

**INVESTIGATING THE EFFECT OF CARBONATION
CURING AND RED MUD UTILIZATION ON
CHARACTERISTICS OF CEMENT COMPOSITES**

BY
MUHAMMAD TALHA SHAFIQUE

A Thesis Presented to the
**COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS**

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CIVIL AND ENVIRONMENTAL ENGINEERING

DECEMBER 2024

KING FAHD UNIVERSITY OF PETROLEUM and MINERALS
DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

This thesis, written by **MUHAMMAD TALHA SHAFIQUE** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CIVIL ENGINEERING**.



Prof. Shamsad Ahmad
Department Chairman



Dr. Suliman Al- Homidan
Dean of Graduate Studies

Date



Dr. Hammad Raza Khalid
(Advisor)



Prof. Shamsad Ahmad
(Co-Advisor)



Dr. Saheed Kolawole Adekunle
(Member)



Dr. Asad Hanif
(Member)



Prof. Salah Al-Dulaijan
(Member)

© Muhammad Talha Shafique

2024

I DEDICATE THIS WORK TO
MY BELOVED PARENTS,
AND
MY SIBLINGS
AND
MY WIFE |

ACKNOWLEDGMENTS

Firstly, I would like to thank Almighty Allah (S.W.T), the most merciful and compassionate, for allowing me to study at KFUPM and providing the knowledge, patience, and strength to complete my thesis work.

I want to extend gratitude to my family members for their firm support and love throughout my journey. Their understanding and encouragement were a constant source of energy for me. I want to acknowledge King Fahd University of Petroleum and Minerals for providing me with an opportunity to complete my graduate studies and for providing me with financial support. I also acknowledge the support of the research centers and core research facilities in KFUPM for providing research support to complete my Master's.

I am sincerely indebted to my advisor, Dr. Hammad Raza Khalid, for his unwavering support, insightful guidance, and invaluable contributions throughout my research. His mentorship has been a cornerstone of this work. I also express my deep appreciation to my co-advisor, Prof. Shamshad Ahmad, for his encouragement, constructive feedback, and immense support at every stage of this study. My deepest thanks also go to my committee members, Dr. Asad Hanif, Dr. Saheed Adekunle, and Dr. Salah Al-Dulaijan, for their constructive suggestions, cooperation, and expert guidance, which greatly enriched the quality of this research. I want to express gratitude to Dr. Salman Siddique, who was a mentor for my research and gave his valuable insights and time throughout the research.

I am immensely grateful to the laboratory team at IRC-CBM, including Engr. Khalid Mohammed and Engr. Abdur Rehman El Tohfa, their dedication, and assistance during the experimental phase were invaluable. Special thanks to Dr. Najamuddin and Engr. Imran for their technical support during the research, which facilitated the smooth execution of my experiments.

I am grateful to my colleagues and peers at KFUPM for their camaraderie and encouragement throughout my academic journey. I am also truly grateful to all those who contributed to the success of this thesis, directly or indirectly.

TABLE OF CONTENT

ACKNOWLEDGMENTS	v
TABLE OF CONTENT	vi
LIST OF TABLES.....	x
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS	xiv
ABSTRACT.....	xv
ملخص الرسالة	xvii
CHAPTER 1	1
INTRODUCTION.....	1
1.1 Research Gap.....	3
1.2 Need for Research	4
1.3 Research Objectives:	6
CHAPTER 2	8
LITERATURE REVIEW.....	8
2.1 Carbon Capture and Storage:	8
2.2 Carbonation of Cementitious Materials	12
2.3 Microstructural Changes Due to Carbonation	15
2.3.1 Enhancement of Pore Structure of Cement Composites.....	16

2.3.2 Enhancement of Interfacial Properties of Cement Matrix	17
2.4 Effect of Carbonation on Mechanical and Durability Properties	19
2.4.1 Mechanical Properties	19
2.4.2 Durability Properties	21
2.5 Red Mud Utilization.....	22
2.6 Impact of Red Mud on Cement Composite Properties.....	25
2.7 Carbonation of Red Mud.....	28
CHAPTER 3	32
RESEARCH METHODOLOGY	32
3.1 Materials	32
3.2 Preparation of Samples	33
3.2.1 Optimization of Carbonation Parameters	33
3.2.2 Red Mud Incorporated Cement Pastes and Mortar.....	34
3.3 Carbonation Curing.....	36
3.3.1 Optimization of Carbonation Parameters	37
3.3.2 Red Mud Incorporated cement pastes and Mortar.....	39
3.4 Specimen Testing.....	40
3.4.1 Fresh State Properties	40
3.4.2 Heat of Hydration	42

3.4.3 Compressive Strength	42
3.4.4 pH of pore solution and Carbonation Degree	43
3.4.5 Drying Shrinkage	44
3.4.6 Particle Size Distribution.....	45
3.4.7 TGA	46
3.4.8 XRD	46
3.4.9 FTIR	47
3.4.10 SEM-EDS	48
CHAPTER 4	49
IMPACT OF PRE-CARBONATION DURATION ON CARBONATION-INDUCED	
PHYSICOCHEMICAL CHANGES IN OPC	49
4.1 Strength development.....	49
4.2 CO ₂ uptake and TGA.....	52
4.3 XRD	56
4.4 FT-IR Spectra.....	59
4.5 SEM-EDS	62
4.6 pH analysis	64
4.7 Drying Shrinkage.....	66
CHAPTER 5	70

IMPACT OF CARBONATION CURING ON RED MUD-INCORPORATED	
CEMENT COMPOSITES	70
5.1 Material Characterization.....	70
5.2 Fresh state properties and heat of hydration	73
5.3 Carbonation degree and pH of pore solution	75
5.4 Compressive strength	78
5.5 Drying Shrinkage.....	82
5.6 XRD	85
5.7 FT-IR.....	89
5.8 TGA	93
5.9 SEM-EDS	97
5.10 Carbon strength factor	99
5.11 Discussions	100
CHAPTER 6.....	102
CONCLUSION AND RECOMMENDATIONS	102
6.1 Conclusions	102
6.2 Future Recommendations.....	104
REFERENCES.....	106
Vitae.....	139

LIST OF TABLES

Table 1. Chemical Composition of OPC and Red Mud.....	32
Table 2. Mix design of mortar specimen	35
Table 3: Experimental plan matrix for early-age carbonation curing	38
Table 4. CO ₂ uptake and portlandite content of specimens	56
Table 5. pH of cement pastes specimens at various depths for carbonated and control specimens	77

LIST OF FIGURES

Fig. 1. Summary of CO ₂ utilization and storage in cementitious materials	13
Fig. 2. Pore volume in carbonated cement paste in various diameter ranges. Adopted from [97].....	17
Fig. 3. SEM micrographs of fiber-cement composites: (a) without carbonation curing, (b) with carbonation curing. Adapted from [104]	18
Fig. 4. Comparison of compressive strength of specimens after carbonation curing and subsequent water curing. Adapted from [14]	20
Fig. 5. Carbonation degree of belite-rich cement after 3 and 7 days of carbonation curing. Adapted from [107]	31
Fig. 6. The physical appearance of red mud and OPC.....	33
Fig. 7. Carbonation Curing Chamber	37
Fig. 8. Carbonation Summary of Optimization of Parameters	39
Fig. 9. Summary of Carbonation of Red Mud incorporated cement paste and Mortars.	40
Fig. 10. Flow Table Test for Cement Paste.....	41
Fig. 11. Setting Time Test for Cement Paste.....	41
Fig. 12. Isothermal Calorimeter Setup	42
Fig. 13. Compression Testing Machine	43
Fig. 14. pH calculation using digital pH meter	44
Fig. 15. Length comparator setup for drying shrinkage.....	45
Fig. 16. Particle Size Analyzer.....	45
Fig. 17. TGA device.....	46

Fig. 18. Ultima IV RIGAKU diffractometer	47
Fig. 19. FT-IR Machine Manufactured by NICOLET	48
Fig. 20. SEM Experimental Set-up	48
Fig. 21. Thermal profile for hydration of OPC	52
Fig. 22. Compressive strength of cement pastes specimens	52
Fig. 23. TGA curves for C-60-0 (E-Ettringite, CH- Portlandite, C- Calcite, M- Monosulfoaluminate).....	54
Fig. 24. XRD spectra of cement paste at 28-days (Alite -A, Belite-B, Ettringite-E, Calcite-C, Portlandite-CH, Aragonite-Ar)	59
Fig. 25. FT-IR spectra of control and carbonated specimens (1: O-H in Ca(OH)_2 , 2: ν_2 of H-O-H, 3: ν_3 of CO, 4: ν_3 of CO, 5: ν_2 of CO_3^{2-} , 6: ν_4 of CO_3^{2-}).....	62
Fig. 26. SEM images and EDS spectra of carbonated specimens.	64
Fig. 27. pH analysis of specimens	66
Fig. 28. Drying shrinkage of specimens	69
Fig. 29. Particle Size Distribution of OPC, Red Mud, and Dune Sand.....	70
Fig. 30. XRD Spectra of OPC and red mud	71
Fig. 31. TGA curves for OPC and red mud	72
Fig. 32. SEM images of red mud and OPC with respective EDS spectra	73
Fig. 33. Thermal Profile for hydration of OPC with different replacements of red mud	74
Fig. 34. Fresh State Properties of Cement Paste.....	75
Fig. 35. Carbonation Degree at 3 and 28 days for Mortar Specimens	76

Fig. 36. Compressive strength of cement pastes and mortar specimens with different replacement of red mud at 3 and 28 days	81
Fig. 37. Drying shrinkage of mortar specimens	84
Fig. 38. XRD of specimens at 28 days (Alite -A, Belite-B, Ettringite-E, Calcite-C, Portlandite-P, Aragonite-Ar, Kaolin-K, Quartz-Q, Cancrinite-Cn).....	88
Fig. 39. FTIR spectra of carbonated and control specimens (1. O-H in $\text{Ca}(\text{OH})_2$ -3642 cm^{-1} , 2. ν_2 of H-O-H – 1650 cm^{-1} , 3. ν_3 of CO – 1470 cm^{-1} , 4. ν_3 of CO –1417 cm^{-1} , 5. ν_2 of CO_3^{2-} – –872 cm^{-1} 6. ν_2 of CO_3^{2-} – – 714 cm^{-1}).....	92
Fig. 40. TG results for control and carbonated specimens (Ettringite-E, Calcite-C, Portlandite-P, Mono sulfo-aluminate-M).....	96
Fig. 41. SEM Images for control and carbonated specimens with EDS Spectra	98
Fig. 42. Carbon Strength factor for paste specimen	100

LIST OF ABBREVIATIONS

OPC	:	Ordinary Portland Cement
TGA	:	Thermogravimetric Analysis
XRD	:	X-RAY Diffraction
SEM	:	Scanning Electron Microscopy
EDS	:	Energy Dispersive X-Ray Spectroscopy
FTIR	:	Fourier Transform Infrared Spectroscopy
ACC	:	Amorphous Calcium Carbonate

ABSTRACT

Full Name : [Muhammad Talha Shafique]

Thesis Title : [Investigating the Effect of Carbonation Curing and Red Mud Utilization on Characteristics of Cement Composites]

Major Field : [Civil Engineering]

Date of Degree : [DECEMBER 2024]

Cement production is among the main contributors to CO₂ worldwide, with a ton of greenhouse gas generated per ton of cement. Another industrial waste generated in huge quantities is red mud, with 1.5 tons of red mud being generated per ton of alumina production. Recycling both wastes, including red mud and CO₂, is essential as both adversely affect the ecosystem. Sequestration of CO₂ in cement composites incorporating red mud has yet to be studied widely. This research investigates the impact of replacing cement with red mud on cement pastes' mechanical and microstructural properties and doing subsequent carbonation to enhance the properties of red mud-incorporated cement mortar. The research is divided into two portions. Firstly, parameters for improving the carbonation regimes were studied. For this, the influence of pre-hydration durations on the carbonation curing of OPC paste to improve CO₂ was studied. Cement paste specimens were subjected to 3-hour carbonation curing at pressures of 15 and 60 psi after pre-hydration durations of 0, 3, 7, and 24 hours. Additional curing regimes, including extended carbonation for 48 hours and immediate moisture curing, were assessed. Analytical techniques such as TGA, SEM, XRD, and FTIR were employed to analyze phase composition, strength, shrinkage, and pore solution pH. The findings indicate that shorter pre-hydration durations (0-3 hours) enhance CO₂ uptake, compressive strength, and

calcium carbonate formation, whereas extended pre-hydration reduces carbonation efficiency due to water loss through evaporation.

The second part studied the influence of red mud incorporation at various replacements. Cement pastes and mortar samples with 5%, 10%, and 15% red mud replacement underwent carbonation curing for 72 hours after casting. The results revealed that incorporating red mud in cement mortar improved strength initially compared to the control, although a slight reduction was observed at 28 days. Carbonation curing enhanced strength retention at 28 days across all red mud replacement levels and significantly reduced the drying shrinkage of specimens. FTIR analysis indicated a reduction in portlandite and increased calcites on surfaces, with amorphous calcium carbonate (ACC) forming in the middle layers of carbonated specimens. TGA results showed increased CO₂ uptake with higher red mud content, while SEM-EDS demonstrated nano-filler effects that reinforced the cement matrix through a hybrid structure of calcite and C-S-H gel. These findings highlight the potential of red mud incorporation to improve carbonation efficiency and enhance the durability of cementitious materials.

ملخص الرسالة

الاسم الكامل: محمد طلحة شفيق

عنوان الرسالة: دراسة تأثير معالجة الكربنة واستخدام الطين الأحمر على خصائص مركبات الأسمنت

التخصص: هندسة مدنية

تاريخ الدرجة العلمية: ديسمبر 2024

يعد إنتاج الأسمنت من بين المساهمين الرئيسيين في ثاني أكسيد الكربون في جميع أنحاء العالم، حيث يتم توليد طن من الغازات الدفيئة لكل طن من الأسمنت. ومن النفايات الصناعية الأخرى المتولدة بكميات ضخمة الطين الأحمر، حيث يتم إنتاج 1.5 طن من الطين الأحمر لكل طن من إنتاج الألومينا. تعد إعادة تدوير النفايات، بما في ذلك الطين الأحمر وثاني أكسيد الكربون، أمرًا ضروريًا لأن كلاهما يؤثر سلبيًا على النظام البيئي. لم يتم بعد دراسة عزل ثاني أكسيد الكربون في مركبات الأسمنت التي تحتوي على الطين الأحمر على نطاق واسع. يتناول هذا البحث دراسة تأثير استبدال الأسمنت بالطين الأحمر على الخواص الميكانيكية والمجهريّة للمعجون الأسمنتي وإجراء الكربنة اللاحقة لتعزيز خواص الملاط الأسمنتي المحتوي على الطين الأحمر. وينقسم البحث إلى قسمين. أولاً، تمت دراسة عوامل تحسين أنظمة الكربنة. لهذا الغرض، تمت دراسة تأثير فترات ما قبل الترطيب على معالجة الكربنة لمعجون OPC لتحسين ثاني أكسيد الكربون. تم إخضاع عينات عجينة الأسمنت إلى معالجة الكربنة لمدة 3 ساعات عند ضغوط تتراوح بين 15 و 60 رطل لكل بوصة مربعة بعد فترات ما قبل الترطيب البالغة 0 و 3 و 7 و 24 ساعة. تم تقييم أنظمة المعالجة الإضافية، بما في ذلك الكربنة الممتدة لمدة 48 ساعة والمعالجة الفورية للرطوبة. تم استخدام التقنيات التحليلية مثل TGA و SEM و XRD و FTIR لتحليل تكوين الطور والقوة والانكماش ودرجة الحموضة في محلول المسام. تشير النتائج إلى أن فترات الترطيب المسبق الأقصر (0-3 ساعات) تعزز امتصاص ثاني أكسيد الكربون، وقوة الضغط، وتكوين كربونات الكالسيوم، في حين أن الترطيب المسبق الممتد يقلل من كفاءة الكربنة بسبب فقدان الماء من خلال التبخر.

أما الجزء الثاني فقد درس تأثير دمج الطين الأحمر في البدائل المختلفة. خضعت معاجين الأسمنت والملاط التي تحتوي على 5%، 10%، و 15% من استبدال الطين الأحمر إلى المعالجة بالكربنة لمدة 72 ساعة بعد الصب. أظهرت النتائج أن دمج الطين الأحمر في مونة الأسمنت أدى إلى تحسين القوة في البداية مقارنة بالتحكم، على الرغم من ملاحظة انخفاض طفيف عند 28 يومًا. عززت معالجة الكربنة الاحتفاظ بالقوة لمدة 28 يومًا عبر جميع مستويات استبدال الطين الأحمر وقللت بشكل كبير من انكماش تجفيف العينات. أشار تحليل FTIR إلى انخفاض في نسبة البورتلانديت وزيادة الكالسيوم على الأسطح، مع تشكل كربونات الكالسيوم غير المتبلورة (ACC) في الطبقات الوسطى من العينات الغازية. أظهرت نتائج TGA زيادة في امتصاص ثاني أكسيد الكربون مع ارتفاع محتوى الطين الأحمر، في حين أظهرت SEM-EDS تأثيرات حشو النانو التي عززت مصفوفة الأسمنت من خلال بنية هجينة من الكالسيوم وهلام C-S-H. تسلط هذه النتائج الضوء على إمكانية دمج الطين الأحمر في تحسين كفاءة الكربنة وتعزيز متانة المواد الأسمنتية.

CHAPTER 1

INTRODUCTION

The increasing concentration of CO₂ has become an alarming situation worldwide. Since the start of the Industrial Revolution in Britain in 1760, the concentration of CO₂ has risen significantly, with around 36 billion tons of CO₂ being released globally into the atmosphere. [1]CO₂ is among the leading greenhouse gases that block solar radiation in the atmosphere, causing a global rise in temperature. Other greenhouse gases include Nitrogen oxide and methane, with CO₂ accounting for almost 75% of all greenhouse gases. [2,3]. Due to the high emission of greenhouse gasses, the global temperature has risen 1 °C between 1860 and 2000 [4,5]According to a WMO (World Meteorological Organization) report, the average global temperature rose 1.15°C in 2022 compared to the preindustrial revolution. It was also claimed that the years from 2015 until 2022 were the hottest in 173 years. [6].

Cement manufacturing is also among the main contributors to CO₂ emissions worldwide. These emissions account for around 5-7% of human-caused emissions globally, with the cement industry being ranked among the top 3 contributors of CO₂ [7–9]. Cement manufacturing is continuously rising, and by 2030-2050, the annual global production of cement is expected to reach 5 billion tons, with CO₂ emissions amounting to 10% of global emissions. [9]. Moreover, aluminum production accounts for 1% of greenhouse gas emissions. [10].

The issue of CO₂ emissions is becoming more critical, and effective measures are required to address the problem. A report published in 2019 claimed that the CO₂ concentration in the atmosphere reached 414.7 ppm, which was around 45% higher than the recorded CO₂ levels in 1990 [11]. Moreover, the data suggested that the CO₂ concentration has risen by 2ppm annually during the past 10 years [12]. Moreover, the human-related CO₂ has risen about 400% since 1950 [13]. To address these issues, scientists worldwide are trying to advance carbon management technologies to reduce the concentration of CO₂. As a part of this effort, different CO₂ sequestration technologies have emerged [14]. There is a growing trend among researchers to capture and utilize CO₂. Different approaches, including pre-combustion, oxy-combustion, and post-combustion, are used to store CO₂ [15,16] Additionally, using renewable energy approaches with CO₂ utilization is an environmentally friendly option that can contribute to a sustainable economy and align with the United Nations' sustainability goals [17].

Another major issue with industrialization is the storage of industrial waste produced while manufacturing various valuable metals. Red mud is a industrial waste that is produced as a byproduct during the manufacturing of alumina. It is created using the Bayer procedure, which uses bauxite to produce alumina with red mud as a byproduct. Almost 1.8 tons of red mud is produced, with each ton of alumina produced [18]. The accumulated red mud has reached around 4 billion tons globally, becoming a significant industrial waste [19]. Almost 200 million tons of red mud are produced annually, which makes it an essential industrial waste [20]. The standard treatments for red mud incorporate dewatering and dry waste storage. The long-term storage of the waste results in the loss of land resources, with the alkalinity of red mud causing problems for the environment and humans [21,22]. A

leakage of red mud in Ajka, a region in Hungary, resulted in the contamination of several villages in 2010 [23].

Various approaches for utilizing red mud can decrease industrial waste [24–26]. The high alkalinity of red mud makes it a suitable candidate for the storage of CO₂ through carbonation [27]. Utilizing the red mud for CO₂ storage can reduce the alkalinity of red mud and help reduce the CO₂ footprint [28]. In the cement industry, CO₂ sequestration is carried out via carbon capture and storage techniques. This includes reacting the calcium-bearing components of cement with CO₂ to form stable carbonates [29–31]. Research has indicated that using pressurized CO₂ to carbonate cement composites at an early age increases the strength of specimens [32,33]. This approach involves placing specimens in sealed chambers and filling the chamber with CO₂ gas [34]. Inside the chamber, the gaseous CO₂ reacts with cement components to form stable carbonates [35]. Considering carbon capture and utilization research, the data on early-age carbonation has resulted in forming a curing process suitable for the pre-cast industry. The pre-cast sector accounts for about 20-30% of the concrete market, including dry and wet products. Carbonation has been carried out to manufacture masonry units and hollow slabs with enhanced durability and strength [36–38].

1.1 Research Gap

Despite extensive research on carbonation and utilization of red mud, many significant gaps still need to be found in the literature. Details on optimizing carbonation parameters, including pre-hydration durations, carbonation pressure, and post-carbonation curing techniques and their impact on mechanical properties, especially drying shrinkage and pH

of pore solution, have yet to be widely studied. The literature mainly focuses on compressive strength and microstructural characterization, with little data on other parameters. Similarly, researchers have researched carbon capture and utilization using red mud separately. However, the partial replacement of red mud in cement using early-age carbonation to improve the properties has yet to be widely studied. Red mud usually causes a decrease in strength at 28 days and affects the other properties of cement composites, like drying shrinkage. Using carbonation on red mud incorporated pastes and mortar to enhance the mechanical and microstructural characteristics at early pre-hydration duration has yet to be widely studied.

Additionally, data on the effect of red mud on the pH of the cement paste pore solution needs to be included. The carbonation reduces the pH of the pore solution, which can cause reinforcement corrosion. However, red mud, being alkaline, has the potential to regulate the pH, which needs to be studied extensively.

1.2 Need for Research

The pressing environmental challenges posed by the increasing concentration of CO₂ and the accumulation of industrial wastes necessitate innovative solutions that address both issues concurrently. Cement production, a significant contributor to global CO₂ emissions, and the disposal of red mud, a hazardous byproduct of alumina manufacturing, represent critical areas where sustainable interventions are urgently needed. The environmental and economic burdens are substantial, with cement manufacturing contributing approximately 5-7% of global anthropogenic CO₂ emissions and red mud production exceeding 200 million tons annually. Traditional methods for mitigating CO₂ emissions, such as carbon

capture and storage CCS and the disposal of red mud through dewatering or dry storage, offer limited benefits in isolation and often involve significant resource consumption. Integrating CO₂ sequestration into red mud utilization promises to transform these challenges into opportunities. Red mud's inherent alkalinity and high mineral content make it suitable for CO₂ storage through carbonation, potentially reducing its environmental risks and lowering the carbon footprint of cementitious materials. Despite advances in early-age carbonation techniques to enhance the mechanical properties of cement composites, significant gaps remain, particularly in understanding the interplay of red mud with carbonation parameters and its impact on long-term properties such as drying shrinkage and pore solution pH. This study also addresses the limited understanding of the effects of early-age carbonation on ordinary Portland cement (OPC), particularly during the mixing stage. While carbonation is recognized for altering the properties of cementitious materials, its specific impact on the microstructure and fresh state properties of OPC remain inadequately explored. The nucleation of calcium carbonate during carbonation and its role in enhancing the densification of cement composites hold significant potential for optimizing carbonation curing techniques, yet these mechanisms are not well understood. These gaps hinder the development of systematic approaches to improving OPC performance and durability through carbonation. Addressing these gaps through systematic investigation is critical to optimizing red mud's potential as a partial cement replacement, enhancing carbonated cement composites' mechanical and microstructural properties, and contributing to a sustainable construction industry.

1.3 Research Objectives:

"To investigate the effects of carbonation curing on the microstructural and mechanical properties of ordinary Portland cement (OPC) and red mud-incorporated cement composites, with a focus on optimizing carbonation parameters, enhancing the performance of cement composites and contributing to CO₂ sequestration."

1. To analyze the microstructural transformations induced by carbonation in OPC and red mud-incorporated cement composites, with a focus on the morphology, distribution, and crystal structure of calcium carbonate, using advanced characterization techniques such as SEM-EDS, XRD, TGA, and FTIR.
2. To investigate the nucleation and growth mechanisms of calcium carbonate crystals during carbonation curing by considering the effects of pre-hydration durations, carbonation pressures, and curing regimes and to evaluate their role in densification and improved performance of cementitious composites.
3. To evaluate the impact of carbonation curing on the mechanical properties of OPC and red mud-replaced cement composites, including compressive strength and drying shrinkage at early and later stages.
4. To examine the chemical and microstructural changes in the pore solution of carbonated cement composites, focusing on pH regulation in red mud-incorporated systems and its implications for mitigating reinforcement corrosion.

5. To assess the potential of red mud as a partial cement replacement in improving carbonation efficiency, enhancing CO₂ uptake, and promoting the durability and sustainability of cementitious materials.
6. To provide insights into the optimization of carbonation curing techniques, including the effects of pre-hydration durations, carbonation pressures, and curing regimes, to maximize CO₂ sequestration and improve the mechanical and microstructural properties of OPC and red mud-incorporated composites.

CHAPTER 2

LITERATURE REVIEW

This literature review details CO₂ Emissions and their capture and storage techniques, focusing on carbonation curing. It also highlights the gaps in the current literature related to red mud and carbonation utilization. Additionally, this review provides the impact of carbonation on cement properties, focusing on giving details that need to be included in the literature.

2.1 Carbon Capture and Storage:

CO₂ is usually formed during combustion to produce energy across various industries. The type of combustion process affects the removal method of CO₂ as well. Although numerous carbon capture technologies are currently available, their implementation remains economically challenging, contributing to 70–80% of the total cost associated with the capture, transportation, and sequestration of CO₂ [39]. Carbon capture systems are broadly categorized into three types: post-combustion, pre-combustion, and oxyfuel combustion, each presenting distinct advantages and limitations. Post-combustion capture involves extracting CO₂ from flue gases following combustion, making it a practical solution for retrofitting existing power plants. Despite its technological maturity and ability to recover up to 800 tons of CO₂ daily, this method faces significant parasitic energy demands. The low concentration of CO₂ in flue gases (7–14% for coal-fired plants and 4% for gas-fired plants) necessitates substantial energy input to achieve the required purity levels (95.5%)

for transportation and storage [40,41]. Consequently, this process can escalate electricity production costs by 32–65%, depending on the type of plant [42].

On the other hand, pre-combustion capture involves processing the fuel before combustion through techniques such as gasification or reforming to produce syngas enriched in hydrogen and CO₂. This method benefits from higher CO₂ concentrations ($\geq 20\%$), facilitating more efficient separation. Primarily applied in Integrated Gasification Combined Cycle (IGCC) plants, pre-combustion capture offers significant potential but is hindered by high capital and operational costs for existing sorption systems, coupled with efficiency losses of approximately 7–8% [43]. However, recent advancements suggest that this approach can achieve CO₂ capture efficiencies of up to 80% at competitive costs, particularly in advanced plant configurations. [44,45].

Oxyfuel combustion utilizes pure oxygen instead of air during combustion, resulting in flue gases with elevated CO₂ concentrations (80–98%). This reduces the energy required for CO₂ separation and offers additional benefits, such as lower nitrogen oxide (NO_x) emissions. Despite these advantages, the process is burdened by the energy-intensive production of cryogenic oxygen, leading to substantial energy penalties and increased costs. Furthermore, the high sulfur dioxide (SO₂) content in exhaust gases may pose corrosion risks. While promising, the full-scale application of oxyfuel combustion is currently limited to demonstration projects [27,46,47].

CO₂ separation technologies are essential components of carbon capture and storage (CCS), enabling the isolation of CO₂ from flue gas or fuel gas streams. Among the available methods, absorption using liquid sorbents, such as monoethanolamine (MEA) and diethanolamine (DEA), achieves separation efficiencies exceeding 90%. However,

challenges include the degradation of sorbents, corrosion issues, and the emission of harmful byproducts during operation [48–50]. Adsorption, which utilizes solid sorbents like activated carbon and zeolites, offers CO₂ recovery rates above 85%, employing techniques such as pressure swing adsorption (PSA) or temperature swing adsorption (TSA). While PSA is more energy-efficient, TSA incurs higher operational costs, limiting its large-scale application [51–53].

Chemical looping combustion, leveraging metal oxides to facilitate CO₂ separation, has demonstrated promising efficiency gains over pre-combustion methods. Recent studies highlight its potential for widespread adoption due to improved net energy efficiency [54,55]. Membrane separation employs selective composite polymers to achieve CO₂ capture efficiencies of 82–88%, although low CO₂ concentrations and pressure levels in flue gases remain significant barriers to scalability [56,57]. Hydrate-based separation, which captures CO₂ through hydrate formation with the aid of additives such as tetrahydrofuran (THF), has shown promise for achieving high efficiency and reduced energy consumption, as THF significantly lowers the formation pressure [58,59]. Cryogenic distillation, another method, achieves CO₂ recovery rates of 90–95% through low-temperature distillation but is hindered by high energy requirements (600–660 kWh/ton), necessitating further optimization for cost-effectiveness [60,61].

Globally, CO₂ storage technologies are being implemented through diverse approaches. Enhanced oil recovery (EOR) and coalbed methane recovery represent viable sequestration methods involving CO₂ injection into depleted oil and gas reservoirs [62,63]. EOR, a mature technology, enables simultaneous hydrocarbon extraction and CO₂ storage, as demonstrated by large-scale projects like the Weyburn initiative in Canada, which has

successfully stored over 30 million tons of CO₂ [64]. Similarly, CO₂-enhanced coalbed methane (CO₂-ECBM) storage utilizes coal seams for dual purposes—CO₂ sequestration and methane recovery. However, scalability is limited by challenges such as low permeability in coal seams [65–67].

Similarly, deep sea aquifers can also be used to store injected CO₂ [68,69]. Deep saline aquifers offer significant CO₂ storage capacity, with multiple trapping mechanisms, including hydrodynamic and mineral trapping. Projects like Statoil's Sleipner operation exemplify the potential of saline aquifers, though research gaps persist regarding the long-term behavior of stored CO₂ post-injection [70]. Deep ocean storage, another technique, involves injecting CO₂ into sediments below 3 km depth, where high pressures cause it to liquefy. Despite its promise, the method requires further exploration to address safety and environmental concerns [71,72].

Another approach for CO₂ sequestration is the mineral carbonation of deposits containing magnesium or calcium, where CO₂ can react with such minerals and form stable carbonates [73]. The issue with these methods is the need for value-added products generated from these processes. This questions the economic feasibility of such approaches, with some methods having safety concerns like leakage of captured gas as well [15].

Adequate carbon dioxide storage is crucial to mitigating its adverse environmental impacts. Conventional storage methods, such as enhanced oil recovery (EOR), saline aquifers, and mineral carbonation, have demonstrated significant potential but need to be improved by challenges related to economic feasibility, scalability, and safety risks, including the leakage of stored gas. In this context, the carbonation of cementitious materials emerges as a promising alternative. This approach not only facilitates CO₂ sequestration but also

enhances the mechanical properties of cement-based materials, providing additional value. Continued research and optimization are necessary to improve its efficiency and scalability, enabling it to serve as a practical and impactful solution for addressing global CO₂ emissions.

2.2 Carbonation of Cementitious Materials

The carbonation of cement-based materials offers a promising pathway for CO₂ sequestration, leveraging the chemical reactivity of cement and its hydration products with carbon dioxide. This process can be integrated into manufacturing through three main approaches: carbonation of raw materials, CO₂ injection into fresh-state composites, and carbonation curing. Carbonation of raw materials, such as recycled aggregates and waste cement, improves density, reduces water absorption, and enhances mechanical performance [74,75]. Similarly, injecting CO₂ into fresh-state cement composites provides mechanical benefits but demonstrates lower sequestration efficiency [76,77]. Fig. 1 highlights the summary of CO₂ utilization and storage in concrete.

Among these methods, carbonation curing emerges as the most effective by achieving CO₂ sequestration rates 3 to 4 times higher than alternative approaches within the U.S. concrete industry [78]. This method improves the mechanical properties and durability of cement-based composites and offers distinct advantages over conventional curing techniques. Compared to steam curing, carbonation curing is less energy-intensive and more time-efficient than moisture curing. Additionally, it stabilizes industrial waste, reduces cement consumption, and mitigates CO₂ emissions [79,80].

The carbonation process involves exposing cementitious mixtures to a controlled CO₂ environment for a specified duration. This can be carried out in two reaction systems: flow-through reactors and enclosed chambers. Flow-through reactors operate under atmospheric pressure with high gas flow rates, whereas enclosed chambers accommodate pressurized gas, which is particularly advantageous for laboratory-scale studies. Pressurized environments facilitate CO₂ diffusion and enable higher carbonation rates and degrees of carbonation [81,82]. High-purity CO₂ gas is commonly employed in laboratory research, as it ensures optimal carbonation performance[83]. However, some researchers have argued that using flue gas directly is a more sustainable and cost-effective alternative, bypassing the need for CO₂ separation. While curing rates may decrease with flue gas, adjustments such as extended curing durations or increased pressure can offset this limitation [84,85].

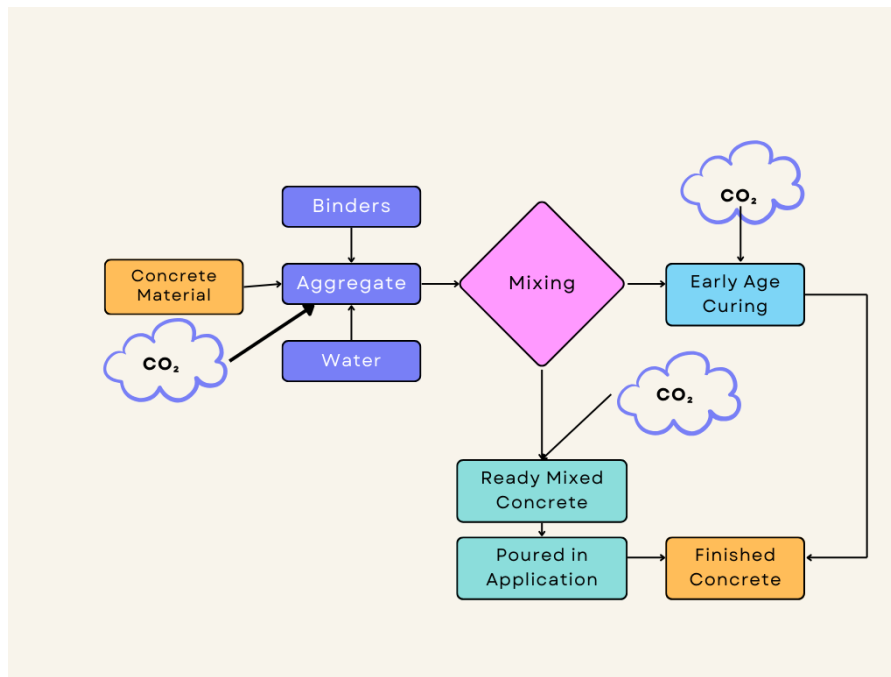
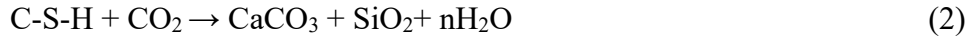


Fig. 1. Summary of CO₂ utilization and storage in cementitious materials

When cement clinkers come into contact with water, they undergo hydration reactions. The carbonation reaction occurs with hydrated cement and involves the reactions of calcium-bearing components of cement with CO₂ for the formation of carbonates of calcium [29–31,33,86,87]. These reactions are given by equations (1) –(4).



The carbonation process in cementitious materials involves a series of reactions between CO₂ and the cement matrix, encompassing the transport and dissolution of CO₂, its diffusion through the material, and the subsequent precipitation of calcium carbonate (CaCO₃) through interactions with calcium ions [88,89]. The primary CO₂-reactive components are the un-hydrated calcium silicates, tricalcium silicate (C₃S), and dicalcium silicate (C₂S). Under moist conditions, these compounds carbonate to form calcium silicate hydrate (C-S-H) and CaCO₃, as illustrated in the referenced equations.

While tricalcium aluminate (C₃A) shows limited direct reactivity with CO₂, its hydration product, ettringite, readily carbonates, forming various secondary compounds [90]. Conversely, tetra-calcium alumino-ferrite (C₄AF) exhibits minimal carbonation, generating calcite, calcium aluminate hydrate (C₃AH₆), and trace amounts of vaterite, aragonite, and gibbsite [91]. Hydration products such as calcium hydroxide (CH) and C-S-H are also susceptible to carbonation. Prolonged exposure to CO₂ results in their decalcification, transforming C-S-H into silica gel, which can contribute to shrinkage and reduced long-

term stability [92,93]. The primary carbonation products include CaCO_3 , which forms in polymorphic structures such as calcite, vaterite, and aragonite, along with polymerized C-S-H gel. The embedded calcite crystals within the matrix contribute to enhanced early-age strength, demonstrating the dual benefits of CO_2 sequestration and mechanical performance improvements [94,95].

Although carbonation of cement-based materials offers significant promise for CO_2 sequestration and improved mechanical properties, several challenges must be addressed to realize its full potential. Key issues include optimizing carbonation efficiency, assessing its long-term impact on durability, and mitigating risks such as reinforcement corrosion, sulfate attack, and alkali-silica reaction. While research has made strides in understanding carbonation in conventional cementitious systems, critical gaps remain in exploring the behavior of alternative binders, such as red mud, during carbonation. Existing studies have primarily focused on traditional cement systems, with limited attention to composite materials incorporating industrial byproducts like red mud. These interactions require deeper investigation to evaluate their carbonation potential, mechanical performance, and durability under diverse conditions. Bridging these knowledge gaps is crucial for advancing carbonation curing beyond laboratory-scale experiments to industrial-scale implementation, enabling the development of sustainable, high-performance materials that integrate waste utilization with effective CO_2 sequestration.

2.3 Microstructural Changes Due to Carbonation

Carbonation affects the microstructure of cementitious materials. The following paragraphs highlight the microstructural changes induced by carbonation in the pore structure and interfacial properties of cementitious materials in the presence of fibers.

2.3.1 Enhancement of Pore Structure of Cement Composites

Carbonation curing plays a crucial role in modifying the pore structure and transport properties of cement-based composites by promoting microstructural densification through the precipitation of calcium carbonate. This process results in a reduction of capillary and total porosity, leading to improved permeability and water absorption characteristics, thereby enhancing the transport properties and overall durability of the material [84]. Notably, carbonation curing is particularly effective in reducing larger pores (>50 nm), whereas hydration processes are more significant in decreasing smaller pores (<50 nm) [96]. As evidenced by mercury intrusion porosimetry (MIP) analysis presented in Fig. 2, carbonation-cured cement paste exhibits an increase in finer pores (<50 nm) alongside a marked reduction in more prominent pores, reflecting the densification of the matrix [97].

Over time, post-conditioning hydration further enhances the material's density by filling the remaining voids with hydration products [98]. Although the apparent porosity of cement paste subjected to either carbonation or moisture curing becomes similar after 28 days, carbonation-cured samples demonstrate a denser surface layer [96]. This refined microstructure contributes to improved transport properties like water absorption, Chloride penetration, air permeability, and surface resistivity. This increases the material's resistance to environmental degradation and enhances its durability.

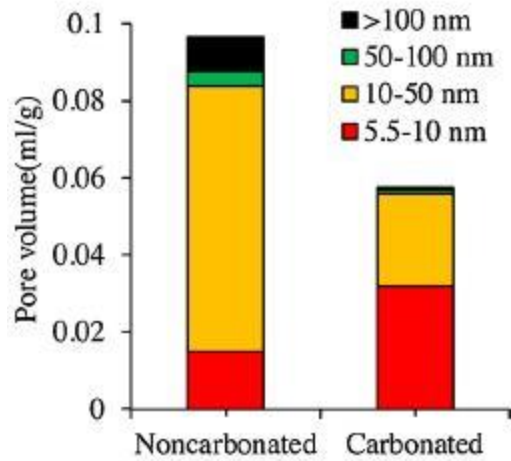


Fig. 2. Pore volume in carbonated cement paste in various diameter ranges. Adopted from [97]

2.3.2 Enhancement of Interfacial Properties of Cement Matrix

Fibers embedded in cement-based materials are susceptible to degradation in the highly alkaline environment of cementitious matrices, which can lead to a decline in durability. Carbonation curing addresses this challenge by neutralizing the alkalinity and forming stable calcium carbonate, enhancing the durability of fiber-reinforced composites. [86]. Basalt and glass fibers, with their silica-based structures, experience lime crystal infiltration during cement hydration, which causes corrosion and gradual strength loss. Glass fiber-reinforced composites, in particular, have demonstrated significant reductions in toughness and strength over 10 years [99,100].

Carbonation curing helps mitigate this issue by lowering the cement matrix's alkalinity by reducing Ca(OH)_2 content and densifying the structure via CaCO_3 precipitation. These changes help prevent moisture ingress, reducing fiber degradation and limiting wet expansion in natural fibers. In conventional hydrated composites, the fiber-matrix interface

is often weakened by increased porosity around the fibers, primarily due to absorbed water [101]. However, carbonation curing improves these interfacial properties by precipitating CaCO_3 crystals within the pores and voids surrounding the fibers [102,103]. As shown in Fig. 3, carbonation curing densifies the matrix near the fibers, enhancing the bond strength at the fiber-matrix interface. The formation of CaCO_3 in voids surrounding the fibers further improves the interfacial bond strength [104].

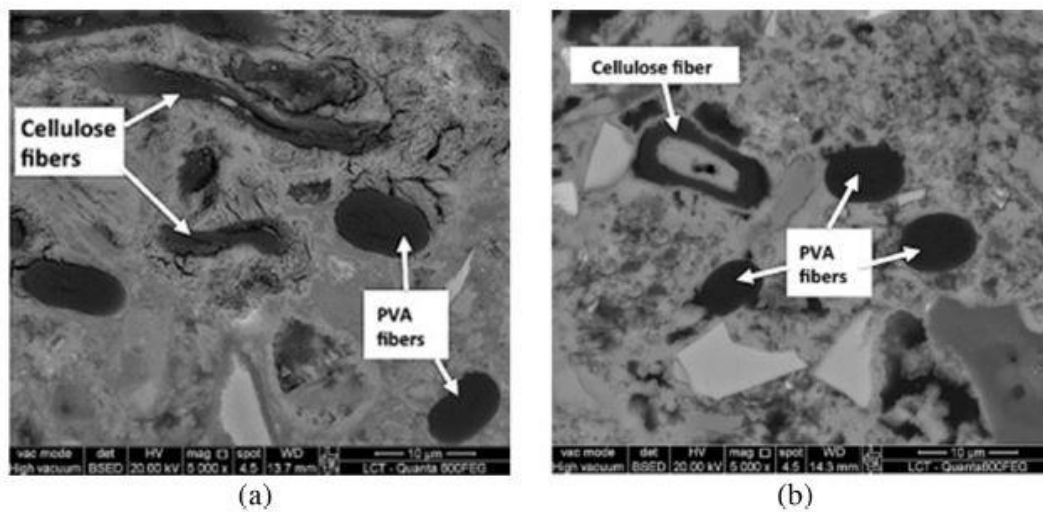


Fig. 3. SEM micrographs of fiber-cement composites: (a) without carbonation curing, (b) with carbonation curing. Adapted from [104]

Although carbonation curing has been extensively examined for its effects on the microstructure and interfacial properties of cement-based composites, significant gaps remain in understanding the optimization of pre-hydration duration before carbonation. In particular, the impact of pre-hydration duration on the distribution of hydration products, the development of early-stage microstructural characteristics, and their subsequent influence on carbonation efficiency and durability enhancements remain unclear. Additionally, the effects of varying pre-hydration durations on the neutralization of

alkalinity and stabilization of fibers within the matrix during carbonation have yet to be thoroughly explored. Addressing these gaps is crucial for refining pre-hydration practices to optimize carbonation-induced improvements, particularly for fiber-reinforced composites susceptible to degradation.

2.4 Effect of Carbonation on Mechanical and Durability Properties

Carbonation also improved the mechanical and durability properties of cement composites. The following sections highlight these improvements.

2.4.1 Mechanical Properties

Carbonation curing has been widely recognized for its ability to accelerate strength development in cement-based composites, as evidenced by numerous studies [14]. As shown in Fig. 4, carbonation-cured samples demonstrate significantly higher early-age strength compared to moisture-cured specimens, with one-day strength reaching 40%–100% of the 28-day strength of water-cured references [81,84,96,105–107]. While subsequent water curing continues to enhance the strength of carbonation-cured specimens, the rate of improvement slows due to the high carbonation degree, which limits further hydration. Nevertheless, the 28-day strength of carbonation-cured samples is generally comparable to that of water-cured references despite a lower hydration degree at early stages. The reaction degree of cement increases more rapidly under carbonation curing than with water curing, promoting rapid hardening and strength gain [96].

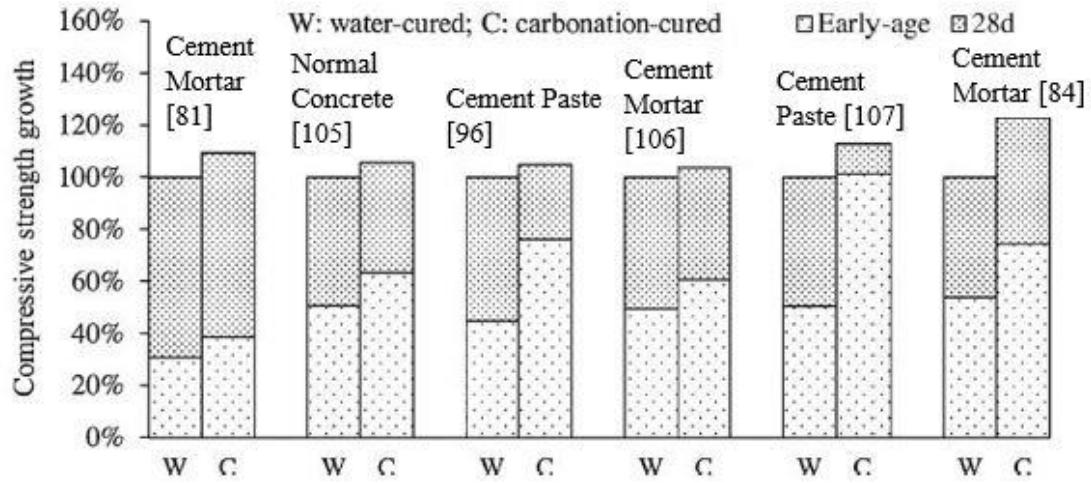


Fig. 4. Comparison of compressive strength of specimens after carbonation curing and subsequent water curing. Adapted from [14]

The accelerated reaction observed during carbonation curing is primarily attributed to the precipitation of calcite, which provides nucleation sites that enhance the growth of reaction products, thus promoting matrix densification [77,108]. As a result, carbonation-cured composites exhibit increased formation of reaction products and a reduction in porosity. In contrast to water-cured composites, which primarily consist of CH and C–S–H gel, carbonation-cured composites are composed of a mixture of C–S–H gel and CaCO_3 . The strong bond between these components improves the toughness and hardness of the matrix, contributing to the early-age strength gain [109,110]. The strength improvement is directly linked to the carbonation degree, as higher carbonation levels lead to denser matrices with enhanced C–S–H and CaCO_3 precipitation [111,112]. However, post-carbonation hydration progresses more slowly due to the reduced amount of unreacted cement in highly carbonated matrices.

2.4.2 Durability Properties

The durability of carbonation-cured cement-based composites has been extensively investigated, with findings indicating significant improvements across several performance areas. Drying shrinkage is notably reduced compared to moisture or steam curing due to carbonation-induced transformations, such as the decalcification of C–S–H and the formation of CaCO_3 , which enhance volumetric stability and cracking resistance [113]. Additionally, carbonation mitigates secondary carbonation shrinkage by densifying the pore structure, reducing CO_2 diffusion from the atmosphere, and decreasing both long-term carbonation depth and shrinkage when compared to conventionally hydrated concrete [114].

Improved freeze-thaw resistance is attributed to the refinement of the pore structure and a reduction in water permeability, which limits freezing damage, as evidenced by lower mass loss in carbonation-cured samples compared to steam-cured or everyday hydrated references [115]. Carbonation curing also enhances abrasion resistance by creating a more robust surface with intermixed C–S–H and CaCO_3 phases, resulting in increased micro-hardness and reduced mass loss during abrasion tests [116].

In terms of high-temperature stability, carbonation-cured composites exhibit less strength loss up to 600°C , owing to the transformation of CH into thermally stable CaCO_3 ; however, significant degradation occurs at higher temperatures due to the decomposition of CaCO_3 [117]. Carbonation curing also improves corrosion resistance, as early carbonation reduces pore connectivity and water absorption, slowing the ingress of chlorides and moisture. Subsequently, water curing can partially restore pH levels, maintaining reinforcement protection [118].

About sulfate attack resistance, carbonation curing limits external sulfate ingress by reducing free calcium ions and pore connectivity. However, variations in the extent of this resistance indicate a need for further research [119]. It also enhances resistance to internal sulfate attack by inhibiting delayed ettringite formation, thus preserving dimensional stability over time [120]. Preliminary studies suggest that carbonation curing may improve alkali-silica reaction (ASR) resistance by altering the physical and chemical environment, though the exact mechanisms remain unclear [121]. Overall, carbonation curing emerges as a promising technique for improving the durability of cement-based composites against multiple degradation mechanisms.

2.5 Red Mud Utilization

The chemical composition of red mud is influenced by the bauxite source, with the primary constituents being Al_2O_3 , CaO , SiO_2 , Na_2O , and Fe_2O_3 [122]. The mineralogical phases of red mud predominantly include quartz (SiO_2), hematite (Fe_2O_3), gibbsite ($\text{Al}(\text{OH})_3$), katoite ($\text{Ca}_3\text{Al}_2\text{SiO}_4(\text{OH})_{12}$), and sodium aluminum silicate ($\text{Na}_6[\text{AlSiO}_4]_6$) [123]. The presence of heavy metals and its high alkalinity pose considerable challenges for its direct application [124]. However, utilizing red mud for CO_2 sequestration has been proposed as a dual-benefit approach, addressing alkalinity reduction in red mud and mitigating CO_2 emissions. Various strategies for red mud utilization present opportunities for minimizing industrial pollution [125]. Given its widespread use in construction, integrating red mud into concrete offers a promising solution for addressing environmental concerns while capitalizing on its global applicability [126].

Neutralizing red mud is crucial for ensuring safe storage and effective management of deposits post-closure, providing opportunities for reuse while mitigating its high pH. Achieving an optimal pH of around 8.0 is ideal, as it facilitates the release of chemically adsorbed sodium, neutralizes alkaline buffer minerals, and ensures the insolubility of toxic metals [127]. Current research is focused on several pH-reduction techniques, such as acid neutralization, CO₂ treatment, seawater neutralization, bioleaching, and sintering. CO₂ gas, or CO₂-rich flue gas, reacts with aqueous slurries of red mud to form carbonic acid, effectively lowering pH by neutralizing the essential components [128,129]. However, gaseous CO₂ neutralization is limited by short contact times, with pH rising again due to the leaching of additional alkaline materials. Studies have explored high-pressure liquid CO₂ for more efficient pH reduction to address this. Additionally, multiple-cycle CO₂ treatments for red mud neutralization have been investigated to improve process efficiency [130].

Efforts to utilize red mud have focused on converting it into a secondary resource or valuable material, addressing the stockpiling challenges since the 1950s. Red mud, rich in Fe₂O₃, Al₂O₃, SiO₂, and compounds such as TiO₂ (up to 24% in Indian red mud), holds the potential for the recovery of rare earth elements like Ga, Sc, and Ti. Iron recovery techniques include roasting magnetic recovery, reducing smelting, and leaching-extraction, with successful global applications reported. For example, the Chinese Metallurgical Research Institute achieved an 86% iron recovery rate using red mud-magnetic separation technology, while Sun et al. optimized magnetic roasting for concentrated iron recovery [131,132]. Aluminum and sodium recovery methods include the Sub-Molten Salt Method

(88% Al_2O_3 recovery) and soda lime processes, which have achieved up to 95% recovery of aluminum and sodium [133].

Red mud has been investigated for construction materials, including cement, bricks, and geopolymers. Geopolymers synthesized through the geo-polymerization of red mud and alkali metal silicates have demonstrated compressive strengths of up to 21 MPa and water absorption rates below 3% [134]. In the production of clay-based products, red mud has been successfully employed to enhance compressive strength and reduce hydraulic conductivity [135]. In cement manufacturing, the inclusion of red mud has been shown to improve sulfate resistance and early strength development, particularly when combined with fly ash, lime, and gypsum [136].

Red mud also finds practical applications as a filling material across various sectors, such as road construction, mining, and plastics. Red mud-derived high-grade road base materials have demonstrated significant potential for large-scale implementation in road construction. A notable example is a 15-meter wide, 4-kilometer highway constructed in Zibo, Shandong Province, which met all required strength and stability standards based on tests conducted by relevant authorities [137].

In the mining sector, researchers at the Institute of Changsha Mining Research developed a "pumped red mud paste cemented filling" technique in collaboration with Shandong Aluminum Company. This method utilizes a mixture of red mud, fly ash, lime, and water in specific proportions to create a backfill material, effectively preventing subsidence in bauxite mines. With a 28-day strength of 3.24 MPa, this approach enhances safety, reduces costs, and improves overall mining efficiency [138].

In the plastics industry, red mud serves as a reinforcing filler for polyvinyl chloride (PVC), significantly extending the lifespan of PVC products due to its thermal stability and anti-aging properties. Its excellent fluidity improves processing efficiency, making it particularly suited for fire-retardant plastic composites, solar water heaters, and construction profiles [139].

2.6 Impact of Red Mud on Cement Composite Properties

Numerous researchers are exploring the application of red mud in concrete, given its extensive global consumption [140]. Numerous studies have explored its potential as a partial replacement for cement, with substitution levels ranging from 15% to 25% [141]. The integration of red mud into cement composites has also been extensively studied. Experimental studies highlight the feasibility of using red mud to improve concrete properties.

Sethy et al. [143] studied that replacing up to 10% of cement with red mud had no substantial effect on concrete strength, although strength decreased at higher replacement levels. Similarly, Metilda et al. [142] Red mud could effectively replace up to 15% of cement without compromising compressive or tensile strength, with reductions observed beyond this threshold. Further, Sapna and Aravindhraj [144] reported a 17% improvement in strength when red mud was used in conjunction with hydrated lime at varying replacement levels.

Studies by Sawant et al. [145] and Rathod et al. [140] confirmed the impact of red mud on both setting time and compressive strength. While lower replacement levels (5–10%) maintained strength, higher proportions (20–25%) yielded mixed results. Wang et al. [146],

utilizing advanced analytical techniques such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), evaluated the microstructural properties of red mud in masonry applications and found that Bayer red mud demonstrated considerable reuse potential. However, researchers generally agree that the optimal cement replacement lies within the 10–20% range to preserve structural integrity and performance [147–149].

The workability of concrete, measured through slump tests, also varies with red mud substitution. Ashok and Sureshkumar observed that slump values increased with higher red mud content, likely due to its porous nature and water absorption properties. However, other studies, including those by Sai and Suresh [150], reported a decline in slump values as red mud content increased, suggesting a reduction in workability. Tang et al. [151] corroborated these findings, noting decreased flowability in self-compacting concrete due to the porous characteristics of red mud.

The hardened properties of concrete, particularly compressive strength, have been extensively studied across varying levels of red mud replacement. Metilda et al. [142] and Ghalehnovi et al. [152] observed that strength reached its peak with 15–25% replacement, with reductions occurring beyond this range due to a lack of sufficient calcium hydroxide for hydration. Ashok and Sureshkumar [153] reported a 21.7% increase in strength at 15% red mud replacement and a 7.5% reduction in costs. Tensile strength tests by Sethy et al. [143] and Bishetti and Pammar [154] showed similar trends, with optimal performance achieved at 10–15% red mud replacement, after which strength declined.

Flexural strength tests, which assess the bending stress of concrete, yielded mixed results when red mud was used as a partial cement replacement. Matilda et al. [142] found improvements in flexural strength with red mud substitution, peaking at 15% replacement,

while Cholkar et al. [155] observed a 15.56% increase in flexural strength compared to the control samples. Similarly, Viyasun et al. [155] also reported consistent increases in flexural strength with red mud content up to 30%. Ashok and Sureshkumar [153] observed a peak flexural strength of 92 kN at 15% replacement, but further increases in red mud content led to a reduction in strength, consistent with findings by Palaniappan et al. [156], who recommended a 10% replacement for optimal results.

In water absorption studies, red mud substitution consistently reduced water uptake (Viyasun et al. [155] reported a decrease in absorption from 1.55% in the control mix to 0.97% at 30% red mud replacement. Similarly, Ghalehnovi et al. [152] observed negligible differences in water absorption between red mud-modified mixes and control mixes, suggesting that the fine red mud particles effectively sealed the pores in the concrete. Venkatesh et al. [157] corroborated these findings, noting reductions in water absorption as the level of substitution and curing time increased, attributing the observed effect to the filler properties of red mud particles.

The modulus of elasticity (MOE), a key measure of resistance to elastic deformation, exhibited varying trends across different studies. Ghalehnovi et al. [152] while MOE slightly decreased with increasing red mud content, the 25% replacement mix achieved a modulus (32 GPa) comparable to the reference mix (33 GPa). Conversely, Liu et al. [158] observed an increase in MOE with red mud content up to 30%, followed by a decline. Nikbin et al. [148] reported consistent reductions in MOE with higher red mud content, attributing this to the reduced aggregate volume, which in turn lowered stiffness. These discrepancies suggest that maintaining MOE's optimal red mud content depends on the specific design and application requirements.

Mechanical strength results reveal a concerning trend with the compressive strength of red mud-incorporated mortars decreasing over time, particularly after 28 days of curing. This reduction is attributed to the high red mud content, which reduces the aggregate volume in the mix, leading to lower stiffness and compromised structural integrity over extended curing periods. Furthermore, the inclusion of amorphous red mud particles, which initially promote hydration reactions and densification, appears to limit long-term strength development as the red mud content increases [159][160].

To address this challenge, carbonation curing has emerged as a promising solution. This process accelerates the formation of stable carbonate compounds, such as calcite, through the reaction of CO_2 with hydration products, thereby enhancing the mechanical properties of red mud-incorporated mortars. Carbonation curing could mitigate the long-term decline in strength by densifying the matrix and filling micropores, reducing the adverse effects of increased red mud content. By optimizing carbonation curing conditions, red mud can be used in cement replacement while meeting strength requirements for more extended hardening periods and contributing to the sustainability of cementitious materials.

2.7 Carbonation of Red Mud

Research on the carbonation of red mud has primarily focused on direct and indirect mineral carbonation methods, with a particular emphasis on the pH changes and carbonation efficiencies observed during these processes. In direct carbonation, red mud undergoes carbonation in a single step [161,162], whereas indirect carbonation involves first extracting metals, such as Na^+ and Ca^{2+} , and soda from red mud, followed by carbonation [163]. The efficiency of carbonation is influenced by various factors, including the liquid limit, which is a critical parameter in slurry carbonation [164].

The carbonation process is highly dependent on the calcium (CaO), sodium (Na₂O), and magnesium (MgO) content of red mud, as these elements participate in carbonation reactions with CO₂. However, the actual CO₂ uptake often falls short of the theoretical maximum carbonation potential (TMCP), primarily due to slow CO₂ diffusion and the limited solubility of calcium-bearing minerals [165]. The carbonation reaction predominantly occurs on the surface of red mud particles, which restricts further CO₂ diffusion into the matrix. This process is typically monitored through pH shifts, FTIR spectroscopy, and total inorganic carbon (TIC) analysis [128,166].

Yadav et al. [167] conducted an extensive study on the carbonation of red mud. The physical properties of red mud were characterized, revealing a density of 2.0 g/cm³, porosity of 0.45%, and a surface area of 10.8 m²/g, as determined by the BET method. The study explored the carbonation of different red mud fractions (RM I, RM II, RM III) by exposing them to a CO₂ atmosphere for reaction times ranging from 0.5 to 12 hours at an average pressure of 3.5 bar. Initial findings indicated that most CO₂ uptake occurred within the first 3.5 hours, with RM I, RM II, and RM III capturing 77%, 82%, and 76% of CO₂, respectively. After this period, the rate of CO₂ uptake significantly slowed, indicating that the reaction had reached saturation. As a result, a reaction time of 3.5 hours was chosen for subsequent experiments.

The CO₂ uptake was highest in RM II, attributed to its higher cancrinite content, a mineral phase that facilitates carbonation. Interestingly, despite RM I having the smallest particle size (5 μm), it exhibited lower CO₂ uptake than RM II, highlighting the greater importance of mineral composition over particle size in the carbonation process. A key observation from the study was that CO₂ uptake was more efficient at liquid-to-solid (l/s) ratios of 0.5, 0.35, and 0.3 for RM I, RM II, and RM III, respectively. This suggests that while water is essential for carbonation,

excessive water can impede CO₂ absorption by restricting its diffusion into the solid phase's pores.

2.8 Effect of carbonation on pH

During carbonation curing, the products formed from cement hydration interact with CO₂, resulting in the neutralization of the cement pore solution pH [168]. In the case of precast concrete subjected to carbonation curing after 12 hours of air curing, a significant reduction in surface pH was observed, reaching a value of 9.9, while the pH near the steel reinforcement remained around 12. A decrease in the concrete pore solution pH to 11.0 can compromise the passive layer on the steel surface, potentially initiating corrosion. The pH level in concrete is a critical factor influencing corrosion; studies have shown that active corrosion of mild steel bars is likely to occur when the pH falls between 9.4 and 10 [169].

Pu et al. [170] conducted an in-depth study on the pH evolution of carbonated concrete specimens. Their research focused on the changes in pH and the chemical composition of the pore solution under various degrees of carbonation. Concrete samples made with ordinary Portland cement and fly ash were subjected to accelerated carbonation conditions, with a CO₂ concentration of 5% and relative humidity at 40%. The results indicated a significant decrease in pH during the first 15 days of carbonation, with a near-linear relationship observed between pH reduction and carbonation duration. After 15 days, the pH reduction stabilized, reaching a final value of around 7.2 for the carbonated concrete, compared to a pH of 12.96–13.41 for the non-carbonated samples. The study further revealed that factors such as water-to-cement ratio, cement content, and fly ash incorporation substantially influenced the pore solution pH. Higher cement content

resulted in a higher initial pH, while incorporating more fly ash led to a lower pH due to the consumption of hydration products.

Siddiqui et al. [107] investigated the carbonation degree of belite-rich cement (BRC) at 3 and 7 days of carbonation curing. They found that the carbonation degree of BRC specimens was generally higher than that of ordinary Portland cement (OPC) throughout the curing period, except at 3 days. The water-to-cement ratio (W/C) played a critical role, as specimens with higher W/C ratios (0.5, 0.6, 0.7) exhibited more excellent carbonation due to developing a more porous cement matrix, which enhanced CO₂ permeability. The faster hydration rate of OPC led to a quicker reduction in free water, facilitating CO₂ diffusion and increasing carbonation. At later ages (7 and 28 days), OPC showed a slower increase in carbonation due to the formation of a dense C–S–H network, which restricted CO₂ penetration. The degree of carbonation at 3 and 7 days of carbonation is illustrated in Fig. 5.

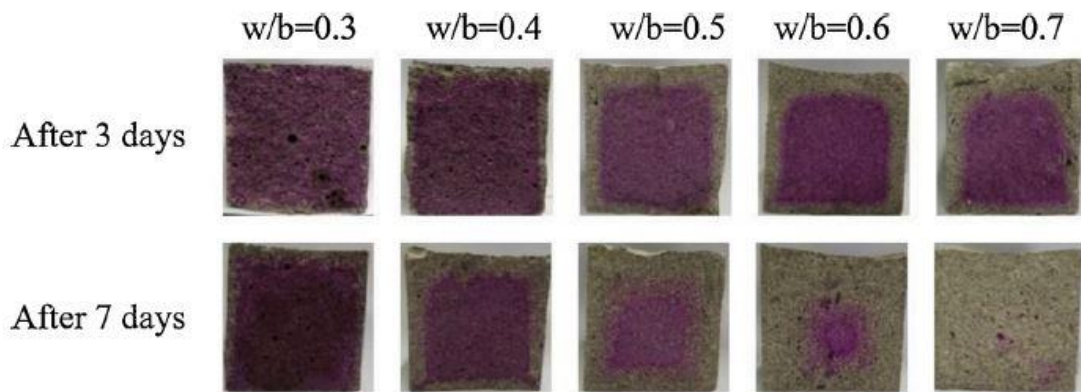


Fig. 5. Carbonation degree of belite-rich cement after 3 and 7 days of carbonation curing. Adapted from [107]

CHAPTER 3

RESEARCH METHODOLOGY

This research was conducted in two phases, which are mentioned below. The phases were conducted separately. The phases are as follows:

1. Optimization of pre-hydration durations and post-carbonation curing regimes.
2. Impact of carbonation on red mud incorporated cement paste and mortars.

3.1 Materials

This experimental study utilized OPC Type 1 and red mud sourced from a local industry. The chemical compositions of OPC Type 1 and red mud are presented in Table 1. Locally sourced dune sand, with a specific gravity of 2.59, was employed in preparing mortar specimens for evaluating carbonation depth, compressive strength, and drying shrinkage. Fig. 6 shows the dried red mud and OPC paste for physical characterization.

Table 1. Chemical Composition of OPC and Red Mud

Chemical Composition	Al ₂ O ₃	SiO ₂	CaO	ZnO	TiO ₂	Fe ₂ O ₃	SrO	Others
OPC Type 1	3.71	16.27	73.97	0.05	0.44	3.96	0.07	1.53
Red Mud	29.55	20.69	8.74	-	9.73	27.47	0.37	3.45



(a) Dried Red Mud



(b) OPC

Fig. 6. The physical appearance of red mud and OPC

3.2 Preparation of Samples

Cement paste and mortar specimens were made using specific standards for both studies.

The details of sample preparation are given below.

3.2.1 Optimization of Carbonation Parameters

Cement paste samples were prepared for chemical analysis, strength testing, and microstructural characterization of hydration products. The cement paste samples were explicitly designed to examine the impact of carbonation on hydration products at varying pre-hydration intervals. A consistent water-to-cement (w/c) ratio of 0.4 was maintained across all paste samples to optimize the carbonation curing process, which relies on sufficient free water to sustain CO_2 reactions. [37].

Mixing was conducted using a Hobart mixer under controlled conditions of $24 \pm 1^\circ\text{C}$ temperature and $65 \pm 10\%$ relative humidity. For cement paste, mixing involved adding

80% of the water at 62 rpm for 3 minutes, then adding the remaining water and an additional 2 minutes of mixing. This was concluded with high-speed mixing at 125 rpm for 1.5 minutes. For mortar samples, cement, and sand were initially dry-mixed for 3 minutes, after which water was introduced, and mixing continued for 3 minutes at 62 rpm, followed by a final high-speed mix at 125 rpm for 2 minutes. These procedures ensured uniform consistency across all paste and mortar specimens.

Sample coding followed the format C-x1-x2, where x1 indicated the carbonation pressure and x2 represented the pre-hydration duration. An extra C was added to the code for samples undergoing additional carbonation curing after initial curing.

3.2.2 Red Mud Incorporated Cement Pastes and Mortar

In this study, paste samples of OPC with varying red mud replacement levels were prepared for microstructural characterization and compressive strength analysis. At the same time, mortar specimens were fabricated to evaluate compressive strength, carbonation degree, and drying shrinkage. Specimen identification followed the format P/Mx-Gx-Rx, where P and M denoted paste and mortar specimens, respectively, G represented carbonation gauge pressure, and R indicated the percentage of red mud replacement. The subscript x after P or M denoted the water-to-cement (w/c) ratio, x after G specified carbonation pressure, and the final x indicated the red mud replacement percentage. For mortar specimens using red mud as a sand replacement, the identifier SR was used instead of R to differentiate the specimens. Control specimens labeled as G0 underwent no carbonation.

The w/c ratio for paste specimens was set at 0.4 to facilitate effective carbonation by ensuring adequate free water for the CO₂ reaction [37]. Both paste and mortar specimens

were mixed using a Hobart mixer under controlled conditions of relative humidity ($65 \pm 10\%$) and temperature ($25 \pm 1^\circ\text{C}$). For paste specimens, mixing involved dry blending the cement and red mud for 2–3 minutes, then adding 80% of the water at 62 rpm for 3 minutes. Subsequently, the remaining water was added, mixing continued for 2 minutes at the same speed, followed by high-speed mixing at 125 rpm for 2 minutes. Mortar specimens underwent similar preparation, with an initial 3-minute dry mix, followed by water addition and mixing for another 3 minutes, concluding with high-speed mixing for 2 minutes. This approach ensured homogeneity for both paste and mortar mixes.

Mortar proportions were maintained at a 1:2 ratio of cement (with red mud replacement) to sand. For specimens where red mud partially replaced sand, a consistent cement quantity was used across all mixes, with sand replaced by red mud at varying percentages and a fixed w/c ratio of 0.5. Red mud was oven-dried before specimen preparation to eliminate excess moisture. Specimens were cast into 50 mm cubes for both paste and mortar, while prismatic bars ($25 \times 25 \times 285$ mm) were prepared for drying shrinkage tests. The mixed design of mortar is given in Table 2.

Table 2. Mix design of mortar specimen

Sample ID	Cement	Red Mud	Sand	Water
	g	g	g	g
M40-G0-R0	1000	-	2000	400
M40-G0-R5	950	50	2000	400
M40-G0-R10	900	100	2000	400
M40-G0-R5	850	150	2000	400

M50-G0-SR0	1000	0	2000	500
M50-G0-SR5	1000	100	1900	500
M50-G0-SR10	1000	200	1800	500
M50-G0-SR5	1000	300	1700	500

3.3 Carbonation Curing

Carbonation curing was conducted using an airtight chamber with a CO₂ inlet valve, pressure gauge, and pressure regulator. Fig. 7 shows the detail of the carbonation chamber. The chamber design ensured a controlled environment for the carbonation process. The inlet valve was connected to a pressurized CO₂ cylinder, and the pressure regulator allowed the adjustment of chamber pressure to the desired levels. During carbonation, the specimens were placed inside the chamber filled with CO₂. The pressure was monitored via the gauge, and once the desired pressure (either 15 psi or 60 psi) was reached, the inlet valve was closed to maintain a sealed environment. The specimens were exposed to CO₂ under these controlled conditions at a laboratory temperature of $24 \pm 1^{\circ}\text{C}$ and relative humidity (RH) of 60%. After carbonation, the samples were removed and subjected to subsequent curing regimes or testing procedures. This process was consistent for all paste and mortar specimens, ensuring repeatability and accuracy.

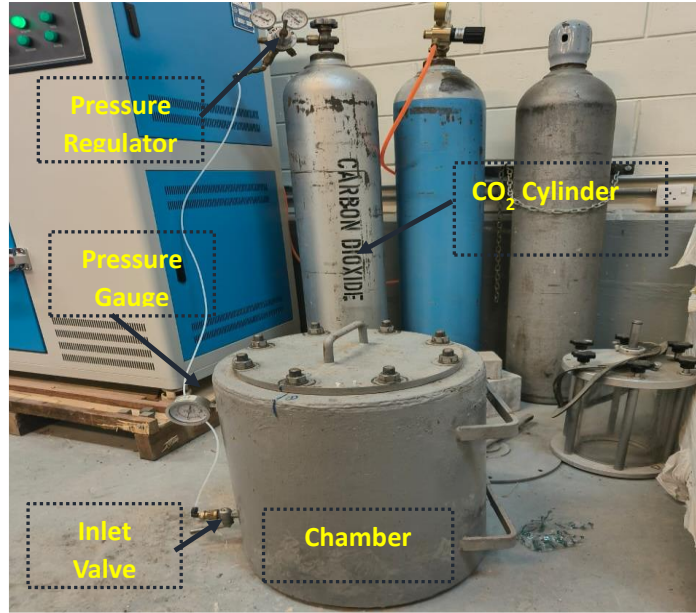


Fig. 7. Carbonation Curing Chamber

3.3.1 Optimization of Carbonation Parameters

For early-age carbonation of hydrating OPC, four different ages of initial hydration were selected (i.e., 0, 3, 7, and 24 h from the duration of casting), before exposing specimens for carbonation. These initial hydration durations were selected considering the pre-cast industry pre-conditioning duration which has been investigated earlier [171]. The carbonation was carried out for 3 h at two different gas pressures (15 and 60 psi). The experimental matrix and protocol are summarized in Table 3 and Fig. 8, respectively. As shown in Fig. 2, the carbonation process comprised of three steps: 1) Initial curing up to the selected initial hydration durations, 2) in-mold carbonation curing for 3 h at the selected pressure, and 3) post-carbonation curing for up to 28 days of curing age under two different regimes. In the first regime, specimens were placed directly in water once the molds were removed. In the second regime, the de-molded specimens were placed again in the carbonation chamber and further carbonation was carried out for 48 h which was followed

by moisture curing till 28 days of curing age. The whole carbonation process was carried out at room temperature of 24 ± 1 °C and R.H. of 60%. After the carbonation curing and demolding, the mortar specimens prepared for drying shrinkage, were submerged in the lime-saturated water for 48 h.

Table 3: Experimental plan matrix for early-age carbonation curing

No.	Designation	Carbonation pressure (psi)	Initial hydration (h)	Extended carbonation
1	C (control)	-	-	-
2	P60-T0	60	0	-
3	P60-T3	60	3	-
4	P60-T7	60	7	-
5	P60-T24	60	24	-
6	P15-T0	15	0	-
7	P15-T3	15	3	-
8	P15-T7	15	7	-
9	P15-T24	15	24	-
10	P60-T0-C	60	0	Yes
11	P60-T3-C	60	3	Yes
12	P60-T7-C	60	7	Yes
13	P60-T24-C	60	24	Yes

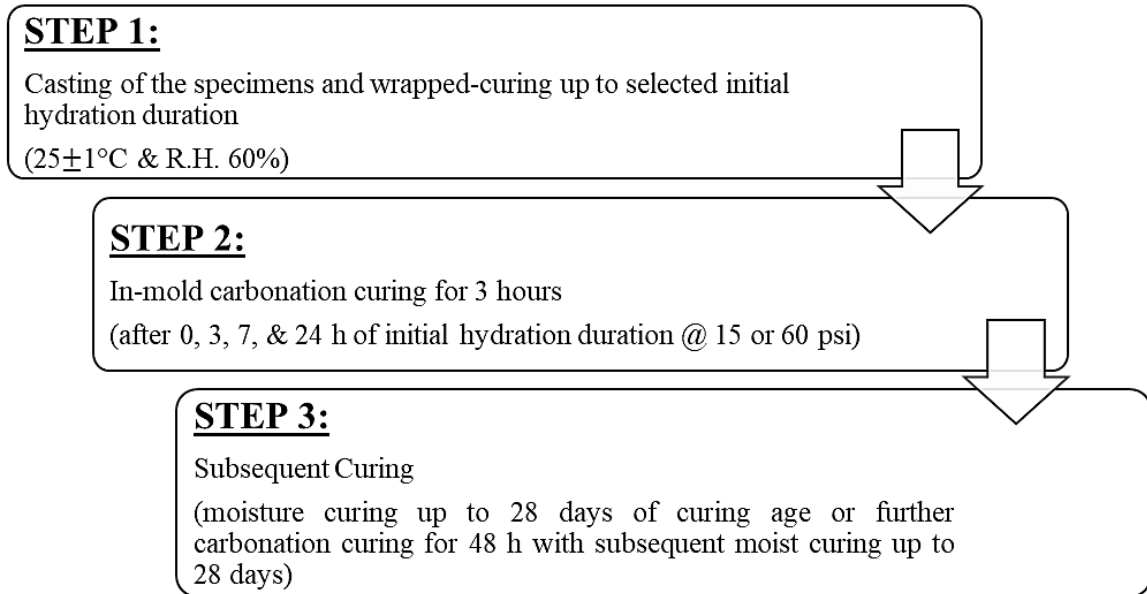


Fig. 8. Carbonation Summary of Optimization of Parameters

3.3.2 Red Mud Incorporated cement pastes and Mortar

The carbonation curing of cement pastes incorporating red mud as a replacement material followed a similar setup, with carbonation performed at pressures of 15 psi and 60 psi. Early-age carbonation was conducted for 24 hours in the mold. After demolding, the specimens were subjected to another 48 hours of carbonation curing. These long curing durations were selected to maximize carbonation efficiency. Compressive strength tests were performed at 3 days, and subsequent specimens underwent moisture curing until 28 days for additional testing. The summary of the carbonation procedure is shown in Fig. 9.

Control specimens, which did not undergo carbonation, were left for 24 hours of air curing before being de-molded and submerged in water for curing at $23 \pm 1^\circ\text{C}$. The carbonation process for red mud-modified mortars was also evaluated. Specimens were carbonated for 24 hours in the mold, followed by an additional 48 hours of carbonation curing.

Hydration was terminated using iso-propanol immersion followed by vacuum desiccation to prepare specimens for microstructural analysis, as this approach minimizes microstructural alterations. Pulverized samples were stored in sealed bags for further study. These procedures ensured consistent and reliable data collection across all specimens [172].

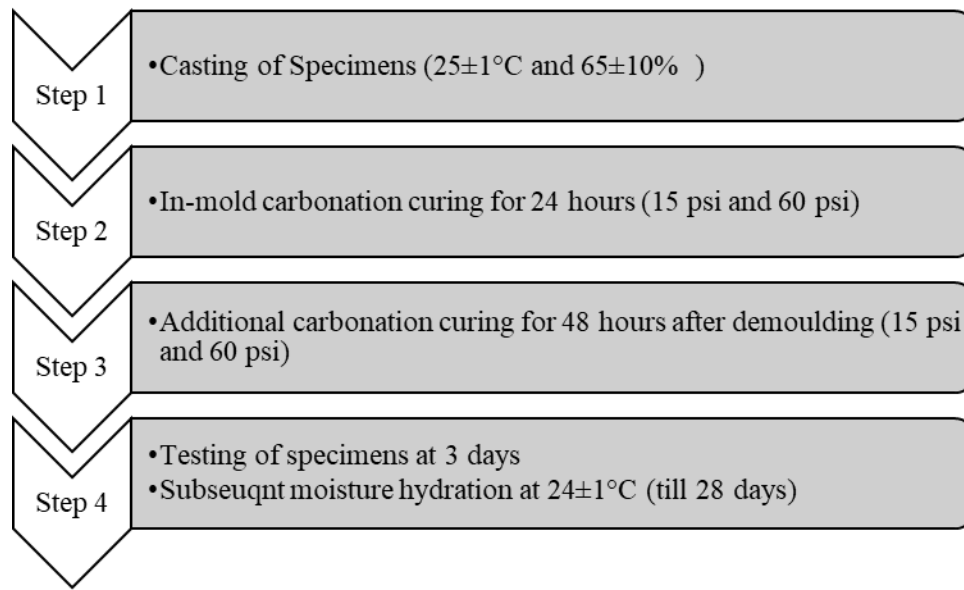


Fig. 9. Summary of Carbonation of Red Mud incorporated cement paste and Mortars

3.4 Specimen Testing

The following tests were carried out to characterize specimens prepared for both experimental plans.

3.4.1 Fresh State Properties

The initial and Final setting time of cement paste with replacements of red mud was conducted using Vicat Apparatus following standard ASTM C403. The flow table test was also performed using the flow table apparatus following ASTM C1437 standard. 25 blows

were given after mixing, and the average flow value was taken from the diameter of the paste. Fig. 10 and 11. It shows the flow test and Setting Time Apparatus, respectively.



(a) Flow Table



(a) Flow of Paste

Fig. 10. Flow Table Test for Cement Paste



Fig. 11. Setting Time Test for Cement Paste

3.4.2 Heat of Hydration

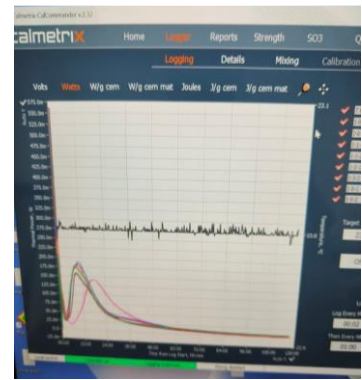
The heat of hydration of cement pastes of the control sample and red mud replacement was carried out using an I-CAL 8000 Isothermal Calorie Meter. The setup could run 8 samples at once. The temperature was set at 23°C, and the heat of hydration was measured. The specimens were also brought to the same temperature before mixing to remove errors. Fig. 12 shows the setup of the Calorie Meter.



(a) Calorimeter



(b) Specimens Placing



(b) Data Logger

Fig. 12. Isothermal Calorimeter Setup

3.4.3 Compressive Strength

The compressive strength of paste and mortar specimens was conducted using an Automated Compression Testing Machine with a loading rate of 0.5 KN/s. For each type of specimen, three cubic samples of 50mm were tested in the machine, and the average

values were taken for each specimen. The compression testing machine is shown in Fig. 13.



Fig. 13. Compression Testing Machine

3.4.4 pH of pore solution and Carbonation Degree

The carbonation degree of mortar specimens was carried out by spraying phenolphthalein on the surface of the mortar. The mortar cubes were cut into a thickness of 12.5mm from the cube using a concrete cutter, and the internal surfaces were sprayed with the indicator. The colorless region identified the carbonated area where the pH is below 9 [173]. The carbonation degree was calculated using Eq. 1 [107].

$$C.D = \left(\frac{\text{Colorless Area}}{\text{Total Area}} \right) \times 100 \quad \text{Eq. 1}$$

The pH of the cementitious matrix is also very critical. Carbonation results in a reduction of pH of the pore solution, which in turn can result in the formation of lower quality passive films on reinforcement in concrete [174]. The pH of the pore solution for cement paste specimens was calculated from the top surface exposed to the center by cutting out discs

of 6 mm thickness with the help of a concrete cutter. For pH calculation, 40 g of distilled water was infused with 5g of cement paste powder in a beaker for 10 minutes while shaking at intervals of 3 minutes. After the infusion was completed, the suspension was filtered in a flask using a No. 50 filter paper, and the pH of the filtered water was recorded using a digital pH meter [175]. The pH meter setup is shown in Fig. 14.

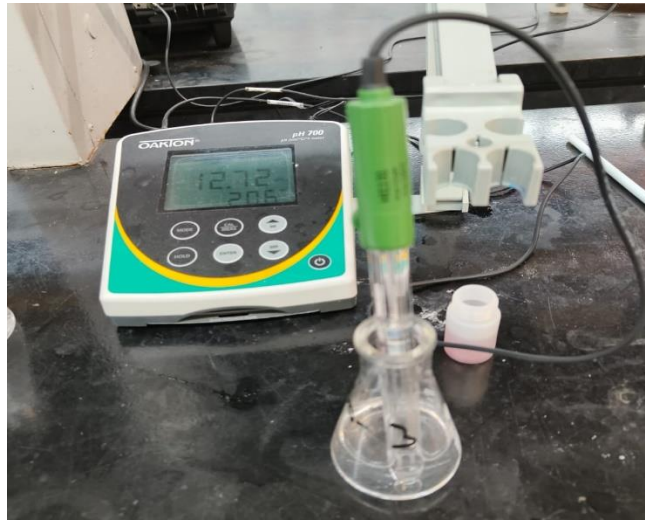


Fig. 14. pH calculation using digital pH meter

3.4.5 Drying Shrinkage

Drying shrinkage measurements were conducted in accordance with ASTM C596-18 standards. The specimens were made and placed in lime saturated water for 48 hours. After curing the specimens were taken out and the excess moisture was cleared. The length readings were taken after curing and the specimens were left to dry in the open air. The length readings were taken at regular intervals and the difference between the length was plotted against time. Fig. 15 shows the length comparator setup for drying shrinkage. The comparator was set to zero by placing the standard-length bar between points. Afterwards the readings were taken for specimens.



Fig. 15. Length comparator setup for drying shrinkage

3.4.6 Particle Size Distribution

The particle size distribution of OPC, red mud, and dune sand was carried out using a particle size analyzer, as shown in Fig. 16. The percentage passing of the raw materials is also shown in Fig. 17. The red mud used in the experimental work was finer than the OPC.



Fig. 16. Particle Size Analyzer

3.4.7 TGA

Thermogravimetric Analysis (TGA) of powdered samples was also conducted using a thermal analyzer (SDT Q600) using nitrogen gas as a shielding agent, as shown in Fig. 17. TGA was carried out to study the stability and composition of minerals. The thermal rate of the analyzer was set at 10°C/min, and the weight loss was logged at 30 °C to 950 °C for the specimens.



Fig. 17. TGA device.

3.4.8 XRD

To understand the phase changes of cement paste, XRD for all powdered samples was carried out using Ultima IV RIGAKU manufactured X-ray Diffractometer shown in Fig. 18. The scanning of specimens was carried out between 5° and 60° using θ -2 θ configuration at scan speed of 2.5°/min.



Fig. 18. Ultima IV RIGAKU diffractometer

3.4.9 FTIR

FTIR spectra of powdered specimens were also obtained using an IS50- FT-IR machine manufactured by NICOLET, as shown in Fig. 19. The Attenuated Total Reflection (ATR) function was used to generate the FTIR spectra of specimens. The range of 4000-400 cm^{-1} was recorded for wavenumber at a resolution of 2cm^{-1} . 32 scans were recorded to register each specimen.



Fig. 19. FT-IR Machine Manufactured by NICOLET

3.4.10 SEM-EDS

SEM-EDS was carried out to study the morphological characteristics of cement paste specimens with various replacements of red mud. The EDS was performed by coating the dehydrated specimens with gold, shown in Fig. 20 a, and point EDS analysis was carried out to get accurate results. The specimens were SEM-EDSed using an electron microscope with model SM-6610LV, shown in Fig. 20 b.



(a) Gold Coating Apparatus



(b) SM-6610LV SEM

Fig. 20. SEM Experimental Set-up

CHAPTER 4

IMPACT OF PRE-CARBONATION DURATION ON CARBONATION-INDUCED PHYSICOCHEMICAL CHANGES IN OPC

4.1 Strength development

Fig. 22 represents the compressive strength of cement paste specimens tested at 3, 7, and 28 days, exposed to different carbonation and curing regimes. Generally, the carbonated specimens showed higher strengths than the control specimens at all the tested ages, except for the early-age strength of the specimens which were subjected to subsequent carbonation (48 h after initial carbonation and demolding). The increase in the compressive strength of carbonated specimens was higher for specimens which were put for carbonation at lower pre-carbonation durations i.e., the earlier the specimens were put for carbonation after molding, the higher the strength gain was observed. Hence, the specimens that were carbonated for 3 h right after the casting showed the highest increase in the strength. The specimens P60-T0 and P15-T0 showed about 20% and 21% strength increase at 3 days compared to the control uncarbonated specimen, respectively. By 28 days, the strength gains of these specimens increased to about 41% and 52%, respectively. Conversely, the specimens P60-T24 and P15-T24 which were put for carbonation after 24 h of initial hydration, exhibited comparable values to the control specimen.

The carbonation curing results in diffusion of CO₂ into specimens which densifies the microstructure [84]. The carbonation is an exothermic process that releases heat as the calcium oxides transform into stable carbonates [176]. The thermal energy has the potential to increase the rate of hydration resulting in a strength gain of specimens [177]. Moreover, the diffusion of CO₂ into the hydrating cement paste when put for carbonation at an early age, is relatively easier. Since the cement matrix is not fully solidified and the reaction rate is high (evident from the heat of hydration shown in Fig. 21), CO₂ can quickly react with hydration products (mainly portlandite) to make carbonation products. The combined effect of microstructure densification and thermal curing resulted in higher strength gains due to early carbonation curing. On the other hand, CO₂ diffusion becomes difficult because of the solidification of the cement matrix as the hydration degree increases with time. As shown in Fig. 21, the maximum heat release occurs during the first 10 h which is the period when carbonation should be carried out.

The decrease in the early-age strength (specifically 3 days) of specimens put for subsequent carbonation, can be attributed to the possible depletion of water in these specimens [178]. It should be noted that both carbonation and hydration are water-dependent processes, requiring an aqueous environment for optimal reaction. For longer carbonation duration, water depletion can interrupt subsequent reactions [171]. This can result in lower strengths compared to control samples being cured under water. However, the compressive strength at 28 days displayed different trends than 3- and 7-day strength. All the carbonated specimens showed higher strength than the control specimen. This indicates that appropriate curing promotes strength recovery at later stages aligning with previous research [14]. The increase in compressive strength decreased with increasing the initial

hydration duration. The specimens with subsequent carbonation of 48 h showed the least increase in strength at 28 days as well. This can again be attributed to water depletion during the carbonation curing which decreased hydration and resulted in lower strength. The subsequent moisture curing of specimens resulted in an increase of strength from control specimens, but it was lower than the samples that were subjected to moisture curing right after demolding.

The samples carbonated at 15 psi at initial hydration duration of 0 and 3 h showed a slight increase in the strength than the samples carbonated at 60 psi. This suggests that the higher pressure does not attribute to more strength gain for specimens. Hence, it can be concluded that proper initial hydration duration combined with optimum pressure for carbonation should be chosen to maximize the strength gain. These findings are also in agreement with other research studies previously conducted [179].

Some studies showed that addition of CO₂ during mixing can result in a rapid change in the microstructure of cement matrix. The addition of the CO₂ to hydrating cement paste results in the formation of nano carbonate particles with the formation of fibrous C-S-H products. This results in the formation of gel which exhibits better mechanical properties than the control specimen [180]. Additionally, it has been reported that early mixing of CO₂ results in strength gain without affecting the long-term strength of concrete [181]. This is in accordance with our experimental results as well. The carbonation carried out at lower pre-carbonation durations resulted in higher strength gains which can be attributed to the carbonate particulate formed which results as a nucleus for further hydration products resulting in a stronger cementitious matrix [182].

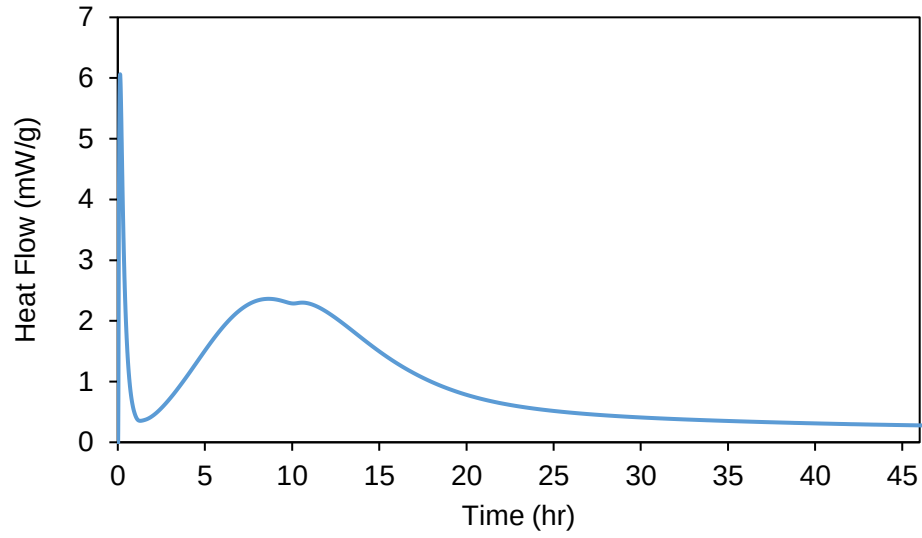


Fig. 21. Thermal profile for hydration of OPC

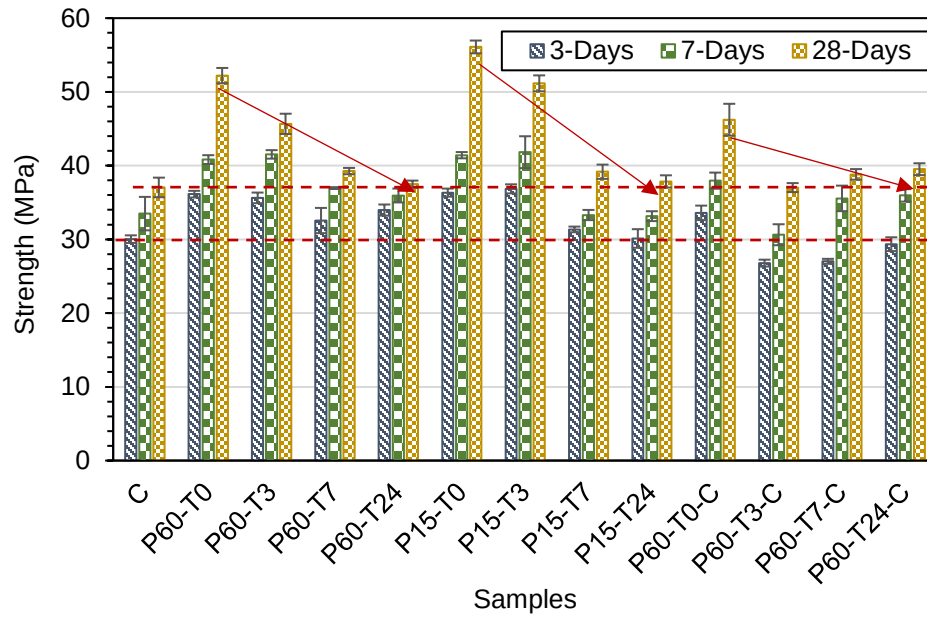


Fig. 22. Compressive strength of cement pastes specimens

4.2 CO₂ uptake and TGA

The thermal decomposition of cement paste generally experiences three main stages which are referred to as dehydration, decarbonation, and dehydroxylation [183]. The percentage

weight loss and derivative weight loss of the representative specimen is shown in Fig. 23. The peaks for portlandite and calcium carbonate were identified in the range of 330- 480 °C and 520- 700 °C, respectively [184]. The initial loss in the range of 50-170 °C is due to decomposition of components related to monosulfoaluminate, C-S-H gel, ettringite, and evaporation of free water [185]. The calcium carbonate can be present in different polymorphs including amorphous calcium carbonate, calcite, aragonite, and vaterite [186]. Among these polymorphs, the calcite shows the best thermal stability and decomposes at higher temperature. At higher temperature, the calcium carbonate completely decomposes into quicklime (CaO) and CO₂ [187]. In comparison to calcite, the amorphous calcium carbonate has the lower thermal stability [188]. From Fig. 23, the decomposition of calcium carbonate can be divided into two stages. First stage from 500-620 and second stage from 620-700. The first peak in the region can be ascribed to the decomposition of amorphous calcium carbonate and the second peak can be attributed to the decomposition of calcite [189].

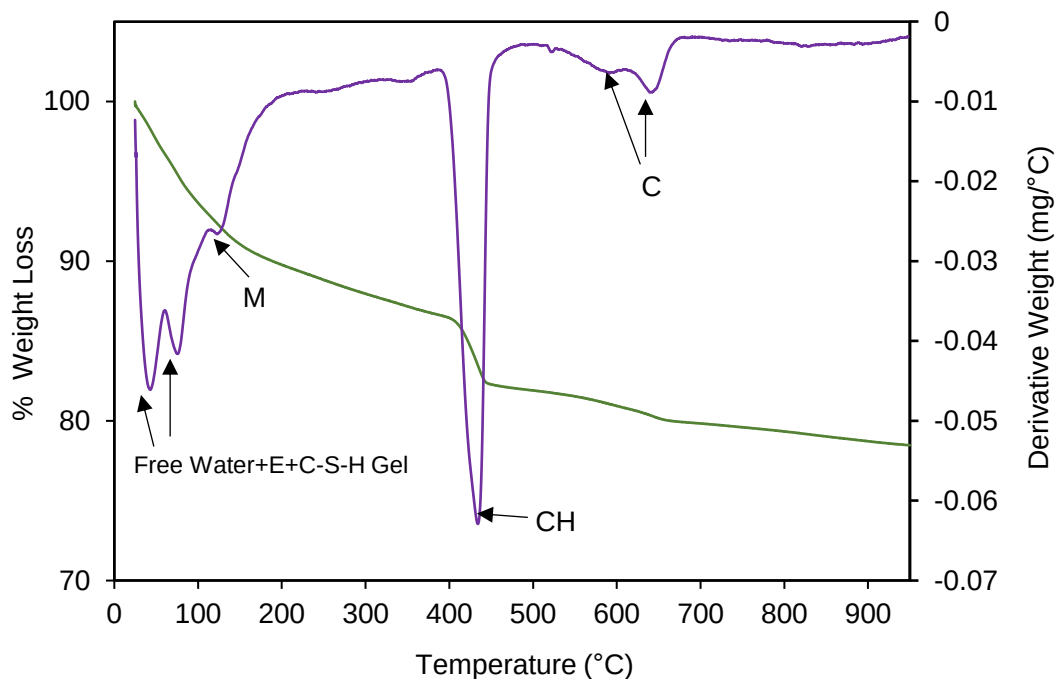


Fig. 23. TGA curves for C-60-0 (E-Ettringite, CH- Portlandite, C-Calcite, M-Monosulfoaluminate)

The mass loss in TGA was used to calculate the CO₂ uptake and the amount of calcium carbonate and portlandite in the specimens due to their carbonations at different pre-carbonation durations. Table 4 represents the summary of CO₂ uptake and content of portlandite and calcium carbonate in specimens. The concentration of these phases was analyzed to gain insights into the hydration and carbonation behavior of the cement paste and to evaluate the associated phase transformations. The loss of mass in the curves showed that the mass of calcium carbonates decreased and of portlandite increased with the increase in the pre-carbonation duration. The carbonation of portlandite is slower as compared to Ca²⁺ ions [190]. As portlandite forms during longer initial hydration durations, carbonation becomes less effective compared to shorter pre-carbonation durations. At early initial hydration stage, abundant Ca²⁺ is directly available for carbonation which results in direct formation of calcium carbonate in the specimens.

The CO₂ uptake was highest in samples carbonated at lower initial hydration ages, as the abundant free Ca²⁺ ions readily available for reaction led to the significant formation of calcite, thereby reducing portlandite formation in the specimens. However, the reduction in portlandite content was not that significant since the carbonation was done for a shorter duration (3 h). With an increase in the initial hydration duration, the CO₂ uptake decreased. This reduction can be attributed to more extensive hydration processes, which consumed the available Ca²⁺ ions, resulting in lower calcite content. This indicates that at higher initial hydration duration, carbonation is not as effective. These results are consistent with the

observed strength increase in the specimens, with samples carbonated at shorter initial hydration durations exhibiting the highest strength. Strength decreased as the initial hydration duration increased.

The specimens that were further carbonated after initial carbonation did not show enhanced carbonation. This indicates that carbonation done in intervals is not as effective. This is also in agreement with strength comparison. The comparison between the specimens that were carbonated at different CO₂ gas pressures, revealed that the pressure does not affect the specimens to a high degree. The high pressure resulted in slightly more diffusion and subsequently slightly increased CO₂ uptake than the samples that were carbonated at 15 psi. For example, a CO₂ uptake of 2.78% and 2.30% was observed for the specimens that were carbonated right after casting at 60 and 15 psi, respectively. It can be concluded from TGA results that the effect of carbonation curing is highly dependent on the carbonation start time after hydration starts.

Additionally, a strength factor based on total CO₂ contribution with respect to strength was calculated for all the specimens. Approximately, 0.822 ton of CO₂ is produced per ton of clinker [191]. This CO₂ released was divided by the strength of the control specimen to find the CO₂/MPa factor which came to be 22.1. Carbonation curing resulted in CO₂ uptake by specimens which reduced the CO₂ footprint of the carbonated specimens. The % of CO₂ uptake was subtracted to find the net CO₂ emissions of the carbonated specimens and was divided by the respective strength of carbonated specimen to find the CO₂/MPa factor, listed in Table 3. It is evident that the CO₂ released per MPa of strength significantly reduced for specimens carbonated at lower pre-carbonation durations. This factor provides strength efficiency of carbonated specimens with lower values indicating higher efficiency.

Table 4. CO₂ uptake and portlandite content of specimens

Specimen ID	CO ₂ uptake (%)	Portlandite (%)	Calcium Carbonate (%)	CO ₂ /MPa
P60-T0	2.78	18.8	4.0	15.3
P60-T3	2.61	17.3	3.8	17.5
P60-T7	2.61	18.3	3.8	20.4
P60-T24	2.70	19.4	3.9	21.3
P15-T0	2.30	17.8	3.3	14.3
P15-T3	1.53	17.5	2.2	15.8
P15-T7	1.49	17.4	2.2	20.7
P15-T24	1.71	18.5	2.5	21.3
P60-T0-C	2.15	17.4	3.1	17.4
P60-T3-C	1.45	18.8	2.1	21.9
P60-T7-C	1.28	19.2	1.8	20.9
P60-T24-C	1.75	18.6	2.5	20.4

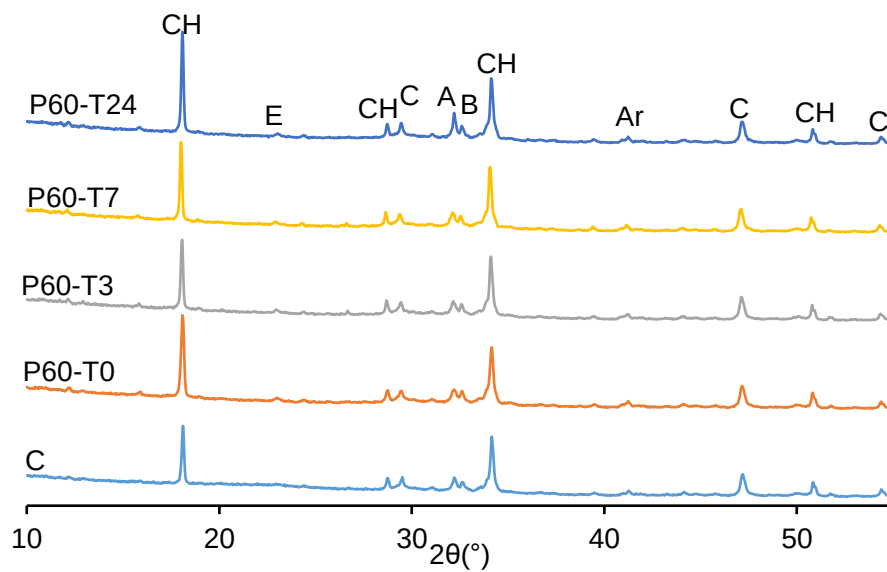
4.3 XRD

XRD was performed on all the specimens to study the mineral composition and identify potential changes due to the carbonation curing of hydrating cement. Fig. 6 represents the XRD patterns of carbonated samples along with the control uncarbonated sample. The initial hydration duration, carbonation pressure, and post-carbonation curing regimes were investigated in the study. The peaks for portlandite, ettringite, calcite, and hydrates were

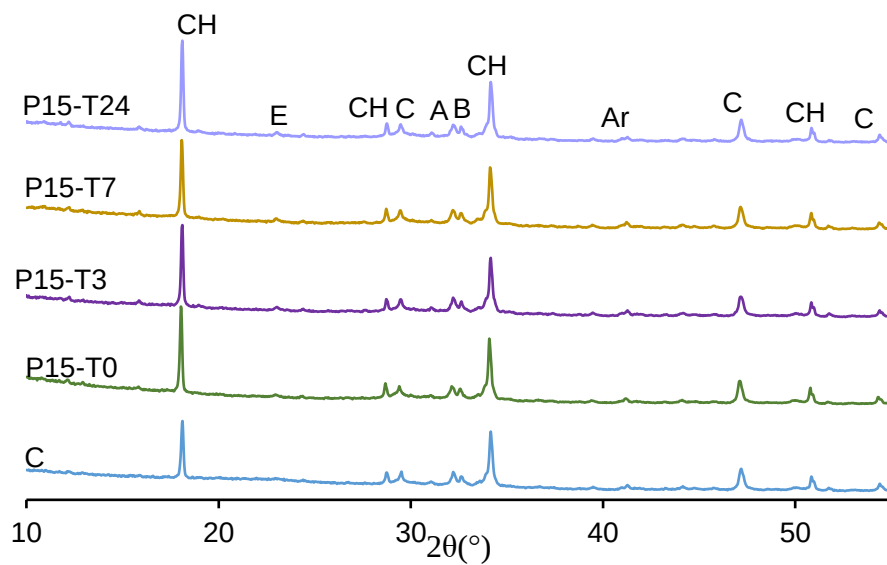
identified in all the samples. Additionally, minor peaks associated to unreacted alite (C_3S) and belite (C_2S) were also present.

The intensity of calcite and portlandite peaks varied across specimens which indicated differences in carbonation levels. The specimens with longer initial hydration durations showed significant portlandite peaks than those specimens carbonated at lower initial hydration durations. For instance, the P60-T24 showed higher intensity of CH at 2θ value of about 18° than other carbonated specimens of the same series as shown in Fig. 24 (a). Similar trends can be seen in the other carbonated specimens as well in Fig 24. (b) and (c). This was also in agreement with TG/DTG which showed higher values of portlandite at longer pre-carbonation durations. This can be attributed to the precipitation of Ca^{2+} and OH^- ions to form portlandite. With longer initial hydration durations, the Ca^{2+} ion decrease in the pore solution while the amount of portlandite increase [192]. Whereas, for shorter initial hydration durations, the Ca^{2+} ions react with the carbonate ion to form calcite without forming portlandite. This results in hindering the formation of portlandite at early ages and allows the formation of portlandite at post-carbonation hydration of cement paste. For longer pre-carbonation durations, well-defined crystalline portlandite is formed in the beginning. The carbonation of portlandite is slower than the carbonation of Ca^{2+} ions [190]. Additionally, the post-carbonation curing allows the continuation of hydration which results in increased portlandite intensity at 28-day testing [178]. This shows that early-age carbonation doesn't hinder further hydration. It has been reported that the concentration of CO_2 plays a vital role during carbonation than its pressure. The pressure does not have significant effects on early age carbonation [193]. Ettringite was also identified in all the specimens. Irrespective of the pre-carbonation duration, the ettringite remained stable in

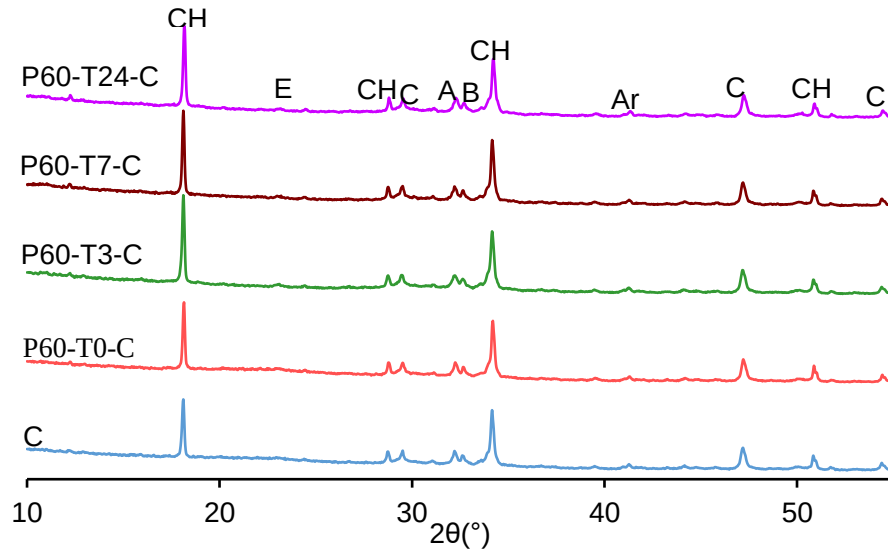
all the samples. Many studies have claimed ettringite to be vulnerable to carbonation which results in the formation of calcite, gypsum and $\text{Al}(\text{OH})_3$ [194,195].



(a) Carbonated at 60 psi



(b) Carbonated at 15 psi



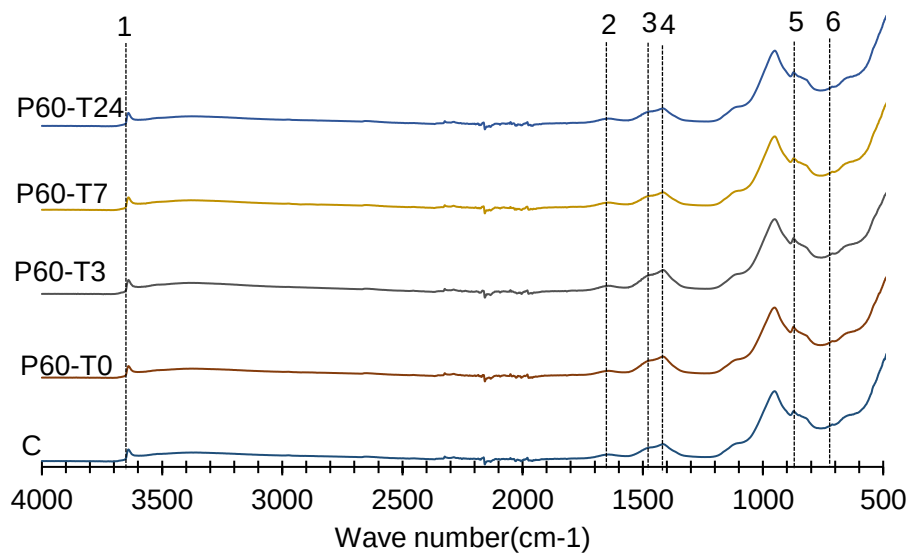
(c) Subsequent carbonation for another 48 h

Fig. 24. XRD spectra of cement paste at 28-days (Alite -A, Belite-B, Ettringite-E, Calcite-C, Portlandite-CH, Aragonite-Ar)

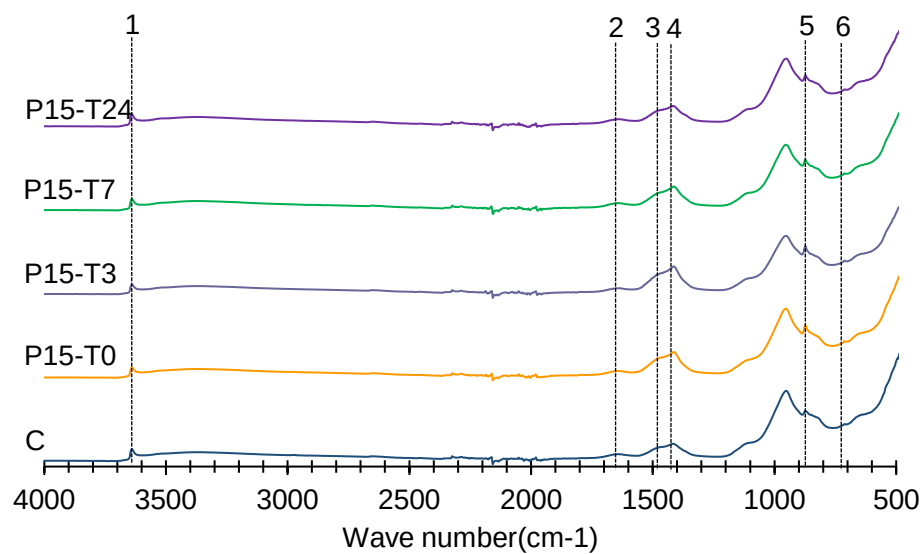
4.4 FT-IR Spectra

FT-IR spectra of control and carbonated specimens are shown in Fig. 25 with initial hydration duration varying from 0 to 24 h. The low transmittance in the spectra corresponds to the higher percentages of chemical components present [196,197]. The O-H bond present in $\text{Ca}(\text{OH})_2$ is assigned at 3642 cm^{-1} , represented by band 1 in Fig. 25 [198]. This band identifies the presence of $\text{Ca}(\text{OH})_2$ and the bond diminished for higher carbonation degrees. The H-O-H present in the chemically bonded water is attributed to the band 2 at 1650 cm^{-1} [199]. The band reduced for specimens with high carbonation degree which indicates that increased carbonation tends to reduce the chemically bonded water [192]. Slight shifts in the corresponding bands were observed for carbonated samples which can be attributed to strongly bonded water with hydration products [193]. The bands 3 and 4

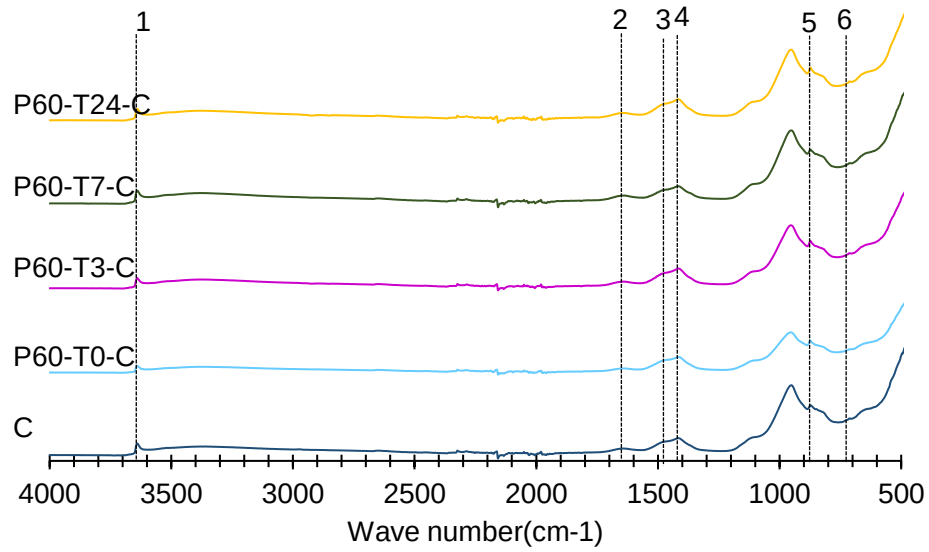
present at 1470 and 1417 cm^{-1} , respectively, can be assigned to the symmetric stretching (ν_3) of C-O bond [200,201]. Additionally, the bands 5 and 6 at 875 cm^{-1} and 714 cm^{-1} respectively are attributed to the in plane (ν_2) and out of plane (ν_4) bending vibration of CO_3^{2-} [202]. These bands represent carbonate groups and as the carbonation increases the peaks of these bands also increase. A slight shift in the phase corresponding to CO_3^{2-} was also observed, with the increase in initial hydration durations. It can be attributed to varying degrees of carbonation. The changes in spectra present between 960 to 1080 cm^{-1} corresponds with the hydrate phases of calcium and silicate. The exact position of these bands depends on the Ca/Si ratio [98]. The shift in this region can be attributed to the synergetic effect of hydration process and silica gel. Moreover, no new peaks were formed with the increase of initial hydration duration for early-age carbonation. It has been reported in the literature that subsequent hydration after carbonation results in modifying the polymerization of C-S-H. This enhances the bonding between calcite and C-S-H resulting in a stronger hybrid [193]. This analysis indicates that optimal initial hydration duration with pressure enhances carbonation and enhances the formation of calcium carbonate.



(a) Carbonated at 60 psi



(b) Carbonated at 15 psi



(c) Subsequent carbonation for another 48 h

Fig. 25. FT-IR spectra of control and carbonated specimens (1: O-H in $\text{Ca}(\text{OH})_2$, 2: ν_2 of H-O-H, 3: ν_3 of CO, 4: ν_3 of CO, 5: ν_2 of CO_3^{2-} , 6: ν_4 of CO_3^{2-})

4.5 SEM-EDS

SEM analysis was conducted for the control and carbonated specimens as shown in Fig. 8. The SEM indicates that the carbonated specimens had a denser microstructure as compared to the control specimen. Fig. 26 (a) shows the microstructure of uncarbonated specimen. Capillary pores are visible in the control specimens. Fig. 26 (b) – (c) represents the microstructure of carbonated samples. The carbonation resulted in reducing the porosity of the cement paste. Similarly, the identified carbonates are shown in Fig. 8 (d) and their corresponding EDS spectra are presented in Fig. 26 (e) and (f). The spectra show the elements of calcium carbonates formed because of carbonation. Carbonation with ambient pressure results in the production of crystalline calcium carbonates. Carbonation tends to generate well-distributed calcium carbonate, filling the pores present in the structure

between the C-S-H. The C-S-H serves as a platform for carbonation reaction and allows the formation of calcium carbonate around its surface [193]. The EDS spectra show high carbon with calcium and silica. This indicates that the calcium carbonate formed is intermingled with the C-S-H gel. This results in generating a hybrid matrix of carbonates and hydrates which contributes to the better performance of carbonated specimens. The literature indicates that longer carbonation duration of specimens results in the improved size of calcium carbonate with better crystallization degree as well [203]. The carbonation forms crystals of calcium carbonate that are placed at irregular intervals on C-S-H surface, leading to enhanced microstructure and reduced porosity. This conclusion agrees with previous studies conducted on carbonation curing [96,97,204,205].

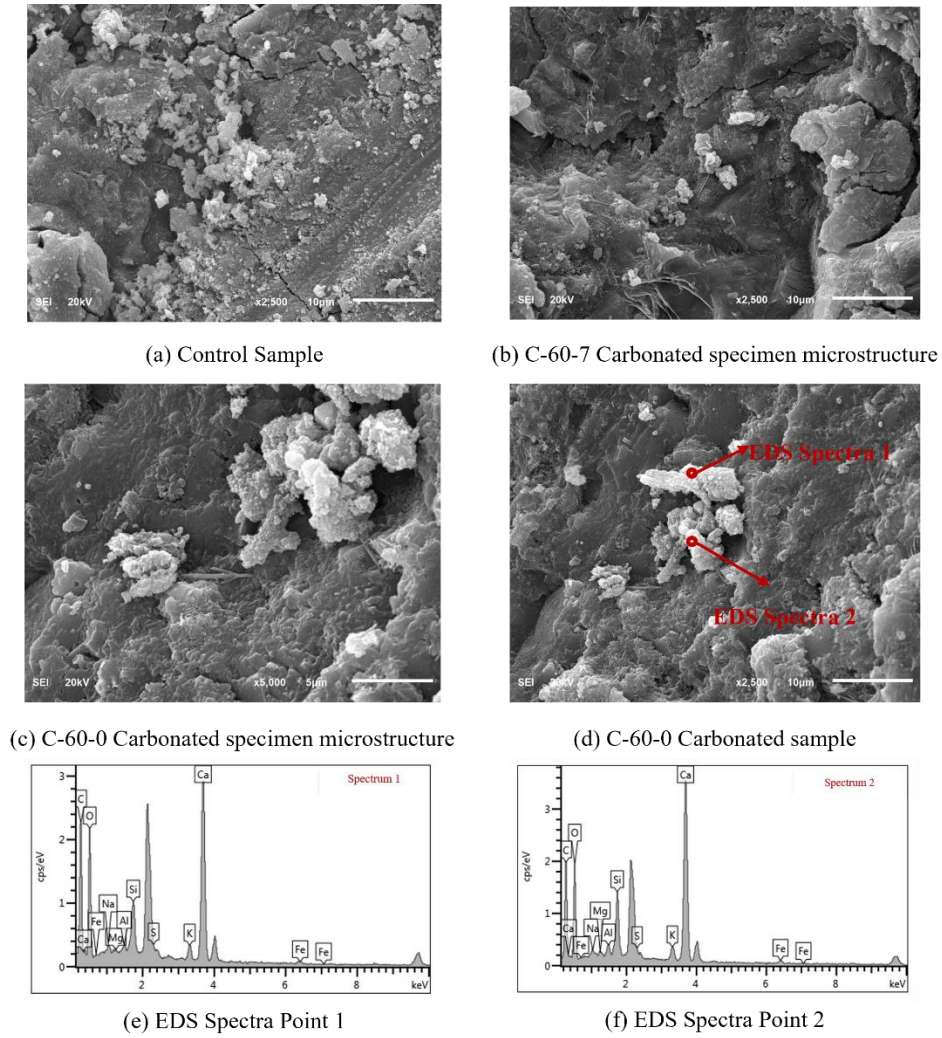


Fig. 26. SEM images and EDS spectra of carbonated specimens.

4.6 pH analysis

Fig. 27 shows the pH values of the specimens. The pH of the specimens was calculated by taking particles from different regions of specimens to get an average pH value. The specimens were carbonated for 3 h at various initial hydration durations and the pH was calculated at 3 and 28 days. The measured pH values of all the samples lie within a range of 12.25–12.79. The uncarbonated control specimens showed the highest pH value at both 3 and 28 days with values of about 12.52 and 12.69, respectively. The specimens that were

further carbonated for 48 h after initial carbonation showed the lowest pH values. The lowest value of pH was 12.25 at 3 days which increased to 12.45 after subsequent moisture curing till 28 days. This indicates that the moisture curing after carbonation slightly enhanced the alkalinity of the pore solution, potentially by the formation of portlandite in the cement paste. These results are in line with the findings from compressive strength, XRD and TG analyses results.

The specimens which showed the highest strength in each group (i.e, carbonation started at 0 h initial hydration), had the lowest pH in their respective groups. For example, specimen C-60-0 showed the lowest pH among the specimens carbonated for 3 h at 60 psi. Similarly, C-15-0 showed the lowest pH among the specimens carbonated for 3 h at 15 psi. This indicates that shorter initial hydration durations have the potential to significantly reduce alkalinity through increased carbonation while maximizing strength gain. In general, the pH values for carbonated specimens were lower than the uncarbonated control specimen, but it is enough to protect the reinforcement in concrete from corrosion. The studies have reported that a pH below 11 can result in the initiation of corrosion of steel reinforcement in concrete [169]. The selected carbonation level resulted in a slight decrease only which is not significant to initiate corrosion. The observed trends highlight that proper carbonation duration combined with initial hydration durations and subsequent curing regimes can result in achieving the optimized properties while avoiding the adverse effects on steel reinforcement present in concrete.

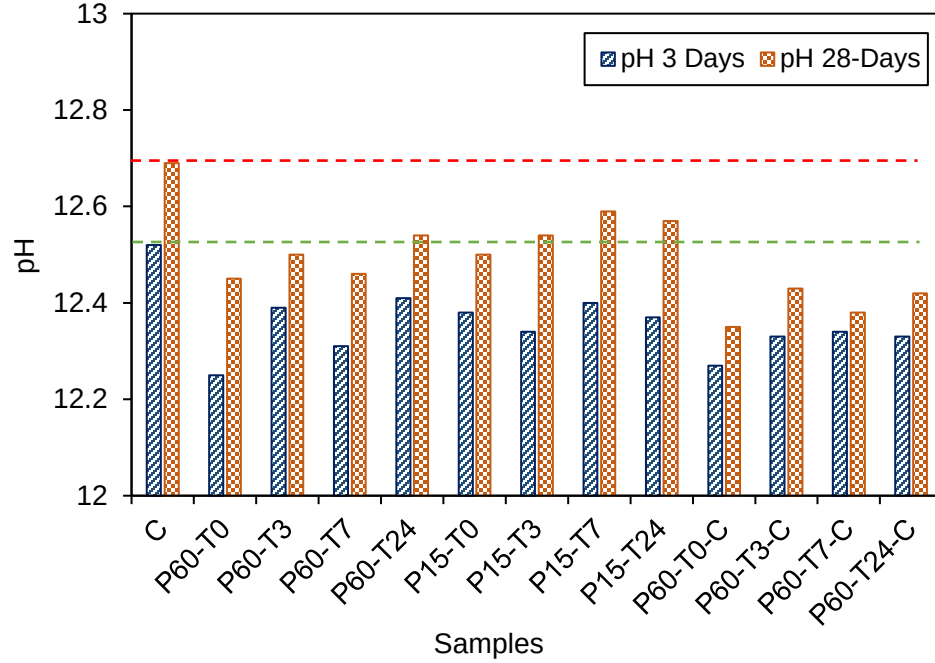


Fig. 27. pH analysis of specimens

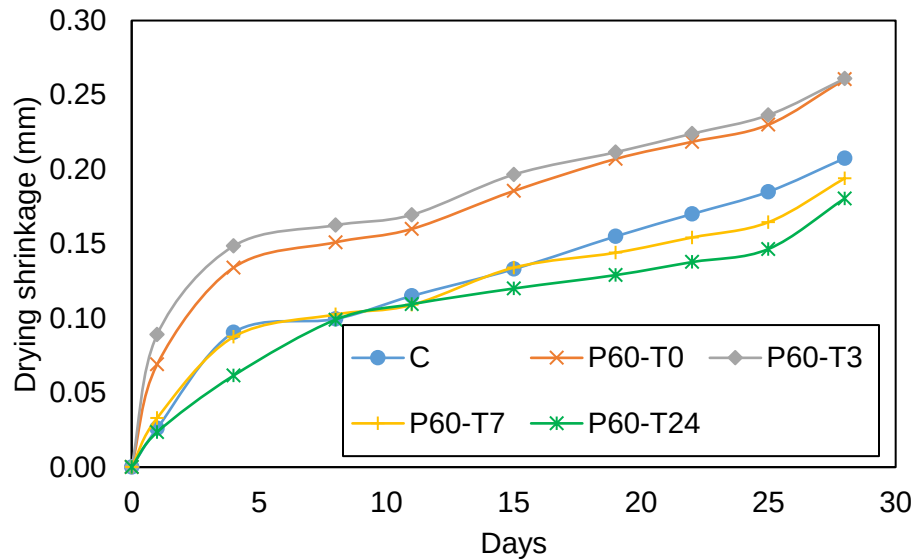
4.7 Drying Shrinkage

Fig. 28 represents the drying shrinkage variations with duration for all the specimens. All the carbonation regimes are plotted against the control specimens to study the effects prominently. All the carbonated specimens with lower pre-carbonation duration showed the highest increase in drying shrinkage. Specimens that were carbonated at 7 and 24 h pre-carbonation duration showed comparable shrinkage with the control samples. The samples that were carbonated at 15 psi showed the most increase in drying shrinkage at all pre-carbonation durations. The high drying shrinkage of carbonated specimens can be attributed to shrinkage associated with shrinkage due to carbonation reaction on the surface of specimens. Moreover, the additional water loss due to the exothermic reaction of carbonation resulted in higher drying shrinkage for carbonated specimens. The specimens that showed the highest increase in strength also had higher shrinkage. This indicates that

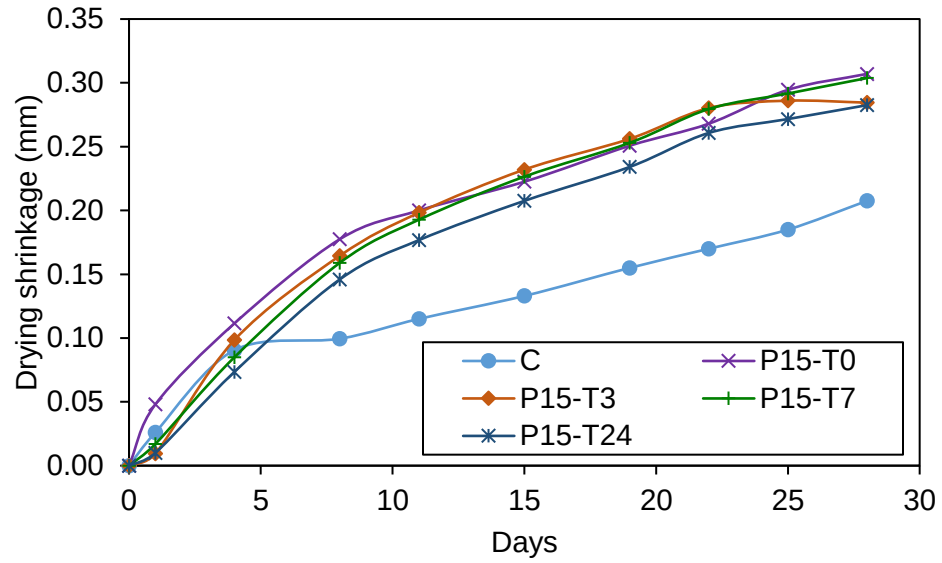
the specimen where more carbonation occurred resulted in higher drying shrinkage. At lower pre-carbonation duration, the abundance of Ca^{2+} ions readily react with CO_2 , forming calcite directly, which contributes to a dense microstructure but also results in considerable shrinkage as water is consumed by carbonation reactions. Comparatively, specimens with extended pre-carbonation durations (7 and 24 hours) exhibited lower shrinkage. This reduced shrinkage is likely due to an increase in hydration products and a decrease in carbonation products. Since the carbonation was low for high pre-carbonation durations, the water loss due to carbonation is also less resulting in lower shrinkage in these specimens. To control the high value of drying shrinkage, it has been reported that spraying water on the surface of specimens immediately after carbonation can be used to control the shrinkage associated with carbonation. This results in compensating water loss due to carbonation reaction [206].

Different conditions result in different drying shrinkage. Shrinkage is an important aspect that needs to be considered during design as well. Different standards have set limits for shrinkage as higher shrinkage can result in impairing the intended functionality of the structure. ASTM C157 limits the shrinkage value at 400 micrometer or lower [207]. Some authors have also provided models to predict shrinkage which also specifies the shrinkage to be around 400 micrometer at 28-days [208]. The maximum value of drying shrinkage observed for our specimens was under the specified limits for all the carbonated specimens. The highest drying shrinkage was shown in P15-T0 specimen with a value of around 300 micrometers. The carbonation resulted in slight increase in shrinkage values, however, they are still within the acceptable limit.

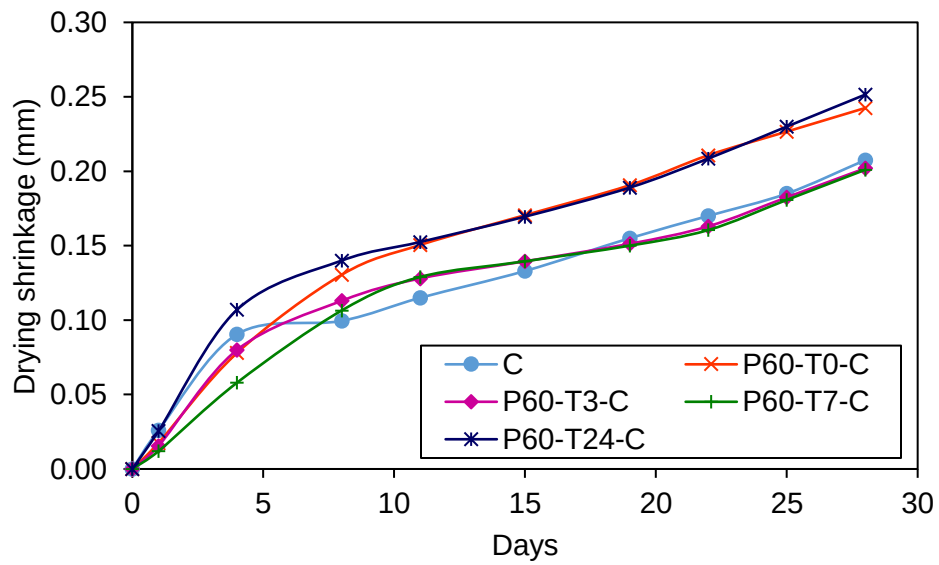
All the cement composites undergo some extent of carbonation due to atmospheric CO₂ during their service life. This carbonation shrinkage results in formation of cracks in the structure as well [114]. In carbonation curing, the specimens undergo some extent of carbonation at early stages, hence the secondary carbonation due to atmospheric CO₂ is lower than the control specimens. Some studies have reported that carbonation-cured samples show less shrinkage in long-duration study due to lower potential of secondary carbonation shrinkage [113,209].



(a) Carbonated at 60 psi



(b) Carbonated at 15 psi



(c) Subsequent carbonation for another 48 h

Fig. 28. Drying shrinkage of specimens

CHAPTER 5

IMPACT OF CARBONATION CURING ON RED MUD-INCORPORATED CEMENT COMPOSITES

5.1 Material Characterization

OPC Type 1 was used along with red mud obtained from local industry. The chemical composition of both OPC Type 1 and red mud are given above in Table 1. Dune Sand taken locally with a specific gravity of 2.59 was used to prepare mortar specimens for carbonation depth, compressive strength, and drying shrinkage. The particle size distribution of OPC, red mud, and dune sand was carried out using a particle size analyzer shown in Fig. 29.

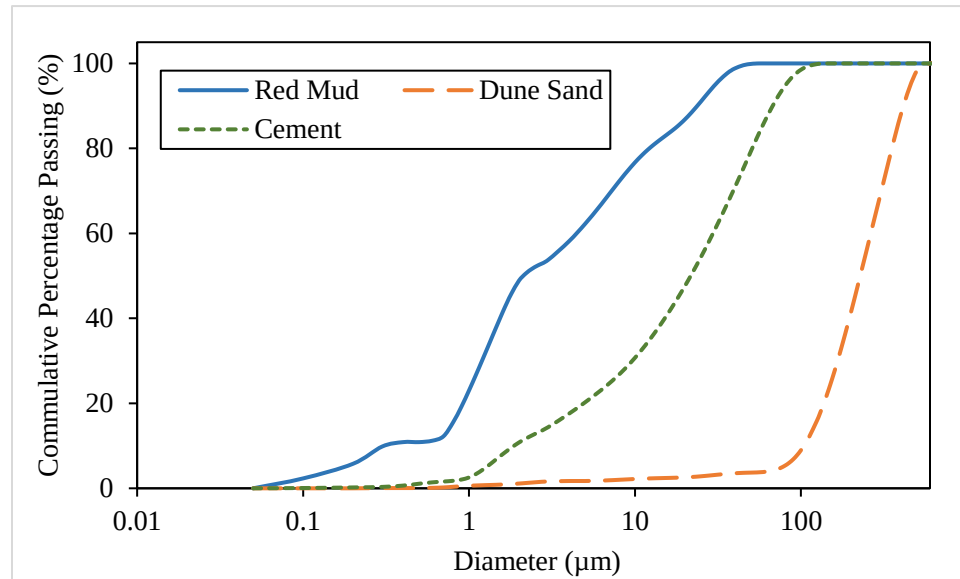


Fig. 29. Particle Size Distribution of OPC, Red Mud, and Dune Sand

Additionally, phase identification of OPC and Red mud was also carried out. Fig. 30 shows the XRD of OPC and red mud. The phases identified for red mud include quartz, calcite,

cancrinite, kaolin, diaspore, and hematite while OPC showed phases of alite, belite, C_3A , and C_4AF . Fig. 31 shows the thermal analysis of red mud and OPC. The OPC showed a stable pattern with a mass loss of around 2 % only which can be attributed to the decomposition of gypsum in cement [210]. While the red mud showed around 12% mass loss with peaks at different intervals. The mass loss of red mud occurs in three stages between 120-500 °C attributed to dihydroxylation and decomposition of amorphous phases in red mud. The mass loss between 550-750 °C is attributed to the decomposition of calcite present in red mud while the mass loss above 800 °C is attributed to the formation of magnetite resulted from decomposition of hematite [211].

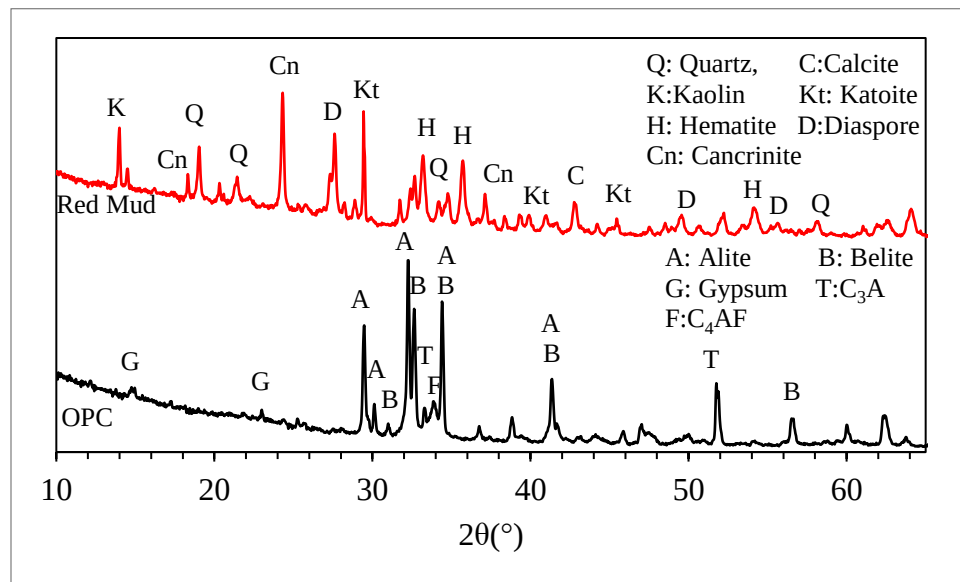


Fig. 30. XRD Spectra of OPC and red mud

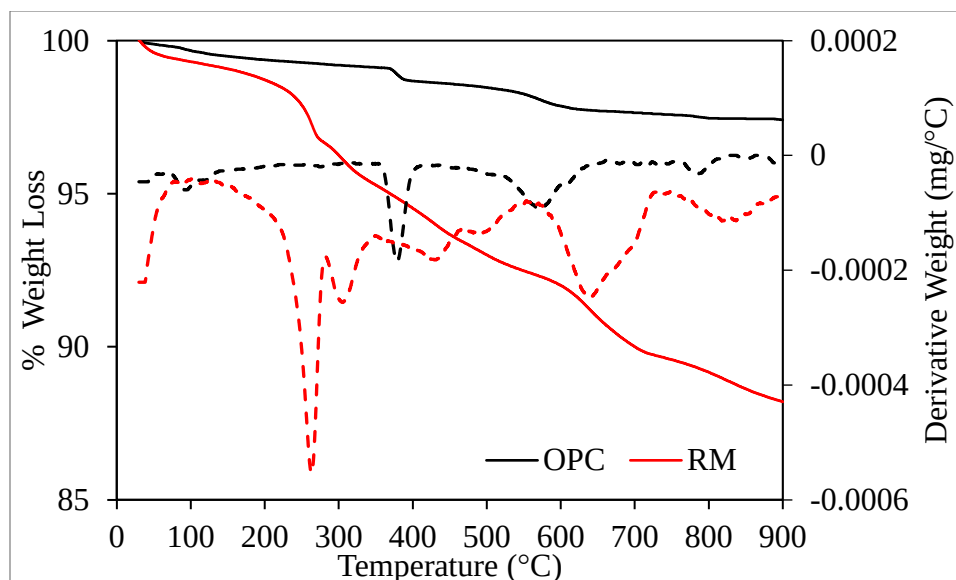
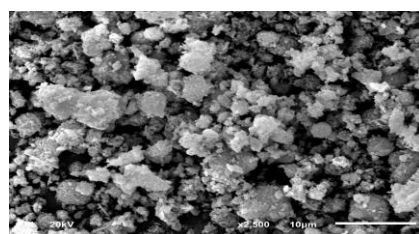
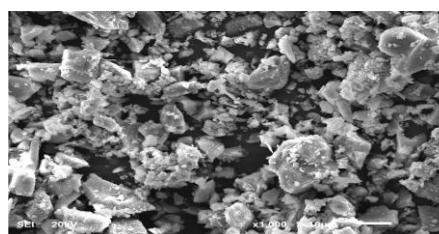


Fig. 31. TGA curves for OPC and red mud

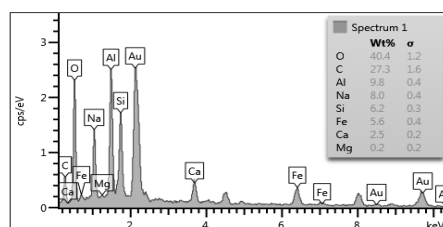
Additionally, shapes of red mud and OPC were observed by using SEM given in Fig. 32. The OPC particles were bigger as compared to red mud with crystalline shapes. The red mud on the other hand is smaller particles with irregular shapes. The EDS of OPC and red mud was also carried out using area EDS to study the elemental composition as well.



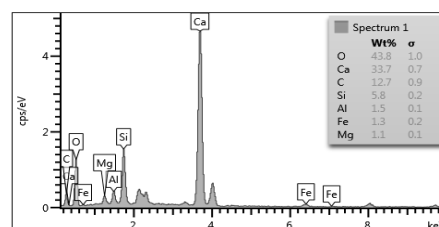
(a) Red Mud



(b) OPC



(c) EDS of Red Mud



(d) EDS of OPC

Fig. 32. SEM images of red mud and OPC with respective EDS spectra

5.2 Fresh state properties and heat of hydration

As the water is mixed with the cement paste, the hydration reaction starts, which contributes to the hardening of the cement paste. During hydration, heat is also released, which is shown in Fig. 33. The other fresh state properties, including initial and final setting time and flow of cement paste, are shown in Fig. 34. During the first stage of hydration, there is an increase in the heat release which is attributed to the wetting and neutralization of charges present on the surface of particles of C_3S and C_3A . During the initial reaction, C_3A reacts with the sulfate to form ettringite converted into calcium mono-sulfoaluminate [212]. After this, the induction stage begins, with a low dissolution rate. During this stage, the concentration of calcium ions is below the saturation limit, and sulfate adsorption causes a decrease in the solubility rate of C_3A [213]. During these stages, the effect of red mud is not significant. When all the alumina is consumed, the system is oversaturated, accelerating the precipitation of portlandite and C-S-H. Red mud is high in alumina content, which increases the matrix's overall alumina content. As we increase the percentage of red mud, there is a delay in initiating the third stage of hydration, which is acceleration, which occurs after approximately 3 hours of mixing water with binder. Similarly, with the increase in the percentage of red mud, the peak of the acceleration period increases. During this period, the nucleation rate is related to the surface area available for reaction. As the red mud is finer than the cement, the increase in heat can be attributed to the increase in surface area due to the fineness of the red mud [214].

The initial and final time of cement paste with the same w/c ratio slightly increased with the increment in the percentages of red mud. This can be attributed to the reduction of

content. The red mud reactivity with increasing amounts showed delayed initiation into the acceleration phase, which correlates with the initial and final setting time. Lastly, the flow of red mud paste indicates that increasing the amount of red mud reduces the flow. This flow can be attributed to the high fineness of red mud. As the red mud is finer, the demand for water to maintain flow increases. It has been reported that the higher surface area produces Van Der Waals force, leading to particle aggregation [215]. From Fig. 32 we can see the fine size and irregular shapes of red mud particles. The increase in the surface area due to increased fineness traps some water between the particles, resulting in a dry mix. This, in turn, increases friction between particles, reducing the plasticity of the paste [216].

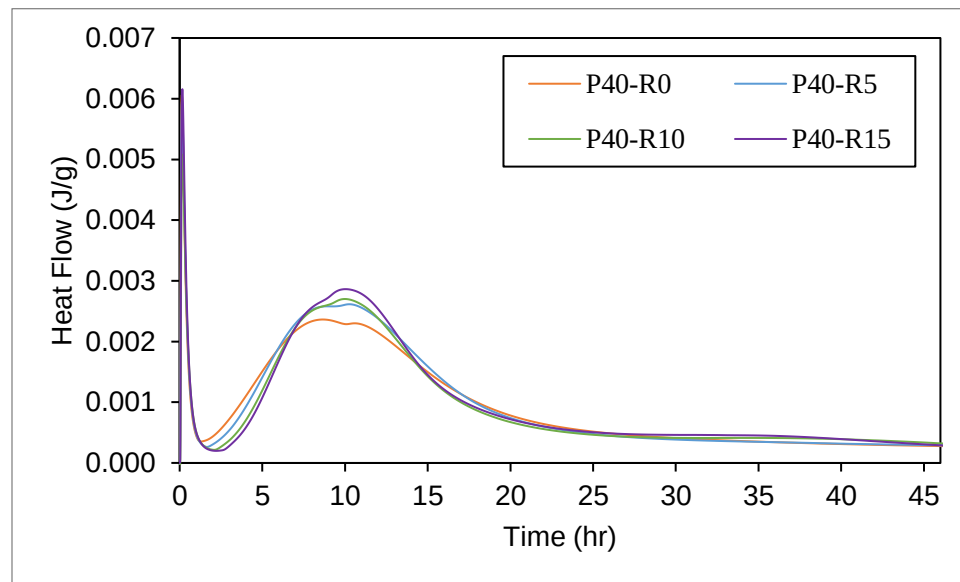


Fig. 33. Thermal Profile for hydration of OPC with different replacements of red mud

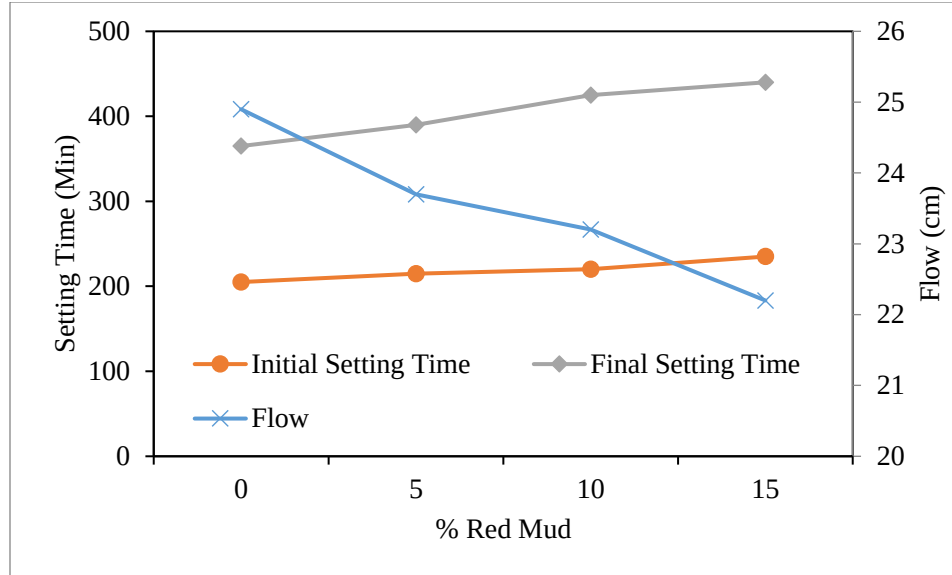


Fig. 34. Fresh State Properties of Cement Paste

5.3 Carbonation degree and pH of pore solution

The carbonation degree of mortar specimens was determined by spraying phenolphthalein indicator on the surface of the discs extracted from the specimen. The test was conducted for red mud as a sand replacement with 0.5 w/c and cement replacement with 0.4 w/c. It was carried out at 3 days after carbonation and at 28 days after subsequent moisture curing after early-age carbonation. Additionally, the pH of the paste specimen was carried out at 28 days on samples taken from various depths of the mortar specimens. The mortar specimen with red mud as cement replacement showed no degree of carbonation. This can be attributed to the less water available for carbonation, resulting in a lower carbonation degree. The mortar specimens with red mud as sand replacement showed some regions where the indicator turned colorless. The colorless region indicates the region with a pH below nine, which is critical for reinforcement corrosion. The remaining region does not mean that no carbonation has occurred, but the level of carbonation is not high enough to

reduce the pH below the threshold limit. The test was again conducted for mortar specimens at 28 days. Fig. 35 showed carbonation degree at 3 and 28 days for specimens. The subsequent hydration after early age carbonation resulted in the formation of more hydration products and resulted in the increased pH at 28 days [178]. The 0.5 w/c ratio showed a carbonation degree in contrast to 0.4 w/c, highlighting the importance of the w/c ratio for carbonation. The higher degree of carbonation can be attributed to the fact that a higher w/c ratio results in the development of a porous cementitious matrix, which increases the permeability and allows more diffusion of CO₂ [217,218]. The carbonation degree of specimens with the colorless region was calculated using Eq. 1, and the degree was estimated to be 31%, 14%, 10%, and 5% for mortar specimens with red mud replacement of 0, 5, 10, and 15.

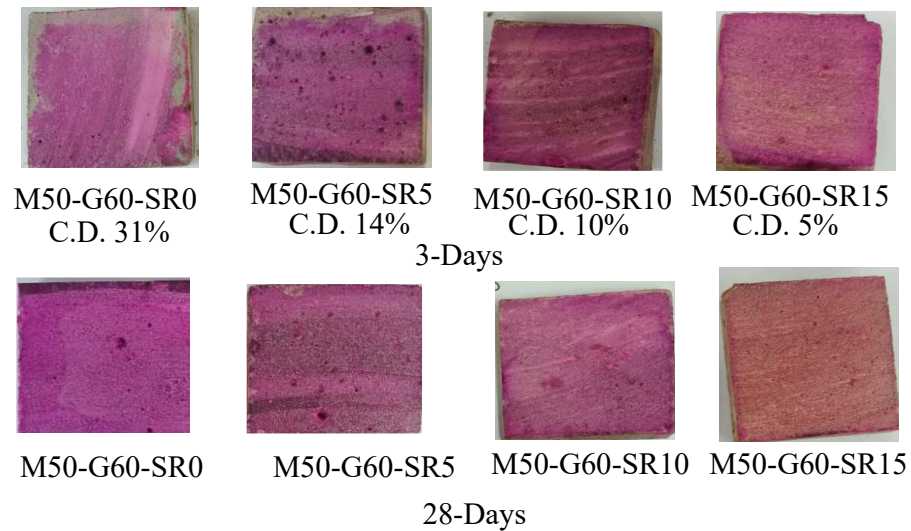


Fig. 35. Carbonation Degree at 3 and 28 days for Mortar Specimens

This indicates that adding red mud, which is alkaline, increases the pH of the pore solution. So, it can regulate the pH of carbonated paste specimens. The pH of paste specimens was also calculated, which is given in Table 5. The control specimens had almost the same pH

in the middle and top regions for all replacements of red mud. The pH of control specimens showed increased red mud content, confirming the carbonation degree results. For carbonated specimens, the pH was calculated at various depths. The outer region showed the lowest pH value, with the value increasing with the depth. This indicates that the top region has the most carbonation, and as the depth increases, the CO₂ diffusion decreases, resulting in reduced carbonation. This result is from the previous research that the carbonation degree increases by increasing the w/c ratio, and the carbonation occurs more on the outer surface than the center region [107]. The red mud has different Na phases present which on reaction with water results in dissolution of strongly basic NaOH. Additionally, the Na₂CO₃ present in red mud also reacts with portlandite to form NaOH [219]. This results in increasing the pH of pore solution of red mud incorporated cement composites.

Table 5. pH of cement pastes specimens at various depths for carbonated and control specimens

Control pH			Carbonated pH				
Sample Id	Top pH	Mid pH	Sample Id	0- 6	7-12	13-18	19-24
				mm	mm	mm	mm
P40-G0-R0	12.76	12.79	P40-G60-R0	12.57	12.67	12.71	12.76
			P40-G15-R0	12.67	12.77	12.78	12.82
P40-G0-R5	12.82	12.86	P40-G60-R5	12.48	12.55	12.7	12.79
			P40-G15-R5	12.52	12.65	12.75	12.85
P40-G0-R10	12.85	12.94	P40-G60-R10	12.56	12.79	12.83	12.85
			P40-G15-R10	12.72	12.86	12.9	12.92

P40-G0-R15	12.9	12.96	P40-G60-R15	12.65	12.85	12.86	12.92
			P40-G15-R15	12.84	12.91	12.95	12.97

5.4 Compressive strength

Fig. 36 represents the compressive strength of cement paste and mortar specimens at 3 and 28 days with different replacements of red mud. Fig. 36 (a) illustrates the strength of cement paste specimens. As indicated in Fig. 36(a), as the replacement percentage of red mud is increased, a decrease in the strength of paste specimens is observed. This can be attributed to the low reactivity of red mud as compared to OPC [220]. The carbonated specimens showed higher strength than the control specimens at 3 and 28 days. The highest strength was demonstrated in specimens containing no red mud at 15 and 60 psi carbonation pressure. The strength of paste specimens containing red mud was increased and was comparable to that of control specimens without red mud at lower replacement of red mud. The increase in the compressive strength of carbonated specimens can be attributed to the formation of calcium carbonate and the densification of pore structure [203]. As the percentage of red mud increased in paste specimens, the strength gained due to carbonation was slightly reduced. This can be attributed to the decrease in the clinker content of cement, which results in the formation of less hydration products. Moreover, the carbonation releases heat due to the formation of stable carbonates from calcium oxide. This generated thermal energy can increase carbonated specimens' compressive strength by improving hydration [176,177]. Additionally, the specimens carbonated at 60 psi showed higher strength gain. This shows that higher pressure resulted in higher degrees of

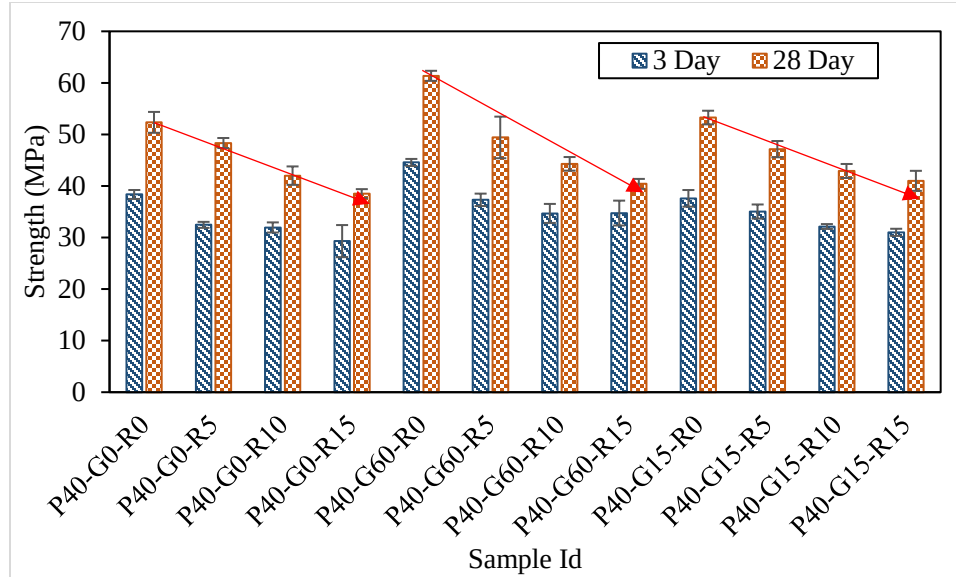
carbonation and strength gain. Higher pressure can help the CO₂ gas diffuse more thoroughly into the cement paste matrix, resulting in higher strength gain.

Fig. 36 (b) shows the compressive strength of cement mortar specimens. The mortar specimens displayed different trends than the cement paste specimens. The strength increases of mortar specimens for normal cured specimens with 0% red mud are also highlighted in Fig 10 (b). The mortar specimens cast with red mud as binder replacement showed an increase in compressive strength up to 10% replacement in 3 and 28 days. For carbonated specimens, the carbonation resulted in a strength gain at 3 days with increasing red mud replacement. However, at 28 days, the specimens' compressive strength decreases compared to control specimens. The carbonated specimen with 0 % red mud has the highest strength increase compared to different replacements of red mud. The subsequent hydration resulted in strength gain for specimens at later stages. As more hydration products are formed due to subsequent hydration, this forms a more dense pore structure [203].

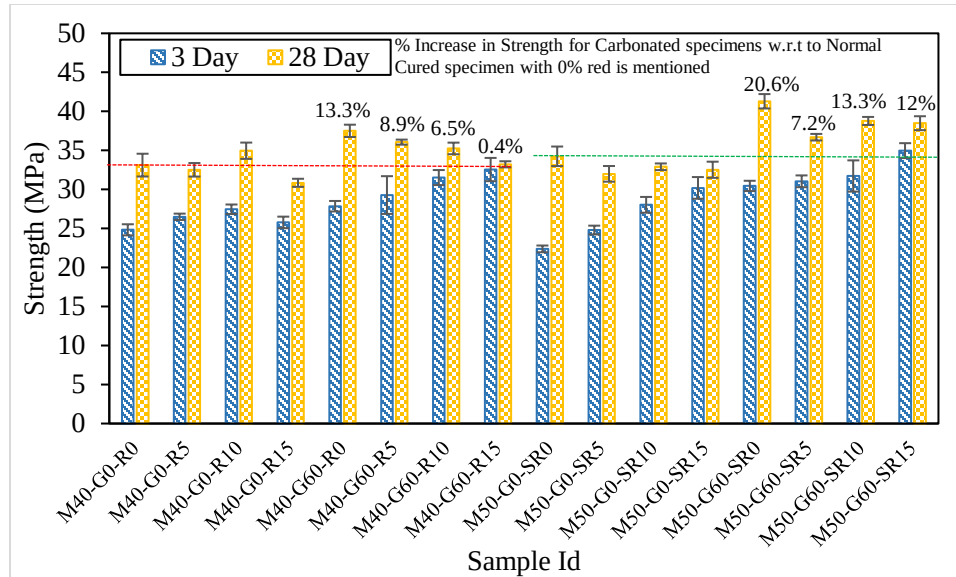
Additionally, all the carbonated specimens had higher strength than the control specimens with 0% red mud and higher strength than the corresponding control specimens. Some studies suggest that using the red mud will gain strength at earlier stages, with the strength decreasing at 28 days [141,221]. Studies have also reported that replacing the red mud up to a specific limit will increase the strength of cement mortar with more increase, resulting in the strength decrease of mortar specimens [222,223]. The effect of different sources of red mud can vary the strength of cement mortar [24]. The carbonation of mortar containing red mud is also enhanced due to the formation of stable carbonates and densification of pore structure. The increase in strength due to incorporating red mud can be attributed to

the higher surface area of the red mud particles. The smaller particle size of red mud makes the mortar denser by filling the voids, which increases strength [224].

Moreover, the mortar prepared with red mud as sand replacement also shows a similar pattern. At 3 days, the increase in the red mud percentage results in an increase in compressive strength. However, at 28 days, the strength of red mud incorporated specimens was lower than the control specimen with 0% red mud. Similarly, the carbonation of specimens resulted in higher strength gain than that of control specimens for all replacements of red mud. The strength increase for carbonated specimens was higher for mortar specimens with a higher w/c ratio. This highlights the role of water in proper carbonation as well. The specimens with a 0.4 w/c ratio showed an increase of 13.3%, 8.9%, 6.5%, and 0.4% with 0, 5, 10, and 15% replacement of red mud from the water-cured control with 0% red mud. While the specimens made with 0.5 w/c showed 20.6%, 7.2%, 13.3%, and 12% gain in strength with 0, 5, 10, and 15% replacement of red mud as compared to water-cured control with 0% specimen red mud for respective series. This study indicates that carbonation can also increase the strength of red mud-incorporated cement mortar. This makes it possible to utilize red mud in cement composites and provide a means for permanent CO₂ storage.



(a) Compressive strength of cement pastes specimens at 3 and 28 days



(b) Compressive strength of mortar specimens at 3 and 28 days

Fig. 36. Compressive strength of cement pastes and mortar specimens with different replacement of red mud at 3 and 28 days

5.5 Drying Shrinkage

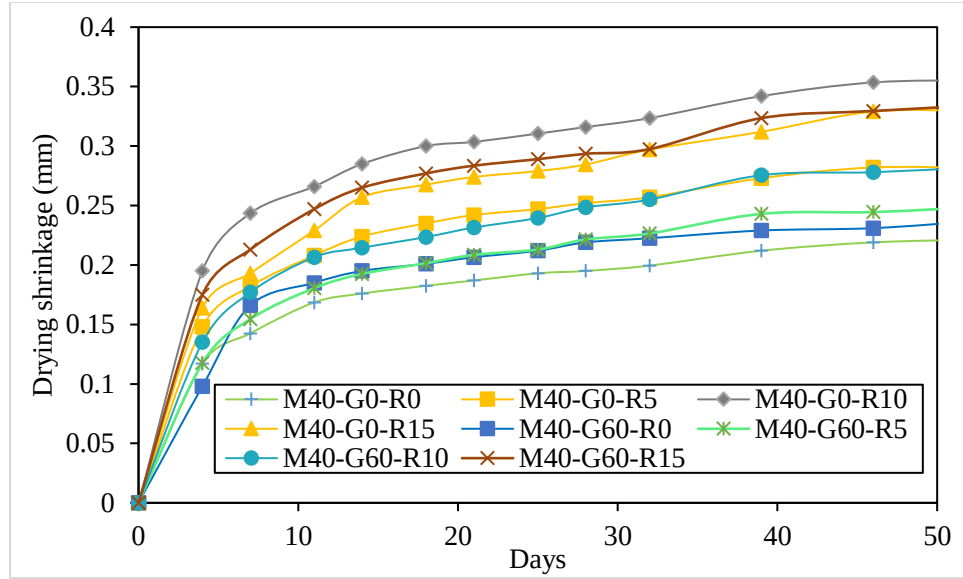
Fig. 37 shows the drying shrinkage of cement mortar specimens. Fig. 37 (a) shows the drying shrinkage of control and carbonated specimens with red mud as cement replacement, while Fig. 37 (b) shows specimens with red mud as sand replacement. As we increase the percentage of red mud in both cases, the drying shrinkage of specimens increases. For the red mud as cement replacement, 10% of red mud showed the highest drying shrinkage. The carbonation of the specimens resulted in a decrease in the drying shrinkage. The highest drying shrinkage of carbonated specimens was also observed for 10% red mud replacement. In both cases, the higher drying shrinkage occurs at earlier stages, which can be attributed to the water moving out of the gel structure, which results in the contraction of capillary walls [225]. The higher w/c ratio resulted in higher drying shrinkage. A higher w/c ratio results in excess water evaporation, resulting in more shrinkage of specimens [226]. The higher content of red mud resulted in higher drying shrinkage values. This increase in the shrinkage can be attributed to higher water loss from the surface of red mud specimens [227,228]. For the specimens with red mud as sand replacement, the highest drying shrinkage was observed for 15% red mud replacement.

The shrinkage of carbonated specimens decreased in both cases. The cement matrix has portlandite content, reacts with CO_2 , and forms stable calcites. CaCO_3 is crystalline and demonstrates excellent dimensional stability. Carbonated specimens have higher stability than controlled specimens [113]. The carbonated specimen with 0% red mud showed a slight increase in the drying shrinkage. The slightly higher shrinkage can be attributed to a higher shrinkage on the specimen's surface and more water loss due to evaporation [206]. Moreover, the control specimen without red mud results in higher carbonation shrinkage.

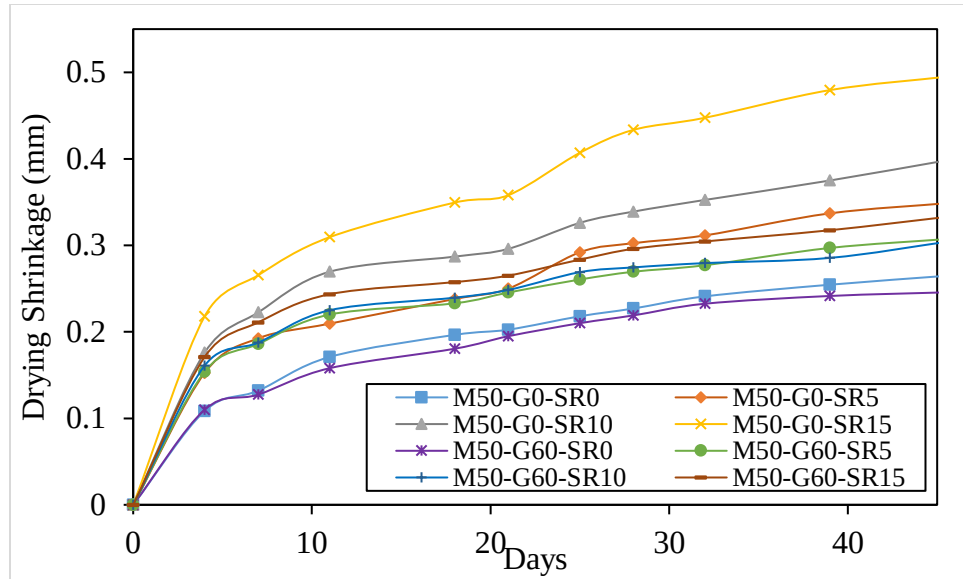
Studies have reported that spraying water on concrete surface can be used to control the shrinkage associated with carbonation [206].

In general, the carbonation resulted in a decrease in the shrinkage for specimens with different replacements of red mud. This indicates that the carbonation can improve the drying shrinkage properties of cement mortar incorporating red mud. The decreased carbonation can be attributed to the red mud's ability to react with CO_2 to neutralize the alkalinity. The carbonation curing of red mud-incorporated mortar results in the sequestration of CO_2 by forming stable carbonates by reaction with oxides of red mud, which does not contribute to carbonation shrinkage. Instead, the formation of stable carbonates results in improving the structural integrity of red mud-incorporated mortar, which reduces the drying shrinkage of carbonated specimens. Many studies have reported that early-stage carbonation results in reduced carbonation in more extended-duration studies. This can be attributed to the low potential of environmental carbonation after early-age carbonation [14,229].

Shrinkage is a critical aspect which needs to be considered during the design of buildings. Different standards have set different limits for shrinkage to ensure that high values of shrinkage do not impair the serviceability of buildings. ASTM C 157 have prescribed limit of 400 micrometer or lower at 28-days [207]. Various studies have reported models to predict shrinkage which also limits the shrinkage at approximately 400 micrometer at 28 days [208]. The values of drying shrinkage for all the specimen under study except P50-G0-SR15 was below 400 micrometer at 28 days. The carbonation curing of the specimen resulted in reducing shrinkage within the limit as well.



(a) Drying shrinkage of mortar specimens red mud as cement replacement



(b) Drying shrinkage of mortar specimens red mud as sand replacement

Fig. 37. Drying shrinkage of mortar specimens

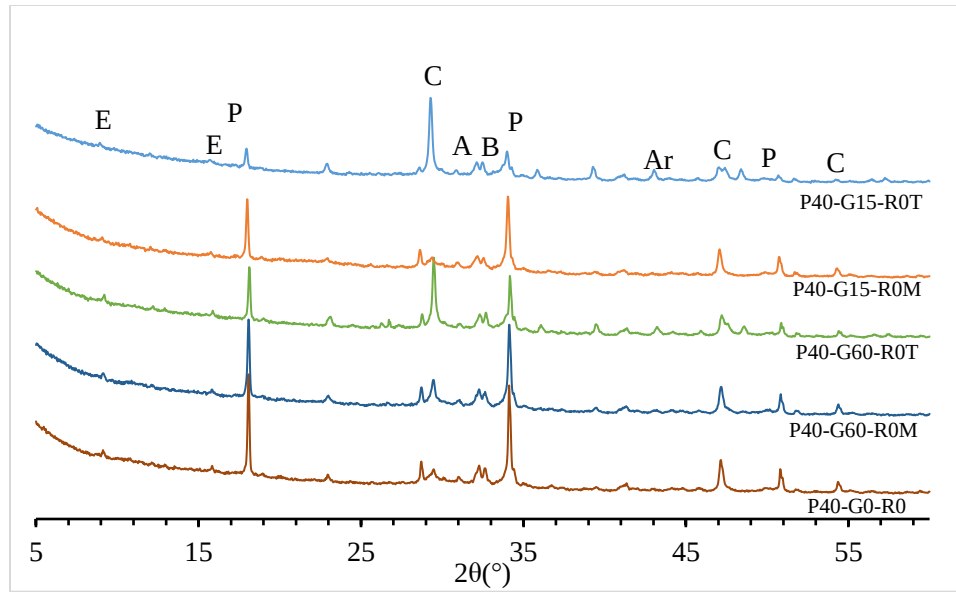
5.6 XRD

XRD was carried out for control, and carbonated specimens were incorporated with different replacements of red mud to identify minerals due to carbonation. The XRD was carried out in two regions for carbonated specimens. The first sample was extracted from specimen top 6 mm thickness, denoted with a T at the end, and the second from the middle region of specimens, denoted with an M at the end of the sample code. Fig. 38 (a)-(d) represents XRD patterns of paste specimens with 0% to 15% red mud replacement. The ettringite, calcite, and portlandite peaks were observed in all specimens. The XRD of specimens also indicates some unreacted C_3S (Alite) and C_2S (Belite) in specimens. The high intensity of calcite peaks in the top region of carbonated specimens were seen for all replacements of red mud indicating a higher degree of carbonation.

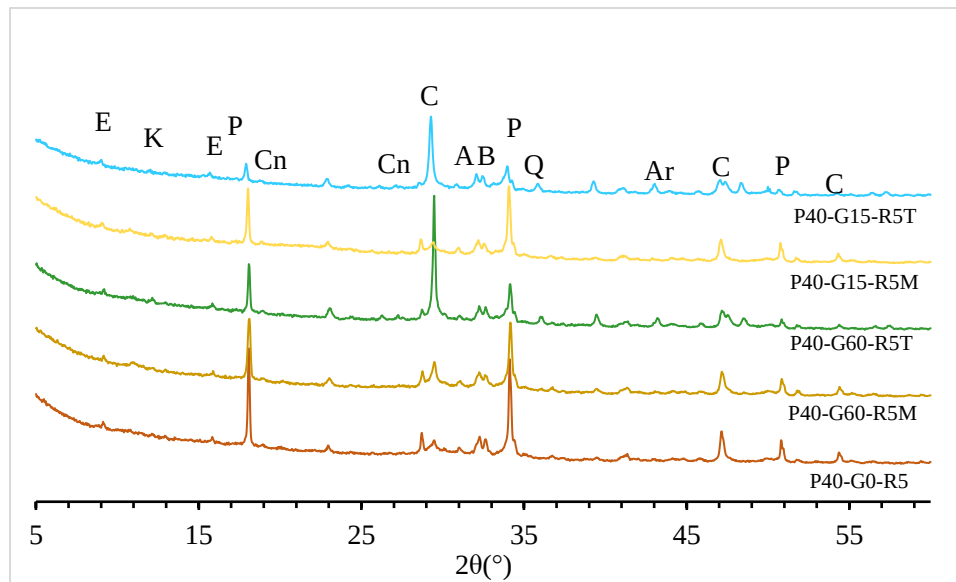
As we move to the middle region, the intensity of the calcite peaks weakened, suggesting that the CO_2 diffusion to the middle region was not that significant and crystalline carbonates were not well formed. All the top region specimens showed sharp peaks for calcite 2θ value of 29.5° . Similarly, the portlandite peaks corresponding to 2θ values of 18° and 28.5° showed decreased intensity. Similarly, the XRD of middle region specimens showed portlandite peaks comparable to control specimens, indicating the presence of more portlandite and less calcite formation. The high portlandite formation can be credited to the precipitation of the OH^- ions with Ca^{2+} together without reacting with the CO_2 gas, whose diffusion is lower in the middle region than the top surface [192]. In contrast, on the top surface, Ca^{2+} ions react with the carbonate ions formed due to the reaction of CO_2 with free water to form stable calcite without forming portlandite. This causes a reduced amount

of portlandite to form on the top surface of specimens. However, the subsequent hydration due to post-carbonation curing results in the formation of portlandite [178].

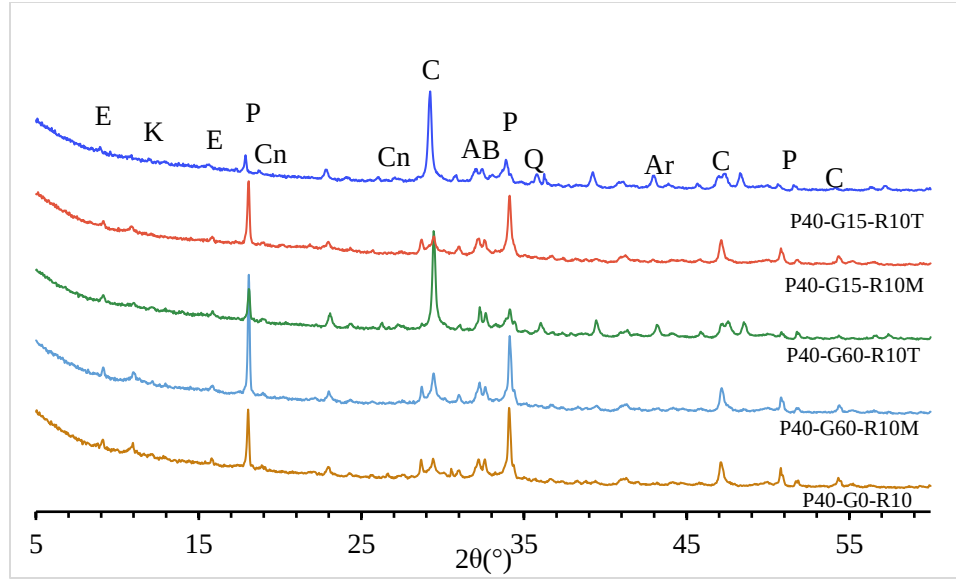
As we increase the percentage of red mud, the intensity of portlandite peaks for uncarbonated specimens reduces. This can be attributed to the reduction of cement which results in the formation of less quantities of portlandite and hydration products. The reduction in portlandite can be observed for the carbonated specimens as well with 15% red mud resulting in least intensities of portlandite peaks. The calcite peaks for carbonated specimen showed an increase in intensities with increasing replacements of red mud. This highlights that the addition of red mud can result in enhancing the CO₂ uptake by cement. Additionally, with the increasing replacement of red mud, some new peaks of unreacted quartz, kaolin, and cancrinite were identified in the specimens. The post-carbonation curing results in the reaction of remaining clinker phases to form additional C-S-H gel and hydration products, suggesting that early-age carbonation does not negatively affect the further hydration of cement paste. The pressure of 60 and 15 psi also showed calcite formation in the top region. Previous studies have reported that the concentration of CO₂ plays a more vital role than the pressure for early-age carbonation [193]. Moreover, Ettringite was also present in all specimens with peaks identified at 2 θ values of 9°, 16° and 23°. The ettringite showed a stable trend in all the specimens. Some studies have reported ettringite to be vulnerable to carbonation, forming Al(OH)₃ and calcite [195].



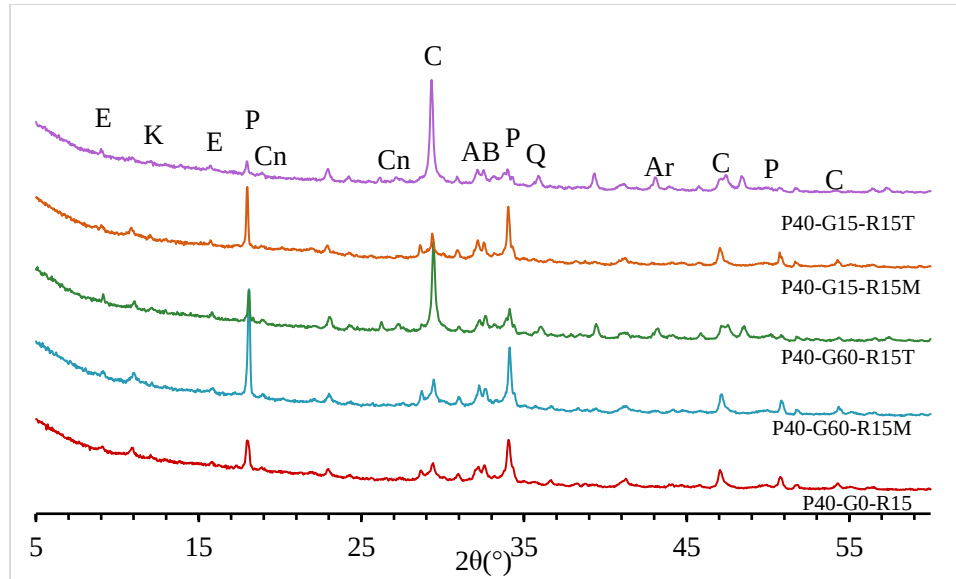
(a) XRD spectra of control and carbonated specimen with 0% red mud



(b) XRD spectra of control and carbonated specimen with 5% red mud



(c) XRD spectra of control and carbonated specimen with 10% red mud



(d) XRD spectra of control and carbonated specimen with 15% red mud

Fig. 38. XRD of specimens at 28 days (Alite -A, Belite-B, Ettringite-E, Calcite-C, Portlandite-P, Aragonite-Ar, Kaolin-K, Quartz-Q, Cancrinite-Cn)

5.7 FT-IR

FT-IR was carried out for all the control and carbonated specimens containing varying replacements of red mud. Fig. 39 (a)-(d) shows FT-IR spectra generated for all the specimens. The low transmittance in the FTIR spectra represents a higher percentage of chemical components [196,197]. Band 1 is assigned to the O-H bond in $\text{Ca}(\text{OH})_2$ at 3642 cm^{-1} [198]. This band represents the presence of portlandite present in the specimen. For all the specimens with different replacements of red mud, this band diminishes for carbonated samples. The top surface showed a higher reduction than the samples from the middle layer. Band 2 is assigned to the H-O-H bond of chemically bonded water at 1650 cm^{-1} [199]. All the specimens showed a reduction in bands for the top carbonated surface compared to the mid, indicating that carbonation uses water and reduces the amount of chemically bonded water. A slight shift in the band was noticed for carbonated specimens, which can be attributed to the bonded water in the hydration products [193].

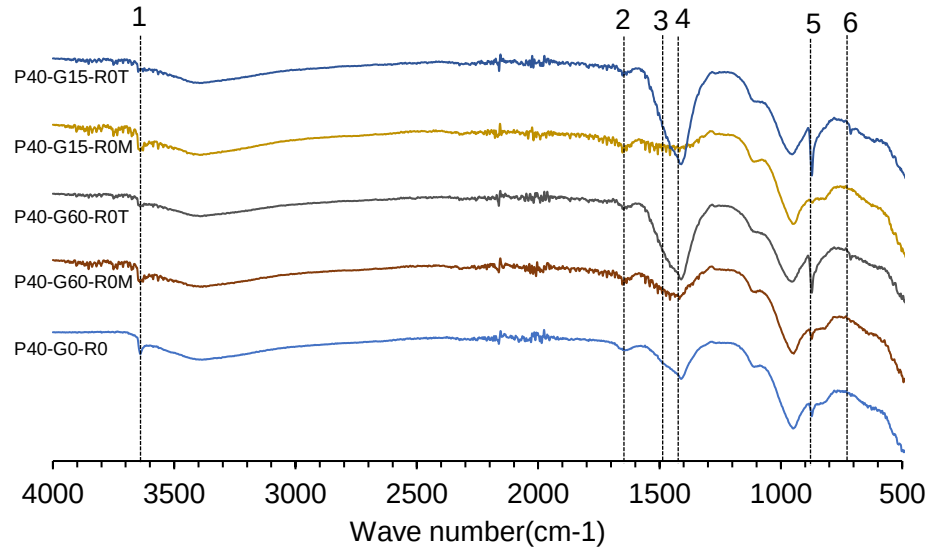
Band 3 and 4 are assigned to the C-O bond symmetric stretching at 1470 cm^{-1} and 1410 cm^{-1} [200,201]. Moreover, bands 5 and 6 are assigned to in-plane and out-of-plane bending vibration of the CO_3^{2-} at 872 cm^{-1} and 714 cm^{-1} [202,230,231]. These bands correspond to the carbonate groups present in the specimens. As the carbonation degree increases, the peaks are generated at the above locations. The slight shift in the band represents varying carbonation degrees in various specimens. The presence of split peaks in the 1420 cm^{-1} to 1480 cm^{-1} region represents the presence of amorphous calcium carbonate (ACC) [232]. All the FTIR spectra of the middle region of carbonated specimens show a split peak in the corresponding region, suggesting the formation of ACC in the middle region. However, a narrow peak in the region of 1420 represents the formation of calcite [231]. All the

specimens on the top surface showed a narrow peak, indicating that ambient concentration of CO₂ resulted in the formation of crystalline calcite. Moreover, a decrease in the transmittance also showed that a higher calcite content was formed due to carbonation in the top region of specimens. Additionally, the reduction in the transmittance of the band at 872 cm⁻¹ also indicates calcite formation. The band transmittance for the middle region was slightly higher, suggesting that less calcite is formed in the middle region with more ACC formed, as evident from bands 3 and 4.

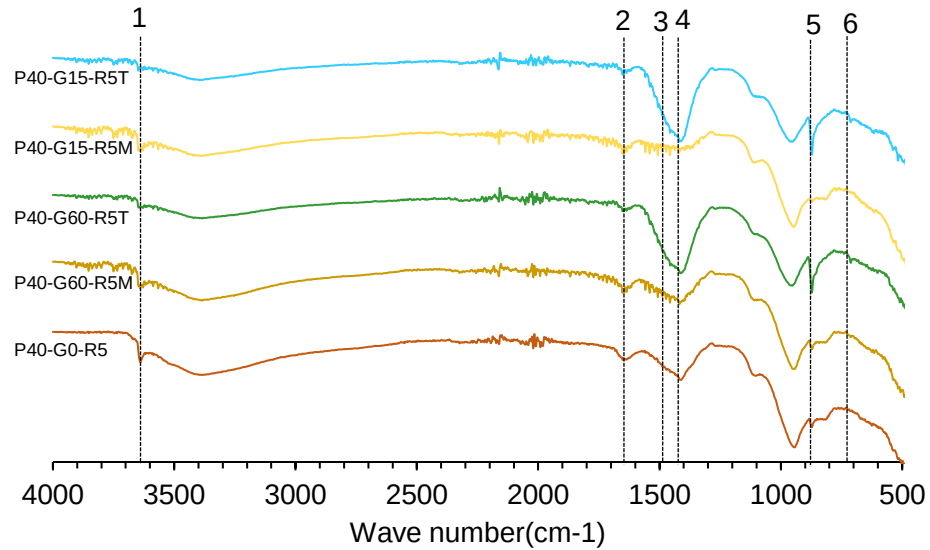
Band 4 showed a slight transition with an increasing percentage of red mud. The peak of the band shifted from 1405 to 1401 cm⁻¹. Additionally, a decrease in the transmittance was observed for the top carbonated specimen showing higher calcite content for higher red mud replacement. Band 5 occurred at 870 cm⁻¹ for all the carbonated specimens with increasing replacement of red mud. A sharp decrease in transmittance was also observed at this band highlighting more formation of calcite. For the specimen taken from middle region of carbonated specimen, split peaks were identified in all the spectra with increasing percentage of red mud highlighting the presence of ACC in all the specimen. Moreover, a slight decrease in the spectra at 815 cm⁻¹ was observed for higher replacement of red mud which is attributed to symmetric stretching of silica gel [233]. The presence of alkali affect the aluminum substitution that results in more Si-O monomers to be available resulting in increase in silica gel content [234].

The shifts in bands between 960 cm⁻¹ and 1080 cm⁻¹ represent the hydrate phases relating to calcium and silicates. These bands' accurate position depends on the Ca/Si ratio [98]. Previous studies also report that post-carbonation hydration causes modification in the C-S-H by polymerization. This enhances the bond between C-S-H gel and calcite, forming a

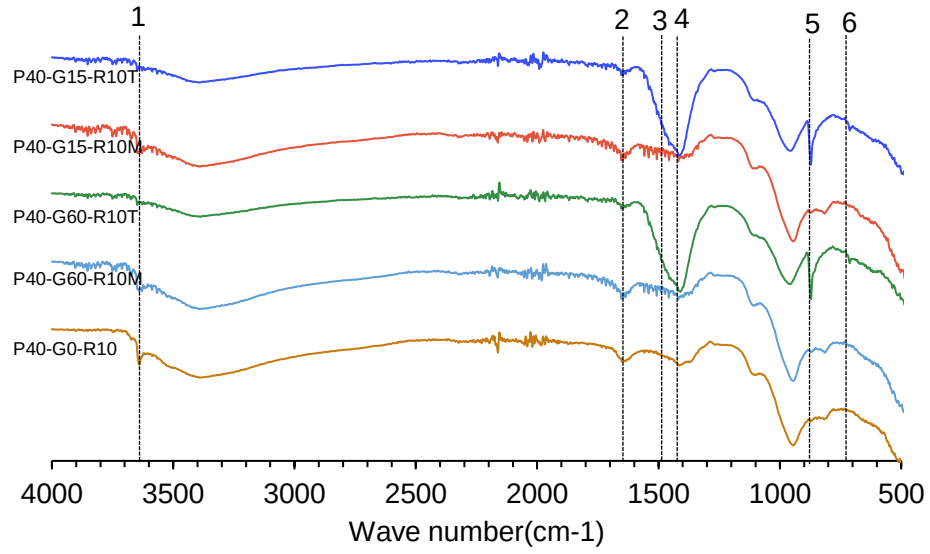
more robust hybrid [193]. This analysis indicates that carbonation results in calcite formation due to ambient pressure and concentration, making a stronger hybrid for various replacements of red mud, confirming the XRD results.



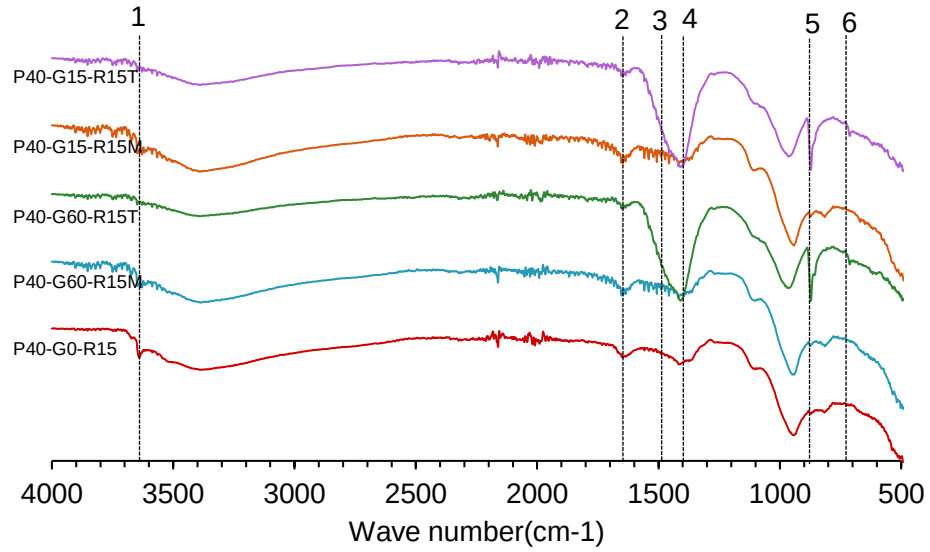
(a) FTIR spectra of control and carbonated specimen with 0% red mud



(b) FTIR spectra of control and carbonated specimen with 5% red mud



(c) FTIR spectra of control and carbonated specimen with 10% red mud



(d) FTIR spectra of control and carbonated specimen with 15% red mud

Fig. 39. FTIR spectra of carbonated and control specimens (1. O-H in Ca(OH)_2 -3642 cm^{-1} , 2. ν_2 of H-O-H – 1650 cm^{-1} , 3. ν_3 of CO – 1470 cm^{-1} , 4. ν_3 of CO – 1417 cm^{-1} , 5. ν_2 of CO_3^{2-} –872 cm^{-1} 6. ν_2 of CO_3^{2-} – 714 cm^{-1})

5.8 TGA

The mass loss from TGA was used to determine the uptake of CO₂ in the carbonated samples. From XRD and FTIR, it was determined that the top region had the highest carbonation. For this reason, we selected the top specimens to run TGA to quantify the CO₂ uptake in the carbonated layer. Fig. 40 shows the TG and DTG curves of control and carbonated specimens. The cement paste decomposes in dehydration, de-hydroxylation, and decarbonation [183]. The peaks of the portlandite usually occur at 330-480 °C, and that of calcite occurs at 520-800 °C [184]. The initial mass loss of specimens in the region of 50-170 °C is due to the evaporation of free water and decomposition of ettringite, C-S-H, and mono-sulfo-aluminate (M) phases [185]. For the carbonated samples, the dehydration intensity decreases compared to the control specimens, which indicates the use of water by carbonation to form calcite. Similarly, the portlandite identified in the temperature range of 330-480 °C showed the highest weight loss for control specimens. However, in the case of carbonated specimens, the weight loss of the portlandite peak was significantly reduced compared to the control specimen. Meanwhile, a significant increase in the decarbonation range of 520-800 °C was observed for the carbonated specimens. This indicates calcite formation from the Ca²⁺ ions instead of forming portlandite during carbonation. Additionally, a slight increase in the calcite content was observed by increasing the percentage of red mud.

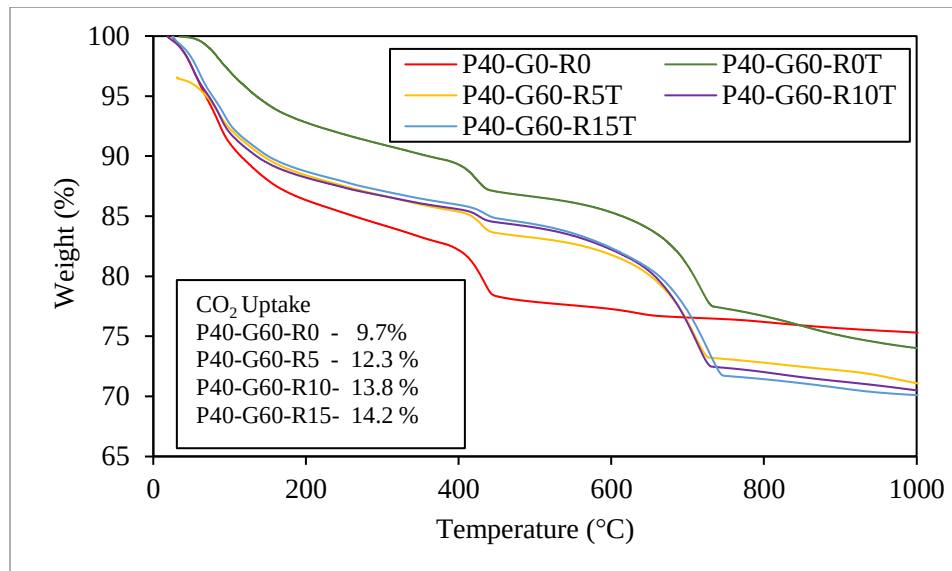
The quantities of calcite, portlandite, and CO₂ uptake were quantified from the weight loss in the respective region. The carbonated specimen showed an increase in the calcite content with reduced quantities of portlandite. As the carbonation started at early ages, abundant Ca²⁺ is directly available for carbonation resulting in the direct formation of calcium

carbonate. The control specimens showed portlandite content of 18.6%, which was reduced to 11.6%, 8%, 5.5%, and 5% for carbonated specimens containing red mud replacement of 0%, 5%, 10%, and 15%, respectively. Similarly, the calcite content for carbonated specimens was recorded as 14.4%, 17.8%, 20.0%, and 20.5%, with CO₂ uptake of 9.7%, 12.3%, 13.8%, and 14.2% with increasing replacement of red mud. The highest calcite content was recorded for specimens with 15% red mud replacement. This highlights that the red mud has the potential to increase the carbonation potential of the cement paste. The increase in intensity of calcite peak was also observed in XRD and FTIR also showed more formation of calcite with increasing replacement of red mud. The increase in the CO₂ uptake can be attributed to the potential of red mud to react with CO₂ to form carbonates. The high CO₂ uptake for red mud has also been reported in previous research [235]. Moreover, the delay in the setting of cement as shown in Fig. 8 can result in the more penetration of CO₂ inside the matrix enhancing the uptake.

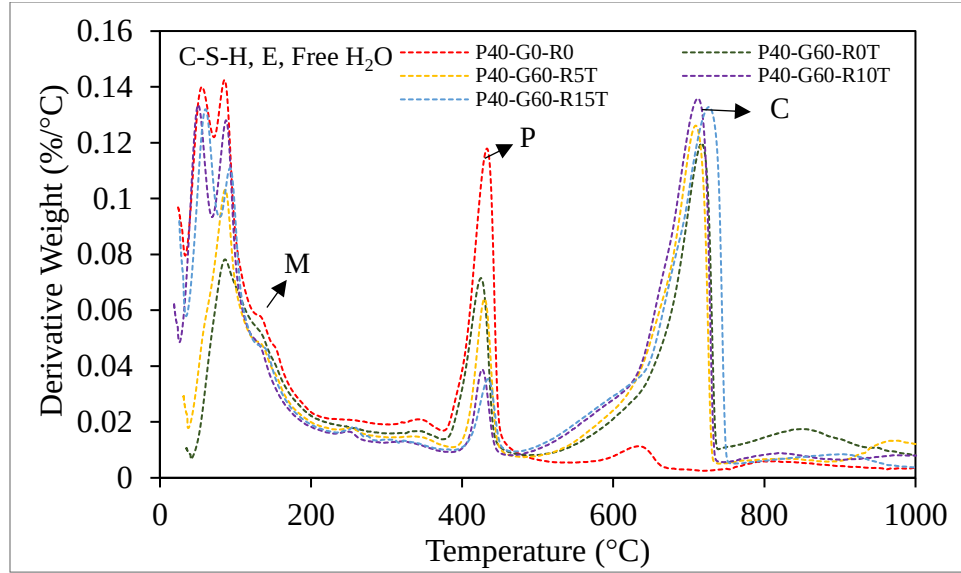
Additionally, the amount of portlandite was reduced with increasing red mud replacement. It can be attributed to the reduction in cement content which resulted in lesser portlandite formation. During early-age carbonation, abundant Ca²⁺ ions are available for reacting with CO₂, which results in a decreased quantity of portlandite initially. This results in a decrease in the amount of Ca²⁺ ions which inhibits the formation of portlandite. The carbonation of Ca²⁺ is faster than portlandite [190]. The post-carbonation curing also results in the formation of portlandite, which increases the alkalinity of the pore solution.

The thermal analysis of specimens carbonated at 15 psi showed similar trends shown in Fig. 40 c. The CO₂ uptake was calculated to be 13%, 14%, 14.56% and 16% for 0, 5, 10, and 15% of red mud replacement. The specimen carbonated at 15 psi showed similar

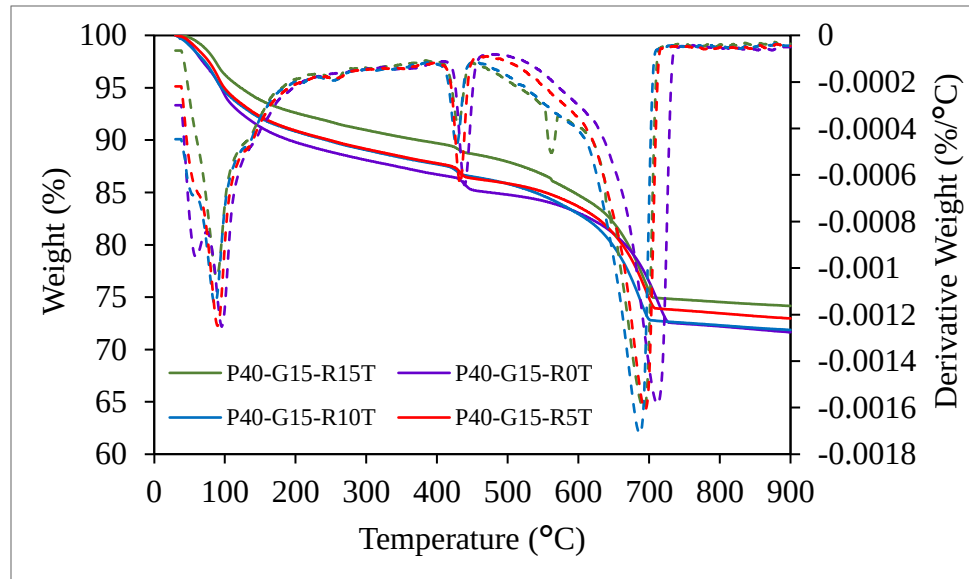
carbonation degrees as 60 psi specimen. This shows that the pressure is not significant during carbonation. Past studies have also reported that the concentration of CO₂ is more significant than the pressure [193]. Similarly, the percentage of portlandite reduced from 6% for specimen with 0% red mud replacement to 3.1% for 15% red mud. This again highlights that carbonation uptake increases with higher red mud replacement. The higher CO₂ uptake at 15 psi can be attributed to slow and homogenous diffusion of CO₂ at lower pressure while the 60 psi can form a more densified layer quickly which can limit penetration.



(a) TG Curves



(b) DTG Curves

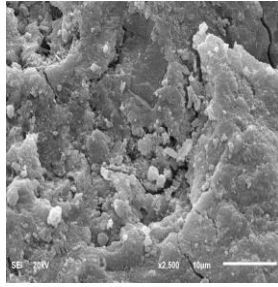


(c) TGA curves for specimen carbonated at 15 psi

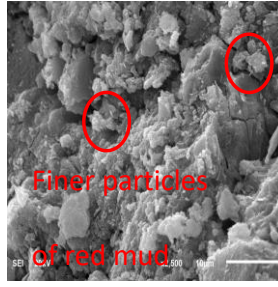
Fig. 40. TG results for control and carbonated specimens (Ettringite-E, Calcite-C, Portlandite-P, Mono sulfo-aluminate-M)

5.9 SEM-EDS

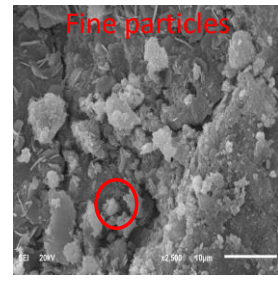
SEM-EDS was carried out to study the microstructure of cement paste incorporating red mud for control and carbonated specimens. Fig. 41 (a)-(c) shows SEM images for control specimens incorporating various percentages of red mud, while Fig. 41 (d)-(f) shows SEM images for carbonated specimens of the corresponding control images. Lastly, Fig. 41 (g)-(j) shows point EDS taken to confirm the calcite formation at different locations in the SEM images. As we increased the percentage of red mud, more fine particles were deposited at various locations in the cement matrix. These smaller particles tend to fill up pores present in cement matrix at an early stage and make an interwoven matrix acting as a nano-filler [236]. Additionally, carbonation results in the formation of calcite filling the pores. The C-S-H acts as a platform for the carbonation process and allows calcite formation on its surface and surrounding areas. [193]The point EDS taken for the specimen indicates higher percentages of carbon and calcium, indicating calcite formation. This calcite is mixed with C-S-H gel, which forms the hybrid matrix, enhancing the mechanical performance of carbonated specimens. Additionally, it has been reported that longer carbonation results in calcite formation with an enhanced crystallization degree. [203]This confirms the results of FTIR and XRD, suggesting that well-crystalline calcite is formed on the top surface while ACC is formed in the middle, where CO₂ diffusion is less. The calcite formed due to carbonation is located irregularly, enhancing microstructure. This conclusion is based on past studies on cement paste carbonation. [84,96,204].



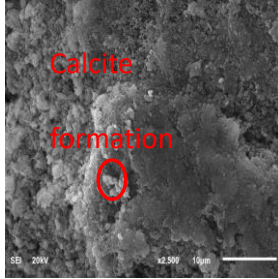
(a) P40-G0-R0



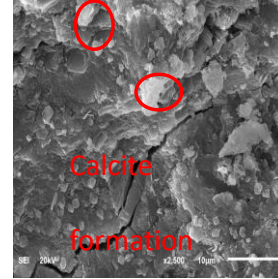
(b) P40-G0-R5



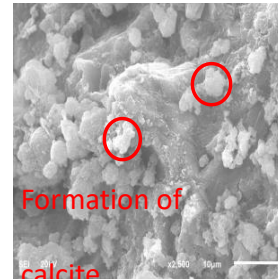
(c) P40-G0-R15



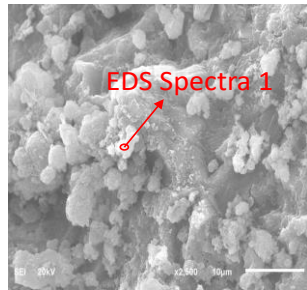
(d) P40-G60-R0



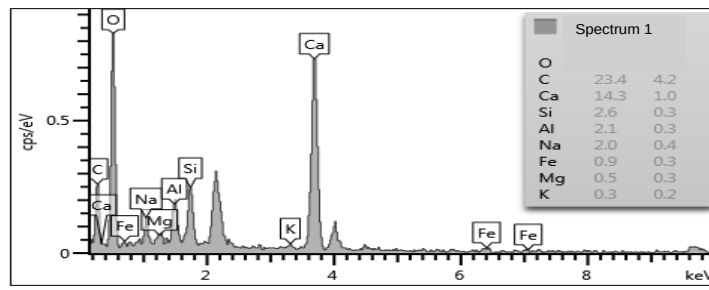
(e) P40-G60-R5



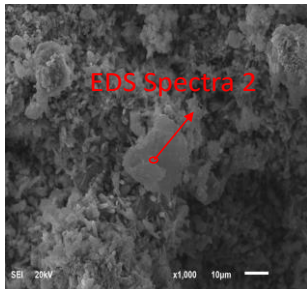
(f) P40-G60-R15



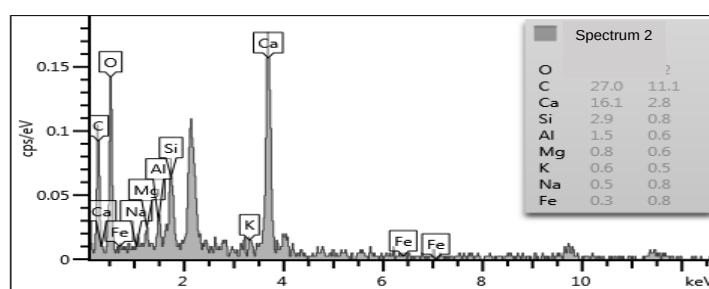
(g) EDS Spectra 1



(h) EDS Spectra Point 1



(i) EDS Spectra 2



(j) EDS Spectra Point 2

Fig. 41. SEM Images for control and carbonated specimens with EDS Spectra

5.10 Carbon strength factor

A carbon strength factor was calculated for the paste specimen based on the net CO₂ emissions for per strength gain in MPa. The production of cement approximately produce 0.822 ton of CO₂. [191]. As we are replacing cement with red mud there will be a reduction in CO₂ emissions due to a reduction in the cement content. Additionally, the carbonated specimen has shown CO₂ uptake which will further reduce the CO₂ footprint of cement used. The net CO₂ emission was divided by the strength of each specimen to calculate the carbon strength factor which is shown in Fig. 42. Net CO₂ emissions were calculated for control specimens by subtracting the percentage of red mud used in the specimen. Furthermore, for carbonated specimens, the CO₂ uptake was further subtracted to find the CO₂ emissions of carbonated specimens.

The paste specimen without red mud showed the least carbon strength factor which is attributed to the higher strength increase after carbonation. The uncarbonated specimen with increasing percentage of red mud showed an increase in the factor which is due to decrease in strength at 28 days attributed to the presence of red mud. The carbonated specimen containing red mud showed a decrease in the carbon strength factor which is attributed to the reduction in net CO₂ emissions as well as the CO₂ uptake in the specimen as well. Additionally, the red mud incorporated cement paste showed an increase in the strength after carbonation. The carbonation at both 15 and 60 psi resulted in reduction of carbon strength factor which highlights that the carbonation at both pressures resulted in strength improvement and carbon sequestration. This has been highlighted by other results as well.

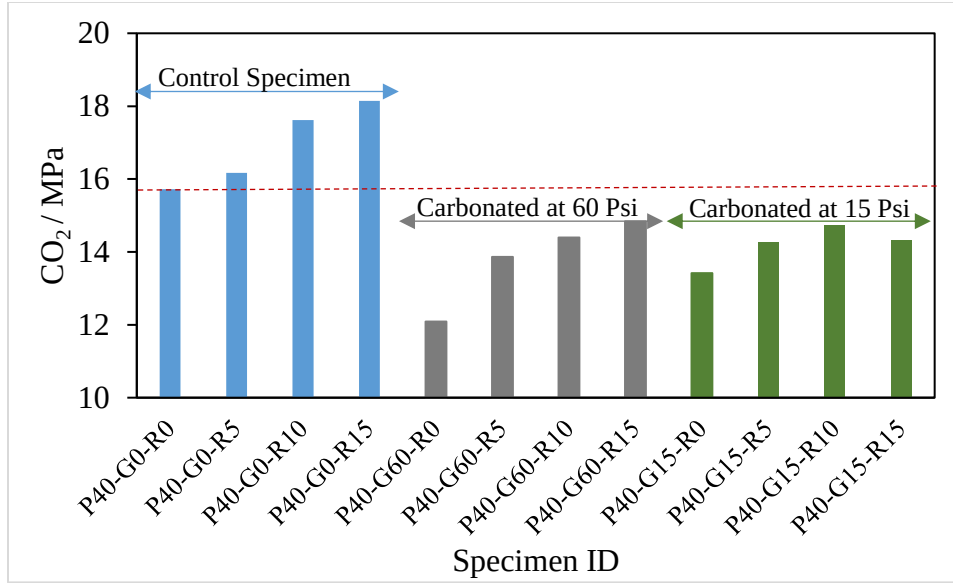


Fig. 42. Carbon Strength factor for paste specimen

5.11 Discussions

The relationship between carbonation degree and CO₂ uptake was carefully examined in this study, revealing critical insights into the limitations of using carbonation degree as a sole indicator of carbonation performance. It was observed that the carbonation degree, assessed using phenolphthalein to determine the depth of the carbonated region in mortar specimens, does not directly correlate with the CO₂ uptake measured through TGA. The carbonation degree reflects the depth of carbonation penetration in the specimen, which is influenced by parameters such as w/b ratio and curing conditions. For instance, at three days post-carbonation, specimens with a higher w/b ratio exhibited a colorless region, indicating carbonation depth and a significant reduction in pH. However, subsequent hydration after carbonation mitigated this effect, resulting in a gradual increase in the pH of the pore solution. Furthermore, the pH development after carbonation highlights the interplay between carbonation and hydration processes. The initial drop in pH in the

carbonated region, particularly in high w/b ratio specimens, was followed by a rebound due to post-carbonation hydration, which forms portlandite and other hydration products. This finding challenges the reliability of pH measurements and carbonation degree as a sole indicator of carbonation performance and underscores the need for integrating multiple characterization techniques to accurately assess carbonation efficiency and CO₂ uptake.

The TGA results demonstrated a consistent increase in CO₂ uptake with higher red mud replacement percentages, irrespective of the carbonation degree. This is attributed to the interaction of abundant calcium ions with CO₂, forming calcite directly during carbonation. However, it was evident that the carbonation degree and pH measurement does not account for the quantity of CO₂ sequestered in the form of calcite or amorphous calcium carbonate (ACC). Instead, it provides a visual representation of carbonation depth, which may vary due to surface densification or heterogeneity in the carbonation process. The microstructural analysis further corroborated the findings from TGA. XRD and FTIR revealed a marked reduction in portlandite content with red mud replacement after carbonation curing. The formation of well-crystalline calcite on the surface and ACC in the middle layers of the specimens was identified, supporting the conclusion that carbonation results in formation of calcite. These results emphasize that CO₂ uptake is primarily governed by the chemical interaction between CO₂ and Ca²⁺ ions rather than the visual extent of carbonation depth.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

This study provides valuable insights into the effects of red mud replacement and varying pre-hydration durations on the mechanical and microstructural properties of cementitious systems subjected to carbonation.

The incorporation of red mud exhibited contrasting impacts on mechanical performance across cement paste and mortar. In cement paste, compressive strength decreased due to the dilution of reactive pozzolanic components. Conversely, in mortar, red mud enhanced early-age strength while contributing to strength reductions at later stages. The carbonation process substantially improved compressive strength for both paste and mortar at the early (3 days) and later (28 days) curing stages. This enhancement was attributed to pore structure densification, the formation of calcite, and the hydration heat generated during carbonation. Additionally, post-carbonation hydration regenerated portlandite and other hydration products, offsetting water loss and further enhancing strength.

Red mud replacement increased drying shrinkage due to its elevated water demand, with higher replacement percentages exacerbating this effect. However, carbonation mitigated shrinkage by densifying the C-S-H pore structure and consuming free water to form calcite, which reduced evaporation. Red mud's alkaline nature elevated the pore solution's pH, serving as a pH stabilizer and ensuring durability. Despite the reduced carbonation degree observed in red mud specimens, the pH remained sufficiently high to inhibit corrosion.

Microstructural analyses revealed that carbonation reduced portlandite content while promoting the formation of crystalline calcite and amorphous calcium carbonate (ACC). XRD and FTIR analyses confirmed these carbonation products, and TGA demonstrated increased CO₂ uptake with higher red mud content. SEM-EDS observations highlighted the nano-filler effect of red mud particles, which enhanced pore filling and facilitated the formation of a robust hybrid matrix with C-S-H gel, leading to improved mechanical performance.

The optimization of pre-hydration durations showed that shorter durations of 0 and 3 hours maximized carbonation efficiency, CO₂ uptake, and strength development. These durations facilitated the rapid availability of reactive Ca²⁺ ions, enabling effective carbonation reactions. Prolonged pre-hydration durations (7 and 24 hours) reduced carbonation efficiency by limiting Ca²⁺ ion availability, resulting in diminished strength gains and lower CO₂ sequestration.

Due to water loss during the exothermic carbonation reaction, carbonation increased drying shrinkage, particularly at shorter pre-hydration durations. Subsequent hydration curing mitigated this shrinkage by replenishing water and enhancing long-term dimensional stability. Although carbonation lowered the pore solution's pH, even at the shortest pre-hydration durations, the pH remained within the range of 12.25–12.79 at 28 days, sufficient to protect steel reinforcement from corrosion.

The findings highlight the potential of combining early-age carbonation with subsequent hydration curing to optimize mechanical performance, improve microstructural characteristics, and achieve environmental benefits. The inclusion of red mud offers a viable approach for CO₂ sequestration, reducing cement's carbon footprint, and enabling

the sustainable utilization of industrial waste. These advancements contribute to the development of environmentally sustainable construction practices.

6.2 Future Recommendations

This study provides valuable insights into the application of carbonation curing and the use of red mud in cementitious systems. However, further research is required to optimize these processes for practical, real-world applications.

1. **Integration with Concrete Systems:** While the present research focused on pastes and mortars, future studies should explore the performance of red mud-incorporated cement in concrete mixtures, especially under different mix designs and curing conditions.
2. **Utilization of Alternative Carbonation Sources:** This study employed pure CO₂ gas; however, flue gas or other CO₂-rich sources should be considered for industrial-scale applications to enhance cost efficiency and scalability.
3. **Exploration of Alternative Supplementary Materials:** Further attention should be given to investigating other industrial by-products, such as fly ash or slag, which have lower environmental impacts, as potential substitutes for cement or sand in combination with red mud.
4. **Long-Term Durability Assessment:** Extended durability tests, including freeze-thaw resistance, chloride penetration, and sulfate attack, are essential to validate the long-term performance of carbonated red mud composites.
5. **Development of Carbonation-Based Design Models:** Future work should aim to develop predictive models that can assess carbonation curing efficiency, strength

development, and CO₂ sequestration potential, aiding in the guidance of industrial applications.

The integration of carbonation curing with red mud utilization represents a promising route toward sustainable construction practices, reducing environmental impacts while maintaining high material performance.

REFERENCES

- [1] H. Ritchie, M. Roser, P. Rosado, CO₂ and greenhouse gas emissions, Our World Data (2020).
- [2] N.A. Rashidi, S. Yusup, An overview of activated carbons utilization for the post-combustion carbon dioxide capture, *J. CO₂ Util.* 13 (2016) 1–16.
<https://doi.org/https://doi.org/10.1016/j.jcou.2015.11.002>.
- [3] Q. Zhang, P. Feng, X. Shen, J. Lu, S. Ye, H. Wang, T. Ling, Q. Ran, Utilization of solid wastes to sequester carbon dioxide in cement-based materials and methods to improve carbonation degree: A review, *J. CO₂ Util.* 72 (2023) 102502.
<https://doi.org/https://doi.org/10.1016/j.jcou.2023.102502>.
- [4] T.F. Stocker, D. Qin, G.-K. Plattner, L. V Alexander, S.K. Allen, N.L. Bindoff, F.-M. Bréon, J.A. Church, U. Cubasch, S. Emori, Technical summary, in: *Clim. Chang. 2013 Phys. Sci. Basis. Contrib. Work. Gr. I to Fifth Assess. Rep. Intergov. Panel Clim. Chang.*, Cambridge University Press, 2013: pp. 33–115.
- [5] A. McMichael, D.H. Campbell-Lendrum, R.S. Kovats, R.J. Nicholls, S. Edwards, P. Wilkinson, T. Wilson, *Global climate change*, (2004).
- [6] W.M. Association, *State of the global climate 2021*, (2022).
- [7] E. Benhelal, G. Zahedi, E. Shamsaei, A. Bahadori, Global strategies and potentials to curb CO₂ emissions in cement industry, *J. Clean. Prod.* 51 (2013) 142–161.
- [8] C.-Y. Zhang, R. Han, B. Yu, Y.-M. Wei, Accounting process-related CO₂ emissions from global cement production under Shared Socioeconomic Pathways,

- J. Clean. Prod. 184 (2018) 451–465.
- [9] R.J. Andres, T.A. Boden, F.-M. Bréon, P. Ciais, S. Davis, D. Erickson, J.S. Gregg, A. Jacobson, G. Marland, J. Miller, A synthesis of carbon dioxide emissions from fossil-fuel combustion, *Biogeosciences* 9 (2012) 1845–1871.
- [10] IEA., Energy technology transitions for industry: strategies for the next industrial revolution, OECD Publishing, 2009.
- [11] F. Apadula, C. Cassardo, S. Ferrarese, D. Heltai, A. Lanza, Thirty years of atmospheric CO₂ observations at the Plateau Rosa Station, Italy, *Atmosphere* (Basel). 10 (2019) 418.
- [12] K. Kelektoglou, Carbon capture and storage: A review of mineral storage of CO₂ in Greece, *Sustainability* 10 (2018) 4400.
- [13] J. Maximillian, M.L. Brusseau, E.P. Glenn, and A.D. Matthias, Pollution and environmental perturbations in the global system, in: *Environ. Pollut. Sci.*, Elsevier, 2019: pp. 457–476.
- [14] Z. Liu, W. Meng, Fundamental understanding of carbonation curing and durability of carbonation-cured cement-based composites: A review, *J. CO₂ Util.* 44 (2021) 101428. <https://doi.org/10.1016/j.jcou.2020.101428>.
- [15] Z. Zhang, S.-Y. Pan, H. Li, J. Cai, A.G. Olabi, E.J. Anthony, V. Manovic, Recent advances in carbon dioxide utilization, *Renew. Sustain. Energy Rev.* 125 (2020) 109799. <https://doi.org/https://doi.org/10.1016/j.rser.2020.109799>.
- [16] B.R. Patra, S.P. Gouda, F. Pattnaik, S. Nanda, A.K. Dalai, S. Naik, A brief

- overview of recent advancements in CO₂ capture and valorization technologies, Carbon Dioxide Capture Convers. (2022) 1–16.
- [17] M. Carus, C. Vom Berg, E. Breitmayer, CO₂ utilisation and sustainability, Carbon Dioxide Util. From Fundam. to Prod. Process. Eds M. North P. Styr. (Berlin Walter Gruyter, GmbH) (2019) 13–30.
- [18] M. Wang, X. Liu, Applications of red mud as an environmental remediation material: A review, J. Hazard. Mater. 408 (2021) 124420.
<https://doi.org/https://doi.org/10.1016/j.jhazmat.2020.124420>.
- [19] E. Mukiza, L. Zhang, X. Liu, N. Zhang, Utilization of red mud in road base and subgrade materials: A review, Resour. Conserv. Recycl. 141 (2019) 187–199.
<https://doi.org/https://doi.org/10.1016/j.resconrec.2018.10.031>.
- [20] Z. Karimi, A. Rahbar-Kelishami, Efficient utilization of red mud waste via stepwise leaching to obtain α -hematite and mesoporous γ -alumina, Sci. Rep. 13 (2023) 8527.
- [21] W.-H. Xie, H. Li, M. Yang, L.-N. He, H.-R. Li, CO₂ capture and utilization with solid waste, Green Chem. Eng. 3 (2022) 199–209.
<https://doi.org/https://doi.org/10.1016/j.gce.2022.01.002>.
- [22] F.W.K. Khudhur, J.M. MacDonald, A. Macente, L. Daly, The utilization of alkaline wastes in passive carbon capture and sequestration: Promises, challenges and environmental aspects, Sci. Total Environ. 823 (2022) 153553.
<https://doi.org/https://doi.org/10.1016/j.scitotenv.2022.153553>.

- [23] P. Renforth, W.M. Mayes, A.P. Jarvis, I.T. Burke, D.A.C. Manning, K. Gruiz, Contaminant mobility and carbon sequestration downstream of the Ajka (Hungary) red mud spill: The effects of gypsum dosing, *Sci. Total Environ.* 421–422 (2012) 253–259. <https://doi.org/https://doi.org/10.1016/j.scitotenv.2012.01.046>.
- [24] A.-R. M., S.L.M. Gómez, C.M.A. Piñeiro, M.B. Olazaran, Uses of Red Mud as a Construction Material, in: *AEI 2017*, 2017: pp. 388–399. <https://doi.org/doi:10.1061/9780784480502.032>.
- [25] S. Samal, A.K. Ray, A. Bandopadhyay, Proposal for resources, utilization and processes of red mud in India — A review, *Int. J. Miner. Process.* 118 (2013) 43–55. <https://doi.org/https://doi.org/10.1016/j.minpro.2012.11.001>.
- [26] C. Venkatesh, S.K. Mohiddin, N. Ruben, Corrosion Inhibitors Behaviour on Reinforced Concrete—A Review *BT - Sustainable Construction and Building Materials*, in: B.B. Das, N. Neithalath (Eds.), Springer Singapore, Singapore, 2019: pp. 127–134.
- [27] X. Wang, J. Qi, H. Zhu, J. Wang, H. Zeng, B. Li, S. Yan, Enhanced sequestration of CO₂ from simulated electrolytic aluminum flue gas by modified red mud, *J. Environ. Manage.* 346 (2023) 118972.
- [28] S. Xue, Y. Wu, Y. Li, X. Kong, F. Zhu, H. William, X. Li, Y. Ye, Industrial wastes applications for alkalinity regulation in bauxite residue: A comprehensive review, *J. Cent. South Univ.* 26 (2019) 268–288. <https://doi.org/10.1007/s11771-019-4000-3>.
- [29] J.G. Jang, G.M. Kim, H.J. Kim, H.-K. Lee, Review on recent advances in CO₂

- utilization and sequestration technologies in cement-based materials, *Constr. Build. Mater.* 127 (2016) 762–773.
- [30] D. Zhang, Y. Shao, Early age carbonation curing for precast reinforced concretes, *Constr. Build. Mater.* 113 (2016) 134–143.
- [31] M. Zajac, A. Lechevallier, P. Durdzinski, F. Bullerjahn, J. Skibsted, M. Ben Haha, CO₂ mineralisation of Portland cement: Towards understanding the mechanisms of enforced carbonation, *J. CO₂ Util.* 38 (2020) 398–415.
- [32] W.A. Klemm, R.L. Berger, Accelerated curing of cementitious systems by carbon dioxide: Part I. Portland cement, *Cem. Concr. Res.* 2 (1972) 567–576.
- [33] J.F. Young, R.L. Berger, J. Breese, Accelerated curing of compacted calcium silicate mortars on exposure to CO₂, *J. Am. Ceram. Soc.* 57 (1974) 394–397.
- [34] S. Monkman, Y. Shao, Assessing the carbonation behavior of cementitious materials, *J. Mater. Civ. Eng.* 18 (2006) 768–776.
- [35] W. Seifritz, CO₂ disposal by means of silicates, *Nature* 345 (1990) 486.
- [36] V. Rostami, Y. Shao, A.J. Boyd, Durability of concrete pipes subjected to combined steam and carbonation curing, *Constr. Build. Mater.* 25 (2011) 3345–3355.
- [37] H. El-Hassan, Y. Shao, Z. Ghoulleh, Effect of Initial Curing on Carbonation of Lightweight Concrete Masonry Units., *ACI Mater. J.* 110 (2013).
- [38] Y. Shao, A.Z. Morshed, Early carbonation for hollow-core concrete slab curing and carbon dioxide recycling, *Mater. Struct.* 48 (2015) 307–319.

- [39] E. Blomen, C. Hendriks, F. Neele, Capture technologies: improvements and promising developments, *Energy Procedia* 1 (2009) 1505–1512.
- [40] E. de Visser, C. Hendriks, M. Barrio, M.J. Mølnvik, G. de Koeijer, S. Liljemark, Y. Le Gallo, Dynamis CO₂ quality recommendations, *Int. J. Greenh. Gas Control* 2 (2008) 478–484. <https://doi.org/https://doi.org/10.1016/j.ijggc.2008.04.006>.
- [41] A.A. Olajire, CO₂ capture and separation technologies for end-of-pipe applications – A review, *Energy* 35 (2010) 2610–2628.
<https://doi.org/https://doi.org/10.1016/j.energy.2010.02.030>.
- [42] M. Kanniche, R. Gros-Bonnivard, P. Jaud, J. Valle-Marcos, J.-M. Amann, C. Bouallou, Pre-combustion, post-combustion and oxy-combustion in thermal power plant for CO₂ capture, *Appl. Therm. Eng.* 30 (2010) 53–62.
<https://doi.org/https://doi.org/10.1016/j.applthermaleng.2009.05.005>.
- [43] T.F. Wall, Combustion processes for carbon capture, *Proc. Combust. Inst.* 31 (2007) 31–47.
- [44] S. Hoffmann, M. Bartlett, M. Finkenrath, A. Evulet, T.P. Ursin, Performance and cost analysis of advanced gas turbine cycles with precombustion CO₂ capture, (2009).
- [45] L.O. Nord, R. Anantharaman, O. Bolland, Design and off-design analyses of a pre-combustion CO₂ capture process in a natural gas combined cycle power plant, *Int. J. Greenh. Gas Control* 3 (2009) 385–392.
<https://doi.org/https://doi.org/10.1016/j.ijggc.2009.02.001>.

- [46] I. Pfaff, A. Kather, Comparative thermodynamic analysis and integration issues of CCS steam power plants based on oxy-combustion with cryogenic or membrane based air separation, *Energy Procedia* 1 (2009) 495–502.
<https://doi.org/https://doi.org/10.1016/j.egypro.2009.01.066>.
- [47] B.J.P. Buhre, L.K. Elliott, C.D. Sheng, R.P. Gupta, T.F. Wall, Oxy-fuel combustion technology for coal-fired power generation, *Prog. Energy Combust. Sci.* 31 (2005) 283–307. <https://doi.org/https://doi.org/10.1016/j.pecs.2005.07.001>.
- [48] F. Bougie, M.C. Iliuta, CO₂ Absorption in Aqueous Piperazine Solutions: Experimental Study and Modeling, *J. Chem. Eng. Data* 56 (2011) 1547–1554.
<https://doi.org/10.1021/je1012247>.
- [49] A. Veawab, A. Aroonwilas, P. Tontiwachwuthikul, CO₂ absorption performance of aqueous alkanolamines in packed columns, in: *ACS Div. Fuel Chem. Prepr.*, 2002: pp. 49–50. <https://www.scopus.com/inward/record.uri?eid=2-s2.0-0344120302&partnerID=40&md5=09bf2331a81bb0d962539f77fba65217>.
- [50] C. Hendriks, *Energy conversion: CO₂ removal from coal-fired power plant*, Netherlands Kluwer Acad. Publ. (1995).
- [51] M. Olivares-Marín, M.M. Maroto-Valer, Development of adsorbents for CO₂ capture from waste materials: a review, *Greenh. Gases Sci. Technol.* 2 (2012) 20–35.
- [52] M.M. Maroto-Valer, Z. Lu, Y. Zhang, Z. Tang, Sorbents for CO₂ capture from high carbon fly ashes, *Waste Manag.* 28 (2008) 2320–2328.

- [53] M. Clausse, J. Merel, F. Meunier, Numerical parametric study on CO₂ capture by indirect thermal swing adsorption, *Int. J. Greenh. Gas Control* 5 (2011) 1206–1213. <https://doi.org/https://doi.org/10.1016/j.ijggc.2011.05.036>.
- [54] Q. Zafar, T. Mattisson, B. Gevert, Integrated Hydrogen and Power Production with CO₂ Capture Using Chemical-Looping Reforming Redox Reactivity of Particles of CuO, Mn₂O₃, NiO, and Fe₂O₃ Using SiO₂ as a Support, *Ind. Eng. Chem. Res.* 44 (2005) 3485–3496. <https://doi.org/10.1021/ie048978i>.
- [55] M. Ishida, M. Yamamoto, T. Ohba, Experimental results of chemical-looping combustion with NiO/NiAl₂O₄ particle circulation at 1200 °C, *Energy Convers. Manag.* 43 (2002) 1469–1478. [https://doi.org/https://doi.org/10.1016/S0196-8904\(02\)00029-8](https://doi.org/https://doi.org/10.1016/S0196-8904(02)00029-8).
- [56] W. Yave, A. Car, S.S. Funari, S.P. Nunes, K.-V. Peinemann, CO₂-philic polymer membrane with extremely high separation performance, *Macromolecules* 43 (2010) 326–333.
- [57] P. Bernardo, E. Drioli, G. Golemme, Membrane Gas Separation: A Review/State of the Art, *Ind. Eng. Chem. Res.* 48 (2009) 4638–4663. <https://doi.org/10.1021/ie8019032>.
- [58] D. Sun, P. Englezos, Storage of CO₂ in a partially water saturated porous medium at gas hydrate formation conditions, *Int. J. Greenh. Gas Control* 25 (2014) 1–8. <https://doi.org/https://doi.org/10.1016/j.ijggc.2014.03.008>.
- [59] Y. Zhang, M. Yang, Y. Song, L. Jiang, Y. Li, C. Cheng, Hydrate phase equilibrium measurements for (THF+SDS+CO₂+N₂) aqueous solution systems in

- porous media, *Fluid Phase Equilib.* 370 (2014) 12–18.
<https://doi.org/https://doi.org/10.1016/j.fluid.2014.02.033>.
- [60] M.J. Tuinier, M. van Sint Annaland, G.J. Kramer, J.A.M. Kuipers, Cryogenic CO₂ capture using dynamically operated packed beds, *Chem. Eng. Sci.* 65 (2010) 114–119. <https://doi.org/https://doi.org/10.1016/j.ces.2009.01.055>.
- [61] M.T. Besong, M.M. Maroto-Valer, A.J. Finn, Study of design parameters affecting the performance of CO₂ purification units in oxy-fuel combustion, *Int. J. Greenh. Gas Control* 12 (2013) 441–449.
<https://doi.org/https://doi.org/10.1016/j.ijggc.2012.11.016>.
- [62] A. Di Maria, R. Snellings, L. Alaerts, M. Quaghebeur, K. Van Acker, Environmental assessment of CO₂ mineralisation for sustainable construction materials, *Int. J. Greenh. Gas Control* 93 (2020) 102882.
- [63] C. Hepburn, E. Adlen, J. Beddington, E.A. Carter, S. Fuss, N. Mac Dowell, J.C. Minx, P. Smith, C.K. Williams, The technological and economic prospects for CO₂ utilization and removal, *Nature* 575 (2019) 87–97.
- [64] M. Blunt, F.J. Fayers, F.M. Orr Jr., Carbon dioxide in enhanced oil recovery, *Energy Convers. Manag.* 34 (1993) 1197–1204. [https://doi.org/10.1016/0196-8904\(93\)90069-M](https://doi.org/10.1016/0196-8904(93)90069-M).
- [65] M. Fujioka, S. Yamaguchi, M. Nako, CO₂-ECBM field tests in the Ishikari Coal Basin of Japan, *Int. J. Coal Geol.* 82 (2010) 287–298.
<https://doi.org/https://doi.org/10.1016/j.coal.2010.01.004>.

- [66] J.R. Kelafant, S.H. Stevens, C.M. Boyer II, Vast resource potential exists in many countries, *Oil Gas J.* 90 (1992) 80–85.
<https://www.scopus.com/inward/record.uri?eid=2-s2.0-0027109738&partnerID=40&md5=7db2bc2d495d924376ce59c498f65725>.
- [67] C.M. White, B.R. Strazisar, E.J. Granite, J.S. Hoffman, H.W. Pennline, Separation and Capture of CO₂ from Large Stationary Sources and Sequestration in Geological Formations—Coalbeds and Deep Saline Aquifers, *J. Air Waste Manage. Assoc.* 53 (2003) 645–715.
<https://doi.org/10.1080/10473289.2003.10466206>.
- [68] R.S. Norhasyima, T.M.I. Mahlia, Advances in CO₂ utilization technology: A patent landscape review, *J. CO₂ Util.* 26 (2018) 323–335.
<https://doi.org/https://doi.org/10.1016/j.jcou.2018.05.022>.
- [69] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, *Renew. Sustain. Energy Rev.* 39 (2014) 426–443. <https://doi.org/https://doi.org/10.1016/j.rser.2014.07.093>.
- [70] S. Garcia, A. Kaminska, M.M. Maroto-Valer, Underground carbon dioxide storage in saline formations, *Proc. Inst. Civ. Eng. Waste Resour. Manag.* 163 (2010) 77–88. <https://doi.org/10.1680/warm.2010.163.2.77>.
- [71] B.A. Seibel, P.J. Walsh, Carbon cycle: Potential impacts of CO₂ injection on deep-sea biota, *Science* (80-.). 294 (2001) 319–320.
<https://doi.org/10.1126/science.1065301>.
- [72] K.Z. House, D.P. Schrag, C.F. Harvey, K.S. Lackner, Permanent carbon dioxide

- storage in deep-sea sediments, *Proc. Natl. Acad. Sci.* 103 (2006) 12291–12295.
- [73] A.A. Olajire, A review of mineral carbonation technology in sequestration of CO₂, *J. Pet. Sci. Eng.* 109 (2013) 364–392.
- [74] B. Zhan, C.S. Poon, Q. Liu, S. Kou, C. Shi, Experimental study on CO₂ curing for enhancement of recycled aggregate properties, *Constr. Build. Mater.* 67 (2014) 3–7.
- [75] V.W.Y. Tam, A. Butera, K.N. Le, W. Li, Utilising CO₂ technologies for recycled aggregate concrete: A critical review, *Constr. Build. Mater.* 250 (2020) 118903.
- [76] S. Monkman, M. MacDonald, On carbon dioxide utilization as a means to improve the sustainability of ready-mixed concrete, *J. Clean. Prod.* 167 (2017) 365–375.
- [77] X. Qian, J. Wang, Y. Fang, L. Wang, Carbon dioxide as an admixture for better performance of OPC-based concrete, *J. CO₂ Util.* 25 (2018) 31–38.
- [78] T. Lim, B.R. Ellis, S.J. Skerlos, Mitigating CO₂ emissions of concrete manufacturing through CO₂-enabled binder reduction, *Environ. Res. Lett.* 14 (2019) 114014.
- [79] V. Rostami, Y. Shao, A.J. Boyd, Carbonation curing versus steam curing for precast concrete production, *J. Mater. Civ. Eng.* 24 (2012) 1221–1229.
- [80] M. Fernández Bertos, S.J.R. Simons, C.D. Hills, P.J. Carey, A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂, *J. Hazard. Mater.* 112 (2004) 193–205.
<https://doi.org/https://doi.org/10.1016/j.jhazmat.2004.04.019>.

- [81] X. Pan, C. Shi, X. Hu, Z. Ou, Effects of CO₂ surface treatment on strength and permeability of one-day-aged cement mortar, *Constr. Build. Mater.* 154 (2017) 1087–1095.
- [82] X. Pan, C. Shi, N. Farzadnia, X. Hu, J. Zheng, Properties and microstructure of CO₂ surface treated cement mortars with subsequent lime-saturated water curing, *Cem. Concr. Compos.* 99 (2019) 89–99.
<https://doi.org/https://doi.org/10.1016/j.cemconcomp.2019.03.006>.
- [83] D. Zhang, Z. Ghouleh, Y. Shao, Review on carbonation curing of cement-based materials, *J. CO₂ Util.* 21 (2017) 119–131.
<https://doi.org/https://doi.org/10.1016/j.jcou.2017.07.003>.
- [84] J.G. Jang, H.K. Lee, Microstructural densification and CO₂ uptake promoted by the carbonation curing of belite-rich Portland cement, *Cem. Concr. Res.* 82 (2016) 50–57. <https://doi.org/https://doi.org/10.1016/j.cemconres.2016.01.001>.
- [85] Z. He, S. Wang, M. Mahoutian, Y. Shao, Flue gas carbonation of cement-based building products, *J. CO₂ Util.* 37 (2020) 309–319.
<https://doi.org/https://doi.org/10.1016/j.jcou.2020.01.001>.
- [86] B. Šavija, M. Luković, Carbonation of cement paste: Understanding, challenges, and opportunities, *Constr. Build. Mater.* 117 (2016) 285–301.
<https://doi.org/https://doi.org/10.1016/j.conbuildmat.2016.04.138>.
- [87] L. Li, M. Wu, An overview of utilizing CO₂ for accelerated carbonation treatment in the concrete industry, *J. CO₂ Util.* 60 (2022) 102000.

- [88] S. Kashef-Haghighi, S. Ghoshal, Physico–Chemical Processes Limiting CO₂ Uptake in Concrete during Accelerated Carbonation Curing, *Ind. Eng. Chem. Res.* 52 (2013) 5529–5537. <https://doi.org/10.1021/ie303275e>.
- [89] I. Mehdipour, G. Falzone, E.C. La Plante, D. Simonetti, N. Neithalath, G. Sant, How Microstructure and Pore Moisture Affect Strength Gain in Portlandite-Enriched Composites That Mineralize CO₂, *ACS Sustain. Chem. Eng.* 7 (2019) 13053–13061. <https://doi.org/10.1021/acssuschemeng.9b02163>.
- [90] D. Zhang, Y. Shao, Enhancing Chloride Corrosion Resistance of Precast Reinforced Concrete by Carbonation Curing., *ACI Mater. J.* 116 (2019).
- [91] D. Wang, J. Chang, Comparison on accelerated carbonation of β -C₂S, Ca(OH)₂, and C₄AF: Reaction degree, multi-properties, and products, *Constr. Build. Mater.* 224 (2019) 336–347.
<https://doi.org/https://doi.org/10.1016/j.conbuildmat.2019.07.056>.
- [92] Y. Li, W. Liu, F. Xing, S. Wang, L. Tang, S. Lin, Z. Dong, Carbonation of the synthetic calcium silicate hydrate (C-S-H) under different concentrations of CO₂: Chemical phases analysis and kinetics, *J. CO₂ Util.* 35 (2020) 303–313.
<https://doi.org/https://doi.org/10.1016/j.jcou.2019.10.001>.
- [93] A. Morandea, M. Thiéry, P. Dangla, Investigation of the carbonation mechanism of CH and C-S-H in terms of kinetics, microstructure changes and moisture properties, *Cem. Concr. Res.* 56 (2014) 153–170.
<https://doi.org/https://doi.org/10.1016/j.cemconres.2013.11.015>.
- [94] V. Shah, K. Scrivener, B. Bhattacharjee, S. Bishnoi, Changes in microstructure

- characteristics of cement paste on carbonation, *Cem. Concr. Res.* 109 (2018) 184–197. <https://doi.org/10.1016/j.cemconres.2018.04.016>.
- [95] H. Cheng, X. Zhang, H. Song, Morphological Investigation of Calcium Carbonate during Ammonification-Carbonization Process of Low Concentration Calcium Solution, 2014 (2014).
- [96] B.J. Zhan, D.X. Xuan, C.S. Poon, C.J. Shi, Mechanism for rapid hardening of cement pastes under coupled CO₂-water curing regime, *Cem. Concr. Compos.* 97 (2019) 78–88.
- [97] D. Zhang, Y. Shao, Surface scaling of CO₂-cured concrete exposed to freeze-thaw cycles, *J. CO₂ Util.* 27 (2018) 137–144.
- [98] P. He, C. Shi, Z. Tu, C.S. Poon, J. Zhang, Effect of further water curing on compressive strength and microstructure of CO₂-cured concrete, *Cem. Concr. Compos.* 72 (2016) 80–88.
- [99] S. Marikunte, C. Aldea, S.P. Shah, Durability of glass fiber reinforced cement composites:: Effect of silica fume and metakaolin, *Adv. Cem. Based Mater.* 5 (1997) 100–108. [https://doi.org/https://doi.org/10.1016/S1065-7355\(97\)00003-5](https://doi.org/https://doi.org/10.1016/S1065-7355(97)00003-5).
- [100] B. Wei, H. Cao, S. Song, Tensile behavior contrast of basalt and glass fibers after chemical treatment, *Mater. Des.* 31 (2010) 4244–4250. <https://doi.org/https://doi.org/10.1016/j.matdes.2010.04.009>.
- [101] B. Kottitum, Q.T. Phung, N. Maes, W. Prakaypan, T. Srinophakun, Early Age Carbonation of Fiber-Cement Composites under Real Processing Conditions: A

- Parametric Investigation, Appl. Sci. 8 (2018). <https://doi.org/10.3390/app8020190>.
- [102] A.E.F.S. Almeida, G.H.D. Tonoli, S.F. Santos, H. Savastano, Improved durability of vegetable fiber reinforced cement composite subject to accelerated carbonation at early age, Cem. Concr. Compos. 42 (2013) 49–58.
<https://doi.org/https://doi.org/10.1016/j.cemconcomp.2013.05.001>.
- [103] G.E. Urrea-Ceferino, D.K. Panesar, H. Savastano, Adjusting curing parameters for innovative and durable vegetable fibre-cement composites, Cem. Concr. Compos. 103 (2019) 121–133.
<https://doi.org/https://doi.org/10.1016/j.cemconcomp.2019.04.028>.
- [104] V.D. Pizzol, L.M. Mendes, L. Frezzatti, H. Savastano Jr., G.H.D. Tonoli, Effect of accelerated carbonation on the microstructure and physical properties of hybrid fiber-cement composites, Miner. Eng. 59 (2014) 101–106.
<https://doi.org/https://doi.org/10.1016/j.mineng.2013.11.007>.
- [105] H. El-Hassan, Y. Shao, Early carbonation curing of concrete masonry units with Portland limestone cement, Cem. Concr. Compos. 62 (2015) 168–177.
<https://doi.org/https://doi.org/10.1016/j.cemconcomp.2015.07.004>.
- [106] T. Chen, X. Gao, Effect of carbonation curing regime on strength and microstructure of Portland cement paste, J. CO2 Util. 34 (2019) 74–86, (n.d.).
- [107] S. Siddique, A. Naqi, J.G. Jang, Influence of water to cement ratio on CO2 uptake capacity of belite-rich cement upon exposure to carbonation curing, Cem. Concr. Compos. 111 (2020) 103616.
<https://doi.org/https://doi.org/10.1016/j.cemconcomp.2020.103616>.

- [108] S. Monkman, M. MacDonald, R.D. Hooton, P. Sandberg, Properties and durability of concrete produced using CO₂ as an accelerating admixture, *Cem. Concr. Compos.* 74 (2016) 218–224.
<https://doi.org/https://doi.org/10.1016/j.cemconcomp.2016.10.007>.
- [109] X. Ouyang, D.A. Koleva, G. Ye, K. van Breugel, Understanding the adhesion mechanisms between CSH and fillers, *Cem. Concr. Res.* 100 (2017) 275–283.
<https://doi.org/https://doi.org/10.1016/j.cemconres.2017.07.006>.
- [110] E. Berodier, K. Scrivener, Understanding the Filler Effect on the Nucleation and Growth of C-S-H, *J. Am. Ceram. Soc.* 97 (2014) 3764–3773.
- [111] P. Librandi, P. Nielsen, G. Costa, R. Snellings, M. Quaghebeur, R. Baciocchi, Mechanical and environmental properties of carbonated steel slag compacts as a function of mineralogy and CO₂ uptake, *J. CO₂ Util.* 33 (2019) 201–214.
<https://doi.org/https://doi.org/10.1016/j.jcou.2019.05.028>.
- [112] K. Behfarnia, M. Rostami, An assessment on parameters affecting the carbonation of alkali-activated slag concrete, *J. Clean. Prod.* 157 (2017) 1–9.
<https://doi.org/10.1016/j.jclepro.2017.04.097>.
- [113] C. Shi, D. Wang, F. He, M. Liu, Weathering properties of CO₂-cured concrete blocks, *Resour. Conserv. Recycl.* 65 (2012) 11–17.
<https://doi.org/https://doi.org/10.1016/j.resconrec.2012.04.005>.
- [114] J. Han, W. Sun, G. Pan, W. Caihui, Monitoring the evolution of accelerated carbonation of hardened cement pastes by X-ray computed tomography, *J. Mater. Civ. Eng.* 25 (2013) 347–354. [https://doi.org/10.1061/\(ASCE\)MT.1943-](https://doi.org/10.1061/(ASCE)MT.1943-)

5533.0000610.

- [115] K. Ebrahimi, M.J. Daiezadeh, M. Zakertabrizi, F. Zahmatkesh, A. Habibnejad Korayem, A review of the impact of micro- and nanoparticles on freeze-thaw durability of hardened concrete: Mechanism perspective, *Constr. Build. Mater.* 186 (2018) 1105–1113. <https://doi.org/10.1016/j.conbuildmat.2018.08.029>.
- [116] H.-K. Kim, K.-I. Song, J.-K. Song, J.G. Jang, Effect of Carbonation on Abrasion Resistance of Alkali-Activated Slag with Various Activators, *Materials (Basel)*. 12 (2019). <https://doi.org/10.3390/ma12172812>.
- [117] S.M. Park, J.H. Seo, H.-K. Lee, Thermal evolution of hydrates in carbonation-cured Portland cement, *Mater. Struct.* 51 (2018) 1–8.
- [118] A. Belda Revert, K. De Weerd, K. Hornbostel, M.R. Geiker, Carbonation-induced corrosion: Investigation of the corrosion onset, *Constr. Build. Mater.* 162 (2018) 847–856. <https://doi.org/https://doi.org/10.1016/j.conbuildmat.2017.12.066>.
- [119] J. Chang, Y. Gu, W.S. Ansari, Mechanism of blended steel slag mortar with CO₂ curing exposed to sulfate attack, *Constr. Build. Mater.* 251 (2020) 118880. <https://doi.org/https://doi.org/10.1016/j.conbuildmat.2020.118880>.
- [120] H.F.W. Taylor, C. Famy, K.L. Scrivener, Delayed ettringite formation, *Cem. Concr. Res.* 31 (2001) 683–693. [https://doi.org/https://doi.org/10.1016/S0008-8846\(01\)00466-5](https://doi.org/https://doi.org/10.1016/S0008-8846(01)00466-5).
- [121] M. Shoji, T. Higuchi, M. Morioka, K. Yokozeki, Inhibitory effect of alkali-silica reaction by the carbonation reaction, *Cem. Sci. Concr. Technol* 69 (2015) 504–

- [122] S. Xue, X. Kong, F. Zhu, W. Hartley, X. Li, Y. Li, Proposal for management and alkalinity transformation of bauxite residue in China, *Environ. Sci. Pollut. Res.* 23 (2016) 12822–12834. <https://doi.org/10.1007/s11356-016-6478-7>.
- [123] D. Bonenfant, L. Kharoune, S. Sauvé, R. Hausler, P. Niquette, M. Mimeault, M. Kharoune, CO₂ Sequestration by Aqueous Red Mud Carbonation at Ambient Pressure and Temperature, *Ind. Eng. Chem. Res.* 47 (2008) 7617–7622. <https://doi.org/10.1021/ie7017228>.
- [124] J. Pradhan, J. Das, S. Das, R.S. Thakur, Adsorption of phosphate from aqueous solution using activated red mud, *J. Colloid Interface Sci.* 204 (1998) 169–172.
- [125] H. Sutar, S.C. Mishra, S.K. Sahoo, H.S. Maharana, Progress of red mud utilization: An overview, *Am. Chem. Sci. J.* 4 (2014) 255–279.
- [126] M.J. Chaddha, S.B. Rai, R.N. Goyal, Characteristics of red mud of Indian alumina plants and their possible utilization, National seminar on environmental concern and remedies in alumina industry at NAICO, India, ENVICON-2007, Damanjodi, India (2007) 41–44.
- [127] D.J. Glenister, M.R. Thornber, Alkalinity of red mud and its application for the management of acid wastes, *Chemica* 85 (1985) 100–113.
- [128] S. Khaitan, D.A. Dzombak, G. V Lowry, Mechanisms of neutralization of bauxite residue by carbon dioxide, *J. Environ. Eng.* 135 (2009) 433–438.
- [129] E. Szirmai, S. Babusek, G. Balogh, A. Nedves, G. Horvath, Z. Lebenyi, J. Pinter,

Method for the multistage, waste-free processing of red mud to recover basic materials of chemical industry, (1991).

- [130] R.C. Sahu, R.K. Patel, B.C. Ray, Neutralization of red mud using CO₂ sequestration cycle, *J. Hazard. Mater.* 179 (2010) 28–34.
- [131] W.D. Li, New Separation Technology Research of Iron from Bayer Progress Red Mud, Cent. South Univ. Libr. Chang. China (2006).
- [132] Y.F. Sun, F.Z. Dong, J.T. Liu, S. WANG, Technology for recovering iron from red mud by Bayer process, *Met. Mine* 9 (2009) 176–178.
- [133] X.F. Zheng, Recycling technology of aluminum and sodium from low temperature bayer progress red mud, *Shandong Met.* 32 (2010) 16–17.
- [134] D.D. Dimas, I.P. Giannopoulou, D. Panias, Utilization of alumina red mud for synthesis of inorganic polymeric materials, *Miner. Process. Extr. Metall. Rev.* 30 (2009) 211–239.
- [135] R.B. Hajela, R.G. Gupta, R.K. Goel, Disposal of solid wastes—red mud and fly-ash in the production of heavy clay products, *Int. J. Environ. Stud.* 33 (1989) 125–132.
- [136] X.R. Qiu, Y.Y. Qi, Reasonable utilization of red mud in the cement industry, *Cem. Technol* 6 (2011) 103–105.
- [137] J.Z. Qi, J. Yang, M. Wang, B. Xiao, Experimental research on road materials of red mud, *Univ. Huazhong Sci. Technol. Wuhan, China* 82 (2005).
- [138] L.G. Yang, Z.L. Yao, D.S. Bao, Pumped and cemented red mud slurry filling

- mining method, *Min. Res. Dev.* 16 (1996) 18–22.
- [139] X.L. Nan, T.A. Zhang, Y. Liu, Comprehensive utilization and analysis of Chinese red mud, *Chin. J. Process Eng* 10 (2010) 264–270.
- [140] R.R. Rathod, N.T. Suryawanshi, P.D. Memade, Evaluation of the properties of red mud concrete, *IOSR J. Mech. Civ. Eng.* 1 (2013) 31–34.
- [141] A.B. Sawant, M.B. Kumthekar, S.G. Sawant, A.R. Mud, Utilization of neutralized red mud (industrial waste) in concrete, *Int. J. Inven. Eng. Sci* 1 (2013) 9–13.
- [142] D.L. Metilda, C. Selvamony, R. Anandakumar, A. Seenii, Investigations on optimum possibility of replacing cement partially by redmud in concrete, *Sci. Res. Essays* 10 (2015) 137–143.
- [143] K. Sethy, R.K. Sitha, S. Barpanda, B.R. Bhoi, Experimental investigation of strength properties of red mud concrete, in: *AIP Conf. Proc.*, AIP Publishing, 2019.
- [144] B.T. Sapna, M. Aravindhraj, Influence of red mud as a partial replacement of cement with hydrated lime, *Int. Res. J. Eng. Technol.* 5 (2018) 1282–1288.
- [145] B. Sawant, D.B. Kamble, T.B. Shinde, Utilization of industrial waste (red mud) in concrete construction, *Int. J. Innov. Res. Sci. Eng.* 2 (2016) 112–121.
- [146] P. Wang, D.-Y. Liu, Physical and chemical properties of sintering red mud and bayer red mud and the implications for beneficial utilization, *Materials (Basel)*. 5 (2012) 1800–1810.
- [147] J. He, Y. Jie, J. Zhang, Y. Yu, G. Zhang, Synthesis and characterization of red

- mud and rice husk ash-based geopolymer composites, *Cem. Concr. Compos.* 37 (2013) 108–118.
- [148] I.M. Nikbin, M. Aliaghazadeh, S.H. Charkhtab, A. Fathollahpour, Environmental impacts and mechanical properties of lightweight concrete containing bauxite residue (red mud), *J. Clean. Prod.* 172 (2018) 2683–2694.
- [149] T. Gupta, Y. Agrawal, K.S. Kanyal, Properties of sustainable concrete containing red mud: a review, *J. Sci. Res. Reports* 27 (2021) 15–26.
- [150] P.S. Sai, C. Sukesh, Strength properties of concrete by using red mud as a replacement of cement with hydrated lime, *Int. J. Civ. Eng. Technol.* 8 (2017) 38–49.
- [151] W.C. Tang, Z. Wang, S.W. Donne, M. Forghani, Y. Liu, Influence of red mud on mechanical and durability performance of self-compacting concrete, *J. Hazard. Mater.* 379 (2019) 120802.
- [152] M. Ghalehnovi, E.A. Shamsabadi, A. Khodabakhshian, F. Sourmeh, J. De Brito, Self-compacting architectural concrete production using red mud, *Constr. Build. Mater.* 226 (2019) 418–427.
- [153] P. Ashok, M.P. Sureshkumar, Experimental studies on concrete utilising red mud as a partial replacement of cement with hydrated lime, *J. Mech. Civ. Eng.* (2014) 1–10.
- [154] P.N. Bishetti, L. Pammar, Experimental study on utilization of industrial waste in concrete, *Int. J. Tech. Res. Appl.* 2 (2014) 49–52.

- [155] K. Viyasun, R. Anuradha, K. Thangapandi, D.S. Kumar, A. Sivakrishna, R. Gobinath, Investigation on performance of red mud based concrete, *Mater. Today Proc.* 39 (2021) 796–799.
- [156] S.M. Palaniappan, V. Govindasamy, A.B. Jabar, Experimental investigation on flexural performance of functionally graded concrete beams using flyash and red mud, *Matéria (Rio Janeiro)* 26 (2021) e12913.
- [157] C. Venkatesh, R. Nerella, M.S.R. Chand, Role of red mud as a cementing material in concrete: A comprehensive study on durability behavior, *Innov. Infrastruct. Solut.* 6 (2021) 13.
- [158] R.-X. Liu, C.-S. Poon, Utilization of red mud derived from bauxite in self-compacting concrete, *J. Clean. Prod.* 112 (2016) 384–391.
- [159] X. Yang, J. Zhao, H. Li, P. Zhao, Q. Chen, Recycling red mud from the production of aluminium as a red cement-based mortar, *Waste Manag. Res.* 35 (2017) 500–507. <https://doi.org/10.1177/0734242X16684386>.
- [160] J.M. Ortega, M. Cabeza, A.J. Tenza-Abril, T. Real-Herraiz, M.Á. Climent, I. Sánchez, Effects of Red Mud Addition in the Microstructure, Durability and Mechanical Performance of Cement Mortars, *Appl. Sci.* 9 (2019). <https://doi.org/10.3390/app9050984>.
- [161] T.D. Rushendra Revathy, A. Ramachandran, K. Palanivelu, Sequestration of CO₂ by red mud with flue gas using response surface methodology, *Carbon Manag.* 12 (2021) 139–151.

- [162] R. Ragipani, K. Sreenivasan, R.P. Anex, H. Zhai, B. Wang, Direct air capture and sequestration of CO₂ by accelerated indirect aqueous mineral carbonation under ambient conditions, *ACS Sustain. Chem. Eng.* 10 (2022) 7852–7861.
- [163] J.-G. Shim, D.W. Lee, J.H. Lee, N.-S. Kwak, Experimental study on capture of carbon dioxide and production of sodium bicarbonate from sodium hydroxide, *Environ. Eng. Res.* 21 (2016) 297–303.
- [164] X. Wang, Q. Zhan, X. Zhang, Y. Su, J. Zhou, Study on improving the carbon sequestration properties of sintered red mud by regulating pressure, *J. Build. Eng.* 84 (2024) 108518.
- [165] Y. Zhang, G. Zhan, Z. Huang, L. Xing, Y. Ying, Z. Chen, J. Li, Performance and mechanisms of alkaline solid waste in CO₂ mineralization and utilization, *Waste Manag.* 175 (2024) 62–72.
- [166] G. Kuntikana, S. Syed, D.N. Singh, S.S. Pandit, N. Kapuri, Amelioration of bauxite residues by sequential slurry carbonation, *Mater. Perform. Charact.* 10 (2021) 391–408.
- [167] V.S. Yadav, M. Prasad, J. Khan, S.S. Amritphale, M. Singh, C.B. Raju, Sequestration of carbon dioxide (CO₂) using red mud, *J. Hazard. Mater.* 176 (2010) 1044–1050. <https://doi.org/10.1016/j.jhazmat.2009.11.146>.
- [168] H.F.W. Taylor, *Cement chemistry*, Thomas Telford London, 1997.
- [169] K. Tuutti, *Corrosion of steel in concrete*, (1982).
- [170] Q. Pu, L. Jiang, J. Xu, H. Chu, Y. Xu, Y. Zhang, Evolution of pH and chemical

- composition of pore solution in carbonated concrete, *Constr. Build. Mater.* 28 (2012) 519–524. <https://doi.org/10.1016/j.conbuildmat.2011.09.006>.
- [171] D. Zhang, Z. Ghoulleh, Y. Shao, Review on carbonation curing of cement-based materials. *J CO2 Util* 21: 119–131, (2017).
- [172] J. Zhang, G.W. Scherer, Comparison of methods for arresting hydration of cement, *Cem. Concr. Res.* 41 (2011) 1024–1036.
- [173] V.M. Bhuchar, V.P. Kukreja, S.R. Das, Evaluation of color changes of indicators. Specific color discrimination of phthalein and sulfonephthalein indicators, *Anal. Chem.* 43 (1971) 1847–1853.
- [174] V.K. Ortolan, M. Mancio, B.F. Tutikian, Evaluation of the influence of the pH of concrete pore solution on the corrosion resistance of steel reinforcement, *J. Build. Pathol. Rehabil.* 1 (2016) 10.
- [175] W.O. Alimi, S.K. Adekunle, S. Ahmad, A.O. Amao, Carbon dioxide sequestration characteristics of concrete mixtures incorporating high-volume cement kiln dust, *Case Stud. Constr. Mater.* 17 (2022) e01414.
- [176] R.M. Santos, J. Van Bouwel, E. Vandavelde, G. Mertens, J. Elsen, T. Van Gerven, Accelerated mineral carbonation of stainless steel slags for CO2 storage and waste valorization: Effect of process parameters on geochemical properties, *Int. J. Greenh. Gas Control* 17 (2013) 32–45.
- [177] P. Rattanadecho, N. Suwannapum, B. Chatveera, D. Atong, N. Makul, Development of compressive strength of cement paste under accelerated curing by

- using a continuous microwave thermal processor, *Mater. Sci. Eng. A* 472 (2008) 299–307.
- [178] D. Zhang, X. Cai, B. Jaworska, Effect of pre-carbonation hydration on long-term hydration of carbonation-cured cement-based materials, *Constr. Build. Mater.* 231 (2020) 117122. <https://doi.org/https://doi.org/10.1016/j.conbuildmat.2019.117122>.
- [179] D. Zhang, X. Cai, Y. Shao, Carbonation curing of precast fly ash concrete, *J. Mater. Civ. Eng.* 28 (2016) 4016127.
- [180] S. Monkman, B.E.J. Lee, K. Grandfield, M. MacDonald, L. Raki, The impacts of in-situ carbonate seeding on the early hydration of tricalcium silicate, *Cem. Concr. Res.* 136 (2020) 106179. <https://doi.org/https://doi.org/10.1016/j.cemconres.2020.106179>.
- [181] M. Thomas, Impact of CO₂ Utilization in Fresh Concrete on Corrosion of Steel Reinforcement, CarbonCure Technol. Inc., Dartmouth, NS, Canada (2019).
- [182] S. Monkman, Y. Sargam, O. Naboka, B. Lothenbach, Early age impacts of CO₂ activation on the tricalcium silicate and cement systems, *J. CO₂ Util.* 65 (2022) 102254. <https://doi.org/https://doi.org/10.1016/j.jcou.2022.102254>.
- [183] K. Scrivener, R. Snellings, B. Lothenbach, C.R.C. Press, A practical guide to microstructural analysis of cementitious materials, Crc Press Boca Raton, FL, USA:, 2016.
- [184] R. Zarzuela, M. Luna, L.M. Carrascosa, M.P. Yeste, I. Garcia-Lodeiro, M.T. Blanco-Varela, M.A. Cauqui, J.M. Rodríguez-Izquierdo, M.J. Mosquera,

- Producing CSH gel by reaction between silica oligomers and portlandite: A promising approach to repair cementitious materials, *Cem. Concr. Res.* 130 (2020) 106008.
- [185] P.K. Mehta, *Concrete. Structure, properties and materials*, (1986).
- [186] Y.-Y. Wang, Q.-Z. Yao, G.-T. Zhou, S.-Q. Fu, Transformation of amorphous calcium carbonate into monohydrocalcite in aqueous solution: a biomimetic mineralization study, *Eur. J. Mineral.* 27 (2015) 717–729.
- [187] F.W. Wilburn, J.H. Sharp, D.M. Tinsley, R.M. McIntosh, The effect of procedural variables on TG, DTG and DTA curves of calcium carbonate, *J. Therm. Anal. Calorim.* 37 (1991) 2003–2019.
- [188] S.-W. Lee, Y.-J. Kim, Y.-H. Lee, H. Guim, S.M. Han, Behavior and characteristics of amorphous calcium carbonate and calcite using CaCO₃ film synthesis, *Mater. Des.* 112 (2016) 367–373.
<https://doi.org/https://doi.org/10.1016/j.matdes.2016.09.099>.
- [189] Y. Li, T. Mi, W. Liu, Z. Dong, B. Dong, L. Tang, F. Xing, Chemical and mineralogical characteristics of carbonated and uncarbonated cement pastes subjected to high temperatures, *Compos. Part B Eng.* 216 (2021) 108861.
<https://doi.org/https://doi.org/10.1016/j.compositesb.2021.108861>.
- [190] E. Ruiz-Agudo, K. Kudłacz, C. V Putnis, A. Putnis, C. Rodriguez-Navarro, Dissolution and carbonation of portlandite [Ca (OH) ₂] single crystals, *Environ. Sci. Technol.* 47 (2013) 11342–11349.

- [191] C. Li, X.Z. Gong, S.P. Cui, Z.H. Wang, Y. Zheng, B.C. Chi, CO₂ emissions due to cement manufacture, in: *Mater. Sci. Forum*, Trans Tech Publ, 2011: pp. 181–187.
- [192] A. Vollpracht, B. Lothenbach, R. Snellings, J. Haufe, The pore solution of blended cements: a review, *Mater. Struct.* 49 (2016) 3341–3367.
- [193] X. Xian, Y. Shao, Microstructure of cement paste subject to ambient pressure carbonation curing, *Constr. Build. Mater.* 296 (2021) 123652.
<https://doi.org/https://doi.org/10.1016/j.conbuildmat.2021.123652>.
- [194] S. Kashef-Haghighi, Y. Shao, S. Ghoshal, Mathematical modeling of CO₂ uptake by concrete during accelerated carbonation curing, *Cem. Concr. Res.* 67 (2015) 1–10.
- [195] T. Nishikawa, K. Suzuki, S. Ito, K. Sato, T. Takebe, Decomposition of synthesized ettringite by carbonation, *Cem. Concr. Res.* 22 (1992) 6–14.
- [196] H.E. Yücel, S. Özcan, Strength characteristics and microstructural properties of cement mortars incorporating synthetic wollastonite produced with a new technique, *Constr. Build. Mater.* 223 (2019) 165–176.
- [197] S. Siddique, J.G. Jang, T. Gupta, Developing marble slurry as supplementary cementitious material through calcination: Strength and microstructure study, *Constr. Build. Mater.* 293 (2021) 123474.
- [198] D.A.D. Silva, H.R. Roman, P.J.P. Gleize, Evidences of chemical interaction between EVA and hydrating Portland cement, *Cem. Concr. Res.* 32 (2002) 1383–1390.

- [199] P. Yu, R.J. Kirkpatrick, B. Poe, P.F. McMillan, X. Cong, Structure of calcium silicate hydrate (C-S-H): Near-, Mid-, and Far-infrared spectroscopy, *J. Am. Ceram. Soc.* 82 (1999) 742–748.
- [200] I.G. Lodeiro, D.E. MacPhee, A. Palomo, A. Fernández-Jiménez, Effect of alkalis on fresh C–S–H gels. FTIR analysis, *Cem. Concr. Res.* 39 (2009) 147–153.
- [201] H.K. Choudhary, A. V Anupama, R. Kumar, M.E. Panzi, S. Matteppanavar, B.N. Sherikar, B. Sahoo, Observation of phase transformations in cement during hydration, *Constr. Build. Mater.* 101 (2015) 122–129.
- [202] T.L. Hughes, C.M. Methven, T.G.J. Jones, S.E. Pelham, P. Fletcher, C. Hall, Determining cement composition by Fourier transform infrared spectroscopy, *Adv. Cem. Based Mater.* 2 (1995) 91–104.
- [203] L. Jiang, Q. Wu, Z. Huo, Z. Zhu, F. Wu, B. Lu, An approach to improve compressive strength of cement paste at low temperature by carbonation curing, *Constr. Build. Mater.* 365 (2023) 130128.
<https://doi.org/https://doi.org/10.1016/j.conbuildmat.2022.130128>.
- [204] V. Rostami, Y. Shao, A.J. Boyd, Z. He, Microstructure of cement paste subject to early carbonation curing, *Cem. Concr. Res.* 42 (2012) 186–193.
- [205] L. Mo, F. Zhang, M. Deng, Mechanical performance and microstructure of the calcium carbonate binders produced by carbonating steel slag paste under CO₂ curing, *Cem. Concr. Res.* 88 (2016) 217–226.
- [206] R.A. Assaggaf, S.K. Adekunle, S. Ahmad, M. Maslehuddin, O.S.B. Al-Amoudi,

- S.I. Ali, Mechanical properties, durability characteristics and shrinkage of plain cement and fly ash concretes subjected to accelerated carbonation curing, *J. South African Inst. Civ. Eng.* 61 (2019) 73–81.
- [207] NRMCA, TIP 17 - Drying Shrinkage of Concrete, *Nrmca* 17 (2018) 6.
- [208] R. Gilbert, Shrinkage, Cracking and Deflection the Serviceability of Concrete Structures, *Electron. J. Struct. Eng.* 1 (2001). <https://doi.org/10.56748/ejse.1121>.
- [209] D. Zhang, T. Liu, Y. Shao, Weathering carbonation behavior of concrete subject to early-age carbonation curing, *J. Mater. Civ. Eng.* 32 (2020) 4020038.
- [210] N.C. Collier, Transition and decomposition temperatures of cement phases—a collection of thermal analysis data, *Ceramics-Silikaty* 60 (2016).
- [211] M.L.P. Antunes, S.J. Couperthwaite, F.T. da Conceição, C.P. Costa de Jesus, P.K. Kiyohara, A.C.V. Coelho, R.L. Frost, Red Mud from Brazil: Thermal Behavior and Physical Properties, *Ind. Eng. Chem. Res.* 51 (2012) 775–779. <https://doi.org/10.1021/ie201700k>.
- [212] O. Chowaniec, Limestone addition in cement, EPFL, 2012.
- [213] E. Berodier, K. Scrivener, Evolution of pore structure in blended systems, *Cem. Concr. Res.* 73 (2015) 25–35.
- [214] R.C.O. Romano, H.M. Bernardo, M.H. Maciel, R.G. Pileggi, M.A. Cincotto, Hydration of Portland cement with red mud as mineral addition, *J. Therm. Anal. Calorim.* 131 (2018) 2477–2490. <https://doi.org/10.1007/s10973-017-6794-2>.
- [215] L. Senff, R.C.E. Modolo, A.S. Silva, V.M. Ferreira, D. Hotza, J.A. Labrincha,

Influence of red mud addition on rheological behavior and hardened properties of mortars, *Constr. Build. Mater.* 65 (2014) 84–91.

- [216] L. Senff, D. Hotza, J.A. Labrincha, Effect of red mud addition on the rheological behaviour and on hardened state characteristics of cement mortars, *Constr. Build. Mater.* 25 (2011) 163–170.
- [217] A. Dureković, Cement pastes of low water to solid ratio: An investigation of the porosity characteristics under the influence of a superplasticizer and silica fume, *Cem. Concr. Res.* 25 (1995) 365–375. [https://doi.org/https://doi.org/10.1016/0008-8846\(95\)00022-4](https://doi.org/10.1016/0008-8846(95)00022-4).
- [218] Y. Malecot, L. Zingg, M. Briffaut, J. Baroth, Influence of free water on concrete triaxial behavior: The effect of porosity, *Cem. Concr. Res.* 120 (2019) 207–216. [https://doi.org/https://doi.org/10.1016/j.cemconres.2019.03.010](https://doi.org/10.1016/j.cemconres.2019.03.010).
- [219] Y. Bo, Y. Sensen, S. Chris, C. Wei, Activation of Binary Binder Containing Fly Ash and Portland Cement Using Red Mud as Alkali Source and Its Application in Controlled Low-Strength Materials, *J. Mater. Civ. Eng.* 32 (2020) 4019356. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0003023](https://doi.org/10.1061/(ASCE)MT.1943-5533.0003023).
- [220] Y. Liu, Y. Zhuge, X. Chen, W. Duan, R. Fan, L. Outhred, L. Wang, Micro-chemomechanical properties of red mud binder and its effect on concrete, *Compos. Part B Eng.* 258 (2023) 110688. [https://doi.org/https://doi.org/10.1016/j.compositesb.2023.110688](https://doi.org/10.1016/j.compositesb.2023.110688).
- [221] M. Kushwaha, S. Akhtar, S. Rajput, Development of the self compacting concrete by industrial waste (red mud), *Int. J. Eng. Res. Appl.* 3 (2013) 539–542.

- [222] I. Vangelatos, G.N. Angelopoulos, D. Boufounos, Utilization of ferroalumina as raw material in the production of Ordinary Portland Cement, *J. Hazard. Mater.* 168 (2009) 473–478.
- [223] D. V Ribeiro, A.S. Silva, J.A. Labrincha, M.R. Morelli, Rheological properties and hydration behavior of Portland cement mortars containing calcined red mud, *Can. J. Civ. Eng.* 40 (2013) 557–566.
- [224] M. Anirudh, K.S. Rekha, C. Venkatesh, R. Nerella, Characterization of red mud based cement mortar; mechanical and microstructure studies, *Mater. Today Proc.* 43 (2021) 1587–1591. <https://doi.org/https://doi.org/10.1016/j.matpr.2020.09.504>.
- [225] E.G. Nawy, *Fundamentals of high-performance concrete*, John Wiley & Sons, 2000.
- [226] M. Kioumars, F. Azarhomayun, M. Haji, M. Shekarchi, Effect of shrinkage reducing admixture on drying shrinkage of concrete with different w/c ratios, *Materials (Basel)*. 13 (2020) 5721.
- [227] R. Liu, C. Poon, Effects of red mud on properties of self-compacting mortar, *J. Clean. Prod.* 135 (2016) 1170–1178. <https://doi.org/https://doi.org/10.1016/j.jclepro.2016.07.052>.
- [228] L. Tang, Study of the possibilities of using Red Mud as an additive in concrete and grout mortar, *Sven. Kärnbränslehantering AB Swedish Nucl. Fuel Waste Manag. Co., Stock. Sweden* (2014).
- [229] B. Lu, C. Shi, Z. Cao, M. Guo, J. Zheng, Effect of carbonated coarse recycled

- concrete aggregate on the properties and microstructure of recycled concrete, *J. Clean. Prod.* 233 (2019) 421–428.
<https://doi.org/https://doi.org/10.1016/j.jclepro.2019.05.350>.
- [230] R.I. Khan, M. Intesarul Haque, S. Siddique, E.N. Landis, W. Ashraf, Effects of amino acids on the multiscale properties of carbonated wollastonite composites, *Constr. Build. Mater.* 374 (2023) 130816.
<https://doi.org/https://doi.org/10.1016/j.conbuildmat.2023.130816>.
- [231] R.I. Khan, W. Ashraf, J. Olek, Amino acids as performance-controlling additives in carbonation-activated cementitious materials, *Cem. Concr. Res.* 147 (2021) 106501. <https://doi.org/https://doi.org/10.1016/j.cemconres.2021.106501>.
- [232] L. Addadi, S. Raz, S. Weiner, Taking advantage of disorder: amorphous calcium carbonate and its roles in biomineralization, *Adv. Mater.* 15 (2003) 959–970.
- [233] I. García Lodeiro, D.E. Macphee, A. Palomo, A. Fernández-Jiménez, Effect of alkalis on fresh C–S–H gels. FTIR analysis, *Cem. Concr. Res.* 39 (2009) 147–153.
<https://doi.org/https://doi.org/10.1016/j.cemconres.2009.01.003>.
- [234] M.O. Yusuf, Bond Characterization in Cementitious Material Binders Using Fourier-Transform Infrared Spectroscopy, *Appl. Sci.* 13 (2023).
<https://doi.org/10.3390/app13053353>.
- [235] J. Yang, H. Xiao, X. He, J. Zeng, Y. Su, W. Li, Y. Wang, Z. Jin, Effect of wet grinding carbonation of sintering red mud on the performance of carbon sequestered mortar, *Constr. Build. Mater.* 445 (2024) 137933.
<https://doi.org/https://doi.org/10.1016/j.conbuildmat.2024.137933>.

- [236] S. Liu, C. Pan, H. Zhang, S. Yao, P. Shen, X. Guan, C. Shi, H. Li, Development of novel mineral admixtures for sulphoaluminate cement clinker: The effects of wet carbonation activated red mud, *J. Build. Eng.* 67 (2023) 105920.
<https://doi.org/https://doi.org/10.1016/j.jobbe.2023.105920>.

Vitae

Name	:Muhammad Talha Shafique
Nationality	:Pakistani
Date of Birth	:10/31/1997
Email	:talhashafiq144@gmail.com
Address	:House No-3, Street -2, Kucha Husnain, Renala Khurd, District Okara, Pakistan, 56130
Academic Background	MSc in Civil Engineering from King Fahad University of Petroleum and Minerals KFUPM, Dhahran, Saudi Arabia From: 2022-2024 BSc in Civil Engineering from National University of Sciences and Technology NUST, H-12, Islamabad, Pakistan From: 2016 - 2020