

**ACCELERATED CARBONATION CURING AS A CO₂
SEQUESTRATION AND WATER CONSERVATION
TECHNIQUE**

A Thesis

*submitted in fulfilment of the requirement
for the award of degree of*

DOCTOR OF PHILOSOPHY

in

CIVIL ENGINEERING

by

DEVENDER SHARMA

Reg. No. 951602009

Under the guidance of

Dr. SHWETA GOYAL

Professor



Department of Civil Engineering

Thapar Institute of Engineering & Technology

Patiala – 147004 (Punjab), INDIA

2021

DECLARATION

I, Devender Sharma hereby declare that the thesis titled, “**Accelerated Carbonation Curing as a CO₂ Sequestration and Water Conservation Technique**” submitted to **Thapar Institute of Engineering and Technology (Deemed University), Patiala**, in fulfillment of the requirements for the award of degree of **Doctor of Philosophy** in Civil Engineering is a record of an original and independent research work done by me during the period July, 2016 to February, 2021 under the supervision and guidance of **Dr. Shweta Goyal**, Professor, Department of Civil Engineering, Thapar Institute of Engineering and Technology, Patiala.

The work contained in this thesis has not been previously submitted to meet the requirements for a degree or diploma at this or any other higher education institution.



Devender Sharma

Reg. No. 951602009

CERTIFICATE

Certified that the work presented in this thesis titled “**Accelerated Carbonation Curing as a CO₂ Sequestration and Water Conservation Technique**” which is being submitted by **Mr. Devender Sharma (Regd. No. 951602009)** in fulfillment of the requirements for the award of degree of **Doctor of Philosophy** in the **Department of Civil Engineering, Thapar Institute of Engineering and Technology, Patiala, India**, is an authentic record of the research work carried out by him under our supervision and guidance.

The contents of this thesis, in full or in part, have not been submitted to any other Institute or University for the award of any degree or diploma.



Dr. Shweta Goyal

Professor

Department of Civil Engineering

Thapar Institute of Engineering and Technology

Patiala – 147004 (Punjab), India

ABSTRACT

Global warming has become one of the biggest problems for a sustainable future ever since the start of the industrial era. CO₂ is a major greenhouse gas which is responsible for global warming, with cement industry contributing towards 5% of worldwide CO₂ emissions. CO₂ sequestration is described as long-term storage of atmospheric CO₂ in stable forms, and is identified as one of the solutions to further mitigate higher levels of CO₂. The ability of cement to react with the atmospheric CO₂ makes cement-based materials viable carbon sinks. The process of interaction of cement with atmospheric carbon dioxide is called natural carbonation. Instead of natural carbonation, the process of deliberately supplying CO₂ to the cement system during very early ages of strength development is called accelerated carbonation curing (ACC). During ACC, the captured CO₂ gas is passed over freshly cast concrete for a certain duration, pressure and relative humidity. In this process, CO₂ reacts with unhydrated cement components (calcium silicates) and hydrated cement compounds (calcium hydroxide and C-S-H) to form CaCO₃ that is stored as stable precipitate in concrete.

The objective of this research work is to evaluate the performance of concrete when subjected to ACC. The testing programme is divided into various subparts. In the first part, the performance of carbonation cured concrete was evaluated vis-à-vis water curing in terms of mechanical properties, permeation properties and microstructural changes of concrete, with special emphasis on surface characteristics. ACC was carried out for a period of 6 hours after initial preconditioning of 2 hours and followed by water spray for three days. The microstructural analysis of the mixes indicated considerable modification of the concrete surface by adopting carbonation curing. It was observed that calcium carbonate formed during the carbonation process gets accumulated in the concrete pores, thereby refining the pore structure and improving the permeation characteristics of concrete. Due to the pore refinement and formation of additional CSH gel formed during the carbonation curing process, an improvement in mechanical properties was also visible. The benefit of ACC was more pronounced on abrasion resistance of concrete as

compared to compressive strength. Both the techniques were further analysed by ANOVA and stoichiometric analysis. ANOVA data indicated that ACC has a more prominent effect on surface of concrete than on the bulk properties.

Further, the effect of carbonation curing duration on the properties of concrete was investigated. For this, the concrete specimens were subjected to carbonation curing duration of 6, 12 or 24 hours and the results were compared with water cured concrete. The mechanical properties of concrete were found to vary significantly with variation in duration of ACC. During the early age testing, the strength of concrete was observed to increase with the increase in carbonation duration. However, at the later ages, highest strength and abrasion resistance was achieved by C12 mixes. Mixes subjected to 24 hours of ACC exhibited lower strength and abrasion resistance; which was attributed to the higher intensity of carbonation in the C24 specimens that resulted in decalcification of CSH into weak silica gel. Secondly, the higher intensity of carbonation led to extensive pore water loss from concrete, which not only created internal voids in the mix, but also depleted the available water required for further hydration in concrete. The durability of concrete subjected to different duration of carbonation curing was analyzed using drying shrinkage test and resistance to weathering carbonation. The drying shrinkage of concrete was observed to be considerably reduced for carbonation cured specimens and the magnitude of reduction in drying shrinkage was observed to be directly proportional to the duration of carbonation curing. In all, carbonation curing of 12 hours was observed to be optimal as it provided better mechanical and durability characteristics to concrete.

In the second part of this work, effect of ACC was studied on performance of mineral admixture based cementitious systems. Three types of mineral admixture based systems were considered: fly ash based portland pozzolana cement (PPC), ground granulated blast furnace slag (GGBS) and cement kiln dust (CKD). Both GGBS and CKD were incorporated as partial replacement of cement in replacement levels varying from 0% to 50%. It was observed that the later age performance of mortars made with fly ash based PPC or GGBS was negatively affected by adopting carbonation curing. It was due to fact

that carbonation curing procedure consumed most of the Ca(OH)_2 formed at early ages in the carbonation reaction and converted it into calcium carbonate. Due to this, Ca(OH)_2 was not available in the matrix to allow the continuation of the pozzolanic reaction. Therefore, the advantage of presence of pozzolanic material could not be achieved in carbonation cured mortars. The post-conditioning of the specimens after carbonation reaction compensated to some extent on the negative effect of carbonation curing on the pozzolanic reaction. On the other hand, the performance of CKD based mortars was observed to be significantly improved with carbonation curing at both the early ages as well as later ages. The cementitious nature and finer particle size of CKD particles was advantageous in carbonation curing regime.

The CO_2 sequestration potential of ACC procedure was investigated for all mixes from the TGA analysis of the mixes. ACC samples registered an effective CO_2 uptake of 14%, 20% and 24% respectively for carbonation curing duration of 6 hours, 12 hours and 24 hours. In terms of CO_2 sequestration ability of different cementitious based systems, it was observed that CO_2 uptake capacity was 18%, 15%, 12% and 20% for OPC, PPC, GGBS and CKD based cementitious systems, respectively.

LIST OF PUBLICATIONS

Publications in SCI indexed journals

1. D. Sharma, S. Goyal, '*Accelerated carbonation curing of cement mortars containing cement kiln dust: An effective way of CO₂ sequestration and carbon footprint reduction*', **Journal of Cleaner Production**, 192 (2018) 844–854. DOI:10.1016/J.JCLEPRO.2018.05.027. Impact Factor- 7.246
2. D. Sharma, S. Goyal, '*Effect of accelerated carbonation curing on near surface properties of concrete*', **European Journal of Environmental and Civil Engineering**, 2020, Taylor and Francis. DOI: [10.1080/19648189.2019.1707714](https://doi.org/10.1080/19648189.2019.1707714). Impact Factor- 1.832

Book Chapter

1. S. Goyal, D. Sharma, 'CO₂ sequestration in cement', **Start-Up Creation**, Elsevier, Woodhead Publishing. 2020 , Page no. 109-194.

Conference Publication

1. D. Sharma, S. Goyal, '*Effect of accelerated carbonation curing on durability properties of concrete*' **International Conference of Rehabilitation and Retrofitting of Structures, Mumbai, Maharashtra, June 24-25, 2019.**

ABBREVIATIONS

Abbreviation	Word(s)
CaO	Calcium oxide
OPC	Ordinary Portland cement
MgO	Magnesium oxide
CaCO ₃	calcite
C-S-H	Calcium silicate hydrate
Ca(OH) ₂	Calcium hydroxide
SEM	Scanning electron microscopy
EDS	Energy dispersive spectroscopy
ANOVA	Analysis of variance
df	Degree of freedom
SS	Sum of squares
MSS	Mean Sum of Squares
LOI	Loss of ignition
CO ₂	Carbon dioxide
BIS	Bureau of Indian Standards
TGA	Thermogravimetric analysis
C ₃ A	Tri Calcium aluminate
ASTM	American Society for Testing and Materials
SiO ₂	Silicon oxide
Al ₂ O ₃	Aluminum oxide
Fe ₂ O ₃	Ferric oxide

SO ₃	Sulfur trioxide
Na ₂ O	Sodium Oxide
K ₂ O	Potassium oxide
F.M.	Fineness modulus
RCPT	Rapid chloride permeability test
CKD	Cement kiln dust
ACC	Accelerated Carbonation Curing
C6	Carbonation Curing for 6 hours
C12	Carbonation Curing for 12 hours
C24	Carbonation Curing for 24 hours
WC	Water Curing
E	Ettringite
V	Voids
d_w	Depth of wear

CONTENTS

Declaration	i
Certificate	ii
Acknowledgement	iii
Abstract	iv
List of Publications	vii
Abbreviations	viii
Table of Contents	x
List of Tables	xvii
List of Figures	xix

CHAPTER – 1 INTRODUCTION

1.1	GENERAL	1
1.2	CARBON DIOXIDE SEQUESTRATION IN CONCRETE	2
1.3	WATER CONSERVATION IN THE CONSTRUCTION SECTOR	3
1.4	CURING OF CONCRETE	4
1.5	MECHANISM OF WATER CURING	5
1.6	ACCELERATED CARBONATION CURING	6
1.6.1	Reaction Mechanism of ACC	7
1.6.2	Laboratory Processing of ACC	10
1.6.3	Laboratory Setup of Carbonation Curing Chamber	12
1.7	SIGNIFICANCE OF THE RESEARCH	13
1.8	GAPS IN THE RESEARCH AREA	13

1.9	OBJECTIVES OF RESEARCH WORK	14
1.10	ORIENTATION OF THE THESIS	15

CHAPTER – 2 LITERATURE REVIEW

2.1	GENERAL	16
2.2	STEPS INVOLVED IN ACC	18
2.2.1	In- Mould Curing	20
2.2.2	Pre-Conditioning	20
2.2.3	Carbonation Phase	22
2.2.4	Post Conditioning Phase	23
2.3	ROLE OF ACC IN CO ₂ SEQUESTRATION	25
2.3.1	Quantification of CO ₂ Uptake	25
2.3.2	Factors Affecting CO ₂ Uptake by ACC	26
2.4	PERFORMANCE OF CARBONATION CURED BUILDING MATERIALS	30
2.4.1	Performance of Cement Paste and Mortars	31
2.4.2	Performance of Concrete Masonry Units	33
2.4.3	Performance of Concrete Subjected to ACC	34
2.5	EFFECT OF ACC ON MORTARS AND CONCRETE MADE WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS	36
2.6	GAPS IN RESEARCH AREA	38

CHAPTER – 3 EXPERIMENTAL PROGRAMME

3.1	GENERAL	39
3.2	MATERIALS	39
3.2.1	Cement	40
3.2.2	Cement Kiln Dust (CKD)	42

3.2.3	Ground Granulated Blast Furnace Slag (GGBS)	43
3.2.4	Fine Aggregates	45
3.2.5	Coarse Aggregates	45
3.2.6	Water	47
3.2.7	Reinforcement Bar	47
3.3	MIX PROPORTIONS	48
3.3.1	Mix Proportions for Mortar Mixes	48
3.3.2	Mix proportions for concrete mixes	48
3.4	CASTING OF SPECIMENS	49
3.5	CURING OF SPECIMENS	51
3.5.1	Water Curing	52
3.5.2	Accelerated Carbonation Curing	52
3.6	TESTING METHODS	56
3.6.1	Compressive Strength	56
3.6.2	Split Tensile strength	58
3.6.3	Water Absorption and Permeable Porosity	59
3.6.4	Sorptivity	59
3.6.5	Abrasion Resistance	61
3.6.6	Rapid Chloride Permeability Test	62
3.6.7	Drying Shrinkage Test	64
3.6.8	Microstructural and Mineralogical Analysis	65
3.6.8.1	<i>X- Ray diffraction (XRD)</i>	65
3.6.8.2	<i>Thermogravimetric Analysis (TGA)</i>	67
3.6.8.3	<i>Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)</i>	67
3.6.9	Carbonation Depth Measurement	68

CHAPTER- 4 EFFECT OF ACCELERATED CARBONATION CURING VIS-À-VIS WATER CURING ON PROPERTIES OF CONCRETE

4.1	GENERAL	74
4.2	EFFECT OF ACC ON MICROSTRUCTURE OF CONCRETE	76
4.2.1	XRD Analysis	76
4.2.2	Thermogravimetric Analysis (TGA)	79
4.2.3	CO ₂ Uptake	82
4.2.4	Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS)	83
4.3	EFFECT OF ACC ON MECHANICAL PROPERTIES OF CONCRETE	86
4.4	EFFECT OF ACC ON PERMEATION PROPERTIES OF CONCRETE	88
4.4.1	Water Absorption	88
4.4.2	Sorptivity	89
4.4.3	Rapid Chloride Permeability Test (RCPT)	92
4.5	NUMERICAL ANALYSIS	93
4.5.1	Stoichiometric Analysis	93
4.5.2	Analysis of Variance	96
4.6	CLOSING REMARKS	97

CHAPTER – 5 EFFECT OF ACCELERATED CARBONATION CURING DURATION ON PROPERTIES OF CONCRETE

5.1	GENERAL	98
5.2	EFFECT OF ACC DURATION ON MECHANICAL PROPERTIES OF CONCRETE	99

5.2.1	Compressive Strength	100
5.2.2	Split Tensile Strength	104
5.2.3	Abrasion Resistance	106
5.3	EFFECT OF CARBONATION CURING DURATION ON pH OF CONCRETE	110
5.4	EFFECT OF ACC DURATION ON PERMEATION PROPERTIES OF CONCRETE	113
5.4.1	Water Absorption	113
5.4.2	Sorptivity	115
5.5	EFFECT OF ACC DURATION ON MICROSTRUCTURE OF CONCRETE	118
5.5.1	XRD Analysis	118
5.5.2	SEM- EDS Analysis	121
5.5.3	Thermogravimetric Analysis	132
5.6	EFFECT OF ACC DURATION ON CO ₂ UPTAKE OF CONCRETE	135
5.7	STOICHIOMETRIC ANALYSIS OF DIFFERENT DURATIONS OF ACC	137
5.8	STATISTICAL ANALYSIS OF EFFECT OF ACC DURATION ON PROPERTIES OF CONCRETE	140
5.8.1	Analysis of Variance	140
5.8.2	Relationship between Abrasion Resistance and Compressive Strength	141
5.9	EFFECT OF ACC DURATION ON LONG TERM PERFORMANCE OF CONCRETE	143
5.9.1	Effect of ACC Duration on Drying Shrinkage of Concrete	143
5.9.2	Effect of ACC Duration on Resistance to Weathering Carbonation	146

5.9.2.1	<i>Carbonation Depth</i>	146
5.9.2.2	<i>Corrosion rate measurement by Linear Polarization Resistance technique</i>	150
5.10	CLOSING REMARKS	154

CHAPTER – 6 PERFORMANCE OF MINERAL ADMIXTURE BASED CEMENTITIOUS SYSTEMS UNDER ACC

6.1	GENERAL	155
6.2	PERFORMANCE OF FLYASH BASED PPC UNDER ACCELERATED CARBONATION CURING	157
6.2.1	Compressive Strength	158
6.2.2	Porosity	163
6.2.3	Microstructure	165
6.3	EFFECT OF ACC ON MORTARS INCORPORATING CKD AS PARTIAL REPLACEMENT OF CEMENT	171
6.3.1	Compressive Strength	171
6.3.2	Porosity of CKD Mortars	176
6.3.3	Microstructure	178
6.4	EFFECT OF ACC ON MORTARS INCORPORATING GGBS AS PARTIAL REPLACEMENT OF CEMENT	181
6.4.1	Compressive Strength	181
6.4.2	Porosity of GGBS Mortars	185
6.4.3	Microstructure of GGBS Mortars	187
6.5	CO ₂ SEQUESTRATION ABILITY	190
6.6	CLOSING REMARKS	191

CHAPTER -7 CONCLUSIONS

7.1	GENERAL	193
-----	---------	-----

7.2	EFFECT OF ACC VIS-À-VIS WATER CURING ON PROPERTIES OF CONCRETE	193
7.3	EFFECT OF DURATION OF ACC ON PROPERTIES OF CONCRETE	195
7.4	PERFORMANCE OF MINERAL ADMIXTURE BASED CEMENTITIOUS SYSTEM UNDER ACC	197
7.5	SCOPE FOR FUTURE WORK	199
REFERENCES		200

LIST OF TABLES

Table No.	Title	Page No.
CHAPTER 1		
Table 1.1	Reaction products obtained after ACC	8
CHAPTER 2		
Table 2.1	Details of duration of steps of ACC used in different studies	19
Table 2.2	Different pre conditioning procedures adopted in different studies	21
Table 2.3	Details of carbonation stage of ACC adopted in different studies	22
Table 2.4	Post conditioning procedures adopted in different studies	24
Table 2.5	CO ₂ uptake data for different parameters of ACC	27
CHAPTER 3		
Table 3.1	Physical properties of Ordinary Portland Cement (OPC)	40
Table 3.2	Chemical composition of Ordinary Portland Cement (OPC)	41
Table 3.3	Physical properties of Portland Pozzolona Cement (PPC)	41
Table 3.4	Chemical composition of Portland Pozzolona Cement (PPC)	41
Table 3.5	Physical properties of Cement Kiln Dust	43
Table 3.6	Chemical composition of Cement Kiln Dust	43
Table 3.7	Physical properties of GGBS	45
Table 3.8	Chemical composition of GGBS	45
Table 3.9	Sieve analysis of fine aggregates	46
Table 3.10	Physical properties of fine aggregates	46
Table 3.11	Physical properties of coarse aggregates	46
Table 3.12	Sieve analysis of coarse aggregate	47
Table 3.13	Concrete mix proportions used in the study	49

Table 3.14	Chloride ion penetration based on charge passed	63
CHAPTER 4		
Table 4.1	Analysis of variance	96
CHAPTER 5		
Table 5.1	Detail of curing regimes adopted in this study	99
Table 5.2	Compressive strength results for different curing regimes and its variation with respect to water curing regime	103
Table 5.3	Si/Ca ratio and C/Ca ratio obtained for different curing regimes	123
Table 5.4	Analysis of variance for compressive strength	141
Table 5.5	Analysis of variance for abrasion resistance	141
Table 5.6	Analysis of variance for split tensile strength	141
Table 5.7	Parameters of the fitted curves with change in curing regime	149
Table 5.8	Corrosion activity from LPR as per RILEM TC 154-EMC	153
CHAPTER 6		
Table 6.1	Chemical composition and physical properties of OPC, PPC, CKD and GGBS	156
Table 6.2	Details of curing regimes used in this study	158

LIST OF FIGURES

Fig. no.	Caption	Page No.
CHAPTER 1		
Fig. 1.1	Projected change in water scarcity by 2050 (“World Water Development Report 2018 UN-Water,” 2018)	2
Fig. 1.2	Hydration speed of the major constituents of ordinary Portland cement (Papadakis et al., 1989)	6
Fig. 1.3	Typical flowchart for steps involved in ACC	10
Fig. 1.4	Typical setup of carbonation curing chamber	13
CHAPTER 2		
Fig. 2.1	Typical steps involved in accelerated carbonation curing (Zhang et al., 2017)	18
CHAPTER 3		
Fig. 3.1	Cement Kiln Dust used in the study	42
Fig. 3.2	SEM and EDS images for CKD sample	43
Fig. 3.3	GGBS used in this study	44
Fig. 3.4	SEM-EDS of GGBS used in this study	44
Fig. 3.5	Steel rebar used in concrete tests	48
Fig. 3.6	Cylindrical concrete specimen for corrosion monitoring	50
	3.6 (a) Schematic diagram of specimen	50
	3.6 (b) Casted specimens	51
Fig. 3.7	Methodology for preparation of specimens	51
Fig. 3.8	Temperature controlled water curing of concrete	52
Fig. 3.9	Setup of Accelerated carbonation curing chamber	53
Fig. 3.10	Accelerated carbonation curing chamber used in the present study	53

Fig. 3.11	Flowchart for process of Accelerated carbonation curing	54
Fig. 3.12	Process of pre-conditioning	54
Fig. 3.13	Specimens placed in carbonation chamber	55
Fig. 3.14	Specimens sealed in plastic bags for post conditioning	56
Fig.3.15	Compressive strength test of concrete	57
Fig. 3.16	Test setup for Split Tensile Strength	58
Fig. 3.17	Testing for Sorptivity	60
Fig. 3.18	Experimental setup for measurement of abrasion resistance of concrete	62
Fig. 3.19	Rapid chloride permeability test	63
Fig. 3.20	Prooveit data processor for measuring charge passed through the concrete	63
Fig. 3.21	Testing setup for drying shrinkage	65
Fig. 3.22	Experimental set up for X-Ray diffraction (XRD) instrument	66
Fig. 3.23	XRD analysis using Xpert Highscore Plus and ICDD reference database	66
Fig. 3.24	Experimental set up for SEM and EDS spectroscopy	67
Fig.3.25	2-D image analysis of SEM images using ImageJ	68
Fig. 3.26	Environment chamber for subjecting the specimens to carbonation exposure	69
Fig. 3.27	Test setup for splitting the cube specimens	70
Fig. 3.28	Measurement of uncoloured part after Phenolphthalein spray	70
Fig. 3.29	Typical polarization curve obtained during LPR	73
Fig.3.30	Test setup for Potentiodynamic (LPR) test	73

CHAPTER 4

Fig. 4.1	Methodology used to study the effect of accelerated carbonation curing vis-à-vis water curing on properties of concrete	76
----------	---	----

Fig. 4.2	XRD spectrum obtained for WC and CC concrete mixes at 26 hours of casting	77
Fig. 4.3	XRD spectrum obtained for WC and CC concrete mixes at 3 days of casting	78
Fig. 4.4	XRD spectrum obtained for WC and CC concrete mixes at 28 days of casting	78
Fig. 4.5	TGA plot at the age of 26 hours of casting	81
Fig. 4.6	TGA plot at the age of 28 days of casting	81
Fig. 4.7 (a)	SEM and EDS analysis of WC specimen at the age of 26 hours	84
Fig. 4.7 (b)	SEM and EDS analysis of CC specimen at the age 26 hours	84
Fig. 4.8 (a)	SEM and EDS analysis of WC specimen at the age of 28 days	85
Fig. 4.8 (b)	SEM and EDS analysis of CC specimen at the age of 28 days	85
Fig. 4.9	Comparative analysis of SEM image (a) WC and (b) CC using ImageJ for specimens tested at 26 hours	85
Fig. 4.10	Compressive strength of WC and CC concrete	87
Fig. 4.11	Abrasion resistance of WC and CC concrete	87
Fig. 4.12	Water absorption for WC and CC concrete	90
Fig. 4.13	Absorption vs square root of time graph at the age of 26 hours	91
Fig. 4.14	Absorption vs square root of time graph at the age of 28 days	91
Fig. 4.15	Sorptivity coefficients for WC and CC concrete	92
Fig. 4.16	Rapid chloride permeability test for WC and CC concrete	93
Fig. 4.17	Stoichiometric representation for WC and CC concrete	95

CHAPTER 5

Fig. 5.1	Test matrix adopted to study the effect of accelerated carbonation curing duration on properties of concrete	99
----------	--	----

Fig. 5.2	Compressive strength of concrete subjected to different curing regimes	100
Fig. 5.3	Split tensile strength of concrete subjected to different curing regimes	105
Fig. 5.4	Abrasion resistance of concrete subjected to different curing regimes	108
Fig. 5.5	Progressive depth of wear at the testing age of 3 days	109
Fig. 5.6	Progressive depth of wear at the testing age of 28 days	109
Fig. 5.7	Progressive depth of wear at the testing age of 90 days	110
Fig. 5.8	pH of specimens subjected to different types of curing regimes	112
Fig. 5.9	Water absorption of concrete subjected to different curing regimes	115
Fig. 5.10	Absorption vs square root of time plot at the age of 3 days	117
Fig. 5.11	Absorption vs square root of time plot at the age of 28 days	117
Fig. 5.12	Sorptivity coefficients of concrete subjected to different curing regimes	118
Fig. 5.13	XRD spectrums for different curing regimes after carbonation phase	119
Fig. 5.14	XRD spectrums for different curing regimes at the age of 3 days	120
Fig. 5.15	XRD spectrums for different curing regimes at the age of 28 days	120
Fig. 5.16	SEM-EDS analysis for different curing regimes just after carbonation	125
Fig. 5.17	SEM-EDS analysis for different curing regimes at the age of 3 days	127
Fig. 5.18	SEM-EDS analysis for different curing regimes at the age of 28 days	128
Fig. 5.19 (a)	2D image analysis of SEM images just after end of carbonation stage	129

Fig. 5.19 (b)	2D image analysis of SEM images at the age of 3 days	130
Fig. 5.19 (c)	2D image analysis of SEM images at the age of 28 days	131
Fig. 5.20	2D porosity of specimens subjected to different curing regimes	131
Fig. 5.21	TGA-DTG analysis of concrete for different curing regimes	133
Fig. 5.22	Content of Calcium Hydroxide, Calcium Carbonate and C-S-H calculated from TGA	134
Fig. 5.23	CO ₂ uptake from different durations of carbonation curing	136
Fig. 5.24	Stoichiometric analysis of different durations of carbonation curing	139
Fig. 5.25	Relationship between depth of wear and compressive strength for carbonation cured specimens	142
Fig. 5.26	Comparison between observed and predicted depth of wear using developed relationship	143
Fig. 5.27	Effect of different curing regimes on drying shrinkage of concrete	145
Fig. 5.28	Carbonation depth test at different ages of exposure	149
Fig. 5.29	Carbonation depth variation with square root of exposure duration	150
Fig. 5.30	Test setup for corrosion rate measurement using LPR	151
Fig. 5.31	Analysis of LPR results using TAFEL extrapolation method	151
Fig. 5.32	Corrosion current density for different curing regimes	153

CHAPTER 6

Fig. 6.1	Flowchart for studying the performance of different mineral admixture based cementitious systems under accelerated carbonation curing	157
Fig. 6.2	Compressive strength of OPC mortars subjected to different curing regimes	160
Fig. 6.3	Compressive strength of PPC mortars subjected to different curing regimes	160

Fig. 6.4	Porosity of OPC based mortars when subjected to different curing regimes	164
Fig. 6.5	Porosity of PPC based mortar mixes when subjected to different curing regimes	165
Fig. 6.6	XRD analysis of OPC mortars at the age of 180 days	167
Fig. 6.7	XRD analysis of PPC mortars at the age of 180 days	167
Fig. 6.8	SEM-EDS of water cured OPC mortar at the age of 180 days	169
Fig. 6.9	SEM-EDS of carbonation cured (O-CC) OPC mortar at 180 days	169
Fig. 6.10	SEM-EDS of carbonation cured (O-CS) OPC mortar at 180 days	169
Fig. 6.11	SEM-EDS of water cured PPC mortar at 180 days	170
Fig. 6.12	SEM-EDS of carbonation cured (P-CC) PPC mortar at the age of 180 days	170
Fig. 6.13	SEM-EDS of carbonation cured (P-CS) PPC mortar at 180 days	170
Fig. 6.14	Compressive strength of CKD mortars at the age of 3 days	173
Fig. 6.15	Compressive strength of CKD mortars at the age of 7 days	174
Fig. 6.16	Compressive strength of CKD mortars at the age of 28 days	174
Fig. 6.17	Compressive strength of CKD mortars at the age of 90 days	175
Fig. 6.18	Compressive strength of CKD mortars at the age of 180 days	175
Fig. 6.19	Porosity of CKD mortars at the age of 3 days	176
Fig. 6.20	Porosity of CKD mortars at the age of 180 days	177
Fig. 6.21	XRD analysis of CKD mortars at the age of 180 days	179
Fig. 6.22	SEM-EDS of Water cured CKD mortars at 180 days	180
Fig. 6.23	SEM-EDS of carbonation cured (CC) CKD mortars at 180 days	180
Fig. 6.24	SEM-EDS of carbonation cured (CS) CKD mortars at 180 days	180

Fig. 6.25	Compressive strength of GGBS mortars at the age of 3 days	183
Fig. 6.26	Compressive strength of GGBS mortars at the age of 7 days	183
Fig. 6.27	Compressive strength of GGBS mortars at the age of 28 days	184
Fig. 6.28	Compressive strength of GGBS mortars at the age of 90 days	184
Fig. 6.29	Compressive strength of GGBS mortars at the age of 180 days	185
Fig. 6.30	Porosity of GGBS mortars at the age of 3 days	186
Fig. 6.31	Porosity of GGBS mortars at the age of 180 days	187
Fig. 6.32	XRD analysis of GGBS mortars at 180 days	188
Fig. 6.33	SEM-EDS of Water cured GGBS mortars at 180 days	189
Fig. 6.34	SEM-EDS of carbonation cured (G-CC) GGBS mortars at 180 days	189
Fig. 6.35	SEM-EDS of carbonation cured (G-CS) GGBS mortars at the age of 180 days	189
Fig. 6.36	Results of TGA-DTG for different materials subjected to ACC	191

CHAPTER 1

INTRODUCTION

1.1 GENERAL

The world is at the cross roads with respect to the two major environmental issues. The first is related to the greenhouse gases emissions. The levels of greenhouse gases in environment have been rising since the start of industrial era. The results of global warming are evident in melting of glaciers, increase in earth's temperature, climate change, etc. The most dominant greenhouse gas is carbon dioxide (CO₂) which is emitted mostly through burning of fossil fuels for energy, manufacturing industries and construction activities. As per the report of the International Energy Agency (IEA), the global CO₂ emissions rose by 1.7% in 2018 as compared to 2017(IEA, 2018). In an effort to tackle the rising CO₂ emissions, United Nations have set up the United Nations Framework Convention on Climate Change (UNFCCC) in 1992. The objective of UNFCCC is to stabilize the atmospheric concentration of CO₂ to a 1990 baseline. At the 21st conference of UNFCCC, known as Paris agreement, 175 countries agreed to make efforts to combat the threat of climate change by limiting the global temperature rise to 2°C with respect to the values registered during the pre-industrial era.

The second major environmental concern is the crisis related to water scarcity. The utilisation of water in agriculture, construction, day to day activities makes it an essential resource for the survival of mankind. With the increasing population, there has been a tremendous rise in the water demand, and with only 3% of world's total water available as fresh water, the problem of water scarcity is only expected to get worse. Also, the climate change and energy demands are expected to amplify this problem. Fig. 1.1 gives the water scarcity prediction by the year 2050 as per World Water Development Report, 2018("World Water Development Report 2018 | UN-Water," 2018).

The present study focuses on addressing both the issues of greenhouse gas emission and water scarcity by adopting a novel curing practice in the construction industry.

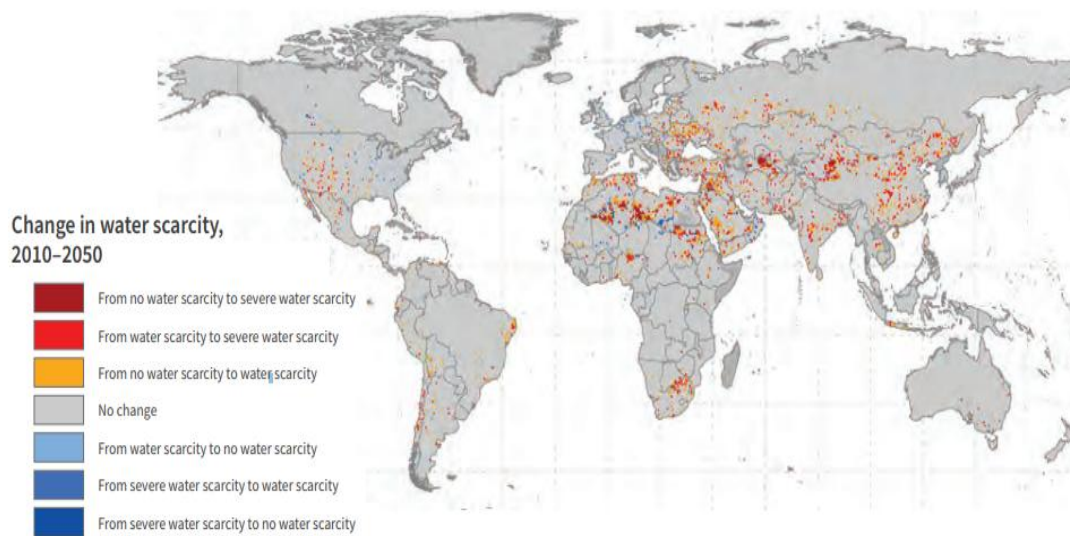


Fig. 1.1: Projected change in water scarcity by 2050 (“World Water Development Report 2018 | UN-Water,” 2018)

1.2 CARBON DIOXIDE SEQUESTRATION IN CONCRETE

Many steps have been taken to counter rising greenhouse emissions and climate change by the nations involved in Paris agreement. It includes incorporating renewable sources of energy, use of bio-fuels in the transportation industry, reducing deforestation rates etc.(National Public Radio, 2011). However, only reducing the future emissions is not sufficient to achieve the target of CO₂ stabilisation. Carbon capture and storage (CCS) or carbon sequestration is identified as one of the solutions to further mitigate higher levels of carbon dioxide. CO₂ sequestration is described as long term storage of atmospheric carbon dioxide in stable forms to mitigate global warming and climate change. CO₂ sequestration is done by capturing the atmospheric carbon dioxide through biological, physical and chemical processes and storing it in stable form for long term. Well equipped CCS systems have the capacity to reduce the carbon dioxide emissions by 80-90%(IPCC, 2005).

The global rise in carbon dioxide emissions come from three main sources: (i) burning of fossil fuels, (ii) land use changes or deforestation, (iii) decomposition of carbonates. Cement industry is the largest contributor to emissions from decomposition of carbonates. The production of cement emits CO₂ in two forms. First is the burning of fossil fuels to generate sufficient energy required to heat all raw materials above 1000°C and also electrical energy required. Second, in production of

clinker, CO₂ gas is released during decomposition of carbonates into oxides and carbon dioxide. Both these processes contribute nearly 8% of global carbon dioxide emissions (Andrew, 2018). Several earlier strategies to reduce CO₂ emissions from cement production included using alternative materials and energy saving production processes (Mikulčić et al., 2013). However, rising demand of cement to cater infrastructure needs has made it difficult to attain the requirement of restricting the temperature rise to below 2°C, as agreed upon in the Paris agreement, by using the conventional CO₂ reducing strategies. Clearly, there is an urgent need to find better and economic ways of carbon dioxide removal from atmosphere.

One such approach for restricting CO₂ levels in the atmosphere is by sequestration of CO₂ in building materials. The concept is based on the ability of cement and its hydrated products to react with atmospheric CO₂. It is well documented that the hydration products react with atmospheric CO₂ over time (Neville and Brooks, 2010), thereby converting the cement hydration products into calcium carbonate. This process of interaction of cement with atmospheric carbon dioxide is called natural carbonation. Instead of natural carbonation, the process of deliberately supplying CO₂ to the cement system during very early ages of strength development is called accelerated carbonation curing (ACC). ACC is a type of mineral carbonation in which captured CO₂ is stored in form of stable inorganic carbonates. The process of ACC is carried out by exposing freshly cast concrete to high concentration of CO₂ for a short duration. Carbonation of cement products is a direct way to sequester CO₂ by converting it into geologically and chemically stable calcium carbonate. ACC has gained the interest of researchers over the last decade, owing to the latest developments in economical CO₂ capture technologies and the urgency to mitigate CO₂ emissions and global warming.

1.3 WATER CONSERVATION IN THE CONSTRUCTION SECTOR

Apart from the contribution of the construction sector in global warming, another rising concern related to construction sector is the consumption of water in various processes of construction. It is well known that water resources have been rapidly depleting over the past few decades, leading to many major cities running out of

groundwater. Water is a necessity for day to day activities. However, with the rising stress on water consumption, the per capita water availability is decreasing drastically.

Construction industry is one of the biggest sectors causing water stress in world. With the increase in population, the demand for infrastructure keeps on increasing. Water is used in construction industry right from the preparation of concrete to the curing till later ages. As per various reports, the water use in cement production can go upto 3500L per ton of cement produced (Kollar and Macauley, 1980). In OPC based concrete, 211 Kg water is required for curing per cubic meter of concrete construction ("masterbuilder.com," 2018). Water is an essential component in curing of concrete as it ensures continuation of hydration reaction in concrete and development of adequate strength and durability properties. Thus, taking in account the large amount of water consumption by construction industry and rapidly rising demand for new projects, it is necessary to look for alternative sources of curing to conserve water.

1.4 CURING OF CONCRETE

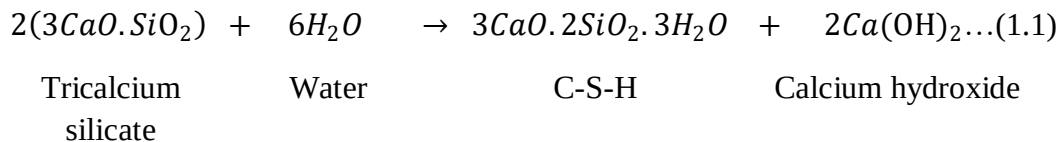
Curing is the process of providing concrete with adequate moisture and temperature in concrete for a particular period of time immediately after placing and finishing so that required properties of concrete can develop. But, both these curing techniques use a large amount of water and energy for their application. Curing has a strong impact on the properties of hardened concrete i.e. proper curing will increase durability, strength characteristics, volume stability, abrasion resistance and resistance to freezing and thawing.

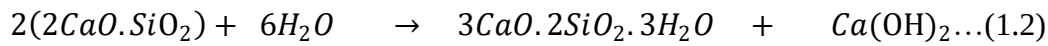
Conventionally adopted curing techniques that invariably use water as the basic constituent are water curing and high pressure steam curing. Water curing is the oldest and most commonly used method of curing for concrete. Easy availability of water and feasibility to use made water curing the most commonly practiced method of curing.

1.5 MECHANISM OF WATER CURING

The cement clinker is composed of a series of calcium-based compounds, commonly referred to as alite (tricalcium silicate or C_3S) and belite (dicalcium silicate or C_2S), aluminate (tricalcium aluminate or C_3A) and ferrite (calcium aluminoferrite or C_4AF). In the process of water curing, the cement compounds on mixing with water undergo hydration reaction to produce various products like calcium hydroxide ($Ca(OH)_2$) and Calcium silicate hydrate (C-S-H) gel. The reactions of these cement constituents with water have been described in chemical equations 1.1-1.4. As per Eqs. 1.1 and 1.2, the tricalcium silicate (alite) and dicalcium silicate (belite) is hydrated to produce calcium silicate hydrates (C-S-H gel) and calcium hydroxide. The C-S-H has a short-networked fiber structure which imparts strength to the concrete. Therefore, hydration of C_3S and C_2S are majorly responsible for strength gain of concrete. Among the two hydration products, calcium hydroxide can be present in amounts up to 26% by volume (Papadakis et al., 1989). As per Eq. 1.3, the tricalcium aluminate reacts with the gypsum in the presence of water to produce ettringite (Calcium aluminosulphate) and once all the gypsum is used up as per reaction (1.3), the ettringite becomes unstable and reacts with any remaining tricalcium aluminate to form monosulfate aluminate hydrate crystals. Tetracalcium aluminoferrite reacts with gypsum and water to produce ettringite and ferric aluminium hydroxide as depicted in chemical Eq. 1.4.

The reaction rates of the cement constituents have been described by Papadakis et al. as shown in Fig. 1.2 (Papadakis et al., 1989). As seen from the reaction rates of Fig. 1.2, C_3S reacts with water at a higher rate as compared to C_2S . Therefore, the C_3S contributes to early strength of concrete, whereas the C_2S hydrates to provide later age strength to concrete.

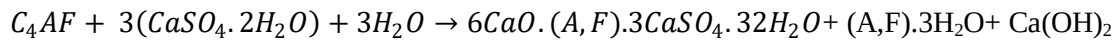




Tricalcium silicate	Water	C-S-H	Calcium hydroxide
------------------------	-------	-------	-------------------



Tricalcium aluminate	Gypsum	Water	Calciumsulfoaluminate
-------------------------	--------	-------	-----------------------



Tetracalcium aluminoferrate	Gypsum	Water	Ettringite	Ferric aluminum hydroxide	Calcium hydroxide
--------------------------------	--------	-------	------------	---------------------------------	----------------------

...(1.4)

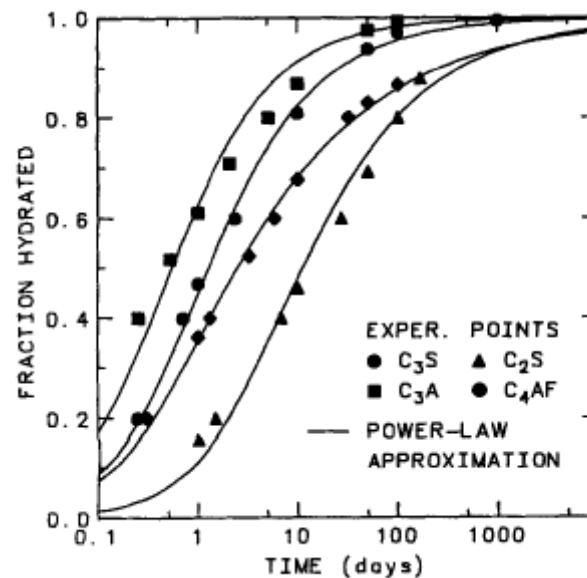


Fig 1.2: Hydration speed of the major constituents of ordinary Portland cement (Papadakis et al., 1989)

1.6 ACCELERATED CARBONATION CURING

While water curing provides an easy and efficient way of curing and strength development to concrete, but the rising scarcity of water in world imposes a restriction on use of water in the construction practices. In order to conserve water, it has become necessary to find alternate curing practices that can ensure satisfactory performance of concrete as provided by water curing. In this regard, the practice of

accelerated carbonation curing (ACC) is being researched for application in precast industry.

ACC is a process of curing for precast concrete components. In this process, after a few hours of casting, concrete is subjected to high concentration of CO₂ for a fixed duration in an enclosed chamber. ACC has the potential to be used as an alternative to steam curing in the field of precast concrete. While the earlier studies for both steam curing and ACC date back to 1970s, the latter did not gain attention due to high costs of CO₂ capture at that time (Berger, 1979; Berger et al., 1972; Berger and Klemm, 1972; Bukowski and Berger, 1979; Goodbrake et al., 1979a, 1979b; Klemm and Berger, 1972; Young et al., 1974). Although the process of steam curing was an energy extensive process and required proper heating and cooling down temperatures, abundant availability of water and already developed heating techniques made steam curing more beneficial for precast concrete. However, the last few decades saw emergence of vast technological advancement in the field of CO₂ capture to tackle the rising CO₂ emissions. The newer methods of CO₂ capture were economical and feasible to implement. With the large scale availability of captured CO₂, efforts are now being made to explore the potential of construction materials to sequester CO₂ in stable form.

ACC offers some advantages as compared to steam curing. Steam curing is a complex process with different stages like steam generation stage, maintaining temperature, pressurised application of steam, cooling stage, etc. General energy requirement of steam curing was found to be 2300KJ to cure one standard concrete block. ACC required only 500KJ of energy to cure same concrete block, which is 1/5th of the energy required by steam curing (Shi et al., 2012c). It indicates that ACC serves the dual advantage of reducing the level of atmospheric CO₂, and also providing a low energy alternative to steam curing.

1.6.1 Reaction Mechanism of ACC

In ACC, partially hydrated cement is subjected to carbonation. Therefore, CO₂ reacts not only with hydration reaction products, but also with anhydrous products of cement clinker. The detailed mechanism of reaction with both anhydrous cement constituents

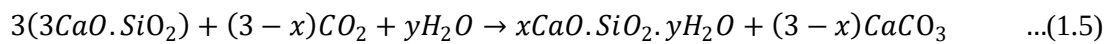
and early hydration products is discussed hereunder. Table 1.1 gives a brief about various reactants and corresponding reaction products obtained after reaction with CO₂.

Table 1.1: Reaction products obtained after ACC

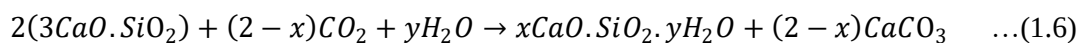
Constituent	Reactivity to CO ₂	Reaction products
Anhydrous products		
Tri Calcium silicate (C ₃ S)	High	C-S-H gel and CaCO ₃
Di Calcium silicate (C ₂ S)	High	C-S-H gel and CaCO ₃
Tricalcium aluminate (C ₃ A)	Low	Aluminium hydroxide and CaCO ₃
Tetracalciumaluminoferrate (C ₄ AF)	Very Low	n/a
Hydration products		
Calcium hydroxide (Ca(OH) ₂)	High	CaCO ₃ and H ₂ O
Calcium silicate hydrate (C-S-H)	High	SiO ₂ , CaCO ₃ and H ₂ O

(a) Carbonation of anhydrous cement constituents

The major constituents of anhydrous cement are tricalcium silicate (C₃S) and dicalcium silicate (C₂S), tricalcium aluminate (C₃A) and tetracalciumaluminoferrate (C₄AF). C₃S and C₂S are known to be reactive to CO₂ in aqueous conditions, but C₃A and C₄AF show minimal to no reactivity (Fernández-Carrasco et al., 2008; Hargis et al., 2017). The reactions of C₃S and C₂S with CO₂ have been shown in equations 1.5 and 1.6 respectively.

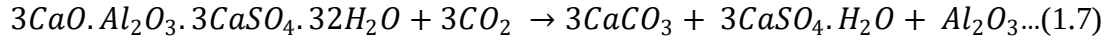


Tricalcium silicate Carbondioxide Water Calciumsilicate hydrate Calciumcarbonate



Dicalcium silicate Carbondioxide Water Calciumsilicate hydrate Calciumcarbonate

C₃A does not show much reactivity with CO₂. However, it hydrates very rapidly to form ettringite in the presence of gypsum (Neville and Brooks, 2010). Ettringite shows reactivity with CO₂ to form aluminium oxide, gypsum and CaCO₃ as shown in Eq.1.7 (Grounds et al., 1988; Nishikawa et al., 1992).



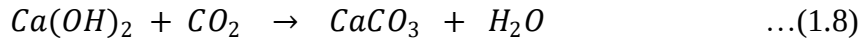
Calcium sulfoaluminate (Ettringite)	Carbon dioxide	Calcium carbonate	Gypsum	Aluminium oxide
--	-------------------	----------------------	--------	--------------------

The reaction of calcium silicates with CO₂ during ACC produces calcium silicate hydrate and calcium carbonate as shown in chemical equations 1.5 and 1.6 (Berger, 1979; Goto et al., 1995; Klemm and Berger, 1972). The sequestration of CO₂ by cement is achieved through formation of CaCO₃ by carbonation curing, which gets precipitated in the pores of material in stable form (Qian et al., 2016). The resulting binding phase after carbonation curing is obtained in the form of CaCO₃ intermingled in an enveloped C-S-H matrix (Rostami et al., 2012b).

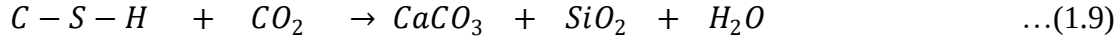
CaCO₃ is obtained in different polymorphs like calcite, vaterite and aragonite, but most dominant polymorph formed upon carbonation of calcium silicates was found to be calcite (Ashraf and Olek, 2016; Chang et al., 2016; Goto et al., 1995; Young et al., 1974). The morphology of C-S-H obtained from carbonation is different from C-S-H obtained by hydration reactions (Chang et al., 2016; Young et al., 1974). Many studies suggest a lower CaO/SiO₂ in C-S-H generated from carbonation as compared to C-S-H produced by hydration of calcium silicates (Berger et al., 1972; Goto et al., 1995; Shtepenko et al., 2006). The structure of C-S-H gel obtained from ACC depends on extent to which carbonation reaction was allowed to proceed and related CO₂ uptake by concrete (Rostami et al., 2012b).

(b) Carbonation of hydrated cement compounds

Calcium hydroxide and calcium silicate hydrate gel are major products formed during hydration of cement. The reaction mechanism of these products with CO₂ has been presented by equations 1.8 and 1.9 (El-Hassan et al., 2013).



Calcium Carbon Calcium Water
hydroxide dioxide carbonate



Calcium silicate Carbondioxide Calcium Silica Water
hydrate carbonate gel

Both the reactions indicate that the common product formed upon carbonation of hydrated cement products is $CaCO_3$, which is precipitated in pores of the mix, thus providing a densification effect in the microstructure and hence, enhanced performance of concrete (Fang and Chang, 2017; Mo et al., 2016a).

Both reactions 1.8 and 1.9 are similar to the reactions observed during natural carbonation of concrete and are considered detrimental when continued over several years. Carbonation reaction of hydration products releases the bound water of concrete owing to its exothermic nature(Song and Kwon, 2007; Zhan et al., 2016). Reaction of $Ca(OH)_2$ with CO_2 causes a drop in pH of pore structure and makes reinforcement steel vulnerable to corrosion. C-S-H gel decalcifies into silica gel upon reacting with CO_2 , deteriorating the performance of concrete.

1.6.2 Laboratory Processing of ACC

As already mentioned, ACC is the process of passing CO_2 gas over precast concrete just after a few hours of mixing. The process of carbonation in ACC is preceded and succeeded by proper pre-conditioning and post conditioning of concrete respectively. The carbonation curing can be divided into a four-step process, as outlined in Fig 1.3.



Fig. 1.3: Typical flowchart for steps involved in ACC

(a) In-Mould Curing

This step is the initial step in ACC process, wherein specimens after casting are allowed to set for few hours. During these initial few hours, hydration reaction takes place and various constituents of cement i.e. C_3S , C_2S , C_3A and C_4AF react with water used for mixing. This step provides initial strength to the specimens and also produces $Ca(OH)_2$ which is predominantly utilized in carbonation process as described in previous section. The in-mould curing is generally carried out in an ambient atmosphere and continued for a few hours ranging from 12-24 hours.

(b) Pre-Conditioning

This phase is essentially a water removal phase. It is necessary to maintain an optimal amount of water for effective carbonation (Fang and Chang, 2017; Rostami et al., 2011; Shao and Shi, 2006; Shi et al., 2012a). Shao and Shi in their study found that CO_2 uptake is affected by moisture condition of concrete. If a wet specimen is subjected to carbonation, the reaction between cement minerals and CO_2 is found to be limited and CO_2 consumption was less (Shao and Shi, 2006). The presence of pore water in concrete blocks the path of CO_2 , thereby hindering the process of carbonation (Shi et al., 2012a; Zhang and Shao, 2016a). Therefore, it is necessary to expose the specimens to drying conditions so that easy passage to CO_2 can be provided. Although, too much drying can cause removal of all the pore water from concrete which would also affect the necessary aqueous condition required for carbonation reaction. It is due to the time interval taken by in mould curing and preconditioning in ACC, that CO_2 is able to react with anhydrous cement constituents as well as early hydration reaction products (Zhang et al., 2017). The process of pre curing is started right after de-moulding and continued till carbonation phase. De-moulding is necessary for efficient preconditioning to ensure water removal from all the faces of concrete and further facilitate maximum penetration of CO_2 . The process of preconditioning is carried out either by air drying or by fan drying for few hours.

(c) Carbonation Phase

Carbonation phase is the most important phase of ACC process. After the initial pre curing, the specimens are placed in the enclosed vacuum chamber. Gaseous CO₂ from the industrial source is allowed to pass through the chamber after an initial vacuum. The vacuuming of chamber is necessary to allow maximum space to be occupied by CO₂ gas only (El-Hassan et al., 2013). The carbonation phase is carried out for a few hours. CO₂ gas is applied at a pressure of 1-5 atm after initially attaining vacuum through a vacuum pump. Captured CO₂ used in ACC maybe either 100% pure or flue gas obtained from industries with concentration of 15-25%.

(d) Post Conditioning Phase

The exothermic behaviour of carbonation reaction causes evaporation of water required for hydration. Therefore, the post carbonation phase is essential to replenish the lost water to enable further hydration of residual cement constituents after carbonation phase. Various studies have stressed on the role of post carbonation water curing in promoting further hydration (El-Hassan and Shao, 2015; He et al., 2016a; Rostami et al., 2011). It has been unanimously concluded in the literature that water curing post carbonation helps in maximizing the strength and caused densification of microstructure (He et al., 2016a; Klemm and Berger, 1972; Monkman et al., 2016; Rostami et al., 2011; Shi and Wu, 2008). Hydration of cement post carbonation helps in production of additional C-S-H gel that provides the additional strength and densification to carbonation cured mix.

1.6.3 Laboratory Setup of Carbonation Curing Chamber

Accelerated carbonation curing chamber consists of an enclosed pressure vessel. The shape of chamber can be cylindrical or cubical as required (Ahmad, 2018; Shi et al., 2012c). The chamber is connected to a vacuum pump that removes the excess air from inside prior to carbonation. CO₂ gas is supplied externally through an industrial CO₂ cylinder and gas pipes. The pressure of CO₂ injection is controlled by pressure regulators on the cylinder. The pressure inside the chamber is controlled by pressure gauges connected to the chamber. The chamber is also provided with input and output nozzles to control the carbon dioxide injection and removal respectively. Safety valve is provided to immediately reduce the pressure inside the chamber in case of any fault

in pressure regulation. The bottom of carbonation chamber is lined with silica gel or water absorbing sheets to absorb water released during carbonation. A typical setup of carbonation chamber is depicted in Fig. 1.4.

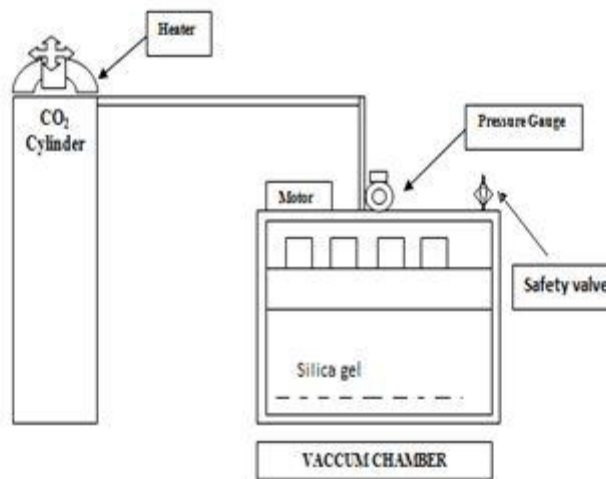


Fig.1.4: Typical setup of carbonation curing chamber

1.7SIGNIFICANCE OF THE RESEARCH

The world infrastructure is growing at a rapid rate; however, the growth of the infrastructure comes at the cost of natural resources and hazardous environmental impacts. Carbon dioxide emissions are eminent from the construction processes. Therefore, it is necessary to find an alternate way through which the impact of carbon dioxide on the environment can be reduced. Accelerated carbonation curing makes use of captured carbon dioxide for curing purposes and can prove as a substitute for water curing. The present study focus on conserving the natural resources and reducing the overall carbon footprint associated with the concrete industry by sequestering carbon dioxide into precast concrete.

1.8GAPS IN THE RESEARCH AREA

Carbonation curing is a developing technique for curing purposes. From the survey of literature and analysis of previously published studies, it is observed that most of the research work is focused on the compressive strength and porosity of carbonation

cured concrete and mortars. For the carbonation curing to be used practically, a comprehensive understanding of the following aspects is required:

1. The role of duration of carbonation curing, preconditioning and post-conditioning required for carbonation curing have not been studied. Each researcher has used a different carbonation curing regime. Hence, an optimum duration of carbonation curing is yet to be studied.
2. Most of the tests have been done with a focus on compressive strength, porosity and chloride penetration of the carbonation cured concrete. Thus, a detailed study needs to be done on long term strength development and durability parameters of concrete
3. Accelerated Carbonation curing can be affected by composition of concrete. Influence of presence of supplementary cementitious materials on the prospects of carbonation cured concrete needs to be understood.
4. Long term performance of carbonation cured concrete in adverse environment has not been studied yet. It is necessary to evaluate the performance of concrete in long run to protect the structure from degradation caused over time.

1.9 OBJECTIVES OF RESEARCH WORK

Accelerated carbonation curing has been researched at laboratory level as a method of curing for precast products and also a technique for CO₂ sequestration in cement based materials. The preliminary studies have reported improved mechanical performance of concrete when subjected to ACC. However, researchers have incorporated different parameters like duration of carbonation, pressure, materials in various studies. In order to develop ACC as a viable curing and CO₂ sequestration technique, the present study has been focused on evaluating the performance of mortars and concrete when subjected to different durations of carbonation, alongwith the performance of ACC concrete against weathering carbonation. Keeping this basic aim in mind, the emphasis of this research is on the following objectives:

1. To investigate the effect of varying accelerated carbonation curing parameters on concrete.

2. To investigate the performance of pozzolanic cements subjected to accelerated carbonation curing.
3. To study the long term performance of accelerated carbonation cured concrete in adverse environments.

1.10 ORIENTATION OF THE THESIS

The present work has been sub-divided into the following sections.

Chapter 1 gives the introduction about the concept and ideology of this study, significance and need of this research.

A comprehensive literature review of various studies carried out on ACC has been given in Chapter 2.

Chapter 3 includes the details of materials, methodology and experimental program used in the present study.

Chapter 4 includes a comparative study on effect of ACC and water curing on properties of concrete

Chapter 5 deals with effect of varying accelerated carbonation curing duration on the overall performance of concrete, including the performance in adverse environments.

Chapter 6 emphasizes on effect of ACC on various types of pozzolanic materials.

Chapter 7 discusses the various conclusions drawn from the present study and future scope of work.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

Carbonation of concrete is based on the ability of cement and its hydrated products to react with atmospheric CO_2 . CO_2 present in the atmosphere reacts with hydrated cement products calcium silicate hydrate and $\text{Ca}(\text{OH})_2$ to form CaCO_3 and silica gel. The reaction of CO_2 with aged concrete is detrimental to the performance of concrete. First, the disintegration of C-S-H into silica gel upon carbonation results in loss of strength of concrete. Secondly, the major effect of carbonation is on the pH of pore solution of concrete. The conversion of $\text{Ca}(\text{OH})_2$ causes a drop in pH of pore solution of concrete, which leads to deterioration of passive layer that protects the reinforcement bar in reinforced concrete.

However, the cement constituents (C_3S and C_2S) on reaction with CO_2 produce C-S-H gel and CaCO_3 which impart additional strength and impermeability to concrete. This application of the carbonation procedure to unreacted cement constituents and early age hydration products was the initial concept behind accelerated carbonation curing (Klemm and Berger, 1972). The process of deliberately supplying CO_2 to the cement system during very early ages of strength development was termed as accelerated carbonation curing. ACC is a type of mineral carbonation in which captured CO_2 is stored in form of stable inorganic carbonates in cement based products. The process of ACC is carried out by exposing freshly cast concrete to high concentration of CO_2 for a short duration. Calcium silicates and $\text{Ca}(\text{OH})_2$ present in the freshly cast concrete react with CO_2 and thus provide a direct way to sequester CO_2 by converting it to geologically and chemically stable calcium carbonate.

The research on ACC was initiated around the same time period as the steam curing i.e. in early 1970s. Many studies have been conducted in 1970s to explore the potential of cement as a carbon sink (Berger and Klemm, 1972; Goodbrake et al., 1979a; Klemm and Berger, 1972; Young et al., 1974). It was observed in these studies that portland cement mortars treated with carbon dioxide immediately after the

process of moulding produced compressive strengths higher than the samples that were hydration cured for one day under normal conditions (Klemm and Berger, 1972). The idea of ACC did not get much attention earlier when it was proposed as a curing regime due to high cost of CO₂ capture and known deteriorating effects of CO₂ on concrete. However, ACC has gained the interest of researchers over the last decade, owing to the latest developments in economical carbon dioxide capture technologies and the urgency to mitigate CO₂ emissions and global warming.

The processes of ACC and steam curing have been primarily developed for the precast concrete products. Steam curing is the most widely used curing method for precast structures in the present time. Abundant availability of water and already developed heating techniques made steam curing a feasible process in the precast industry. Steam curing provides the major advantage of rapid strength gain of precast concrete. The major disadvantage associated with steam curing is being an energy extensive process and requirement of proper heating and cooling down temperatures for producing quality precast concrete.

Due to emergence of vast technological advancement in the field of CO₂ capture to tackle the rising CO₂ emissions in the last few decades, ACC has gained popularity among researchers as a key to sequester carbon dioxide in cement based products. With the large scale availability of captured CO₂, researchers once again tried to explore the potential of construction materials to sequester CO₂ in stable form. It has been estimated in a study that if all concrete masonry units in USA and Canada are produced with ACC, 1.5 million tonnes of recovered CO₂ can be sequestered annually (El-Hassan et al., 2014).

ACC offers various advantages as compared to steam curing. Steam curing is a complex process with different stages like steam generation stage, maintaining temperature, pressurised application of steam, cooling stage, etc. General energy requirement of steam curing was found to be 2300KJ to cure one standard concrete block. ACC required only 500KJ of energy to cure same concrete block, which is 1/5th of the energy required by steam curing (Shi et al., 2012c). It indicates that ACC serves the dual advantage of reducing the level of atmospheric CO₂, and also providing a low energy alternative to steam curing.

In this chapter, detailed review of accelerated carbonation curing has been conducted with focus on available knowledge, performance of resultant products and application of ACC to supplementary cementitious materials.

2.2 STEPS INVOLVED IN ACC

As already mentioned, ACC is the process of passing CO_2 gas over precast concrete just after a few hours of mixing. The process of carbonation in ACC is preceded and succeeded by proper pre-conditioning and post conditioning of concrete respectively as already described in Section 1.6.2. The process of ACC includes four major steps: In-mould curing, preconditioning, carbonation, post conditioning as depicted in Fig. 2.1. The duration of each step is variable in different studies. Table 2.1 gives a brief summary of durations for these steps adopted by various researchers in their study on carbonation curing.

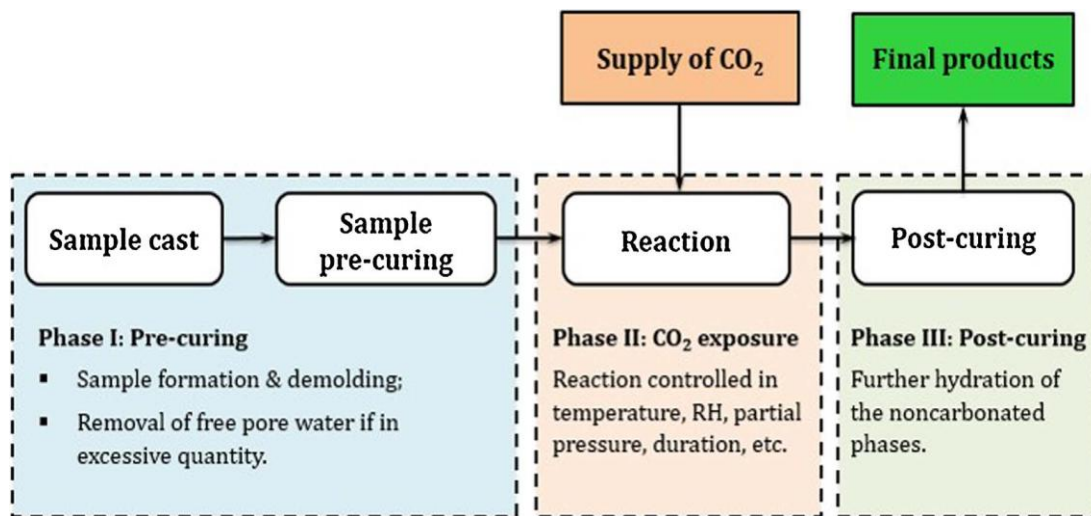


Fig. 2.1: Typical steps involved in accelerated carbonation curing (Zhang et al., 2017)

Table 2.1: Details of duration of steps of ACC used in different studies

Reference	In-mould curing	Pre-conditioning	Carbonation	Post conditioning
Investigations on concrete				
(Zhang and Shao, 2016a)	5 hours	5 hours	12 hours	27 days
(El-Hassan and Shao, 2015)	18 hours	n/a	4 hours	Till surface saturation
(Rostami et al., 2012a)	18 hours	n/a	2 hours	Till surface saturation
(Ahmad et al., 2017)	18 hours	n/a	1 hour - 10 hours	n/a
(Rostami et al., 2011)	18 hours	n/a	2 hours, 4 hours	Water curing, sealed air curing till 28 days
(Shi et al., 2012a)	n/a	2 hours- 18 hours	2 hours	n/a
(Shi et al., 2012c)	6 hours	4 hours	2 hours	n/a
(He et al., 2016a)		2 hours-6 hours	3 hours	0, 7, 28 ,90 days
(Zhan et al., 2013a)	n/a	n/a	3, 12, 24 hours	n/a
(Zhang and Shao, 2016b)	5-6 hours	5.5 hours	12 hours	27 days
(Zhang and Shao, 2018)	5-6 hours	5.5 hours	12 hours	27 days
Investigations on cement paste and mortar				
(Jang and Lee, 2016)	20 hours	n/a	28 days	n/a
(Junior et al., 2015)	6 hours	n/a	1 hour, 24 hours	Ambient curing at RH 100%
(Rostami et al., 2012b)	n/a	18 hours	2 hours	Water spray and sealed bag curing

n/a - data not available

2.2.1 In- Mould Curing

In the initial studies, ACC was applied to dry mix concrete which did not require any in-mould curing and could be subjected to curing right after casting (Klemm and Berger, 1972). The dry mix of concrete was further adopted for studying concrete masonry units and concrete blocks subjected to ACC (El-Hassan and Shao, 2015; Zhan et al., 2016). However, CO₂ uptake was found to be very low for pressure compacted dry mixes (Shao and Shi, 2006). Later, when this procedure was applied to wet mix concrete, it was necessary to provide initial in mould curing to allow early setting of concrete before de-moulding (Zhang and Shao, 2016a). The time taken by in mould curing allows sufficient hydration of cement constituents to produce Ca(OH)₂ that primarily reacts with carbon dioxide during the process of carbonation curing. Initial in-mould curing also allows development of sufficient strength required for handling the precast concrete products.

2.2.2 Pre-Conditioning

The process of pre-conditioning is essentially a water removal phase. Water present in the pores of concrete might hinder the movement of carbon dioxide through pores of concrete. Therefore, it is necessary to remove water from the pores of concrete to ensure effective carbonation (Fang and Chang, 2017; Rostami et al., 2011; Shao and Shi, 2006; Shi et al., 2012a). Several studies have incorporated different durations and methods for preconditioning of concrete as listed in Table 2.2. Preconditioning is carried out either using fan drying or air drying in ambient environment. The process of pre curing is started right after de-molding and continued till carbonation phase. De-moulding is necessary for efficient preconditioning to ensure water removal from all the surfaces of concrete and further facilitate maximum penetration of CO₂. It is also necessary to make sure that the duration of preconditioning does not induce excess removal of water from concrete, as presence of moisture is also a necessity for the carbonation reaction to occur.

Table 2.2: Different pre conditioning procedures adopted in different studies

Reference	Pre conditioning type	Duration	w/c ratio
Investigations on concrete			
(Zhang and Shao, 2016a)	25°C, 50 ± 5% RH, Wind speed 1m/s	5-6 hours	0.3-0.4
(Shi et al., 2012a)	RH 50 ± 5%, 98%, 22 ± 3°C	0-18 hours	0.43-0.5
(Shi et al., 2012c)	Dry windy environment	4 hours	n/a
(He et al., 2016a)	RH 60%, 22°C	2-6 hours	0.25,0.18,0.11
(Zhang and Shao, 2016b)	25°C, RH 50 ± 5%, fan drying at 1 m/s	5.5 hours	0.4-0.5
(Zhang and Shao, 2018)	25°C, RH 50 ± 5%, fan drying at 1 m/s	5.5 hours	0.4
Investigations on cement pastes and mortars			
(Rostami et al., 2012b)	25°C, RH 60%	18 hours	0.36

2.2.3 Carbonation Phase

After the initial pre curing, the specimens are placed in the enclosed vacuum chamber for the process of carbonation. Gaseous CO₂ from the industrial source is allowed to pass through the chamber after providing an initial vacuum. The vacuuming of chamber is necessary to allow maximum space inside the chamber to be occupied by CO₂ gas only (El-Hassan et al., 2013). The carbonation phase is carried out for a few hours. Table 2.3 gives the details of different parameters adopted by researchers while studying ACC.

This phase is the most important part of the process of carbonation curing. It is during this phase only, when carbon dioxide gas reacts with the constituents of cement (calcium silicates) and the hydration products (calcium hydroxide and C-S-H) of cement. The efficiency of this phase of ACC directly affects the performance of resultant mortar or concrete.

Table 2.3: Details of carbonation stage of ACC adopted in different studies

Reference	Purity of CO ₂	Pressure	Temperature (°C)	Relative Humidity (%)	Duration (hours)	Vacuum condition
(Klemm and Berger, 1972)	100	56 psi (0.38 MPa)		-	5 minutes	-
(Zhang and Shao, 2016a)	99.8	5 bars (0.5MPa)	-	-	12	-
(El-Hassan and Shao, 2015)	99	0.1 MPa	Room temperature	-	4	0.7 bars (0.07MPa)
(Rostami et al., 2012a)	99.5	1.5 bar (0.15MPa)	-	-	2	-
(Ahmad et al., 2017)	-	10 psi-60 psi (0.068 MPa – 0.41 MPa)	-	-	1-10	One minute
(Rostami et al., 2011)	99.5	1.5 bar (0.15MPa)	-	-	2	-
(Shi et al., 2012a)	-	10psi,20psi (0.068-0.137MPa)	-	-	2	600mm of Hg (0.07 MPa)
(Shi et al., 2012c)		10 psi (0.068MPa)			2	600mm of Hg (0.07 MPa)
(He et al., 2016a)	-	0.2 MPa	-	-	3	-0.1 MPa
(Zhan et al., 2013a)	-	0.1 bar (0.01 MPa)	23	-	6, 12, 24	-0.5 bar (0.05 MPa)
(Zhang and Shao, 2016b)	99.8	5 bar (0.5 MPa)	-	-	12	-
(Zhang and Shao, 2018)	99.8	5 bar (0.5 MPa)	-	-	12	-
(Jang and Lee, 2016)	5	-	20	60	28 days	
(Junior et al., 2015)	20	-	25	60	1, 24	-
(Rostami et al., 2012b)	99.5	0.15 MPa	-	-	2	-

Concentration and pressure of CO₂, relative humidity (RH) and temperature are important governing factors in determining the extent of carbonation reaction (Kashef-haghighi et al., 2015; Kashef-Haghighi and Ghoshal, 2010; Shi et al., 2012b). The concentration of CO₂ may vary depending on process and source of capturing. Captured CO₂ may be either 100% concentrated carbon dioxide or flue gas obtained from industries with concentration of 15-25%. CO₂ gas is injected at a certain pressure in the carbonation chamber. The reaction rate of early carbonation is majorly influenced by CO₂ diffusion which is governed by concentration and pressure of CO₂ (Kashef-haghighi et al., 2015; Shi et al., 2012b).

Most of the studies on ACC have been conducted at room temperature or a temperature range of 20-25°C (Abdullahi et al., 2016; García-González et al., 2008; Jang and Lee, 2016). Higher temperatures can increase the CO₂ diffusion but might reduce its aqueous solubility. During carbonation curing, temperature of specimens rise to 70°C for cement paste and 58°C for concrete have been observed due to the exothermic nature of carbonation reactions (Monkman and Shao, 2006; Shi et al., 2012b). Higher temperature during carbonation curing might add to the water loss from the concrete, which could further affect the hydration process in concrete.

Ambient relative humidity has been generally preferred in studies for optimal CO₂ diffusion and carbonation (Jang and Lee, 2016; Junior et al., 2015). Although, CO₂ diffusion is promoted under ambient relative humidity, but higher RH can be used to prevent water loss due to elevated temperatures (Bukowski and Berger, 1979; Jang and Lee, 2016; Zhang et al., 2017). Higher relative humidity can also be preferred in case of low water to binder ratio of the mix. As per literature, excessive water content can limit the reaction by blocking the diffusion of CO₂ to the reactants. (Shi et al., 2012a; Zhang and Shao, 2016a)

2.2.4 Post Conditioning Phase

As already described, the carbonation reactions are exothermic in nature, which causes evaporation of water required for hydration. During carbonation curing, temperature of specimens rises to 70°C for cement paste and 58°C for concrete. Therefore, the post carbonation phase is essential to replenish the lost water to enable

further hydration of residual cement constituents after carbonation phase. Various studies have stressed on the role of post carbonation water curing in promoting further hydration (El-Hassan and Shao, 2015; He et al., 2016a; Rostami et al., 2011). It has been unanimously concluded in the literature that water curing post carbonation helped in maximizing the strength and caused densification of microstructure (He et al., 2016a; Klemm and Berger, 1972; Monkman et al., 2016; Rostami et al., 2011; Shi and Wu, 2008). Hydration of cement post carbonation helps in production of additional C-S-H gel that provides the additional strength and densification to carbonation cured mix.

Table 2.4 gives the details of post conditioning procedure adopted by various studies. The duration of post conditioning varies from 3 days to 27 days depending upon the type of post conditioning used. A lot of studies have adopted water spray instead of immersion or ponding as a post conditioning procedure (El-Hassan and Shao, 2015; Rostami et al., 2012b, 2012a). As the effect of ACC on pore water in concrete is more dominant near the surface (Junior et al., 2015), therefore use of water spray for a fixed period might be considered sufficient to replenish water depleted from the surface during ACC. This would also help to reduce the content of water required for the curing of concrete.

Table 2.4: Post conditioning procedures adopted in different studies

Reference	Post conditioning type	Duration of post conditioning
(Zhang and Shao, 2016a)	Moisture room maintained at 25°C, 95% RH	27 days
(El-Hassan and Shao, 2015)	Water spray	Till surface saturation
(Rostami et al., 2012a)	Water spray	-
(He et al., 2016a)	Immersion in Ca(OH)_2 saturated solution	7, 28, 90 days
(Zhang and Shao, 2018)	Moisture room (25°C, 95% RH)	27 days
(Junior et al., 2015)	Ambient conditions, 100% RH	28 days
(Rostami et al., 2012b)	Water spray	-

2.3 ROLE OF ACC IN CO₂ SEQUESTRATION

Accelerated Carbonation curing of concrete is believed to serve dual purpose. Apart from acting as a curing regime to improve the properties of concrete, the major purpose of ACC is to sequester carbon dioxide in the cement based materials.

2.3.1 Quantification of CO₂ Uptake

The sequestration of CO₂ through ACC is measured in terms of CO₂ uptake of concrete. The quantification of CO₂ uptake is done either by mass loss method or by thermogravimetric analysis. CO₂ uptake is obtained as a result of reaction of carbon dioxide with the constituents of cement and the hydration products of cement. The reaction of carbon dioxide during ACC results in change in physical and chemical characteristics of the mix, which is used to quantify the CO₂ uptake either by mass loss method or by thermogravimetry.

In mass loss method, the weights of specimens before and after carbonation curing are noted. After noting down the weights of specimens before and after carbonation curing, the CO₂ uptake is calculated using the Eq. 2.1(Rostami et al., 2012a; Shao et al., 2006c; Shao and Shi, 2006):

$$\text{CO}_2 \text{ uptake (\%)} = \frac{\text{Mass}_{\text{post CO}_2} + \text{Mass}_{\text{lost water}} - \text{Mass}_{\text{pre CO}_2}}{\text{Mass}_{\text{binder}}} \dots (2.1)$$

The major advantage of this method is the simplicity and feasibility to implement. However, the only shortcoming of this method for calculation of CO₂ uptake is the exact measurement of lost water during carbonation reaction. This is due to two major reasons: Firstly, when multiple specimens are collectively placed in the carbonation chamber for the process of ACC, it is difficult to know the exact amount of water lost from each specimen (Ahmad et al., 2017). Secondly, because the process of ACC is carried out in an enclosed chamber, it is difficult to recover the water lost from the samples completely. Therefore, in this method approximate estimate is made for amount of water lost during carbonation reaction.

The second method for determination of CO₂ uptake by specimens is using thermogravimetric analysis on the carbonated specimens. This method has been more

commonly used by researchers in recent studies (Chabannes et al., 2015; Jang and Lee, 2016; Zhang and Shao, 2016a). Thermogravimetric analysis is the process of heating a specimen up to a high temperature and recording the subsequent weight loss in the specimens. In this method, the carbonation cured specimen is heated over a temperature range of 50°C - 800°C and the corresponding weight loss at each temperature is noted. For ACC, it is necessary to heat the specimens up to a temperature of 800°C because the carbon dioxide is released in the temperature range of 600°C – 800°C upon disintegration of carbon dioxide (Lothenbach et al., 2011; Scrivener et al., 2016). Then, the quantification of CO₂ uptake is done as per Eq. 2.2:

$$\text{CO}_2 \text{ uptake (\%)} = \frac{\text{Sample mass at } 550^\circ\text{C} - \text{Sample mass at } 800^\circ\text{C}}{\text{cement mass in the original sample}} \times 100 \dots (2.2)$$

2.3.2 Factors Affecting CO₂ Uptake by ACC

The factors affecting CO₂ uptake by ACC can be classified in three ways:

- (i) Factors related to ACC procedure like duration and pressure of the supplied CO₂ gas, concentration of CO₂ gas, preconditioning, relative humidity, temperature, etc.
- (ii) Factors related to characteristics of sequestering material like cement/binder composition, water to binder ratio, moisture condition, etc.
- (iii) Effect of Alternate Binders on CO₂ Sequestration by ACC

Effect of these factors on CO₂ uptake by ACC as reported in different studies has been summarised in Table 2.5 and discussed in detail in the following section.

(i) Effect of CO₂ concentration, duration and pressure of CO₂ exposure on the CO₂ uptake by ACC

The influence of different parameters of ACC on the degree of CO₂ uptake by concrete has been evaluated by measuring the CO₂ uptake after carbonation. Ahmad et al. studied the effect of both duration of CO₂ exposure and pressure of CO₂ injection on CO₂ uptake ability of concrete (Ahmad et al., 2017). In his study, the duration of

ACC was varied from 1 hour – 10 hours and the pressure was varied from 10 psi to 60 psi. The uptake of CO₂ increased as the time of CO₂ exposure of specimens was increased from 1 hour to 10 hours. However, the rate of CO₂ uptake by concrete diminished as the duration of carbonation was increased. The authors attributed this to precipitation of calcium carbonate in pores after initial carbonation reaction, which hinders the penetration of CO₂ at longer curing durations (Ahmad et al., 2017). It was also noted that the diminishing rate of CO₂ uptake prevailed only at low pressures of 10-40 psi. Higher pressure of 50 psi and 60 psi exhibited over 50% and 100% more CO₂ uptake as compared to low pressures. Zhan et al. also observed an increase in CO₂ uptake from 19% to 30% on increasing the curing time from 6 hours to 24 hours (Zhan et al., 2013a).

Table 2.5: CO₂ uptake data for different parameters of ACC

Reference	Material characteristics		Parameters related to carbonation curing				CO ₂ uptake (% of weight of binder)
	Binder material	Water/binder ratio	Duration of CO ₂ exposure	Pre-conditioning	CO ₂ pressure	Concentration of CO ₂	
(Zhang and Shao, 2016a)	OPC	0.3-0.4	5-6 hours	25°C, 50 ± 5% RH, Wind speed 1m/s	5 bar (0.5 MPa)	99.8%	9.9%- 14.6%
(El-Hassan and Shao, 2015)	Portland limestone cement	0.71	4 hours	-	0.1 MPa	99%	18.3%
(Rostami et al., 2012a)	ASTM type 1 cement	0.36	2 hours	-	1.5 bar (0.15 MPa)	99.5%	7 – 9%
(Ahmad et al., 2017)	ASTM type 1 cement	0.45	1-10 hours	-	10 psi- 60 psi (0.068 MPa– 0.41 MPa)	-	3%- 7%
(Shi et al., 2012a)	ASTM type III Portland cement	0.43-0.50	2 hours	RH 50 ± 5%, 98%, 22 ± 3°C	10 psi, 20 psi (0.068 MPa – 0.137 MPa)	-	10%-24%
(Zhan et al., 2013a)	ASTM type 1 cement	-	6, 12, 24 hours	-	0.1 bar (0.01 MPa)	-	19%-30%

(Zhang and Shao, 2016b)	OPC and fly ash	-	12 hours	-	5 bar (0.5 MPa)	99.8%	14.3% and 17.06%
(Jang and Lee, 2016)	Belite rich Portland cement	0.5	28 days	-	-	5%	13%-16.9%

Apart from the pressure and duration of CO₂, the purity of CO₂ used in the carbonation process also affects the CO₂ sequestration. Studies on carbonation curing have been conducted using 100% CO₂ concentration (pure CO₂) as well as using flue gas obtained from cement and power plants with CO₂ concentration ranging from 15-25% (Monkman and Shao, 2010a; Shao et al., 2006c, 2006a; Shao and El-Hassan, 2013; Wang et al., 2007; Zhan et al., 2013a). To study the effect of concentration of CO₂ gas on CO₂ uptake, Shao et al. carried out ACC for duration of 2 hours using 99.8% and 25% concentration of CO₂. CO₂ uptake by concrete was found to be directly proportional to the concentration of CO₂ used. When the carbonation curing is carried out at 100% concentration level of CO₂, the specimen recorded 16% CO₂ uptake by weight of binder, whereas, the CO₂ uptake level was reduced to 9% for carbonation curing carried out at 25% concentration level (Shao et al., 2006c). Jang and Lee used 5% concentration of CO₂ and carried out the ACC process for 28 days to achieve a CO₂ uptake of 16% (Jang and Lee, 2016). While technologies are available to extract 100% pure CO₂ from the flue gases, the economical constraints of these techniques also needs to be considered to make the process of CO₂ sequestration efficient.

As discussed in section 2.2.2, preconditioning prior to carbonation is necessary to remove excess water from pores so as to provide a clear path to CO₂. Many studies have emphasised on the role of preconditioning for effective CO₂ sequestration (Shao and Shi, 2006; Shi et al., 2012a). Shi et al. studied the effect of different ways of preconditioning during the ACC process on CO₂ uptake by concrete (Shi et al., 2012a). In his study, pre conditioning was done in two ways; dry preconditioning with RH 50% using circulated air and moist preconditioning with RH 98 % up to 18 hours in a closed container. It was observed that specimens subjected to dry preconditioning showed slightly higher CO₂ uptake as compared to moist environment. CO₂

consumption was found to be decreasing beyond the preconditioning time of 5 hours, indicating existence of an optimum moisture content to be achieved for effective CO₂ sequestration.

(ii) Effect of material characteristics on CO₂ uptake by ACC

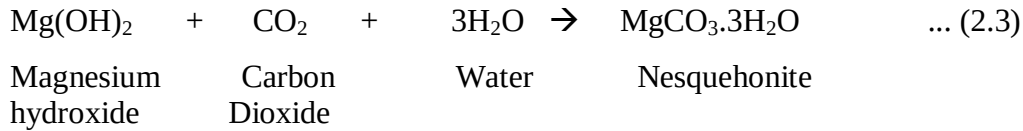
CO₂ uptake by any cementitious material directly depends on the composition of material. Calcium silicates are major reactants during accelerated carbonation curing. A higher Belite (C₂S) content was found to promote the CO₂ uptake by 3% of weight of the binder (Jang and Lee, 2016). In ACC, CO₂ actively reacts with metal oxides bearing materials to form carbonates. Presence of oxides of calcium and magnesium in material enhances the degree of CO₂ uptake significantly (Mo et al., 2016b; Mo and Panesar, 2013, 2012; Vandeperre and Al-Tabbaa, 2007). Addition of supplementary cementitious materials (SCM) like fly ash, blast furnace slag, MgO were also found to improve the CO₂ uptake efficiency of the mix (Monkman and Shao, 2006; Panesar and Mo, 2013; Peethamparan et al., 2003; Zhang et al., 2016).

High replacement levels of cement by supplementary materials leads to more porous microstructure and facilitate higher penetration of CO₂ gas. Also, finer particle sizes of SCMs provide higher specific surface area for reaction and accelerate the rate of carbonation (Monkman and Shao, 2006). In a study by Zhang et al., it was observed that CO₂ uptake increased from 19.5% to 24% and 28% respectively when 20% and 50% OPC was replaced by fly ash (Zhang et al., 2016). On replacing OPC with fly ash, the hydration degree of mix decreased and led to formation of a porous microstructure. The porous microstructure allows CO₂ to penetrate easily in the paste and enhance the CO₂ reaction degree. Therefore, for same water to binder ratio, fly ash concrete was more reactive to CO₂ than OPC concrete.

(iii) Effect of Alternate Binders on CO₂ Sequestration by ACC

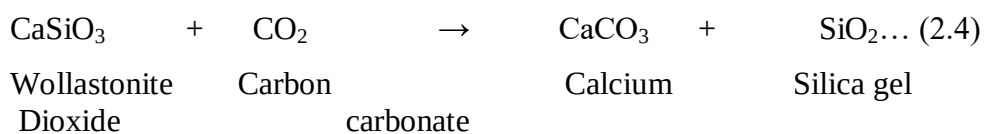
The presence of CO₂ reactive minerals in cement can enhance its CO₂ sequestration capacity. Incorporating such minerals in cement as partial substitutions or additives can improve the CO₂ uptake of resulting concrete (Torgal et al., 2018). Magnesium oxide (MgO) has been utilized as a low dose additive to Portland cement (Zheng et al., 1991). MgO hydrates in presence of water to form magnesium hydroxide. When

subjected to carbonation curing, magnesium hydroxide (Mg(OH)_2) reacts with CO_2 in high RH and CO_2 concentration to form Magnesium carbonate or nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$). The fundamental reaction can be represented as shown in Eq. 2.3 (De Silva et al., 2009).



Many studies have been conducted using MgO in blended cements and subjected to carbonation curing (Mo et al., 2016b; Mo and Panesar, 2013, 2012; Panesar and Mo, 2013; Pu and Unluer, 2016; Unluer, 2018; Unluer and Al-Tabbaa, 2014; Zhang and Panesar, 2018). The researchers have reported enhanced compressive strength owing to formation of matrix composed of nesquehonite, calcite, C-S-H and Ca(OH)_2 . One of the concerns regarding use of MgO is stability of nesquehonite at high temperature and low RH (Jauffret et al., 2015). High temperature might cause disintegration of nesquehonite and alter the binder properties of MgO (Jauffret et al., 2015).

Hydraulic calcium silicates C_3S and C_2S are major participants of both cement hydration as well as carbonation reactions. Wollastonite ($\text{CaO} \cdot \text{SiO}_2$) or CS is a non-hydraulic mineral that is found to be reactive towards CO_2 (Ashraf and Olek, 2016). Reaction of CS with CO_2 yields calcium carbonate, silica gel as main phases instead of C-S-H as is the case in hydraulic silicates (Huijgen et al., 2006). The chemical reaction of wollastonite with CO_2 has been represented in Eq. 2.4.



Possible carbonation of minerals like wollastonite which are otherwise non-cementitious opens up the opportunity for enhanced CO_2 sequestration as well as potential additives to Portland cement.

2.4 PERFORMANCE OF CARBONATION CURED BUILDING MATERIALS

Carbonation curing has been successfully applied on various precast elements to improve the resultant properties. The effect of ACC was initially demonstrated on

mortar specimens, and was later extended to masonry units and concrete specimens. The effect of ACC on the results properties of different materials is discussed hereunder:

2.4.1 Performance of Cement Paste and Mortars

The study on ACC initially began with cement mortars and pastes in the early 1970s (Goodbrake et al., 1979a; Klemm and Berger, 1972; Young et al., 1974). On the studies conducted on dry mixes, low water contents of order 0.15-0.20 have been employed in earlier studies (Klemm and Berger, 1972; Young et al., 1974). Carbonation cured dry mixes gained higher compressive strength at the age of 1 day than the hydration cured specimens. Klemm and Berger studied the effect of accelerated carbonation curing on cementitious systems at different water-cement ratios (Klemm and Berger, 1972). They observed in their study that compressive strength of cement mortars to be decreasing with ACC at very low and very high water cement ratios (Klemm and Berger, 1972). Therefore, an optimum amount of water is also necessary for effective carbonation. Water interacts with CO₂ to form carbonic acid which is responsible for dissolving calcium ions from cement minerals and insufficient water may cause halting of reaction. Klemm and Berger also reported that specimens carbonated for 5 minutes followed by 3 days of hydration were able to achieve compressive strength equivalent to 14-day strength of non-carbonated specimens. The increase in strength was attributed to formation of a matrix composed of C-S-H and CaCO₃ upon carbonation of calcium silicates and Ca(OH)₂.

The strength of carbonation cured specimens was also found to be dependent on the water cement ratio of mortar. Water cement ratio of mortars and post curing hydration had prominent effect on compressive strength of carbonation cured mortars. It has been reported in several studies that post hydration of carbonation cured specimens for 3 days led to approximately 45% increase in strength of mortars (He et al., 2016a; Klemm and Berger, 1972). Similar results for strength gain by carbonation cured mortars were reported in other studies (Farnam et al., 2016; Jang and Lee, 2016; Panesar and Mo, 2013; Shao et al., 2014a).

The results for porosity related properties of mortars and pastes subjected to early carbonation curing have been found to be contradictory in different studies (Junior et al., 2015; Qian et al., 2016). Junior et al. reported an increase in porosity of cement pastes when subjected to carbonation curing (Junior et al., 2015). The increase in porosity was attributed to loss of pore water from the surface and promoting formation of voids in its place. On the other hand, many studies reported a reduction in porosity of carbonation cured mortars and pastes (Ahmad et al., 2017; Qian et al., 2016; Rostami et al., 2012b). The reduction in porosity was reported to be caused by formation of CaCO_3 during the process of carbonation curing. CaCO_3 gets precipitated in the voids and creates a micro aggregate effect that reduced porosity of the mix. .

Microstructure of carbonation cured mortars was studied using X-Ray diffraction (XRD), Scanning electron microscopy (SEM) and Thermogravimetry (TGA). X-Ray diffraction patterns of carbonation cured specimen showed proportion of Ca(OH)_2 to be significantly reduced and formation of calcite as major CaCO_3 phase. Also, C_3S and C_2S peaks were noticeably diminished indicating partial carbonation of silicates (Khoshnazar and Shao, 2018; Rostami et al., 2012b). On further water curing of carbonated specimens, Ca(OH)_2 appeared stronger with weaker calcium silicate peaks, indicating continuation of hydration reaction post carbonation on providing sufficient water (Rostami et al., 2012b).. SEM images of carbonated specimens showed a densified mix with strong peaks of Ca, Si, and O in Energy Dispersive X-ray spectroscopy (EDS) indicating presence of C-S-H with relatively high carbon content. Crystalline CaCO_3 was not observed clearly in the mix, instead intermingled matrix of C-S-H with CaCO_3 was observed (Rostami et al., 2012b). TGA analysis of carbonated mortars confirmed the findings of XRD and SEM. The mass loss of carbonated specimens in the temperature range of 420-460°C was lower than the reference sample indicating lower Ca(OH)_2 decomposition. The mass loss after 540°C was higher for carbonated specimens which indicated loss of bonded CO_2 (Rostami et al., 2012b).

The effect of carbonation curing on strength of pastes was also found to be dependent on duration of CO_2 exposure. Junior et al. studied the effect of two different durations of 1 hour and 24 hours of ACC on properties of high initial strength Portland cement

paste (Junior et al., 2015). 1 hour of carbonation curing enhanced the compressive strength by almost 10%; while 24 hours of carbonation curing considerably reduced the compressive strength as compared to the reference specimens. The increase in strength was attributed to generation of C-S-H along with CaCO_3 which created a microstructure with strength-contributing solids, as explained in earlier studies (Ashraf and Olek, 2016; Guan et al., 2016; Rostami et al., 2012b). However, carbonation curing also led to removal of water from the pore structure. Prolonged duration of carbonation leads to excess removal of water and causes opening up of pore structure. The change in structure composition from loss of water affects the strength of paste negatively. Along with this, high water loss significantly decreased the remaining water content and hindered the subsequent hydration reactions of cement paste.

2.4.2 Performance of Concrete Masonry Units

Concrete masonry units (CMU) are precast products made of plain concrete. CMUs are used for construction of load bearing walls. CMUs represent a low environmental impact construction system and provide superior performance than cast in situ concrete (El-Hassan et al., 2014). Worldwide application of CMUs provides huge scope for CO_2 sequestration with the help of ACC. Several researchers examined the effect of ACC on performance of concrete masonry units made with limestone cement and lightweight aggregate in different studies (El-Hassan et al., 2014; El-Hassan and Shao, 2015; MacMaster and Tavares, 2015; Mahoutian and Shao, 2016; Shao et al., 2014b; Xuan et al., 2016). In the earlier studies by El-Hassan and Shao, CMUs were carbonation cured for 4 hours followed by water spray till surface saturation. The results were compared with 4 hour steam curing and water curing (El-Hassan et al., 2014; El-Hassan and Shao, 2015). Steam curing had the highest early age strength followed by carbonation curing and water curing. Carbonation curing had higher compressive strength than water cured specimens at all testing ages.

The microstructure studies on carbonation cured CMUs revealed similar observations as found in microstructure testing of cement pastes and mortars (El-Hassan and Shao, 2015). XRD and TGA confirmed substantial conversion of Ca(OH)_2 into CaCO_3 . SEM images of CMUs showed microstructure composed of C-S-H, ettringite, Ca(OH)_2 along with poorly crystalline CaCO_3 , wrapped between C-S-H.

CMUs were able to uptake approximately 24% CO₂ by weight of cement(El-Hassan and Shao, 2015). It was estimated in the study that one CMU block of 15 Kg with 13% cement was able to store 0.47 Kg of cement in the form of CaCO₃. This data was extrapolated to estimate that if block and brick plants incorporated ACC, CO₂ - emissions related to cement industry could be reduced by 2.5%.

2.4.3 Performance of Concrete Subjected to ACC

Most of the work on ACC has been concentrated on studying the performance of plain concrete. It has been unanimously concluded in the literature that rapid early strength gain is eminent after ACC(El-Hassan and Shao, 2014; He et al., 2016a; Monkman and Shao, 2010b; Rostami et al., 2012a; Shao et al., 2006b; Shi et al., 2012a, 2012c; Zhan et al., 2013a; Zhang and Shao, 2016b, 2018, 2016a). The increase in compressive strength of ACC cured mixes can be understood due to formation of Calcium Silicate Hydrate gel intermingled with CaCO₃ which generates a more dense microstructure as compared to conventional hydration where major reaction products are Ca(OH)₂ and C-S-H(Shao et al., 2006c; Shao and El-Hassan, 2013; Zhang and Shao, 2016a). CaCO₃ produces a higher solid volume than Ca(OH)₂ and does not leach out easily(Dias, 2000).

It has been concluded in the studies that later age strength of carbonation cured concrete is dependent upon post curing process adopted (El-Hassan et al., 2013; He et al., 2016a; Rostami et al., 2012a). Considerable strength gain has been reported when ACC is followed by subsequent water curing either by immersion in water or by water spray(El-Hassan and Shao, 2015; He et al., 2016a). Post carbonation water spray is necessary to replenish the lost water and allow further hydration of residual cement constituents(Rostami et al., 2011).

Many studies have stressed on role of various factors like duration of CO₂ exposure and pressure on the performance of carbonation cured concrete(Ahmad et al., 2017; Zhan et al., 2013b). While shorter carbonation durations have helped in enhancing the performance of cement paste, higher duration of initial carbonation curing showed a detrimental effect on performance of concrete. Higher duration of carbonation leads to

lesser availability of water for further hydration of cement causing a decrease in strength of concrete (Rostami et al., 2012a).

The densification of microstructure by carbonation curing is found to enhance the durability performance of concrete. The durability of concrete has been evaluated by testing chloride permeability, air permeability, electrical resistivity, sulfate attack and acid attack (Rostami et al., 2012a, 2011; Zhang and Shao, 2016a). Rostami et al. compared the effects of steam curing and carbonation curing on durability performance of precast concrete (Rostami et al., 2012a). Carbonation cured concrete showed higher surface resistivity, and increased resistance to sulfate and chloride attack. The precipitation of CaCO_3 in the surface pores results in a denser and less connected pore structure in precast concrete. Pore size refinement, lesser passage to water and other deleterious substances and subtraction of reactive Ca(OH)_2 from concrete through carbonation curing adds to durability performance of concrete (Zhang and Shao, 2016a). Shi et al. studied the weathering properties of carbonation cured concrete blocks (Shi et al., 2012c). Carbonation cured specimens showed lower drying shrinkage and water absorption as compared to steam cured specimens. The better durability performance was attributed to reduction in total porosity, especially capillary porosities; due to formation of C-S-H intermingled with CaCO_3 . Similar results for chloride penetration and weathering carbonation resistance of carbonation cured concrete were reported by Zhang and Shao (Zhang and Shao, 2016b).

Densification of the mix by carbonation curing has been unanimously accepted as per microstructural assessments in various studies (Ahmad et al., 2017; He et al., 2016a; Rostami et al., 2012a; Zhang and Shao, 2016a). As discussed earlier, the densification is a result of different reaction products formed by carbonation curing as compared to water or steam curing. SEM images of carbonation cured concrete exhibited dense microstructure composed of CaCO_3 crystal wrapped in C-S-H gel (Ahmad et al., 2017; He et al., 2016a). The formation of different phases of CaCO_3 was confirmed by XRD analysis. Based on the participating reactants, vaterite or calcite polymorphs were observed in XRD spectrums (Zhang and Shao, 2016a). The microstructure of carbonation cured concrete was significantly enhanced when sufficient

postconditioning was provided to the specimens. Presence of water enabled further hydration of concrete post ACC and SEM images showed formation of additional C-S-H gel and Ca(OH)_2 (He et al., 2016a).

The only concern regarding use of ACC is reported for reinforced concrete structural elements. Natural carbonation of concrete has been extensively studied and several researchers have stressed on reinforcement corrosion due to prolonged exposure to carbonation (Ahmad, 2003; Belda Revert et al., 2018; Bertolini et al., 2013; Böhni, 2005; Cabrera, 1996; Hobbs, 2001; Ismail et al., 2010; Köliö et al., 2015; Roy et al., 1999; Tonoli et al., 2011; Zhao and Jin, 2016). It is known that Ca(OH)_2 is converted into CaCO_3 during natural carbonation and this lowers the pH from 12.5 to 9, thereby damaging the passive layer that protects reinforcement bar (Zhao and Jin, 2016). Similar to this, some researchers have raised concern over lowering of pH by ACC (Rostami et al., 2011; Shi et al., 2012c; Zhang and Shao, 2016b). However, many studies on pH of carbonation cured mortar concrete have shown the pH of carbonated products to be higher than the threshold value of 10 (Rostami et al., 2011; Zhang and Shao, 2016b). Also, it has been found feasible to raise the decreased pH by following carbonation curing process with adequate water curing process (Rostami et al., 2012a).

2.5 EFFECT OF ACC ON MORTARS AND CONCRETE MADE WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS (SCM)

Cement production is one of the largest contributors to CO_2 emissions. Supplementary cementitious materials (SCMs) have been partially or completely used as replacement of cement or fine aggregates in construction in order to reduce the demand of cement and corresponding CO_2 emissions (Al-Harthi et al., 2003; Babu and Kumar, 2000; Bondar and Coakley, 2014; Cheng et al., 2005; Jia, 2012; Khan and Siddique, 2011; Kunal et al., 2012; Limbachiya and Roberts, 2004; Lothenbach et al., 2011; Maslehuddin et al., 2009; Najim et al., 2014; Nochaiya et al., 2010; Siddique, 2011; Siddique and Bennacer, 2012; Toutanji et al., 2004). Some of the established SCMs are fly ash, silica fume, blast furnace slag, steel slag, etc. Pozzolanic materials like fly ash, steel slag, cement kiln dust when used as replacement to cement, improve the long term performance of concrete as the pozzolanic reaction takes time. But, the

early age strength of SCMs is a concern, as the reduction in cement content causes lesser hydration and consequently, lesser formation of C-S-H gel (Lothenbach et al., 2011). The problem of low early strength of SCMs can be solved by using carbonation curing at early ages.

Apart from CO₂ sequestration, carbonation curing has also been found to act as an activation mechanism for supplementary cementitious materials (Monkman et al., 2018). Many studies have tried to assess the effect of ACC on use of SCMs (Monkman and Shao, 2006; Zhan et al., 2016; Zhang et al., 2016; Zhang and Shao, 2018). ACC not only enhances the hydration degree of alternative cementitious materials, but also improves the early age performance of concrete. Monkman and Shao assessed the carbonation behavior of Ground Granulated Blast Furnace Slag (GGBS), fly ash, electric arc furnace (EAF) slag and lime (Monkman and Shao, 2006). All four materials reacted differently when subjected to carbonation curing of 2 hours. Fly ash and lime showed highest degrees of carbonation, followed by EAF slag; while GGBS showed least reactivity towards CO₂. Calcite was the major reaction product from fly ash, lime and EAF slag; while aragonite was produced by carbonation of GGBS. Several studies tried to assess the CO₂ sequestration ability of steel slag binders (Bonenfant et al., 2008; He et al., 2013; Huijgen et al., 2005; Huijgen and Comans, 2006; Ukwattage et al., 2017). Presence of C₂S component in steel slag makes it a potential cementitious material that could act as a carbon sink for CO₂ sequestration (Johnson et al., 2003).

Zhang et al. in their study found that fly ash concrete was more reactive to CO₂ as compared to OPC concrete (Zhang et al., 2016). With the reduction in OPC content, a porous microstructure was generated due to insufficient hydration reaction. The enlarged distance between cement grains facilitated higher possibility of reaction with CO₂ and hence, a higher degree of CO₂ sequestration. The performance of SCMs subjected to carbonation curing is majorly dependent upon fineness of material and water content post carbonation. Finer particle size of SCMs provides a higher specific area for effective carbonation reaction. Due to this, it was observed in many studies that concrete made with SCMs had better reactivity towards CO₂ than OPC (Monkman and Shao, 2006). Water content post carbonation also plays a dominant

role in determining the performance of SCMs. Sufficient water content post carbonation is necessary for complete hydration and pozzolanic reaction of SCMs (Monkman and Shao, 2006).

2.6 GAPS IN RESEARCH AREA

From the survey of literature and analysis of previously published studies, it has been established as a beneficial alternative to steam curing for precast concrete. The process of ACC not only serves the purpose of carbon dioxide sequestration, but also enhances the properties of concrete and mortar. Concrete cured with carbon dioxide had considerable increase in early age compressive strength and was able to achieve required later age strength. The precipitation of CaCO_3 along with calcium silicate hydrate provided a denser microstructure as compared to hydration cured specimens.

The efficiency of ACC depends upon a number of factors including purity of CO_2 gas, pressure during ACC, duration of curing. It is necessary to optimize the process of ACC by controlling these parameters carefully, so that maximum CO_2 sequestration can be achieved economically and the process as a whole can be optimised. Previous research has been mainly focused on immediate performance of concrete, however, detailed study needs to be done on long term strength development and durability parameters of concrete.

The performance of carbonation cured concrete is found to be dependent majorly on composition of binder material. Supplementary cementitious materials are being widely researched and used these days as a potential replacement of cement. Therefore, there is a need to assess the behaviour of these materials when subjected to carbonation curing.

CHAPTER 3

EXPERIMENTAL PROGRAMME

3.1 GENERAL

The objective of this research work is to evaluate the performance of concrete when subjected to accelerated carbonation curing (ACC). The testing programme was divided into various subparts. In the first part, the performance of carbonation cured concrete was evaluated in terms of mechanical properties, permeation properties, microstructural changes and long term durability aspects of concrete. In this, the effect of carbonation curing duration was also investigated. Further, the CO₂-sequestration potential was investigated from the TGA analysis of the mixes. In the second phase, the performance of mineral admixture based cementitious systems under ACC was investigated. For this, mortar mixes were cast and performance was evaluated in terms of mechanical, permeation and microstructural aspects.

In this chapter, the properties of materials used in the experimental programme are discussed, followed by details of specimen preparation. Along with this, the experimental setups of different curing regimes and curing methodology used in this study are explained in detail. The details of different tests conducted in the present study are also included in this chapter.

3.2 MATERIALS

The present study has been conducted on mortar and concrete specimens. Primary materials required for preparing the mixes were cement, fine aggregate, coarse aggregate and water. Cement acts as a binder and is majorly responsible for imparting strength to the concrete mix. A large fraction of volume of concrete is formed by aggregates which are relatively inert and provide bulk to the concrete. Two types of aggregates based on size are used in preparation of concrete i.e. coarse aggregates and fine aggregates. Water is responsible for the hydration reaction with cement and also provides workability to the mix. Same sets of materials were used throughout this study for casting of specimens. Preliminary testing of materials was done in accordance with relevant codes to examine the physical properties of these materials.

The details of the materials along with their properties have been described in the subsequent sections.

3.2.1 Cement

As discussed in section 1.5 and 1.6, the major reactants in hydration and carbonation reactions are constituents of cement i.e. calcium silicates (C_3S , C_2S) and calcium aluminates (C_3A). The cement used in this study was procured from local market and stored in sealed containers to prevent any interaction with moisture. Ordinary Portland Cement (OPC) of 43 grade conforming to IS 8112:2013 (IS 8112, 2013) and ASTM C150 (ASTM C150, 2011) was used for preparation of specimens. The physical properties of OPC used are listed in Table 3.1. The chemical composition of cement is listed in Table 3.2.

Portland Pozzolona Cement (PPC) was used in the second part of the study, wherein the performance of mineral admixture based cementitious systems under ACC was investigated. Fly ash based - Portland Pozzolona cement (PPC), conforming to Indian standards IS: 1489 (Part -1):1991 (IS 1489, 1991) was used. The physical properties and chemical composition of PPC are listed in Tables 3.3 and 3.4, respectively.

Table 3.1: Physical properties of Ordinary Portland Cement (OPC)

S. No.	Characteristic	Obtained Result	Standard Values as per IS 8112:2013
1.	Fineness	310 m ² /Kg	> 225 m ² /Kg
2.	Specific Gravity	3.14	-
3.	Normal Consistency	30 %	-
4.	Initial Setting Time	123 min	> 30 min.
5.	Final Setting Time	270 min	< 600 min

Table 3.2: Chemical composition of Ordinary Portland Cement (OPC)

Constituent	%
SiO ₂	21.25
CaO	63.49
Fe ₂ O ₃	4.30
MgO	1.02
SO ₃	2.93
Al ₂ O ₃	4.74
Na ₂ O	0.30
K ₂ O	0.78
TiO ₂	0.36
LOI	2.23

Table 3.3: Physical properties of Portland Pozzolona Cement (PPC)

S. No.	Characteristic	Obtained Result	Standard Values as per IS 1489:1991 (Part 1)
1.	Fineness	324 m ² /Kg	>300 m ² /Kg
2.	Specific Gravity	2.88	-
3.	Normal Consistency	32 %	-
4.	Initial Setting Time	150 min.	> 30 min.
5.	Final Setting Time	385 min.	< 600 min.

Table 3.4: Chemical composition of Portland Pozzolona Cement (PPC)

Constituent	%
SiO ₂	35.77
CaO	53.02
Fe ₂ O ₃	0.65
MgO	2.71
SO ₃	2.41
Al ₂ O ₃	2.59
Na ₂ O	0.22
K ₂ O	0.70
TiO ₂	0.39
LOI	1.5

3.2.2 Cement Kiln Dust (CKD)

Cement Kiln Dust (CKD), is a by-product from the cement manufacturing industry and is considered as an industrial waste. The high alkaline content of CKD restricts its reuse into cement for concrete production (Maslehuddin et al., 2009; Najim et al., 2014). Disposal of CKD is also not recommended as it results in contamination of ground water by chemicals and heavy metals leached out from CKD (Sadek et al., 2017). However, the high level of alkalinity along with the fine particle size of the waste product makes it a suitable material that can be used as replacement of cement. This would help in generating economic and ecological value to this waste material.

Cement Kiln Dust used in this study was procured from Ambuja Cement Plant, Darlaghat, Bilaspur. Fig. 3.1 shows the actual sample of cement kiln dust used. CKD is a very fine powdery material of uniform micron sized particles. Fig 3.2 shows EDS and SEM images of CKD. THE EDS image shows peaks of calcium and silica in the graph, which further confirms that the chemical composition of CKD is similar to that of cement. Table 3.5 describes the physical properties of CKD. The chemical composition of CKD is given in Table 3.6. The chemical composition of CKD is similar to ordinary portland cement with lime, silica and alumina as major constituents. CKD contains significant amount of alkalis and is generally considered caustic (Siddique, 2006).

In the present study, CKD was used as replacement of cement in varying percentages of 0,5,10,20,30,40 and 50 % for making mortar mixes, which were subjected to accelerated carbonation curing.



Fig. 3.1: Cement Kiln Dust used in the study

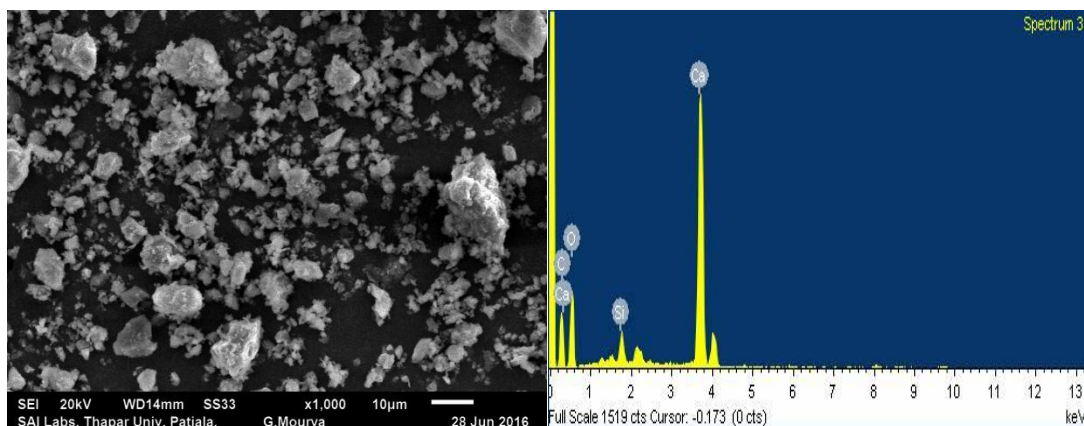


Fig. 3.2: SEM and EDS images for CKD sample

Table 3.5: Physical properties of Cement Kiln Dust

Sr No	Property	Value
1	Specific Gravity	2.7
2	Fineness	460 m ² /Kg

Table 3.6: Chemical composition of Cement Kiln Dust

Constituent	%
SiO ₂	15
CaO	39.4
Fe ₂ O ₃	2.3
MgO	1.8
SO ₃	5.7
Al ₂ O ₃	3.2
Na ₂ O	1.4
K ₂ O	3.1
LOI	19

3.2.3 Ground Granulated Blast Furnace Slag (GGBS)

GGBS is a by-product from the blast furnace process which is used in the production of iron. Molten iron and molten slag are produced in the blast furnace operated at 1500°C. Molten slag is lighter and floats on the top of molten iron. After removal of

the molten iron from the furnace, the remaining molten slag is then water quenched rapidly below 800°C in order to prevent the crystallization of merwinite and melilite, resulting in the formation of coarse sand like granules(Habashi, 2017). GGBS is then obtained after drying of the granules and grinding them to a fine powder. GGBS so produced is a mixture of alumina, silica, magnesium oxide and lime; which are also the basic constituents of Portland cement.

In the present study, GGBS (as shown in Fig. 3.3) was procured from Alcofine of CountoMicrofine Products Pvt. Ltd. The SEM image of the GGBS sample along with EDS is shown in Fig. 3.4, which exhibits a very fine particle size for the GGBS particles. Silica is observed as major constituent of GGBS from the EDS analysis. The physical properties of GGBS and chemical composition of GGBS are given in Table 3.7 and 3.8 respectively.



Fig. 3.3: GGBS used in this study

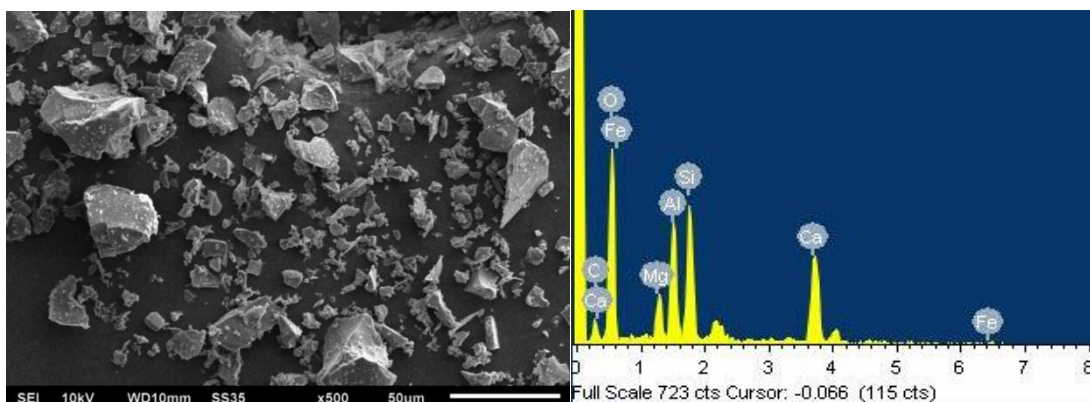


Fig. 3.4: SEM-EDS of GGBS used in this study

Table 3.7: Physical properties of GGBS

Sr. No	Property	Value
1	Specific Gravity	2.9
2	Fineness	449 m ² /Kg

Table 3.8: Chemical composition of GGBS

Constituent	%
SiO ₂	73.47
CaO	12.4
Fe ₂ O ₃	2.3
MgO	2.18
SO ₃	1
Al ₂ O ₃	4.5
Na ₂ O	0.5
K ₂ O	2.1
LOI	1.35

3.2.4 Fine Aggregates

Natural river sand belonging to zone II as per IS:383-2016 (IS 383, 2016) was used as fine aggregates in this study. Physical properties of fine aggregates were tested as per relevant standards prior to their use. The sieve analysis of fine aggregates is presented in Table 3.9. From sieve analysis results, it can be seen that the percentage passing of fine aggregates satisfied the Zone –II recommendations of IS 383-2016 (IS 383, 2016). The physical properties of fine aggregate are presented in Table 3.10. The fine aggregates were washed followed by drying in oven for 24 hours prior to its use for casting of specimens.

3.2.5 Coarse Aggregates

Coarse aggregate is essential for providing bulk to the concrete. Crushed gravel with nominal size of 20 mm and 10 mm was used as coarse aggregates. Both the aggregates were used in a ratio of 60:40 by volume respectively. Therefore, the aggregates were mixes in the same proportion before measuring the physical properties and sieve analysis. The physical properties of coarse aggregates were

measured as per the guidelines of IS 383:2016 (IS 383, 2016) and the results are presented in Table 3.11. The sieve analysis of the coarse aggregates has been presented in Table 3.12. The coarse aggregates were also washed and dried in oven for 24 hours prior to its use for casting of specimens.

Table 3.9: Sieve analysis of fine aggregates

Sieve size	Mass Retained (g)	%age retained	%age passing	Cumulative %age mass retained
4.75 mm	31	3.1	96.9	3.1
2.36 mm	137	13.7	86.3	16.8
1.18 mm	238	23.8	76.2	40.6
600 microns	168	16.8	83.2	57.4
300 microns	316	31.6	68.4	89
150 microns	65	6.5	93.5	95.5
Pan	45	4.5	95.5	100
			Σ %age retained =302.4	
Fineness modulus = 302.4/100 = 3.02				

Table 3.10: Physical properties of fine aggregates

Properties	Observed values
Specific gravity	2.64
Moisture content (%)	0.17
Water absorption (%)	0.87
Fineness modulus	3.02

Table 3.11: Physical properties of coarse aggregates

S. No	Characteristic	20 mm aggregate	10 mm aggregate
1.	Type	Crushed	Crushed
2.	Specific Gravity	2.70	2.69
3.	Fineness Modulus	6.93	6.10
4.	Total Water Absorption (%)	2.04	2.1

Table 3.12: Sieve analysis of coarse aggregate

IS Sieve (mm)	Wt. Retained (gm)	%age weight retained	Cumulative Wt. retained (gm)	Cumulative %age Wt. retained
20	120	2.40	120	2.40
10	3516	70.32	3636	72.72
4.75	1198	23.96	4834	96.68
Pan	166	3.32	5000	100.00
$\Sigma = 5000$				$\Sigma C = 172.29$
Fineness modulus $= \frac{\Sigma C + 500}{100} = (172.29 + 500)/100 = 6.72$				
ΣC = Summation of Cumulative % age retained up to 4.75 mm				

3.2.6 Water

Water is responsible for hydration reactions with the binder material and formation of CSH gel and other products that impart strength to the concrete. Water content is also essential to provide workability to concrete. In this study, potable tap water was used for casting and curing of mortar and concrete mixes. The pH of the water used was checked periodically and was found to be around 8.

3.2.7 Reinforcement Bar

TMT steel bars of 12 mm diameter confirming to IS 1786:2008 (IS 1786, 2008), were used in this study for carrying out the corrosion investigations in concrete specimens. The bars were cut into 230 mm lengths. Before embedding the steel rebar into concrete, it was prepared as per ASTM G 109: 2013 (ASTM G 109-13, 2013). The steel rebar was cleaned by rubbing with emery paper and laboratory grade hexane to remove the rust particles from the surface of rebar. The bars were then coated with 2 layers of epoxy from the top for a length of 50 mm at one end of the rebar in order to leave only a bottom 180 mm portion bar. After air drying of the bar specimens, an insulating tape was applied on the epoxy coated portion. Then, a 3mm thick neoprene tube with 12mm internal diameter was mounted over the insulating tape. To ensure electrical connectivity at the top end of the bar, a 3 mm threaded hole was made. Subsequently, a stainless steel screw was inserted into the hole to ensure proper

electrical connectivity between working electrode and corrosion analyzer for corrosion measurement. The prepared test piece is shown in Fig. 3.5.

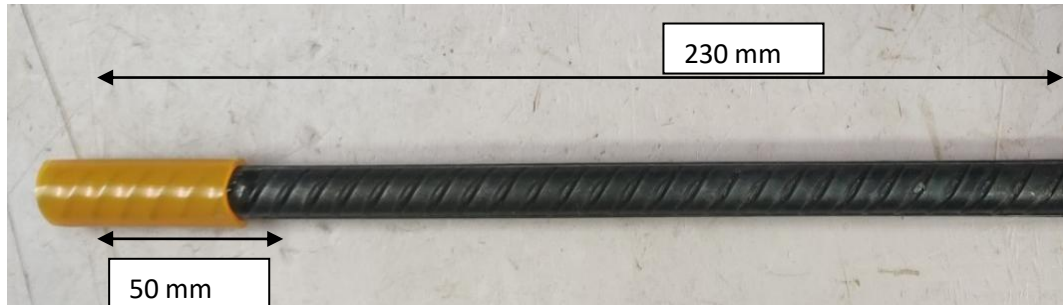


Fig. 3.5: Steel rebar used in concrete tests

3.3 MIX PROPORTIONS

To understand various aspects of accelerated carbonation curing, investigations were carried out on mortar and concrete mixes. The mix proportions were finalized as per the relevant codal provisions. The details are presented in the following sections:

3.3.1 Mix Proportions for Mortar Mixes

Mortar mixes were prepared with a binder to aggregate ratio of 1:3 as per the guidelines of IS 4031(Part 6): 1988 (IS 4031:Part6, 1988). The water to binder ratio for mortar specimens was kept at 0.5.

3.3.2 Mix proportions for concrete mixes

Concrete mix was designed as per IS 10262:2009 (IS:10262, 2009). The grade of concrete used in the study was M25 with a target 28 day compressive strength of 31.6 MPa, using the mild exposure conditions. Water to cement ratio was determined based on strength and workability of trial mixes. Based on the performance of trial mixes, a w/c ratio of 0.45 was used in the present investigation. The mix proportions of the designed mix are listed in Table 3.13.

Table 3.13: Concrete mix proportions used in the study

Constituent	Cement	Fine aggregates	Coarse aggregates	Water
Quantity(Kg/m ³)	400	690	1150	180

3.4 CASTING OF SPECIMENS

For the preparation of mortar specimens, the binder and sand were initially dry mixed with a trowel for at least one minute and then water was added to the dry mix. The mixing was done for nearly three minutes until a uniform mix was obtained. Immediately after mixing, the mortar was placed in cubic moulds in three layers and each layer was prodded 20 times to remove entrained air. The cubic mould was then vibrated for 2 minutes to ensure proper compaction. In mortar mixes, cubes of size 70.6 mm were cast.

For the preparation of concrete specimens , firstly, the aggregates and cement were taken in the required proportions and were dry mixed in a mechanical mixer of capacity 0.06 m³ for two minutes and then the water was added in equal proportions to the dry mix and mixed until a uniform distribution was obtained. Immediately after mixing, concrete was poured into respective moulds. All the moulds were oiled on internal surfaces prior to pouring of concrete.

Different sets of moulds were used in this study based on the requirement of the test. Cubes of size 150 mm were cast for compressive strength test and cubes of size 100mm were cast for testing of water absorption and carbonation depth. Cylinders of diameter 150 mm and length 300mm were cast for carrying out split tensile strength test and cylinders of diameter 100mm and length 50 mm were cast for preparations sorptivity test and rapid chloride permeability test. For abrasion resistance measurements, specimens having size 70 x 70 x 35 mm were prepared. Prism specimens of size 75×75×285mm were cast for the measurement of unrestrained drying shrinkage test. For linear polarization resistance test, reinforced cylindrical specimens of diameter 100 mm and length 200 mm were prepared. The cylinders were reinforced with a single steel rebar of diameter 12 mm.

For casting of concrete specimens, concrete was poured in each mould in three layers and prodded 20 times with a tamping rod each time to remove entrained air as per provisions of IS 516:2004 (IS 516, 2004). The moulds were then compacted over vibrating plate to ensure proper compaction.

For corrosion monitoring, cylindrical specimens of diameter 100mm and length 200 mm were cast and schematic diagram of specimen is shown Fig 3.6(a). The steel bars were concentrically placed with transverse clear cover of 44 mm and bottom cover of 20 mm. Fig 3.6(b) shows the specimen after casting. For casting of specimens, a special moulding system was used so as to accurately maintain the position and placement of the bars with respect to cylinders. To maintain the bottom cover and concentric position of rebar, the specimen were casted in inverted position with the help of special arrangement made in the system. After casting the specimen were demoulded and subjected to their respective curing regime for 28 days.

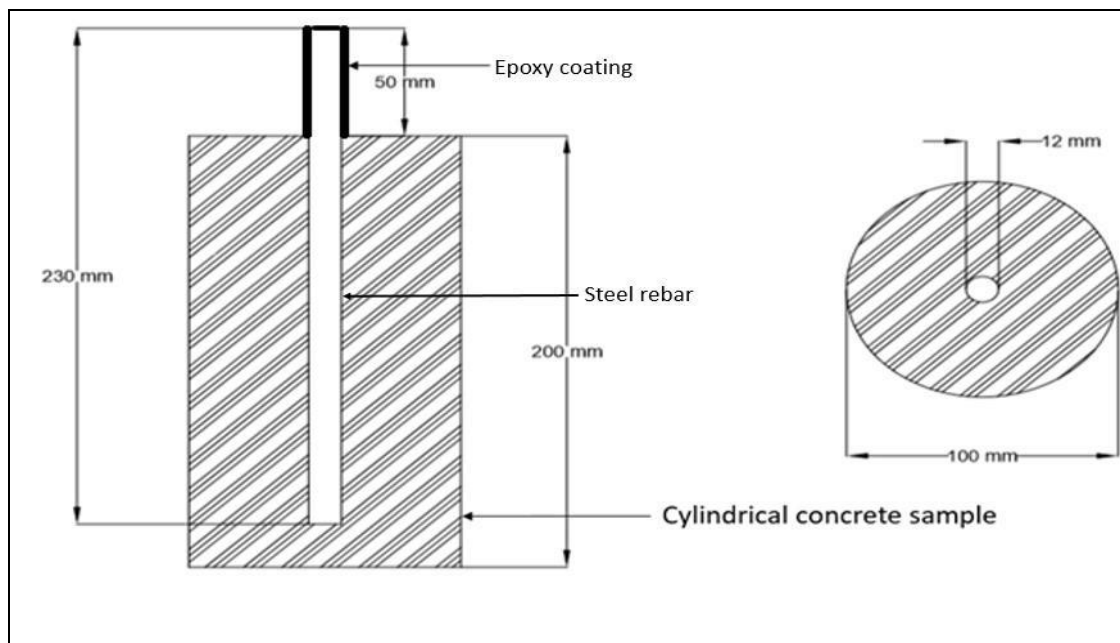


Fig. 3.6(a): Schematic diagram of cylindrical concrete specimen for corrosion monitoring



(b)

Fig. 3.6(b): Casted cylindrical concrete specimen for corrosion monitoring

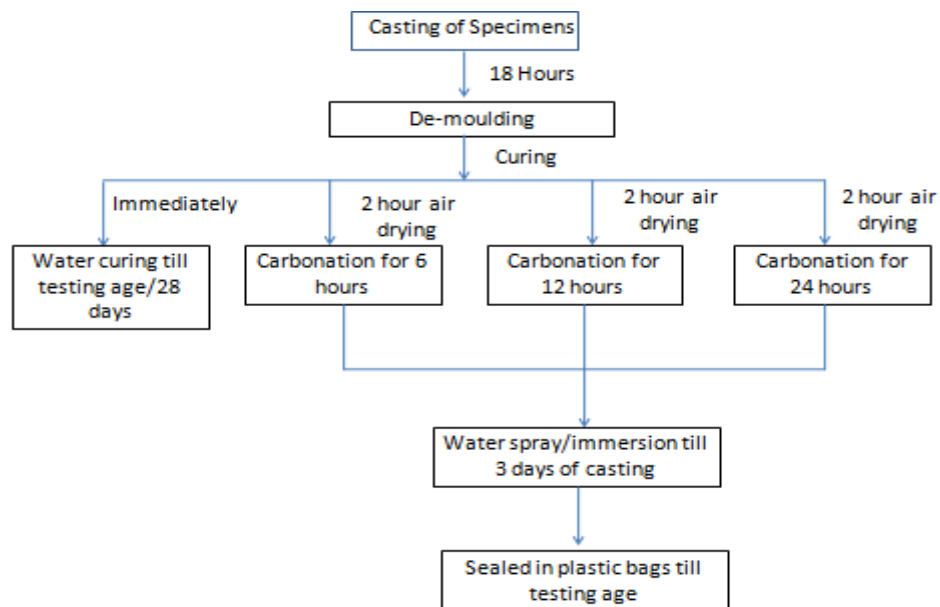


Fig. 3.7: Methodology for preparation of specimens

3.5 CURING OF SPECIMENS

To study the effect of different curing regimes on mortar and concrete, the specimens were separated into different sets after de-moulding and subjected to the required curing regime as shown in Fig 3.7. All the specimens were demoulded after 18 hours as opposed to the normal de-moulding practice of 24 hours. It was to assure that the specimens could be subjected to the carbonation curing regime at the earliest along

with sufficient hydration. In the present study, two different types of curing regimes were used; water curing (WC) and accelerated carbonation curing (ACC). The specifications of these curing regimes have been discussed in the following sections:

3.5.1 Water Curing

For water curing, the specimens were initially kept in laboratory environment till 26 hours of casting and then immersed in a curing tank maintained at a temperature of $27 \pm 2^\circ\text{C}$ as per the guidelines of IS 516:2004 (IS 516, 2004). For water cured regime, the process of water curing was carried out till the testing age. Specimens subjected to water curing are shown in Fig 3.8.



Fig. 3.8: Temperature controlled water curing of concrete

3.5.2 Accelerated Carbonation Curing

The process of ACC was carried out in an enclosed vacuum chamber. The line diagram showing the typical setup for accelerated carbonation curing is outlined in Fig. 3.9; while the actual ACC chamber used in this study is shown in Fig. 3.10. The shape of chamber can be cylindrical or cubical as required. The chamber is connected to a vacuum pump to remove the excess air from inside prior to carbonation. CO_2 gas is supplied externally through an industrial CO_2 cylinder and gas pipes. The pressure of CO_2 injection is controlled by pressure regulators on the cylinder. The pressure inside the chamber is controlled by pressure gauges connected to the chamber. The chamber is also provided with input and output nozzles to control the carbon dioxide

injection and removal respectively. Safety valve is provided to immediately reduce the pressure inside the chamber in case of any fault in pressure regulation. The bottom of carbonation chamber is lined with silica gel or water absorbing sheets to absorb water released during carbonation.

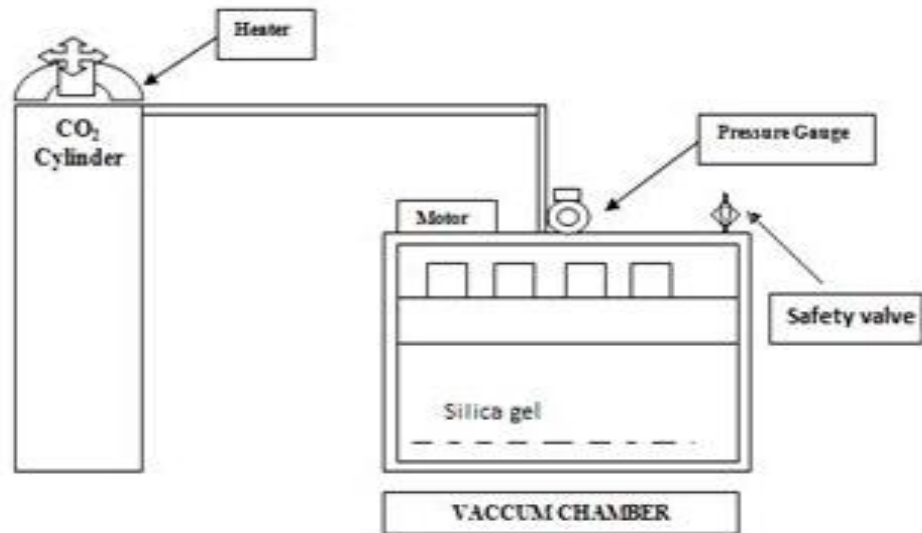


Fig. 3.9: Setup of Accelerated carbonation curing chamber



Fig. 3.10: Accelerated carbonation curing chamber used in the present study

The process of ACC was carried out in three stages after de-moulding namely, preconditioning stage, carbonation stage and postconditioning stage as shown by flowchart in Fig. 3.11.



Fig. 3.11: Flowchart for process of Accelerated carbonation curing

(a) *Preconditioning*: This phase is essentially a water removal phase. It is necessary to maintain an optimal amount of water for effective carbonation. Previous studies have reported that the moisture condition of concrete significantly affects the CO₂ reactivity of concrete (Shao and Shi, 2006; Shi et al., 2012a). The presence of pore water in concrete blocks the path of CO₂, thereby hindering the process of carbonation. Therefore, it becomes necessary to expose the specimens to drying conditions so that easy passage to CO₂ can be provided. However, excessive drying can cause removal of all the pore water from concrete which would also affect the necessary aqueous condition required for carbonation reaction. Preconditioning in the present study was carried out for 2 hours after de-moulding of specimens. In this, the specimens were placed in an environmental chamber maintained at a temperature of 26 °C and RH of 50 ± 5%. The specimens subjected to preconditioning are shown in Fig 3.12.



Fig. 3.12: Process of pre-conditioning

(b) *Carbonation:* After the initial pre curing, the specimens were placed in the enclosed vacuum chamber. After placement of specimens, the chamber lid was closed and tightened with screws. The chamber was provided with pressure gauge, safety valve and was attached to the CO₂ cylinder having industrial grade CO₂ gas with purity of 99%. The chamber was vacuumed up to 400mm of Hg before the injection of CO₂ gas. The vacuuming of chamber is necessary to allow maximum space to be occupied by CO₂ gas only (Shi et al., 2012c). The pressure of gas at the outlet of CO₂ cylinder and in the curing chamber was maintained with the help of pressure gauges. The specimens kept inside the chamber were then subjected to CO₂ gas at a pressure of 10 psi (0.68 bars or 68 kPa). The process of carbonation was carried out for durations of 6, 12 or 24 hours as per requirement. An autocut CO₂ supply was provided to the chamber to maintain a constant exposure of specimens to CO₂. After the completion of carbonation period, the chamber outlet was opened to release the residual gas and then the chamber was opened. Specimens placed in carbonation chamber are shown in Fig. 3.13.



Fig. 3.13: Specimens placed in carbonation chamber

(c) *Postconditioning*: The exothermic behaviour of carbonation reaction causes evaporation of water required for hydration. Therefore, the post carbonation phase is essential to replenish the lost water to enable further hydration of residual cement constituents after carbonation phase. In the present study, post conditioning of specimens was done with help of water spray for 3 days. Water spray was adopted instead of curing under water in order to make the whole process more efficient in terms of water conservation. Water spray was carried out by covering the specimens with gunny bags and spraying them with water twice a day. It was observed that the spraying duration of twice a day was sufficient to maintain the moisture. After the water spray, the specimens were sealed with plastic sheets till the testing age to prevent loss of moisture and allow the continuation of hydration reaction for a sufficient time. The postconditioning process is shown with the help of Fig. 3.14.



Fig. 3.14: Specimens sealed in plastic bags for post conditioning

3.6 TESTING METHODS

The test programme consisted of examining mechanical properties, permeation characteristics, long term durability studies and micro-structural analysis of the mixes. The test procedure adopted for studying each property is underlined in the following sections:

3.6.1 Compressive Strength

Compressive strength of concrete is the maximum compressive stress that concrete can sustain without failure. Specimens after being subjected to respective curing

regimes were tested for compressive strength. The test was conducted on AIMIL Compression Testing Machine (CTM) as shown in Fig 3.15. Compressive strength test on mortars was conducted on cubes of size 70.6 mm as per the guidelines laid down in (IS 4031:Part6, 1988). The load was gradually applied at a loading rate of 35 N/mm²/min and average result of triplicate specimens was considered.



Fig. 3.15: Compressive strength test of concrete

Compressive strength test of concrete was conducted on cubical specimens of size 150mm as per the procedure given in IS 516:2004 (IS 516, 2004). The test was carried out just after carbonation and at the testing ages of 3, 7, 28, 90 and 365 days of casting. The specimens were placed between the loading plates perpendicular to the casting face and the load was applied gradually at a rate of 140kg/cm²/min. The compressive strength was calculated as per Eq. 3.1. Average compressive strength of three specimens was considered as the compressive of the mix. Surface water and grit was wiped prior to all compressive strength tests.

$$f_c = \frac{P}{A} \dots (3.1)$$

f_c = Compressive strength (MPa or N/mm²),

P = Maximum load (N),

A = Cross section area of cube (mm²)

3.6.2 Split Tensile Strength

Split tensile strength test was conducted as per IS 5816:1999 (IS 5816, 1999) on concrete cylindrical specimens of diameter 150mm and length 300 mm. For conducting the test at any desired age, the specimens under water curing were taken out of the curing tank and were dried in the laboratory environment for two hours. The specimens under carbonation curing were taken out of the sealed plastic bags. The specimens were placed horizontally between plates of compression testing machine and a progressive compressive line load at a loading rate of 1.2 N/ (mm²/min) to 2.4 N/ (mm²/min) was applied between the opposite generators of the test specimen continuously till it breaks. The typical test set up for split tensile strength test is shown in Fig. 3.16. The maximum load (P) sustained by specimens during the test was noted and the split tensile strength was calculated as per Eq. 3.2.

$$f_{ct} = \frac{2P}{\pi dl} \dots (3.2)$$

where, f_{ct} = Split tensile strength (MPa or N/mm²),

P = maximum load in N

d = diameter of cylinder in mm

l = length of cylinder in mm



Fig 3.16: Test setup for Split Tensile Strength

3.6.3 Water Absorption and Permeable Porosity

The tests for water absorption and permeable porosity were carried out as per the procedure given in ASTM C642:2008 (ASTM C642-13, 2008a). The test on mortar specimens was carried out on cubes of size 70.6mm. For concrete specimens, the test was carried out on cubes of size 100mm. At the testing age, the specimens were first subjected to oven drying at 100 to 110 °C for a period of 24 hours and mass of oven dried specimens was measured (A). The specimen was then immersed in water at a temperature of 21 °C for a period of 48 hours and then the weight was measured after surface drying the specimen (B). The value of water absorption was then calculated as per Eq. 3.3.

To calculate permeable porosity, the specimen was placed in a container covered with tap water and allowed to boil for 5 hours. The specimen is allowed to cool down to a temperature of 20 to 25°C. The mass was measured again after surface drying the sample (C). After immersion and boiling, the specimen was suspended in water and apparent weight was measured (D). As described in ASTM C642:2008, permeable porosity was calculated as per Eq. 3.4:

$$\text{Water absorption (\%)} = \frac{B-A}{A} \times 100 \dots (3.3)$$

$$\text{Permeable Porosity (\%)} = \frac{C-A}{C-D} \times 100 \dots (3.4)$$

where,

A = mass of oven dried sample in air (g)

B = mass of surface dried sample in air after immersion (g)

C = mass of surface dried sample in air after immersion and boiling (g)

D = apparent mass of sample in water after immersion and boiling (g)

3.6.4 Sorptivity

Capillary pores provide primary route of transport to water and other agents in concrete (McCarter, 1993). Therefore, test for sorptivity is important in context of capillary porosity. Test for sorptivity was carried out as per ASTM C1585:2004 (ASTM C1585-13, 2004) on cylindrical concrete specimens of diameter 100 mm and length 50mm.

For conducting the test at a desired age, the specimens were taken out of the respective curing regimes and were put in an oven maintained at a temperature of 50 ± 2 °C for a period of three days and then kept in a sealable container for 15 days. Cylindrical specimens were covered on all sides with epoxy and bottom surface was left exposed. The initial weight of the specimen was measured with an accuracy of 1mg. The bottom surface was then exposed to water as shown in Fig. 3.17. Mass gain by the specimens at 1, 5, 10, 15, 20, 30, 60, 120, 180, 240, 300, 360 minutes and 1, 2, 3, 5, 6, 7 and 8 days of immersion was measured. The value of absorption was calculated as per the Eq. 3.5 and was designated as 'I'.

$$I = \frac{m_t}{a \times d} \dots (3.5)$$

where, I = adsorption (mm)

m_t = change in mass of specimen in grams at time t

a = exposed area of specimen in mm^2

d = density of water in g/mm^3



Fig 3.17: Testing for Sorptivity

The rate of water absorption was then plotted against the square root of time, taken in seconds. The obtained curve is generally divided into two parts; the data upto 6 hours of absorption is taken as primary curve and the data after 6 hours till the end of test represents secondary curve. The value of initial and secondary absorption was given by the slope of the best-fit lines for initial and secondary curves, respectively. The slope of the best fit regression line of primary curve was taken as sorptivity value of

the specimen. While the constant of the best fit line equation gives the sorptivity coefficient. The code further states that the water absorption rate cannot be determined from the data points, if the correlation coefficient (R^2) is less than 0.98 (linear relationship is not followed by the curve). In the present study, the sorptivity coefficient of all mixes was calculated by using the data of absorption till 6 hours of testing.

3.6.5 Abrasion Resistance

The test for abrasion resistance was carried out at the age of 3 days, 7 days and 28 days of casting. The test was conducted as per the guidelines of IS 1237: 2012 (IS 1237, 2012) on concrete specimens of size 35mm x 70mm x 70mm. The set up used for conducting abrasion test is shown in Fig.3.18. For conducting abrasion resistance test, the specimens at the desired testing age were taken out of the respective curing regime and were oven dried at a temperature of $110\pm 5^\circ\text{C}$ for 2 hours. The initial weight of specimen was then recorded on a digital balance, having least count of 0.01 gram. The initial thickness of oven dried specimen was measured at five locations with the help of vernier caliper having least count of 0.02 mm. The test specimen was then fixed in the holding device of the abrasion testing machine and a load of 300 N was applied at the centre. Thereafter, the grinding of specimen was done at a speed of 22 revolutions per minute. The grinding path of the disc of the abrasion testing machine was evenly distributed with 20 gram of abrasive powder. Weight of the specimen was measured after each 22 revolutions and then the specimen was turned about the vertical axis through an angle of 90° in clockwise direction until the end of test (220 revolutions). The extent of abrasion of each specimen was determined from the difference in values of thickness measured before and after the abrasion test, by using the formula given in Eq. 3.6.

$$T = \frac{(w_1 - w_2)t}{w_1} \dots (3.6)$$

where, T = Average loss in thickness (mm)

w_1 = Initial mass of specimen (g)

w_2 = Final mass of abraded specimen (g)

t = Initial average thickness of the specimens (mm)

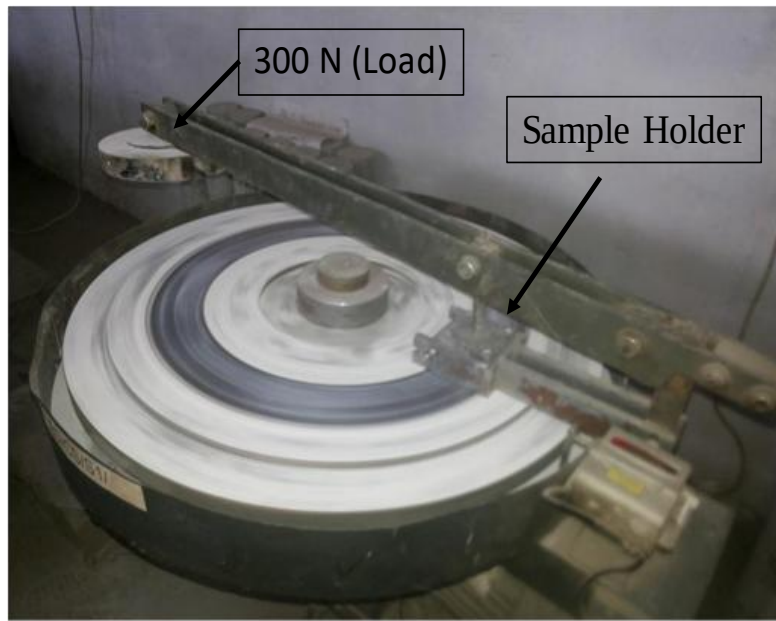


Fig. 3.18: Experimental setup for measurement of abrasion resistance of concrete

3.6.6 Rapid Chloride Permeability Test

Rapid Chloride Permeability Test (RCPT) is a method to determine resistance of concrete to chloride ions. The test was performed on cylindrical concrete specimens of diameter 100mm and length 50 mm as per the guidelines of ASTM C1202 (ASTM C1202, 2012). The preconditioning of specimens was done in a desiccator as per the guidelines of the code. For conducting the test, the specimens were placed in specially made cells (as shown in Fig 3.19) containing 3 % NaCl solution and 0.3 N Na(OH) solution. One end of the specimen was immersed in sodium chloride solution and the other end was immersed in sodium hydroxide solution. A voltage of 60 V DC was applied across ends and the charge passed was recorded for a period of 6 hours. Prooveit data processor was used in this study to measure the chloride ion permeation as shown in Fig 3.20. The average of total charge passed in coulombs through the three concrete specimens was reported as the RCPT value of that mix. The charge passed was related to the resistance of the mix to chloride ion penetration by using the rating scale provided in the code and is presented in Table 3.14. The charge passed provides a qualitative rating of chloride permeability of concrete.

Table 3.14: Chloride ion penetration based on charge passed

S.No.	Charge passed (Coulombs)	Chloride ion penetration
1	>4000	High
2	2000 – 4000	Moderate
3	1000 – 2000	Low
4	100 – 1000	Very low
5	<100	Negligible

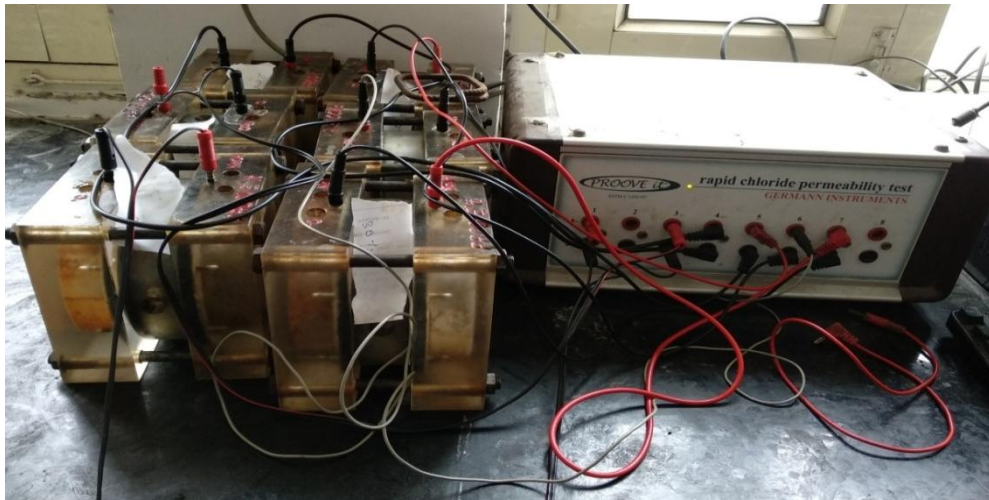


Fig. 3.19: Rapid chloride permeability test

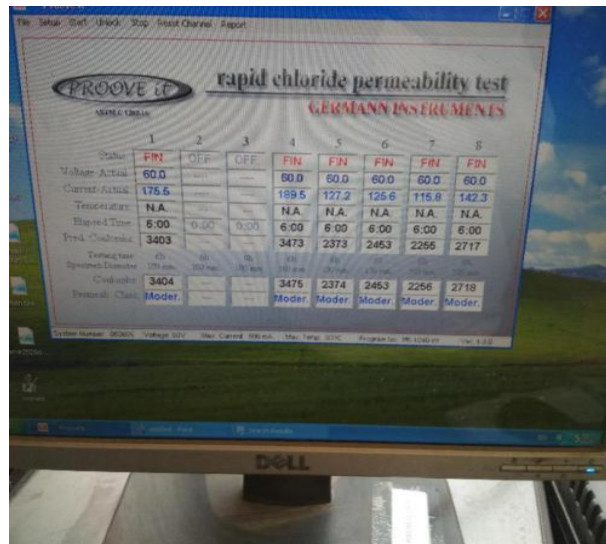


Fig. 3.20: Prooveit data processor for measuring charge passed through the concrete

3.6.7 Drying Shrinkage Test

Drying shrinkage is defined as the change in dimensions of concrete with time caused by moisture loss upon drying. The test for drying shrinkage was carried out as per ASTM C157- 2017 (ASTM C157, 2017) on prism specimens of dimensions 75mm×75mm×285 mm. The test is called unrestrained drying shrinkage test and is based on monitoring the variation in length of a specimen from the moment it is taken out of mould till its length stabilizes. The unrestrained shrinkage test set-up consists of a dial gauge and length comparator instrument, as shown in Fig. 3.21. The least count of the dial gauge was 0.01 mm.

For conducting the test, the specimens were taken out of the respective curing regimes and an initial reading was taken with the test set-up. The specimens were then air stored for 270 days in the laboratory environment with relative humidity between 60–80 %, keeping minimum clearance of 25 mm between the specimens. The length comparator readings were taken at several intervals during the drying period, which were used to calculate drying shrinkage strain as per ASTM C157-2017 (ASTM C157, 2017). The drying shrinkage strain was then calculated as per Eq. 3.7. During the first month of drying, the shrinkage strain was measured at 4, 7, 10, 14, 21 and 28 days of drying. In the subsequent months, as shrinkage slowed down, drying shrinkage readings were taken at 15 days interval and the specimens were monitored till the drying period of 9 months.

$$L_x = \frac{CRD - \text{Initial CRD}}{G} \quad \dots(3.7)$$

where,

L_x = length change in specimen at any age (%)

CRD = comparator reading of the specimen

Initial CRD = Comparator reading taken just after de-moulding of specimens

G = Gage length (250mm)



Fig 3.21: Testing setup for drying shrinkage

3.6.8 Microstructural and Mineralogical Analysis

The analysis of the mixes at micro structural level was done in order to understand the changes occurring at the micro scale in the mineralogical composition of the mixes. The microstructure of concrete/mortar was studied by obtaining the powder specimens, taken either from the surface or from the core of the specimens. The hydration reaction in collected powder was stopped by solvent exchange method using ethanol and subsequent drying. Microstructure analysis of the mix was done by adoption various techniques: X-Ray Diffraction (XRD), Thermo-gravimetric analysis/Differential Thermogravimetry (TGA/DTG), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS). The details of the tests performed are underlined in the following sections:

3.6.8.1 X- Ray diffraction (XRD)

XRD analysis was done to analyze different phase changes occurring during accelerated carbonation curing process. XRD was performed with Cu-K α radiation ($\lambda=1.54 \text{ \AA}$) over a 2θ range of $10-70^\circ$ in steps of 0.02° . The test was performed on Panalytical XRD analyzer PW 1140/09 as shown in Fig. 3.22. The X- ray diffraction (XRD) technique is to identify the crystalline phases present in concrete, which includes calcium hydroxide, calcium-silicate-hydrate, ettringite etc. Along with this, the presence of aggregates results in the peaks corresponding to the minerals present

in that aggregate. The various crystalline phases of any mineral have a unique diffraction image. XRD analysis was done with the help of XpertHighscore Plus and ICDD reference database as shown in Fig. 3.23.



Fig. 3.22: Experimental set up for X-Ray diffraction (XRD) instrument

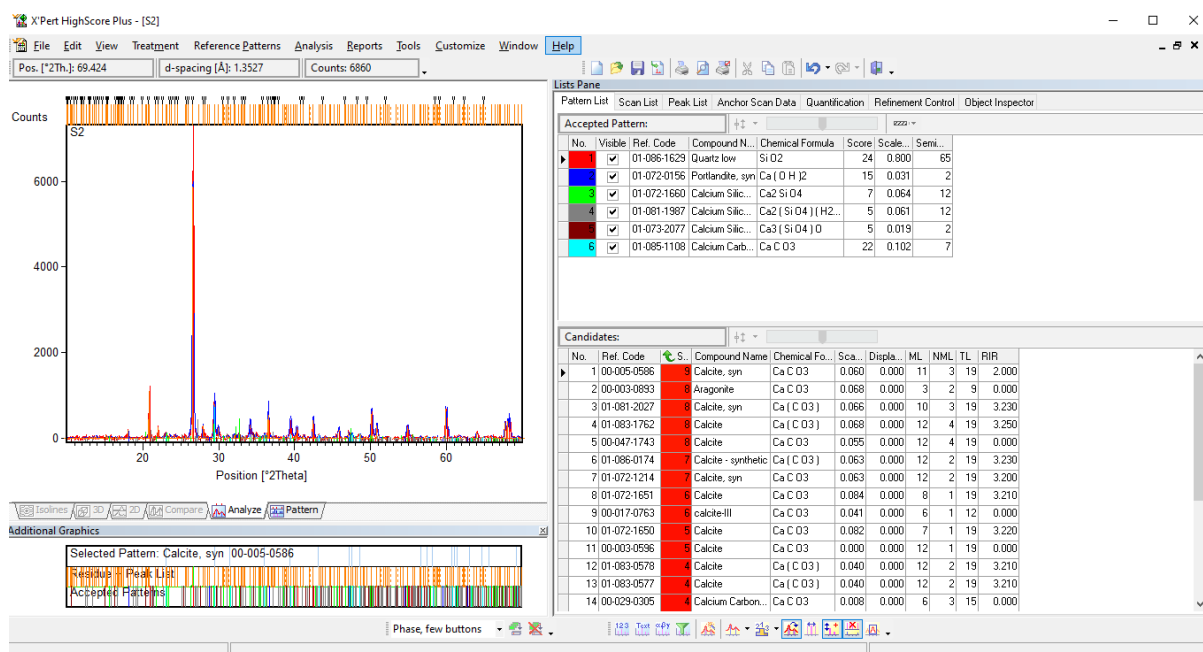


Fig. 3.23: XRD analysis using XpertHighscore Plus and ICDD reference database

3.6.8.2 Thermogravimetric Analysis (TGA)

TGA/DTG was performed to quantify the amount of Ca(OH)_2 and CaCO_3 , C-S-H present in different specimens. TGA was done with a NETZSCH STA 449F3 analyzer over a temperature range of 100–800°C. Powder specimens were procured for TGA from the top layer of cubical specimens. Specimens were placed on the heating tray in a Nitrogen environment and the temperature was raised gradually at a heating rate of 10°C/minute. The corresponding weight loss with change in temperature was recorded. For TGA, the percentage loss in mass is plotted against increase in temperature. CO_2 uptake of concrete was also measured with the help of TGA.

3.6.8.3 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM gives the information regarding the topographic and compositional behaviour of the material; while, EDS identifies the different phases present in the chemical composition. For performing the test, fractured small pieces of specimens were obtained from the sample crushed under compression testing machine during compression test. The morphology of concrete mixes was studied using SEM images that were captured by a JSM-6510LV microscope at 20 kV as shown in Fig. 3.24. EDS was performed to identify the elemental composition of microstructural crystals. Specimens were gold coated prior to SEM using ion sputter technique.



Fig. 3.24: Experimental set up for SEM and EDS spectroscopy

The SEM images were further analyzed for surface porosity using 2D image analysis with the help of ImageJ software as per the procedure previously described by various researchers (Plessis et al., 2014; Stutzman et al., 2016). A typical example of 2-D image analysis using ImageJ is shown in Fig 3.25.

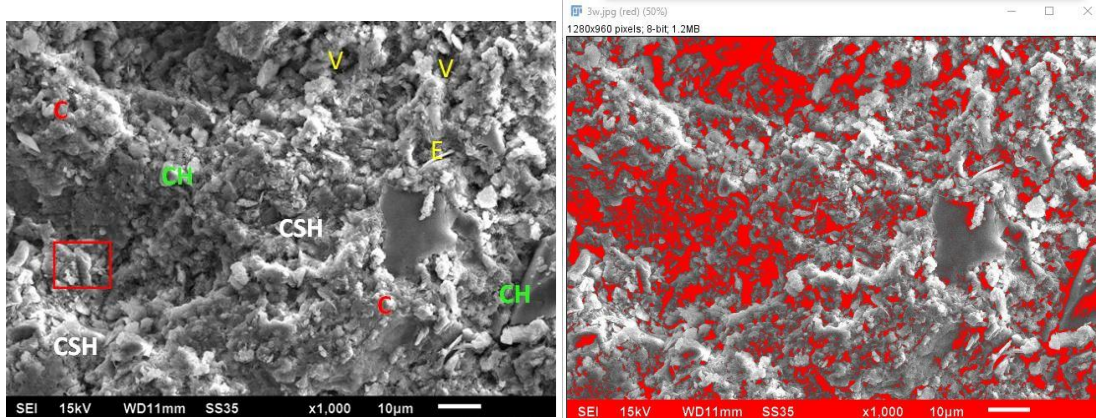


Fig 3.25: 2-D image analysis of SEM images using ImageJ

3.6.9 Carbonation Depth Measurement

Carbonation depth test is conducted to measure the resistance of concrete to carbon dioxide penetration. The test was carried out on cubical specimens of size 100mm. After 28 days of casting, the specimens were taken out of their respective curing regimes and were kept in the laboratory environment for 7 days, with relative humidity between 60 – 80%. The specimens were then sealed from five faces with epoxy and one face was left exposed. It was done to ensure unidirectional flow of carbon dioxide gas during exposure.

The samples were placed in the environmental chamber which was capable of maintaining temperature, relative humidity and CO₂ concentration in the range of 20-50°C, 30-70% and 0-10% by volume respectively. Carbon dioxide was supplied to the chamber by connecting CO₂ gas cylinder externally through the gas supply pipes. The gas pressure was monitored with the help of a pressure gauge mounted on the top of the gas cylinder. An industrial grade gas cylinder was used in the present study. Inside the chamber, the specimens were subjected to carbonation exposure at CO₂ concentration of 5± 0.5 %, 60-70% relative humidity and 30± 2°C temperature.

The typical set up for the carbonation exposure to the specimens is shown in Fig. 3.26.

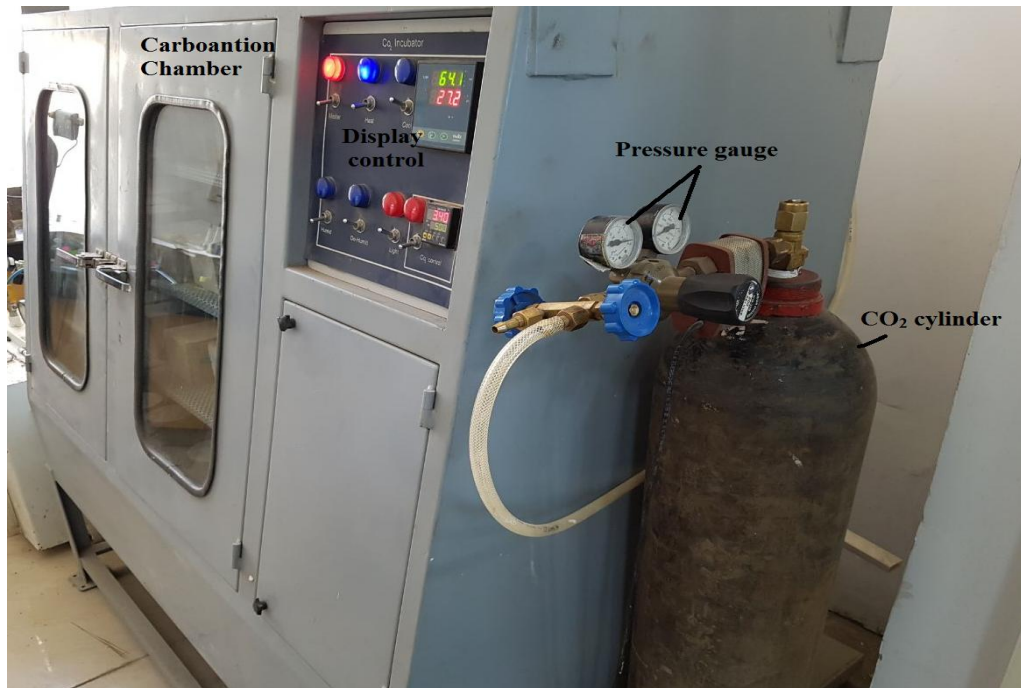


Fig. 3.26: Environment chamber for subjecting the specimens to carbonation exposure

The specimens were tested for carbonation depth at 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 360 days of CO₂ exposure. For measuring carbonation depth at a specific age, the specimens were taken out of the environment chamber and were split centrally into two halves so that the exposed surface is split. The test set up for splitting the specimens is shown in Fig. 3.27. Immediately after splitting, the exposed surface was cleaned and 1% phenolphthalein solution was sprayed on the freshly exposed surface. A typical split specimen after spraying the phenolphthalein indicator is shown in Fig. 3.28. The surface had two regions: colored part and the uncolored part. The uncolored part represented the carbonated area and colored part represented non carbonated area. The average depth of uncoloured part is taken as the representative depth of carbonation for the specimen. On each split surface, the depth of carbonation was measured at five locations (as marked in Fig. 3.28) by using a vernier calliper with the least count of 0.1 mm. Therefore, for each sample, 10 readings were taken and the average of these readings was taken as the carbonation

depth of the specimen. Further, the test was conducted on triplicate specimens and average result of three was considered as the representative value for a mix under particular curing regime.



Fig. 3.27: Test setup for splitting the cube specimens



Fig. 3.28: Measurement of uncoloured part after Phenolphthalein spray

3.6.10 Linear Polarization Resistance Test

To ascertain the effect of accelerated carbonation curing on rebar corrosion, reinforced concrete specimens of 100 mm diameter and 200 mm length were prepared and were subjected to respective curing regimes. After 28 days of curing, the specimens were taken out and were subjected to carbonated environment in environment chamber at 5% CO₂ concentration with RH between 50-70%. The

corrosion rate of the specimens were measured periodically after every 30 days of exposure by using linear polarization resistance (LPR) technique and Tafel Extrapolation (polarization) measurements, till the end of exposure duration of 360 days.

LPR technique is a rapid and non-intrusive technique used to determine the instantaneous corrosion rate of the rebar embedded in concrete. This technique was introduced by Stern and Geary in 1957 and has now become most widely used technique for the evaluation of corrosion rate of the embedded rebar (Alonso et al., 1996; Broomfield et al., 2002; Huang et al., 1996; Song, 2000). During LPR measurement, the rebar is perturbed from its equilibrium potential by a small potential scan (0.167mV/s) through auxiliary electrode. This perturbation can be done either potentiostatically or galvanostatically. In potentiostatic perturbation, the potential of the rebar is varied between a fixed amount (ΔE) and the current decay (ΔI) is monitored after a fixed time. While in galvanostatic perturbation, current is supplied to the rebar by a fixed amount (ΔI) and potential change (ΔE) is monitored after a fixed time (Saraswathy and Song, 2007). The polarization resistance (R_p) of the rebar is estimated by using the following Stern-Geary equations (Saraswathy and Song, 2007; Song, 2000):

$$R_p = (\Delta E / \Delta I) \quad \dots(3.8)$$

Corrosion current, I_{corr} is then calculated from the measured value of R_p and the relationship is provided in eq. (3.9)

$$I_{corr} = B / R_p \quad \dots(3.9)$$

Where, R_p refers to polarization resistance (Ωcm^2)

B refers to the Stern- Geary constant which depends upon the Tafel constant of the polarization curve and is calculated by using eq. 3.10.

$$B = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c)} \quad \dots(3.10)$$

where, β_a is the slope of the anodic curve of Tafel curve and β_c is the slope of the cathodic branch of the Tafel curve.

Further, corrosion current density (i_{corr}) from the calculated value of corrosion current (I_{corr}), is obtained by dividing value of I_{corr} the polarized surface area of the rebar as shown in eq. (3.11)

$$i_{corr} = I_{corr} / A \quad \dots(3.11)$$

The polarized surface area of the rebar is assumed to be that area which lies directly beneath the auxiliary electrode.

LPR measurements were done by using ACM field machine (Serial No. 1463). For polarization measurement, potentiostatic perturbation method was used and the working electrode was polarized to $\pm 25\text{mV}$ from the equilibrium potential at a sweep rate of 10 mV/min . Prior to that start of testing, the specimens were taken out of the environment chamber and were saturated for six hours, in order to make better electrical connectivity. The sample is then placed in soap solution for ionic movement. Then, the electric connections were made for taking LPR measurements. The test setup and specimens are shown in Fig. 3.30. In the test setup, the cylindrical specimens were covered with steel mesh acting as an auxiliary electrode and saturated colomel electrode was dipped in solution serving as reference electrode. The connections were made between the working, auxiliary and reference electrode with ACM field machine setup. The rest potential was noted and then the working electrode was polarized to $\pm 25\text{mV}$ from the equilibrium potential at a sweep rate of 10 mV/min . The typical polarization curve obtained during LPR measurement is shown in Fig. 3.29. Polarization curve consisted of two well defined region i.e. Anodic and cathodic. Tafel slops were adjusted and then the value of corrosion current density (i_{corr}) was noted from the instrument.

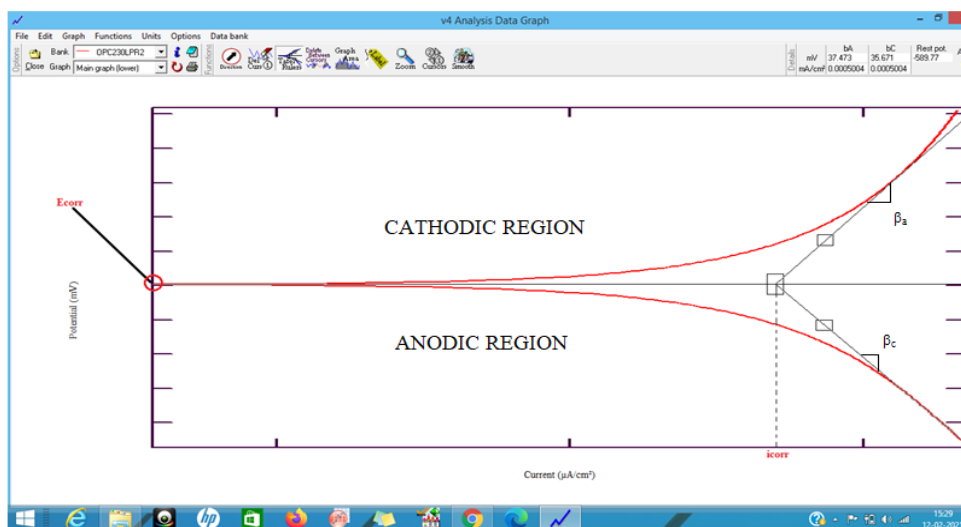


Fig. 3.29: Typical polarization curve obtained during LPR

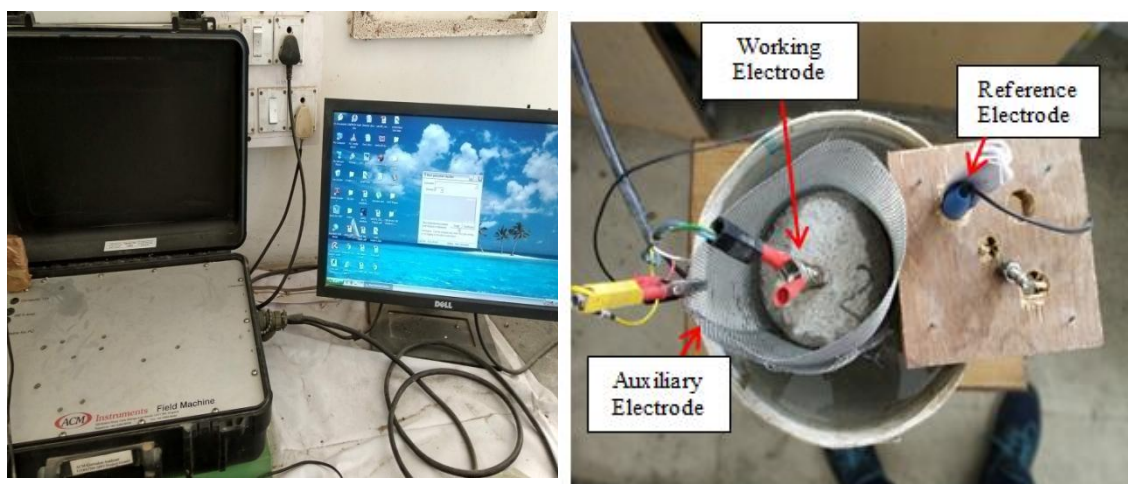


Fig. 3.30: Test setup for Potentiodynamic (LPR) test

CHAPTER 4

EFFECT OF ACCELERATED CARBONATION CURING VIS-À-VIS WATER CURING ON PROPERTIES OF CONCRETE

4.1 GENERAL

Curing of concrete is an important process that is essential for developing the required mechanical and durability properties of concrete. In the first phase of this study, the effect of accelerated carbonation curing (ACC) on various properties of concrete has been analysed and the results have been compared with water curing. The major focus of this part of the study is to assess the two curing regimes in terms of surface characteristics. Most of the previous work on ACC considered mechanical properties of the resultant mix (mainly compressive strength) as the major performance parameter. It has also been concluded in the literature that ACC has a more prominent effect on early age strength of bulk concrete.

Further, concerns have been raised regarding long term performance of carbonation cured concrete due to utilisation of Ca(OH)_2 in the basic ACC reactions. Since, long term performance is affected by ingress of aggressive ions in concrete, the characteristics of near surface concrete become more significant than mechanical properties of bulk concrete. It is also well documented that the surface layer of concrete is very distinct from the core because of the porosity gradient and movement of particles that occur during the compaction of concrete (Siddique and Kaur, 2011). The near surface layer of concrete is said to be weaker and most permeable part (Long et al., 2001). Therefore, the durability and service life of concrete should be assessed from the near-surface properties of concrete, rather than compressive strength which is an indicator of concrete core.

That is why; this study focuses on near surface concrete. For this, after 18 hours of casting and in-mould curing, the specimens were de-moulded and were separated into two sets. While one set of specimens was subjected to traditional water curing (WC) till the testing age, the other set of specimens was subjected to 6 hours of accelerated

carbonation curing (CC). For water curing, the specimens were initially kept in laboratory environment till 26 hours of casting and then immersed in a curing tank maintained at a temperature of 27 ± 2 °C as per the guidelines of IS 516:2004 (IS 516, 2004). For ACC, the specimens were initially subjected to a preconditioning of 2 hours. Preconditioning was carried out in an environmental chamber maintained at a temperature of 26 °C and RH of $50 \pm 5\%$. The preconditioning was followed by curing with CO₂ in a vacuum chamber for 6 hours, in which CO₂ gas of 99% purity was passed at a constant pressure of 0.068 MPa (10 psi) with the temperature maintained at 25 ± 2 °C. Thereafter, the specimens were subjected to water spray for 3 days till the saturated surface condition was obtained. The water spray was vital to replenish the water consumed due to exothermic carbonation reaction and hence promote further hydration (He et al., 2016b). Water spray was adopted instead of curing under water in order to make the whole process more efficient in terms of water conservation. After the water spray, all the specimens were sealed in plastic bags till the testing age.

The performance of near surface concrete of both the mixes were assessed, in which microstructure has been studied using XRD, TGA/ DTG and SEM-EDS; permeation characteristics have been studied using water absorption, sorptivity, rapid chloride permeability. Also, the mechanical performance of surface has been studied in terms of abrasion resistance. The findings are further supported by Analysis of Variance (ANOVA) and stoichiometric analysis of different curing regimes. Along with this, compressive strength of the mixes were obtained as a reference value. The test results obtained from the experimental programme are discussed in the following sections. The methodology followed in this study is depicted in Fig. 4.1.

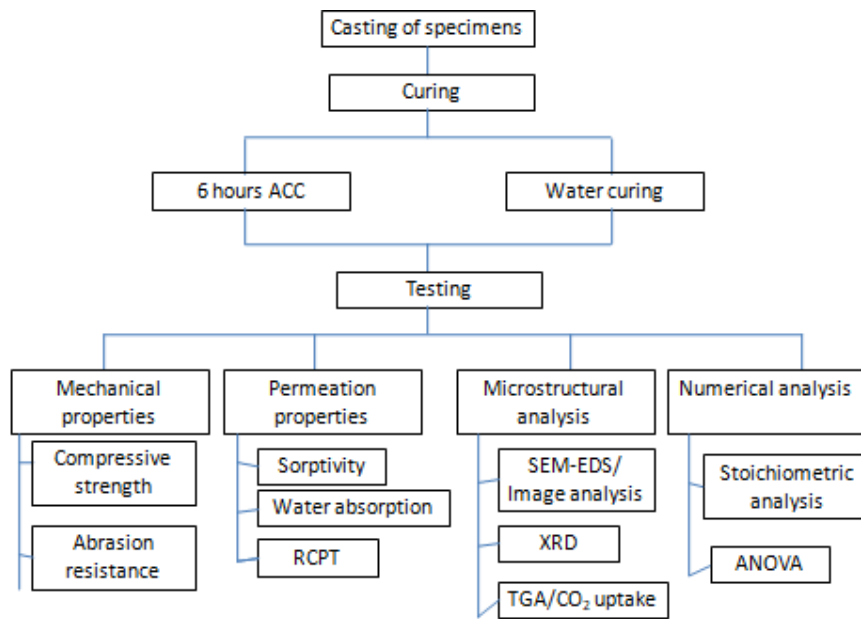


Fig. 4.1: Methodology used to study the effect of accelerated carbonation curing vis-à-vis water curing on properties of concrete

4.2 EFFECT OF ACC ON MICROSTRUCTURE OF CONCRETE

Curing of concrete is responsible for physiochemical reactions in concrete. Therefore, on varying the curing procedure, microstructure evaluation becomes necessary to understand these physiochemical changes. The microstructure of the surface layer of concrete was studied by obtaining the powder specimens from surface layer up to a depth of 5 mm. The hydration reaction in collected powder was stopped by solvent exchange method using ethanol and subsequent drying. Microstructure analysis of the mix was done by X-Ray Diffraction (XRD), Thermo-gravimetric analysis/Differential Thermogravimetry (TGA/DTG) and Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS). 2-D image analysis was also performed on SEM images using image analysis software ImageJ to get an idea about surface porosity.

4.2.1 XRD Analysis

Figs. 4.2, 4.3 and 4.4 give the XRD spectra for water cured (WC) and carbonation cured (CC) specimens at the ages of 26 hours, 3 days and 28 days of casting, respectively. The testing age of 26 hours corresponds to the end of carbonation period

in the carbonation curing regime. The various peaks and their intensity indicate relative quantities of certain compounds in the specimen. All the peaks were matched with ICDD reference database using XpertHighscore Plus.

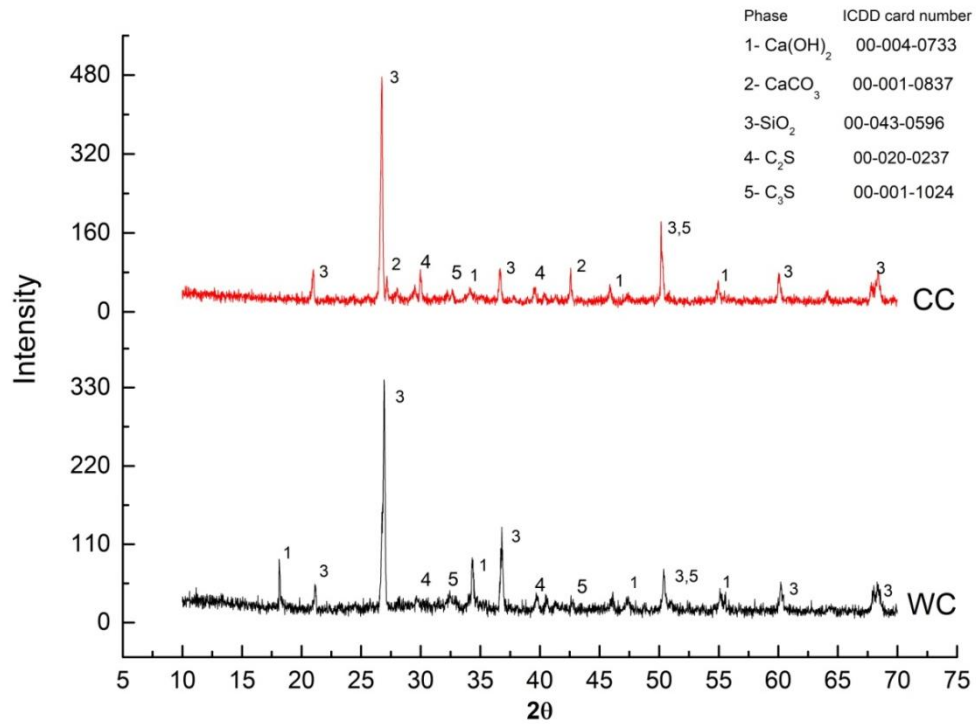


Fig. 4.2: XRD spectrum obtained for WC and CC concrete mixes at 26 hours of casting

The XRD analysis of WC concrete at the age of 26 hours of casting (Fig. 4.2) showed major peaks of silicates of calcium (C_3S and C_2S) accompanied with portlandite ($\text{Ca}(\text{OH})_2$) and quartz. At an early age of 26 hours, the CC specimens exhibited additional peaks of calcium carbonate (CaCO_3) along with the major hydration products, evidencing the incidence of carbonation reaction and CO_2 uptake. Also, the intensity of portlandite peaks and Calcium Silicate peaks was observed to be diminished in CC specimens owing to the reaction of calcium silicates with carbon dioxide and conversion of $\text{Ca}(\text{OH})_2$ into CaCO_3 during accelerated carbonation curing process.

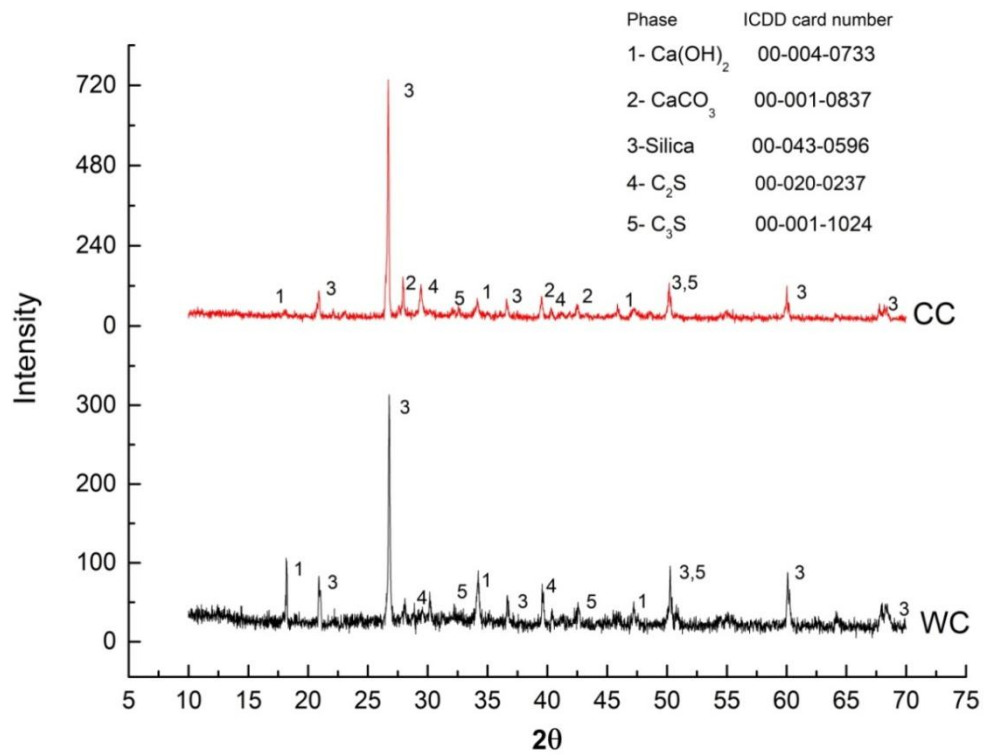


Fig. 4.3: XRD spectrum obtained for WC and CC concrete mixes at 3 days of casting

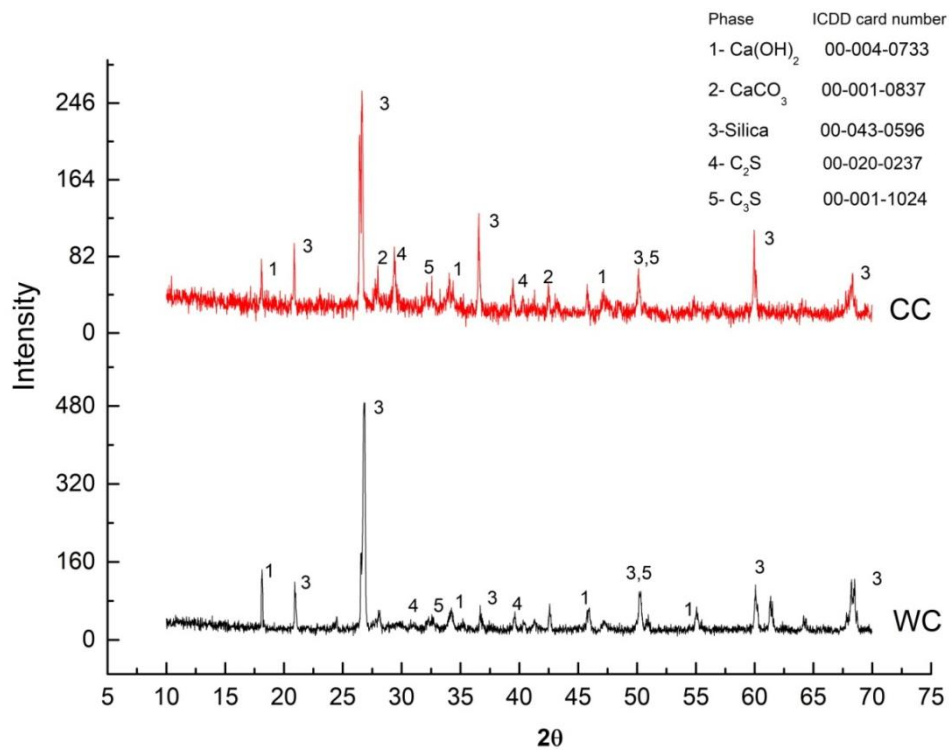


Fig. 4.4: XRD spectrum obtained for WC and CC concrete mixes at 28 days of casting

In Fig. 4.3, a coexistence of hydration (Ca(OH)_2) and carbonation products (CaCO_3) was observed in CC specimens at the testing age of 3 days of casting. On providing subsequent hydration post carbonation in CC specimens, Ca(OH)_2 peaks grew stronger with time, while the intensity of C_3S and C_2S peaks diminished; indicating the continuation of hydration reaction in till later ages. At the age of 28 days of casting, significant peaks of Ca(OH)_2 were observed from the XRD spectra of both CC and WC curing regimes as shown in Fig. 4.4, owing to the progress of hydration reaction of cement at later ages. Also, the peaks of CaCO_3 were observed to be maintained till the later ages, indicating stability of the calcium carbonate produced during the carbonation reaction.

4.2.2 Thermogravimetric Analysis (TGA)

The findings of XRD analysis were further confirmed by performing thermogravimetry on the samples at 26 hours and 28 days of casting. For TGA, the specimens were heated up to 800°C and the mass loss at regular intervals was measured. The mass loss in a specific temperature range can be correlated to a particular compound formed during curing process. Typically, the TGA plots can be divided into three temperature zones. The mass loss in 100°C - 400°C zone corresponds to the loss of water due to early dehydration of C-S-H. The mass loss in 400°C - 460°C zone is related to the dehydration of lime and gives a quantitative estimate of Ca(OH)_2 . The mass loss above 600°C corresponds to disintegration of CaCO_3 and estimates the amount of CaCO_3 present in the sample. The water loss below 100°C is related to loss of pore water. The mass curve obtained by TGA was also used for quantitative estimation of CO_2 uptake by concrete (Scrivener et al., 2016; Zhang and Shao, 2016a).

The TGA/DTG plots of WC and CC specimens at the ages of 26 hours and 28 days of casting are presented in Figs. 4.5 and 4.6 respectively. By using the data of mass loss in the respective temperature ranges, the formation of particular compound formed (i.e. Ca(OH)_2 , CaCO_3 and C-S-H) at any testing duration was obtained by using the eqs. 4.1, 4.2 and 4.3 respectively. The compounds formed under both the curing regimes at 26 hours and 28 days of casting are shown in bar graphs in Fig. 4.5 and 4.6 respectively.

$$Ca(OH)_2,measured = WL_{Ca(OH)_2} \times \frac{m_{Ca(OH)_2}}{m_{H_2O}} \dots (4.1)$$

$$CaCO_3,measured = WL_{CaCO_3} \times \frac{m_{CaCO_3}}{m_{CO_2}} \dots (4.2)$$

$$CSH,measured = WL_{CSH} \times \frac{m_{CSH}}{m_{H_2O}} \dots (4.3)$$

where,

$WL_{Ca(OH)_2}$ = Weight loss in the range of 400-460°C

m = molar mass of the compound

WL_{CaCO_3} = Weight loss in the range of 600-800°C

WL_{CSH} = Weight loss in the range of 100-400°C.

At the age of 26 hours of casting, the major variation in TGA plots of WC and CC specimens was observed in the temperature range of 600°C - 800°C. CC specimens exhibited a mass loss of 3.6% in this range in comparison to mass loss of 0.9% by WC specimens in this range. DTG curve of CC specimen also shows a strong peak in the range 600-750°C, which is associated to decarbonation of calcium carbonate. Since mass loss in this range corresponds to disintegration of $CaCO_3$ and loss of CO_2 from carbonates, the higher mass loss in CC samples clearly indicate formation of $CaCO_3$ and corresponding CO_2 uptake by the samples during ACC process. The DTG peak between 600-720°C also shows that $CaCO_3$ formed by carbonation curing is poorly crystalline (Goto et al., 1995; Rostami et al., 2012b). The mass loss in carbonate range of WC samples (although very small) is attributed to pre-treatment of specimens by ethanol, which gets liberated during TGA and results in formation of calcium carbonate (Scrivener et al., 2016; Zhang and Scherer, 2011). The mass loss in 400°C - 460°C which is associated with dehydration for calcium hydroxide is more dominant for WC specimen as evident in DTG curves. The dehydration of $Ca(OH)_2$ is less intensive in carbonation cured specimen indicating partial consumption of $Ca(OH)_2$ in the carbonation reaction. The content of C-S-H gel was quantified by the loss of bound water in temperature range of 100-400°C. CC specimens exhibited higher content of C-S-H gel at the age of 26 hours of casting, which can be attributed to the higher reaction rate of carbonation reactions.

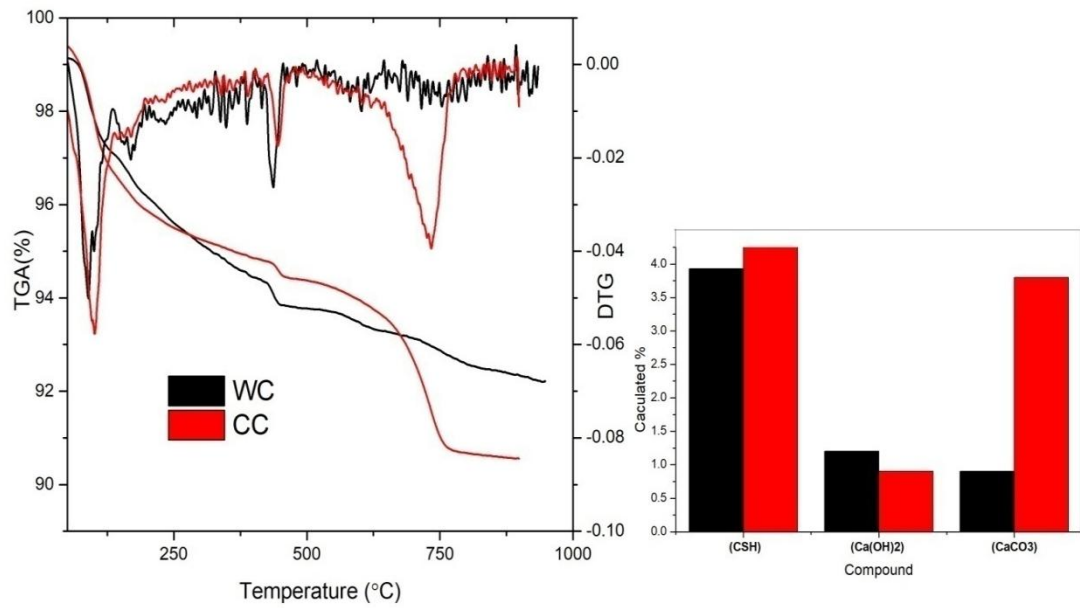


Fig. 4.5: TGA plot at the age of 26 hours of casting

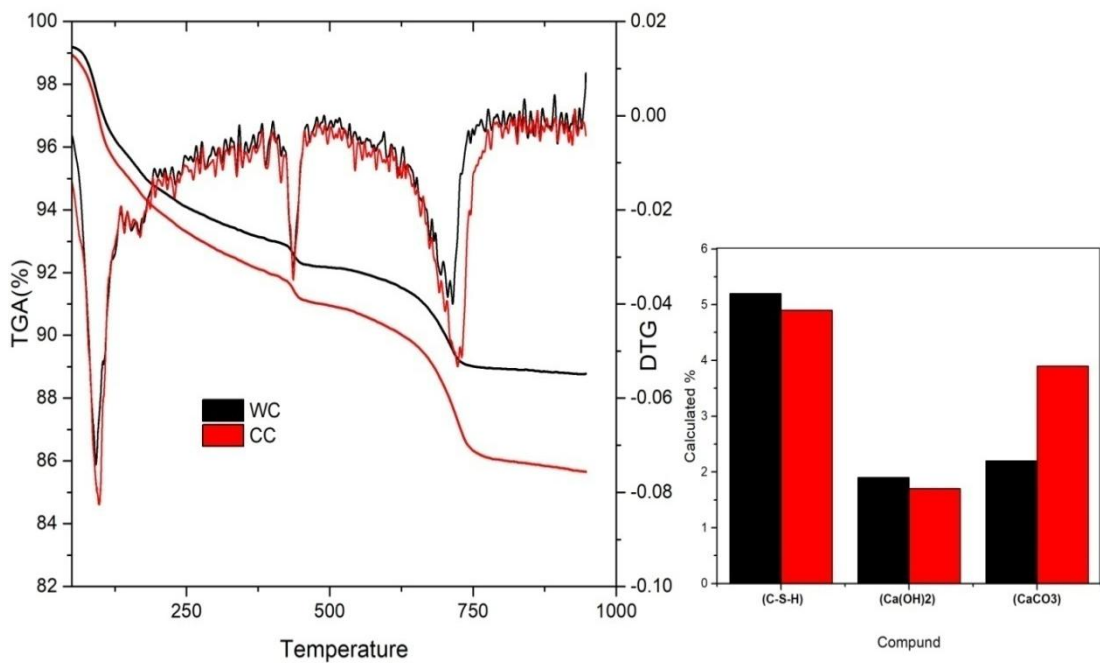


Fig. 4.6: TGA plot at the age of 28 days of casting

In Fig. 4.6, at the later age of 28 days of casting, the mass loss in 600°C - 800°C zone is still higher for CC specimens, indicating precipitation of CaCO_3 during ACC regime and its stability till later ages. The mass loss in 400°C - 460°C zone is similar for both the curing regimes indicating continuation of hydration reaction in CC

specimens post accelerated carbonation process that was facilitated by providing water spray till 3 days of casting, indicating continuous formation of C-S-H gel in both the curing regimes at the age of 3 days of casting. This is similar to what was observed in XRD spectra of CC specimens wherein CaCO_3 peaks were observed along with peaks of Ca(OH)_2 . Similar observations have been made by various researchers regarding the TGA of carbonated concrete (El-Hassan et al., 2014; Rostami et al., 2012a; Zhang and Shao, 2016a). The C-S-H content at the age of 28 days is observed to be slightly higher for the water cured specimens, owing to the hydration of concrete till the age of 28 days.

4.2.3 CO_2 Uptake

TGA plots can further be used to quantify CO_2 uptake by concrete (Scrivener et al., 2016; Zhang and Shao, 2016a). The mass loss in the third temperature zone of 600-800°C can be correlated to CO_2 uptake by using the relation given in Eq. 4.4 (Scrivener et al., 2016; Zhang and Shao, 2016a)

$$\text{CO}_2 \text{ uptake (\%)} = \frac{\text{Sample mass at } 600^\circ\text{C} - \text{sample mass at } 800^\circ\text{C}}{\text{cement mass in original sample}} \times 100 \dots (4.4)$$

TGA plot obtained at the end of 26 hours of casting (Fig. 4.5) was used to quantify CO_2 uptake during the carbonation reaction. The data from this graph was used in Eq. 4.4. to obtain the values of CO_2 uptake. The observed values of CO_2 uptake was found to be 6.7% for WC specimens, and 20.8% for CC specimens. Therefore, the higher value observed in the CC specimens clearly indicates CO_2 sequestration in the carbonation curing regime. The CO_2 uptake in WC specimens can be observed due to presence of pre-existing carbonates in the concrete mix, possibly because of aggregates (El-Hassan and Shao, 2015). So, if this pre-existing content is excluded from CC mixes, an effective CO_2 of 14.1% was utilized and stored in concrete during the ACC process. The CO_2 uptake further demonstrates the efficiency of ACC procedure for successfully sequestering CO_2 in concrete.

4.2.4 Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS)

The morphology of the concrete mixes under both the curing regimes at 26 hours and at 28 days of casting was studied through SEM images and EDS conducted on crushed concrete specimens and are presented in Figs. 4.7 and 4.8 respectively. SEM micrographs showed the presence of C-S-H gel, calcium hydroxide, ettringite in WC mixes whereas precipitation of calcium carbonate were observed in the CC mixes along with other major hydration products. A considerably densified microstructure was observed in SEM images of CC specimens at the age of 26 hours owing to the precipitation of CaCO_3 in the pores of concrete and also production of additional C-S-H gel in the process of ACC.

Formation of CaCO_3 was further confirmed by performing EDS at locations marked in Figs. 4.7 and 4.8. Major peaks of Ca, C, Si, Fe, Al were observed in EDS graphs. At the age of 26 hours, WC specimen exhibited a Si/Ca ratio of 0.70 and C/Ca ratio of 0.13; while CC specimen showed Si/Ca ratio of 0.45 and C/Ca ratio of 0.64. CC specimens showed a lower Si/Ca value and higher C/Ca value, indicating formation of a gel like amorphous phase with Si/Ca ratio less than that of C-S-H generated from hydration reactions. Similar observation regarding the variation in Si/Ca ratio and C/Ca ratio with the carbonation curing process has been reported by Qian et al. (Qian et al., 2016).

With the progress of hydration reaction at the age of 28 days, the WC specimen exhibited a Si/Ca ratio of 0.47 and C/Ca ratio of 0.16, whereas the similar values for CC specimen was 0.55 and 0.51, respectively. It indicated increase in relative proportion of C-S-H in CC specimens due to continuation of hydration process facilitated by water spray till 3 days of casting, post carbonation. It also indicated similar concrete composition in both water curing and accelerated carbonation curing procedures, with additional CaCO_3 formation in the later curing regime.

2D analysis of SEM images was done by using ImageJ software in order to estimate the pore fractions of the surface. Multiple SEM images of each type of specimen were analysed using ImageJ and average porosity measurement was considered. Fig. 4.9

shows comparative analysis of pore fractions of WC and CC specimens at the age of 26 hours using ImageJ. From the analysis, it was observed that at 26 hour testing, the porosity of CC specimen was 20.7% as compared to 24.9% for WC specimens. Hence, a more dense microstructure was observed for CC mixes, that can be attributed to the formation of CaCO_3 which precipitates in the voids and produces a micro-aggregate effect (Qian et al., 2016). Densification of the mix can be observed as the age progresses from 26 hours to 28 days, irrespective of the curing regime, with CC and WC mixes showing surface porosity values of 15.8% and 17.1% respectively.

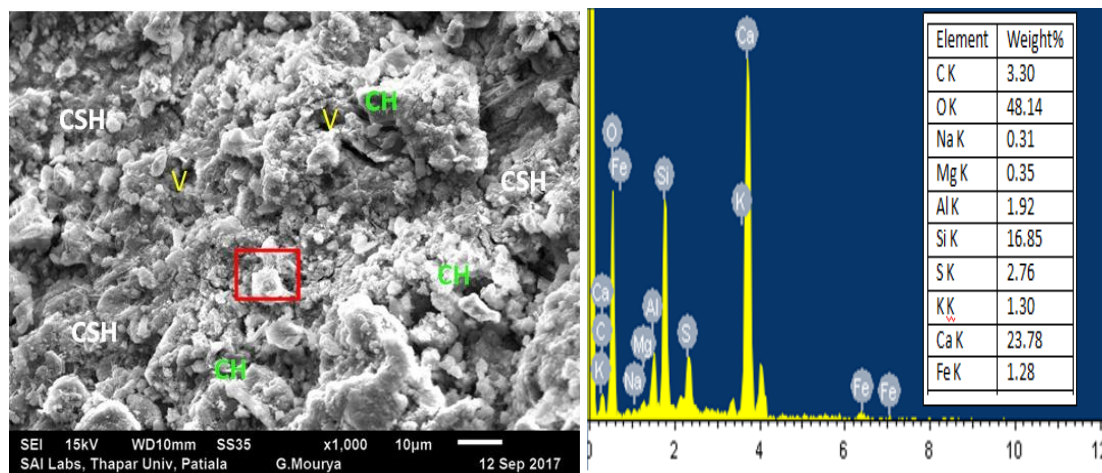


Fig.4.7(a): SEM and EDS analysis of WC specimen at the age of 26 hours(C-S-H- Calcium silicate hydrate gel, V- Voids, C- Calcium Carbonate, CH- Calcium Hydroxide, E-Ettringite)

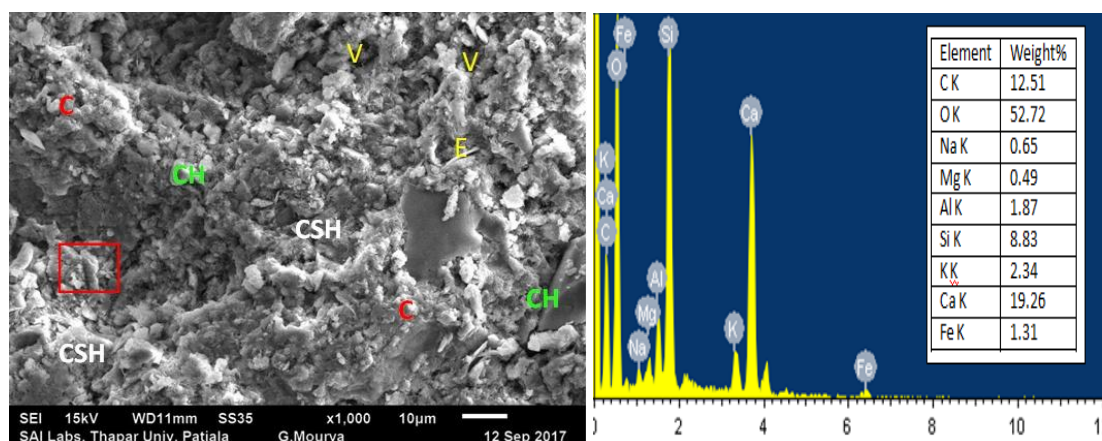


Fig. 4.7(b): SEM and EDS analysis of CC specimen at the age 26 hours

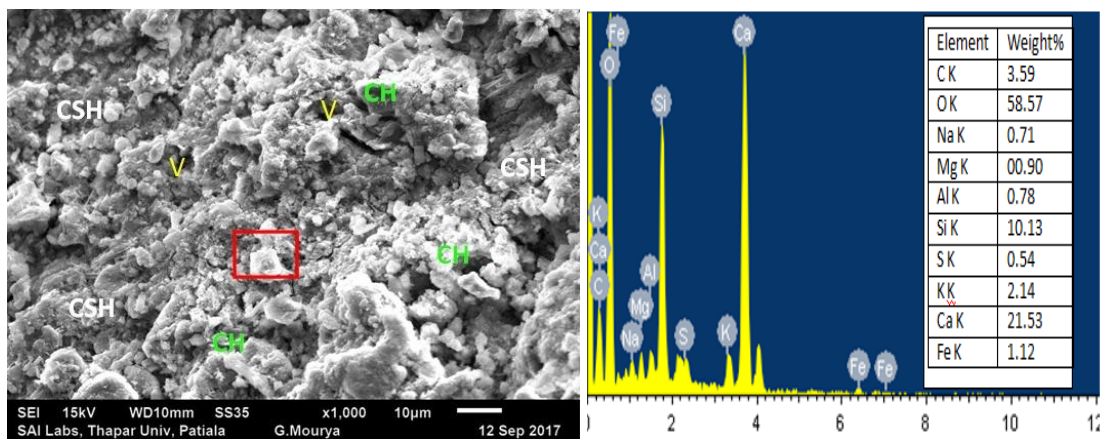


Fig. 4.8(a): SEM and EDS analysis of WC specimen at the age of 28 days

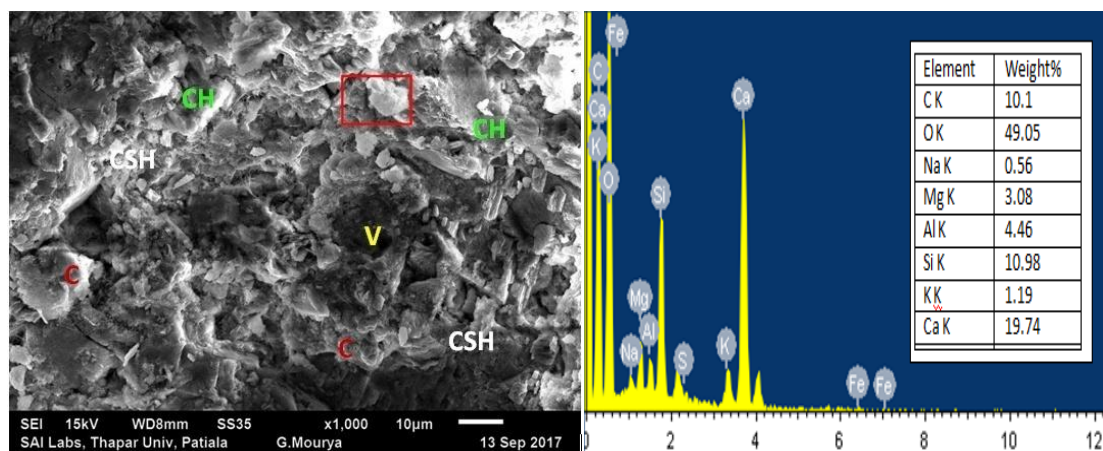
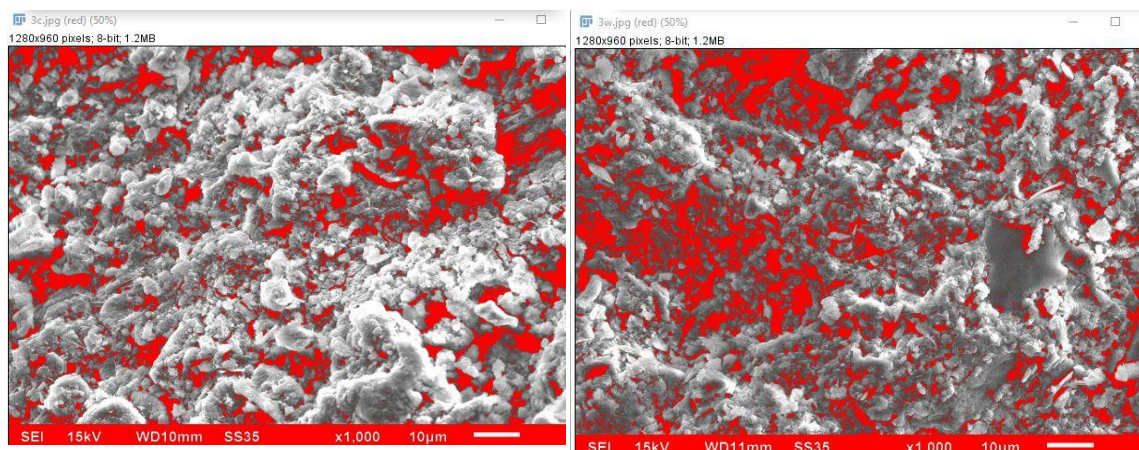


Fig. 4.8(b): SEM and EDS analysis of CC specimen at the age of 28 days



(a) WC

(b) CC

Fig. 4.9: Comparative analysis of SEM image (a) WC and (b) CC using ImageJ for specimens tested at 26 hours

4.3 EFFECT OF ACC ON MECHANICAL PROPERTIES OF CONCRETE

The mechanical performance of concrete subjected to WC and CC was studied at the age of 26 hours, 3, 7 and 28 days of casting. While the compressive strength test was conducted to study bulk concrete, abrasion test was performed to evaluate the mechanical performance of surface concrete. Compressive strength development under the two curing regimes was studied by conducting compressive strength tests as per the guidelines of IS 516:2004 (IS 516, 2004) and results are presented in Fig. 4.10. The abrasion resistance of concrete was measured as per IS 1237: 2012 (IS 1237, 2012) on specimens of size 70.6 x 70.6 x 35 mm. The test was performed on a grinding disc using an abrasive powder comprising of 95% aluminium oxide by mass. The results for abrasion test are presented in Fig. 4.11.

As can be seen in Figs. 4.10 and 4.11, the mechanical performance of concrete enhanced with accelerated carbonation curing regime. The CC specimens, which were carbonation cured for 6 hours, exhibited higher compressive strengths than WC specimen irrespective of the testing age. Similarly, the depth of wear was found to be considerably lower for CC specimens as compared to WC specimens. The lower depth of wear is indicative of better performance of concrete surface under abrasive action. The enhanced performance of CC specimens as compared to WC specimen can be attributed to higher rate of carbonation reaction and conversion of un-hydrated C_2S and C_3S into calcium carbonate and C-S-H gel. Also, the carbonation reaction during ACC causes conversion of $Ca(OH)_2$ produced by hydration reaction to thermodynamically stable $CaCO_3$. The formation of $CaCO_3$ was also confirmed by additional peaks of Calcite in the XRD spectrum and higher mass loss observed in the temperature range of 600°C -800°C which is associated with $CaCO_3$ disintegration in TGA of CC specimens.

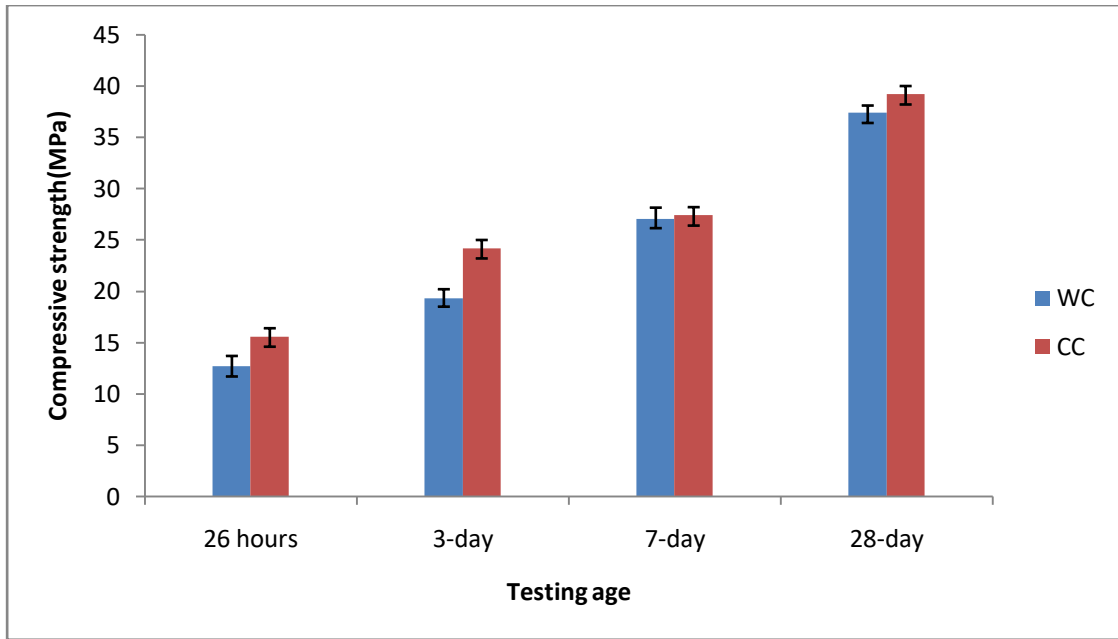


Fig.4.10: Compressive strength of WC and CC concrete

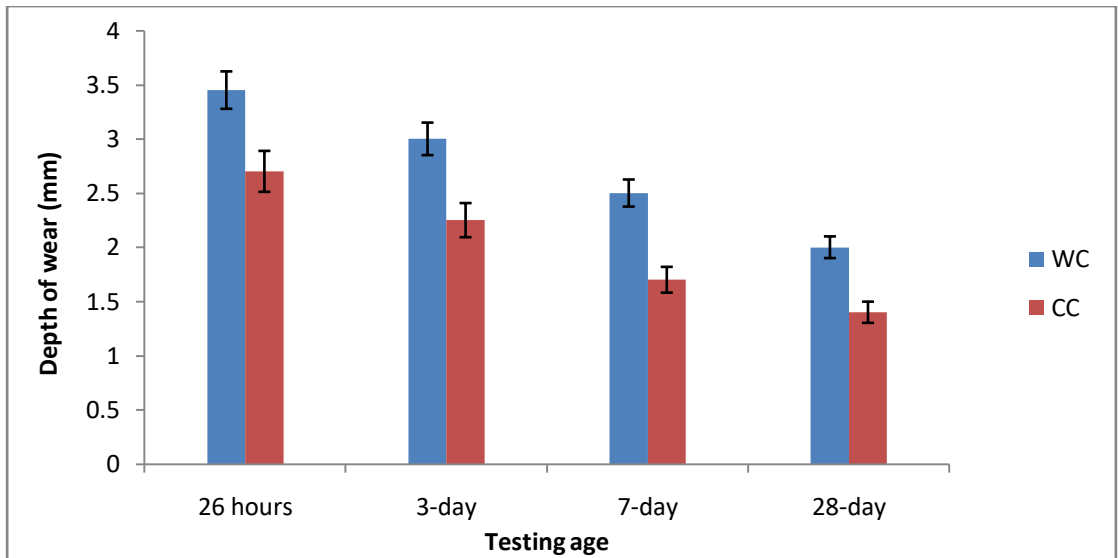


Fig.4.11: Abrasion resistance of WC and CC concrete

The mechanical performance of both WC and CC specimens goes on improving with time. A loss in compressive strength of CC specimens has been reported in some previous researches due to lack of hydration process (Rostami et al., 2011; Zhan et al., 2016). The loss of strength in CC specimens was not observed in present study, owing to the water spray provided for 3 days post carbonation. This water spray allows for

continuation of hydration reaction and corresponding gain in strength. On comparing the mechanical performance of both curing regimes with age, it was observed that the compressive strength of CC samples is about 30 % higher than WC samples at the early ages of 26 hours and 3 days of casting. However, the compressive strengths of WC and CC specimens are comparable at the age of 7 and 28 days, whereas the WC specimens exhibit a much higher depth of wear than CC specimens even at later ages. This indicates a more prominent effect of ACC on surface performance of concrete than on bulk properties.

4.4 EFFECT OF ACC ON PERMEATION PROPERTIES OF CONCRETE

The water permeation characteristics of concrete surface subjected to WC and CC regimes was evaluated with the help of sorptivity, water absorption and rapid chloride permeability tests (RCPT) at the ages of 26 hours and 28 days of casting. Measure of sorptivity gives an idea of moisture transport in concrete through capillary action and water absorption gives the amount of water absorbed by concrete surface in case of immersion. RCPT is an indirect measure to determine resistance of concrete to chloride ions. Water absorption was measured as per the guidelines of ASTM C642:2008 (ASTM C642-13, 2008b) on cubical specimens of size 100 mm and sorptivity was evaluated as per the guidelines of ASTM C1585:2004 (ASTM C1585-13, 2004) on cylindrical specimens of diameter 100 mm and length 50 mm. RCPT test was performed on cylindrical concrete specimens of diameter 100 mm and length 50 mm as per the guidelines of ASTM C1202 (ASTM C1202, 2012). The test results are discussed hereunder.

4.4.1 Water Absorption

The results of water absorption are presented in Fig. 4.12. It can be seen from the figure that the water absorption of the carbonation cured concrete was found to be lesser than the water cured at both the testing ages. This indicates enhanced impermeability of the surface layer of concrete when subjected to accelerated carbonation curing. CaCO_3 precipitated from the carbonation reactions of ACC occupies the void spaces in concrete surface and acts as a barrier to passage of water. Therefore, lower values of water absorption are observed in the carbonation cured

specimens as compared to water cured specimens. However, it was also noted that the difference in water absorption of two curing regimes was more significant at early testing ages. This can be attributed to higher rate of carbonation reaction than the hydration reaction during the earlier ages of testing. As the testing age progresses, the water cured concrete undergoes sufficient hydration reaction which is observed to be lacking in case of carbonation cured specimens.

4.4.2 Sorptivity

The test for sorptivity was carried out as per the guidelines of ASTM C1585:2004 (ASTM C1585-13, 2004) on cylindrical specimens of diameter 100mm and length 50mm. For obtaining sorptivity of the mix, the specimens were allowed to absorb water through one surface only and the mass gained due to capillary rise of water was noted. The change in mass of the specimen was recorded at 1, 5, 10, 20, 30, 60, 120, 180, 240, 300, 360 minutes and 1, 2, 3, 4, 5, 6, 7 and 8 days. The slope of absorption vs square root of time plot for the first six hours gives the value of primary sorptivity coefficient, which helps in analysing the water transport properties and characteristics of concrete pore structure (Khatib and Mangat, 1995; Pan et al., 2017).

Figs. 4.13 and 4.14 exhibit the results of sorptivity test at the age of 26 hours and 28 days of casting. Fig. 4.13 indicates that CC specimens had lower capillary absorption right from the beginning of the test. The final absorption of CC specimens at 26 hours of casting was 18.5% lower than the corresponding WC specimens. At the testing age of 28 days, both CC and WC specimens had almost the similar values of absorption throughout the testing duration. However, the WC specimens initially indicated a higher value of absorption, which can be owed to the better surface characteristics of CC concrete which are observed to persist till the later ages.

The data points of absorption vs square root of time plot till 360 minutes of testing were taken separately and a best fit line was drawn for the data points. The slope of the best fit regression line of this curve was taken as sorptivity value of the specimen. Fig. 4.15 shows the value of primary sorptivity coefficients at the age of 26 hours and 28 days of casting, as observed in Fig. 4.13 and 4.14.

It can be observed from Fig. 4.15 that the sorptivity coefficient for the carbonation cured specimens at the age of 26 hours was considerably lesser than the water cured specimens. This can be attributed to an increase in solid volume due to conversion of anhydrous C_3S , C_2S and $Ca(OH)_2$ to $CaCO_3$. It was observed by Dias that carbonation of $Ca(OH)_2$ to $CaCO_3$ brings about an 11% increase in volume (Dias, 2000). $CaCO_3$, so formed, occupies the large pores on concrete surface, producing a micro-aggregate effect and acts as a nucleation site for further hydration.

As the testing age progressed from 26 hours to 28 days, sorptivity coefficients were observed to decrease for both the curing regimes owing to further hydration of cement. The difference in sorptivity coefficients also reduced at the age of 28 days, owing to the hydration of water cured specimens which produces a denser microstructure at the later ages.

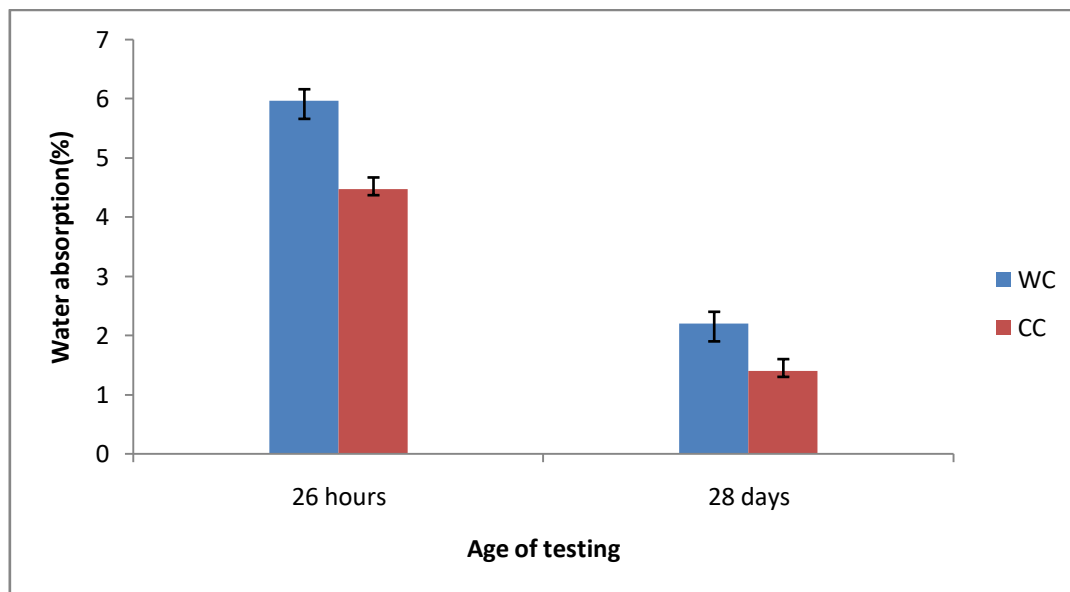


Fig.4.12: Water absorption for WC and CC concrete

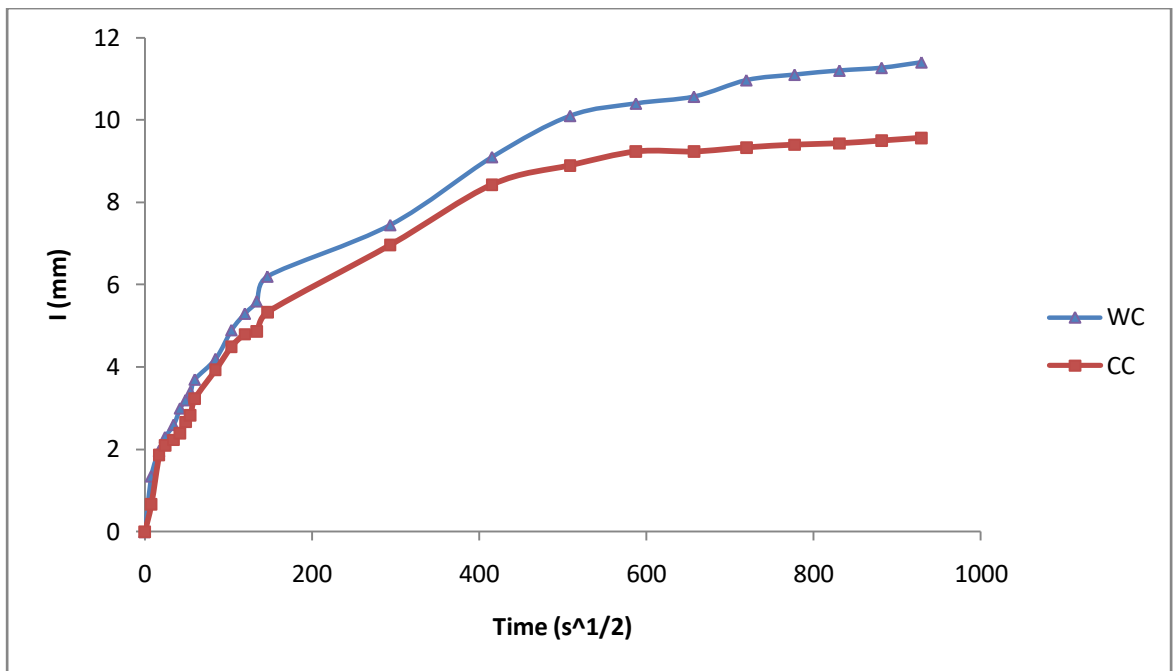


Fig. 4.13: Absorption vs square root of time graph at the age of 26 hours

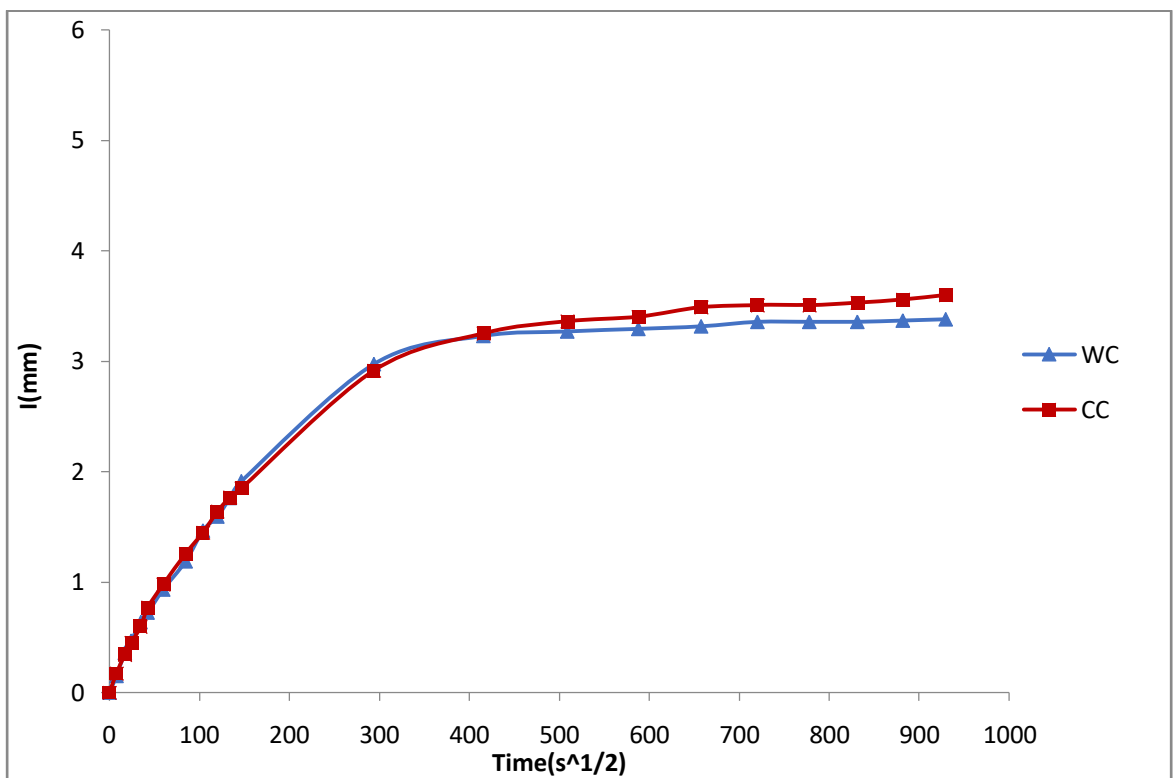


Fig. 4.14: Absorption vs square root of time graph at the age of 28 days

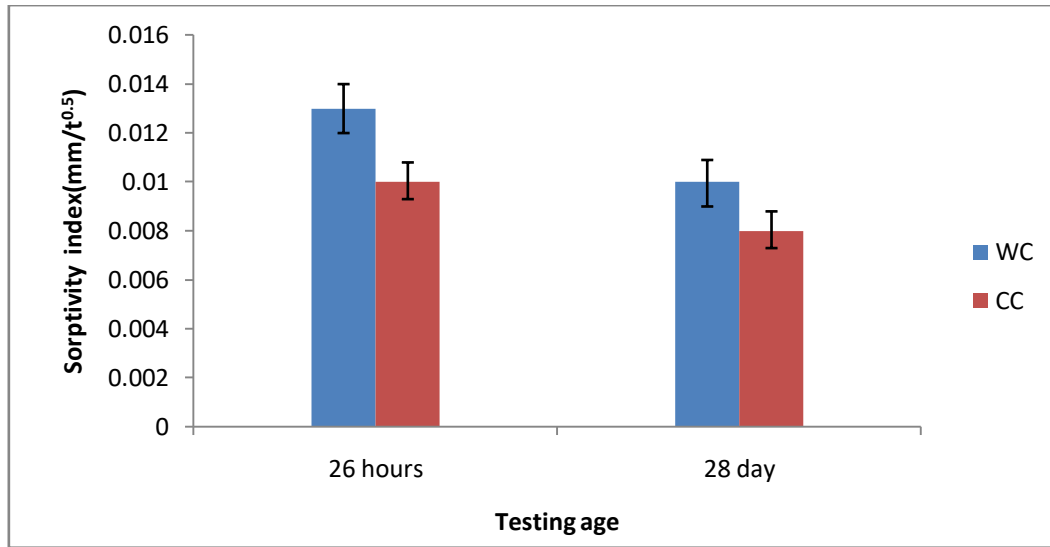


Fig. 4.15: Sorptivity coefficients for WC and CC concrete

4.4.3 Rapid Chloride Permeability Test (RCPT)

RCPT test was carried out as per the guidelines of ASTM C1202: 2012 (ASTM C1202, 2012) on cylindrical specimens of diameter 100mm and length 50mm. The results of RCPT at the age of 3 and 28 days are reported in Fig. 4.16. It can be seen clearly that carbonation cured concrete allows notably less electric charge to pass as compared to water cured specimens. The lower chloride permeability of ACC specimens can be attributed to lower hydroxyl ion concentration and higher packing density of surface due to precipitation of CaCO_3 (Rostami et al., 2012a).

Irrespective of the curing regime followed, both type of specimens showed lower electrical conductivity at the testing age of 28 days. The difference in the charge passed between two curing regimes at the age of 28 days is found to be smaller than the difference observed at early ages. The lesser difference can be understood due to higher hydroxyl ion concentration produced by subsequent hydration of concrete. However, subsequent hydration post initial carbonation curing produces additional C-S-H gel which causes reduced porosity and hence, restricts the ion movement through surface. The lesser charge passed in ACC specimens indicates poor pore connectivity as compared to water cured concrete.

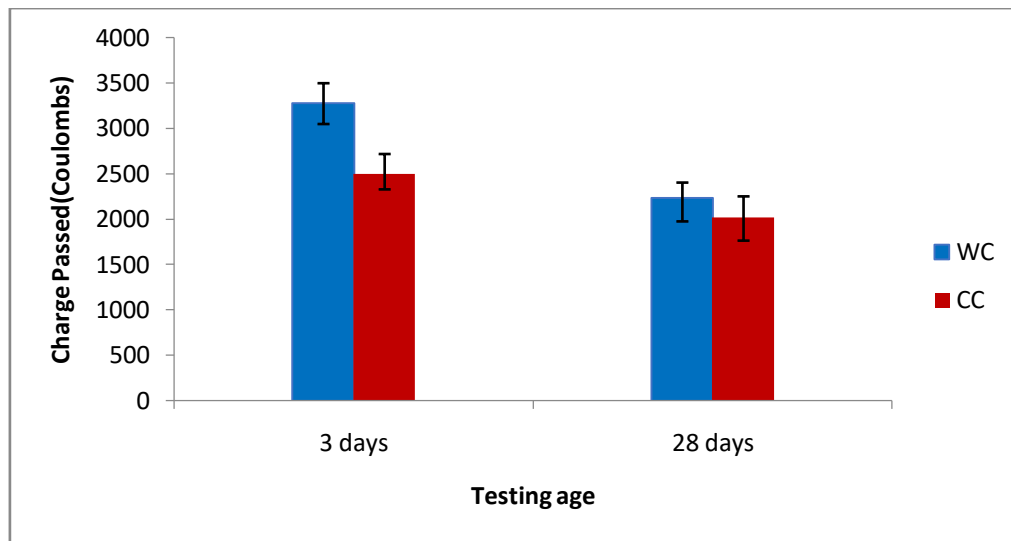


Fig. 4.16: Rapid chloride permeability test for WC and CC concrete

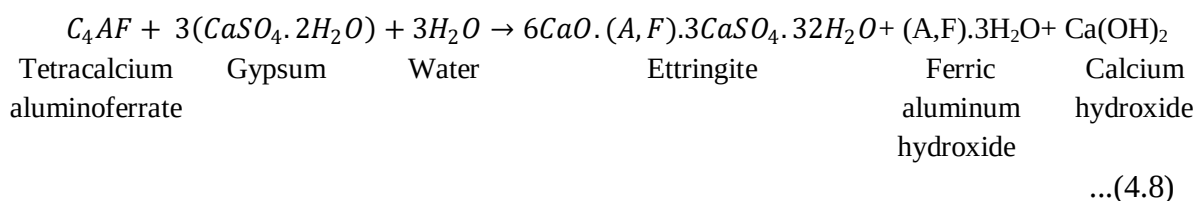
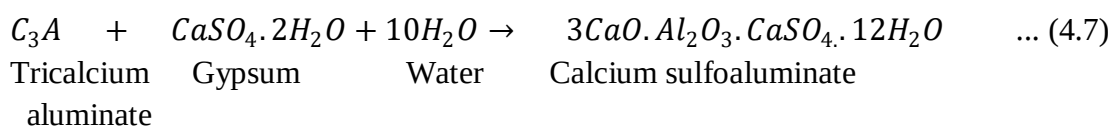
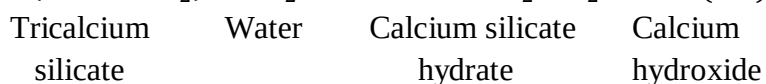
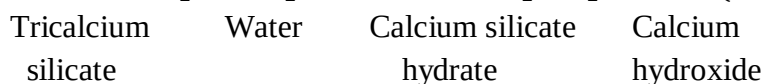
4.5 NUMERICAL ANALYSIS

The two types of curing regimes were analysed mathematically with the help of Stoichiometric Analysis and Analysis of Variance (ANOVA). The results of these analyses have been presented in the following section:

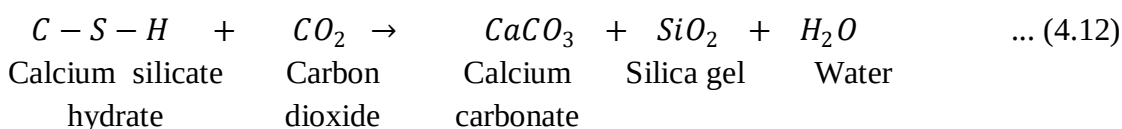
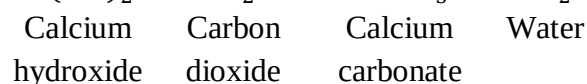
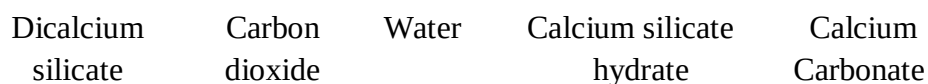
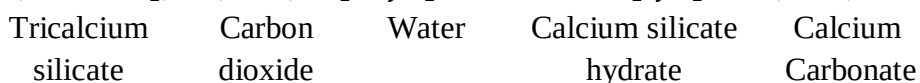
4.5.1 Stoichiometric Analysis

Stoichiometric analysis was performed for both WC and CC concrete to measure the net change in phase configurations in both curing processes. The analysis was carried on the basis of reaction mechanism of hydration and carbonation curing regimes. While water curing process involves hydration of cement, carbonation curing involves both hydration and carbonation of cement compounds. The comparison of both the curing regimes was made at the age of 3 days of casting and variations in relative composition of various compounds are reported in Fig. 4.17.

Hydration of cement begins as soon as water is added to the dry mix. The major components of cement are C_2S , C_3S , C_3A and C_4AF and their hydration mechanism is summarised in Eqs. 4.5-4.8 (Papadakis et al., 1989). Major compounds formed during hydration of C_2S , C_3S are $Ca(OH)_2$ and C-S-H gel; whereas hydration of C_3A and C_4AF results in formation of ettringite and ferric aluminium hydroxide respectively.



During the ACC process, along with the normal hydration reactions, additional carbonation reactions take place involving hydration products (namely C-S-H and Ca(OH)_2) and anhydrate C_3S and C_2S , which are summarized in Eqs. 4.9-4.12.



Stoichiometric analysis of ACC concrete was performed using hydration rate of unhydrated cement compounds given by Papdakisetal.(1989) and CO₂ uptake data obtained from TGA graphs shown in Fig. 4.5. For carrying out the stoichiometric analysis, 1 unit of cement was assumed and the relative fractions of various constituents and resultant reaction products were calculated based on chemical reactions 4.5-4.12 and the molecular weights of the respective compounds. The results obtained from stoichiometric analysis at the end of 3 days of hydration are presented in Fig. 4.17 for CC and WC specimens. It can be seen from the figure that accelerated carbonation curing leads to an increase in quantity of C-S-H gel and formation of additional compound, i.e. CaCO₃ which precipitates in the pores causing reduction in concrete porosity.

The stoichiometric analysis of WC and CC concrete confirms higher C-S-H content for CC concrete mixes and hence a higher compressive strength which was also observed in the compressive strength tests. Also, CaCO₃ production as observed in stoichiometric analysis correlated well with the findings of permeation tests and microstructure analysis, where lesser permeation was observed in the carbonation cured concrete owing to formation of a denser microstructure.

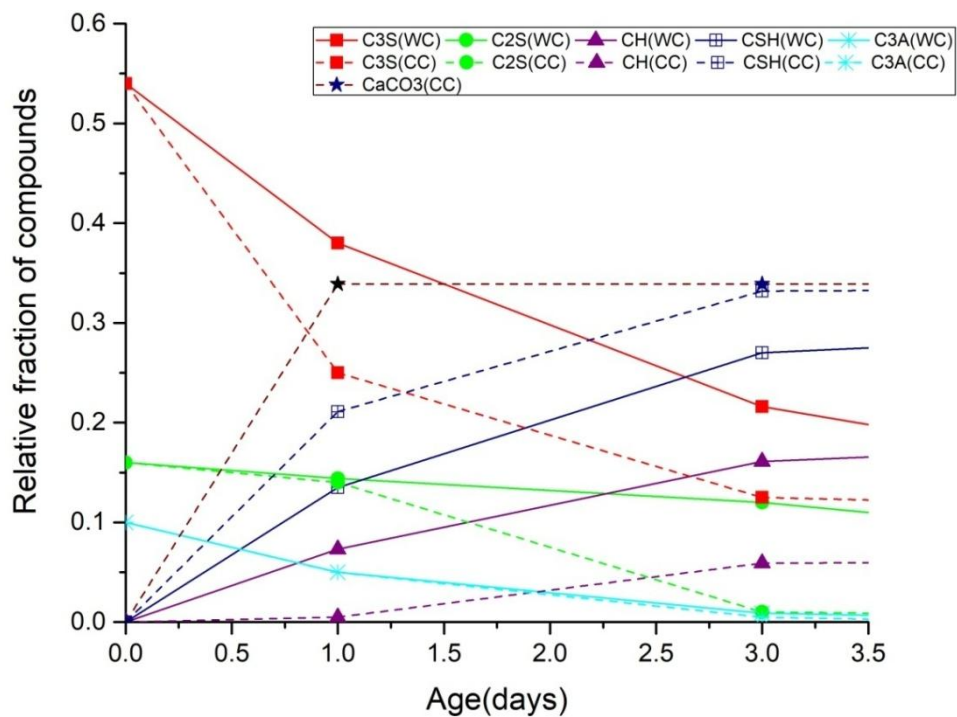


Fig. 4.17:Stoichiometric representation for WC and CC concrete

4.5.2 Analysis of Variance

The objective of ANOVA was to determine the significance of varying the curing regime on mechanical properties of concrete. Two mechanical properties were assessed in the present investigation, representing bulk strength (compressive strength) and surface characteristics of concrete (abrasion resistance). One- way analysis of variance (ANOVA) was performed using IBM SPSS statistics. Adopting a null hypothesis that means for varying curing regime are same, ANOVA was performed on both the tested mechanical properties. A level of significance of 0.05 was considered for the analysis.

Table 4.1 gives the descriptive analysis of compressive strength and abrasion resistance respectively for change in the curing regime. Since, the P-value is less than 0.05 for both compressive strength and abrasion resistance, this is enough evidence to reject the null hypothesis and it can be inferred that means vary significantly. Thus, mechanical properties of concrete change significantly on varying the type of curing. However, the p-value for abrasion resistance is lesser than the p-value for compressive strength. This further indicates ACC has a more prominent effect on surface of concrete than on the bulk properties.

Table 4.1: Analysis of variance

Parameter		Sum of Squares	df	Mean Square	F	p-value	Significance (Significant if $P < 0.05$)
ANOVA for compressive strength	Between Groups	7.042	1	7.042	7.853	0.040	Significant
	Within Groups	3.587	4	0.897			
	Total		5				
ANOVA for abrasion resistance	Between Groups	0.003	1	0.003	10.316	0.033	Significant
	Within Groups	0.001	4	0.001			
	Total	0.005	5				

4.6 CLOSING REMARKS

In this chapter, the effect of accelerated carbonation curing and water curing on the properties of resultant concrete was studied, with the special emphasis on the characteristics of the concrete surface. ACC was carried out for a period of 6 hours after initial preconditioning of 2 hours and followed by water spray for three days. The microstructural analysis of the mixes indicated considerable modification of the concrete surface by adopting carbonation curing. It was observed that calcium carbonate formed during the carbonation process gets accumulated in the concrete pores, thereby refining the pore structure and improving the permeation characteristics of concrete. Due to the pore refinement and formation of additional C-S-H gel during the carbonation curing process, an improvement in mechanical properties was also visible. Both abrasion resistance and compressive strength showed considerable improvement till the age of 3 days as compared to water curing regime. However, benefit of ACC on later ages was more pronounced on the surface strength, with substantial improvement in abrasion resistance of concrete at 28-days as compared to compressive strength. ANOVA data further indicates that ACC has a more prominent effect on surface of concrete than on the bulk properties.

ACC samples also registered an effective CO₂ uptake of 14.1% when compared with the water cured specimens, which exhibits the ability of ACC process to successfully sequester CO₂ inside concrete in the form of stable products like calcium carbonate and C-S-H.

CHAPTER 5

EFFECT OF ACCELERATED CARBONATION CURING DURATION ON PROPERTIES OF CONCRETE

5.1 GENERAL

From the first phase of the study on the performance of accelerated carbonation curing and water curing regime, it has already been established that ACC has the potential to enhance the mechanical and permeation characteristics of concrete. However, it has been observed in the literature that researchers have used varying parameters of carbonation. In this chapter, the effect of ACC duration on performance of concrete has been discussed in terms of mechanical, permeation, microstructural and shrinkage properties. The long-term performance of concrete exposed to adverse weathering environment has also been investigated in terms of carbonation depth and linear polarization resistance.

For this part of the study, the specimens were demoulded after 18 hours of casting and were then divided into four sets. One set of specimens was subjected to continuous water curing at $27^{\circ}\text{C} \pm 2^{\circ}$ temperature and 100% RH till the testing age. Other three sets were subjected to accelerated carbonation curing for variable durations. The accelerated carbonation curing duration was kept at 6 hours, 12 hours and 24 hours. Prior to carbonation curing, the specimens were subjected to a preconditioning of 2 hours in an environmental chamber maintained at a temperature of 26°C and RH of $50 \pm 5\%$. After the carbonation curing process, the specimens were further subjected to water spray up to three days to replenish some water lost during the carbonation process and to continue the hydration reaction. Thereafter, the specimens were sealed in plastic bags till the testing age. The details of the curing procedure and the mix designations are shown in Table 5.1. The test matrix adopted for this part of study is summarized in Fig. 5.1. The test results are discussed in the following sections.

Table 5.1: Detail of curing regimes adopted in this study

Curing Scheme	Mix Designation	Details of curing scheme		
		Pre Conditioning	Curing	Post Conditioning
Water curing	WC	-	Water curing at 27±2°C temperature and 100% RH	-
Carbonation curing (CC)	C6	Initial pre conditioning for 2 hours	Carbonation curing for 6 hours	Water spray for 3 days and then sealed in plastic bag
	C12		Carbonation curing for 12 hours	
	C24		Carbonation curing for 24 hours	

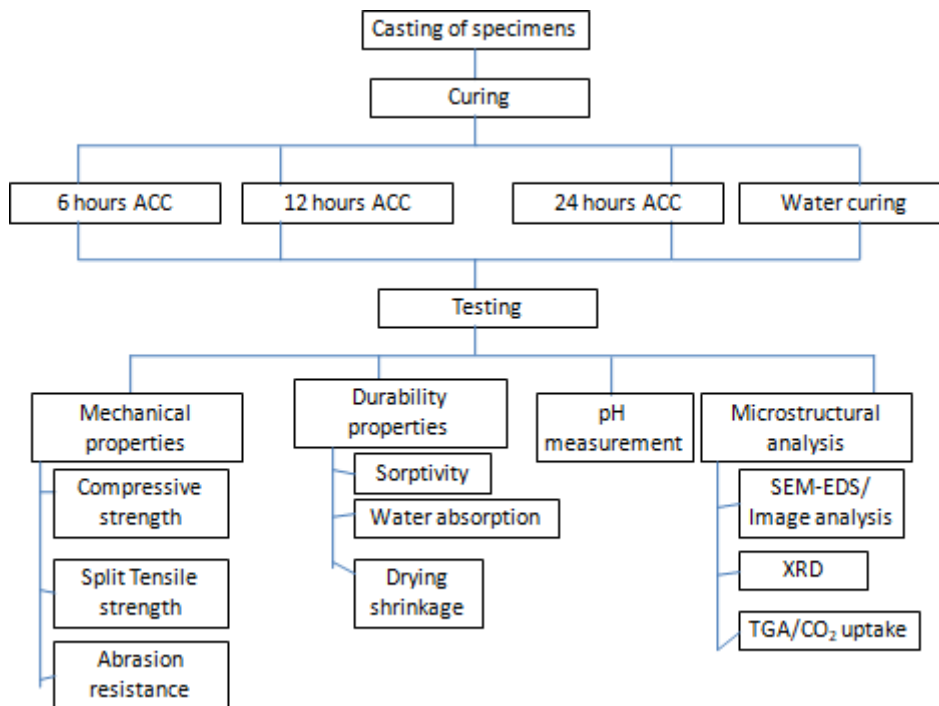


Fig. 5.1: Test matrix adopted to study the effect of accelerated carbonation curing duration on properties of concrete

5.2 EFFECT OF ACC DURATION ON MECHANICAL PROPERTIES OF CONCRETE

The effect of duration of accelerated carbonation curing has been studied on various mechanical properties of concrete, which includes the development of compressive

strength, split tensile strength and abrasion resistance of concrete. The test results are discussed in the following sections:

5.2.1 Compressive Strength

The compressive strength is one of the primary properties that govern the performance of concrete. In the present study, M25 mix was cast and was subjected to respective curing regime after de-moulding. It included water curing till the testing age, carbonation curing for variable duration of 6 hours, 12 hours and 24 hours; followed by water spray for three days. The compressive strength of mix was measured initially right after the carbonation stage of ACC; that is after 26 hours for carbonation curing duration of 6 hours, after 32 hours for carbonation curing duration of 12 hours and after 44 hours for carbonation curing duration of 24 hours. For reference, compressive strength test was performed after 26 hours of casting for water cured (WC) specimens. After that, compressive strength under all the curing regimes was measured at the age of 3, 28, 90 and 365 days of casting. The test was carried out as per the guidelines of IS 516: 2004 (IS 516, 2004) and the results have been presented in Fig. 5.2. Table 5.2 represents the percentage change in compressive strength of carbonation cured specimens with respect to water cured concrete.

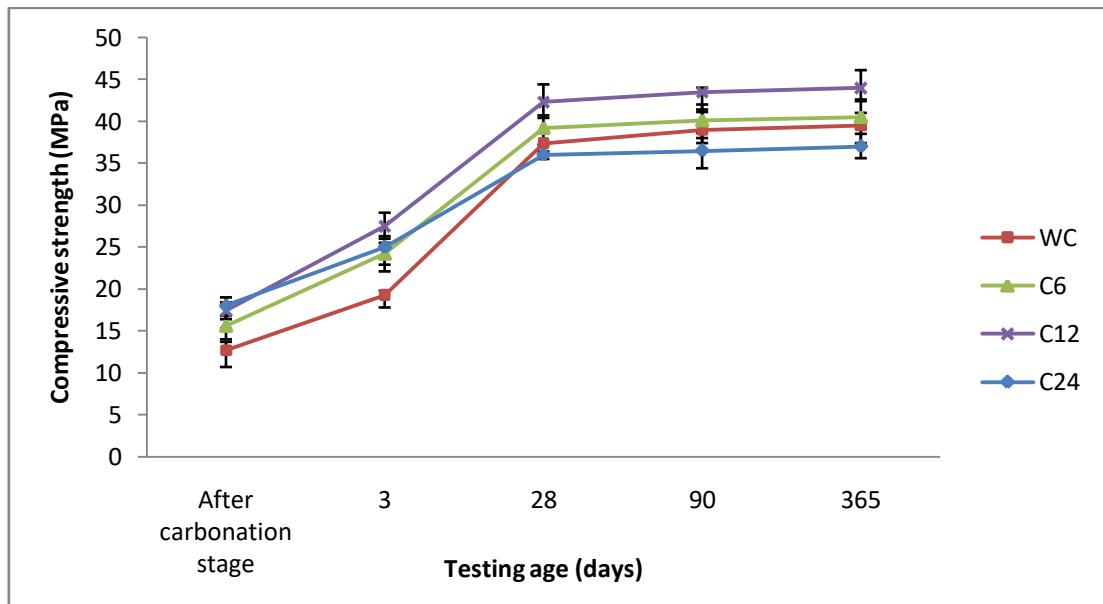
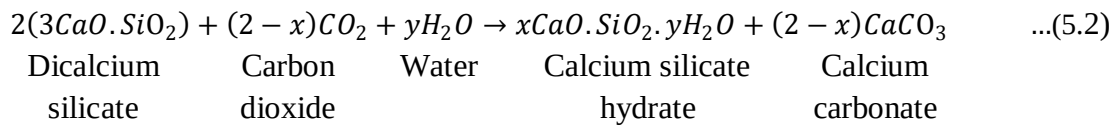
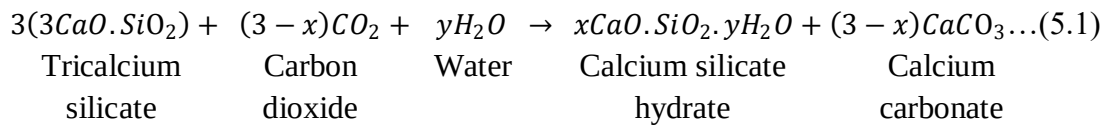
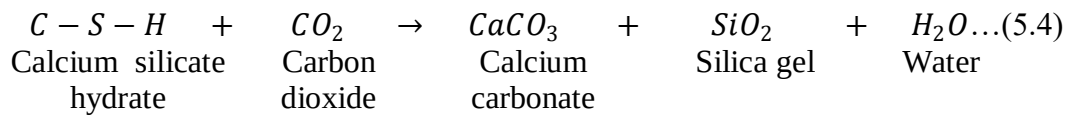


Fig. 5.2: Compressive strength of concrete subjected to different curing regimes

Fig. 5.2 shows the compressive strength results for different curing regimes opted in this study. The compressive strength just after carbonation stage and at the age of three days can be considered as early age compressive strength of concrete; while the results at 28, 90 and 365 days represent the later age compressive strength of the concrete. It can be observed from the results that C6, C12 and C24 specimens obtained 22.8%, 39% and 41% higher compressive strength respectively than water cured concrete just after carbonation stage, that is nearly at one day of casting. Similarly, at the age of three days; C6, C12 and C24 specimens obtained 25.3%, 42.4% and 29.5% higher strength respectively than water cured specimens. This indicated that ACC enhanced the early strength of concrete considerably for all carbonation durations.

The higher early strength of ACC specimens can be attributed to the carbonation reaction, leading to the formation of C-S-H gel and CaCO_3 , which directly act as strength contributing solids. The basic carbonation reactions are listed in equations 5.1-5.4. It can be seen from the equations that CO_2 reacts with both unhydrated cement constituents (C_3S and C_2S) and hydration compounds ($\text{Ca}(\text{OH})_2$ and C-S-H) to form additional C-S-H gel and CaCO_3 . The CaCO_3 crystals get deposited in the pores present in concrete. The CaCO_3 crystals get intermingled with C-S-H gel and provide a densified mass which imparted higher strength to concrete. Liu et al. and Mo and Panesar also found in their studies that carbonation curing resulted in improved early age compressive strength (Liu et al., 2016; Mo and Panesar, 2012).





Among the three carbonation curing durations, it was also observed from the results that C12 and C24 specimens obtain the highest early age strengths. This indicated a higher degree of carbonation with increased duration of ACC, which resulted in production of greater amount of $CaCO_3$ and C-S-H gel and hence higher compressive strength of the respective mix. At the end of carbonation process, C24 specimens had the highest compressive strength. It can be due to higher carbonation of the specimens. However, at the testing age of three days, the highest strength was obtained by C12 specimens, followed by C24 and C6 mixes. It further indicated that excessive carbonation curing would provide initial benefits in terms of compressive strength that could soon be lost after the carbonation process is over.

At later age of testing, it was observed that C6 and C12 specimens still had higher strength than the corresponding water cured specimens; however, C24 specimens registered strength levels lower than the water cured specimens. Also, the rate of improvement in strength levels was found to be lower than the strength improvements obtained at early ages of testing. At the age of 28 days, specimens from all curing regimes were found to achieve the target strength of 31.6 MPa, but the highest strength was achieved by C12 curing regime which achieved approximately 13% higher compressive strength than the water cured concrete. As compared to this, C6 specimens had 4.8% higher strength than the corresponding water cured specimens; while C24 specimens achieved strengths lower than the water cured specimens. It clearly indicated that prolonged carbonation curing was detrimental to later age strength of concrete.

In all the three curing regimes, the carbonation curing period was followed by three days of water spray to replenish the water lost during carbonation reaction and to allow subsequent hydration of specimens so that the basic hydration reactions of the binder with water could take place leading to the formation of C-S-H gel. Therefore, in all the carbonation curing procedures, the total compressive strength gained by the

mix is due to the products formed during the carbonation reactions and the hydration reactions.

Table 5.2: Compressive strength results for different curing regimes and its variation with respect to water curing regime

Testing age(days)	Compressive strength and its variation with respect to water curing regime	Curing Regime			
		WC	C6	C12	C24
After carbonation	CS (MPa)	12.7	15.6	17.4	18
	% change	-	+22.8	+37	+41.7
3 days	CS (MPa)	19.3	24.2	27.5	25
	% change	-	+25.3	+42.4	+29.5
28 days	CS (MPa)	37.4	39.2	42.3	36
	% change	-	+4.8	+13.1	-3.7
90 days	CS (MPa)	39	40.1	43.5	36.5
	% change	-	+2.8	+11.5	-6.4
365 days	CS (MPa)	39.5	40.5	44	37
	% change		+2.5	+11.3	-6.3

*CS = Compressive Strength

As the carbonation curing duration was increased, the carbonation reaction and hence the products formed during the carbonation reaction (CaCO_3 and C-S-H) was increased. However, the higher carbonation duration also led to higher water loss from the specimens due to the basic nature of carbonation reactions. The reason of water spray after carbonation curing phase was to replenish some amount of water loss. In C6 and C12 mixes, the higher strength achieved at 28 days of curing indicated that the carbonation reaction and the subsequent hydration reactions could achieve higher strengths than water curing regime. However, the lower strength of C6 specimens than C12 specimens can be understood due to relatively lesser intensity of carbonation reaction in this case. C24 specimens achieved approximately 4% lower strength than the WC concrete. The lower strength for C24 specimens can be

attributed to two major reasons: Firstly, the water loss from concrete caused by exothermic nature of carbonation reactions. It has been previously reported in literature that higher duration of carbonation might lead to significant water loss and hence, act as a hindrance to subsequent hydration (Junior et al., 2015). In the case of C24 specimens, a higher intensity of carbonation caused excessive removal of pore water from concrete, which hindered the subsequent hydration reactions and resulted in loss of strength of concrete. Secondly, higher duration of carbonation also led to intensive reaction of CO_2 with C-S-H, which caused disintegration of C-S-H into weak silica gel (Goodbrake et al., 1979b). The disintegration of C-S-H into silica gel caused loss in the binding property of concrete and resulted in lower strength of concrete.

The comparison of strengths at later ages of 90 days and 365 days indicated similar trend as observed at the age of 28 days. Specimens from all types of curing regimes continued to gain strength from the hydration of cement. The maximum compressive strength was achieved in C12 mixes, indicating the positive effect of sufficient carbonation curing even at later ages. C6 mixes had strength almost equivalent to the water curing regime; while C24 mixes achieved a little lower strength. It clearly indicated that 12 hours of carbonation curing would provide best mechanical performance even at later ages. Also, the test results further confirmed the usefulness of water spray followed by sealed plastic bag curing; rather than the continuous water curing. It would help in water conservation without compromising on the mechanical performance of concrete.

5.2.2 Split Tensile Strength

Split tensile strength test was conducted on specimens subjected to different curing regimes at the age of 28 days and 90 days. The test was conducted as per the guidelines of IS 5816:1999 (IS 5816, 1999) and the results are presented in Fig. 5.3. The trend observed in split tensile strength result was similar to the one observed in compressive strength results. At both the testing ages, split tensile strength of C6 and C12 mixes were found to be higher than the corresponding value achieved in water cured specimens; while C24 mixes achieved lower split tensile strength than water cured concrete. The higher split tensile strength for carbonation curing duration

of 6 hours and 12 hours is indicative of a denser concrete microstructure, attributed to precipitation of CaCO_3 and additional C-S-H gel during carbonation. However, lower tensile strength in C24 mixes indicated that the lack of hydration and higher water loss due to carbonation reaction has detrimental effect on both the compressive and split tensile strengths of concrete. It further indicated the importance of duration of carbonation curing on the properties of resultant concrete.

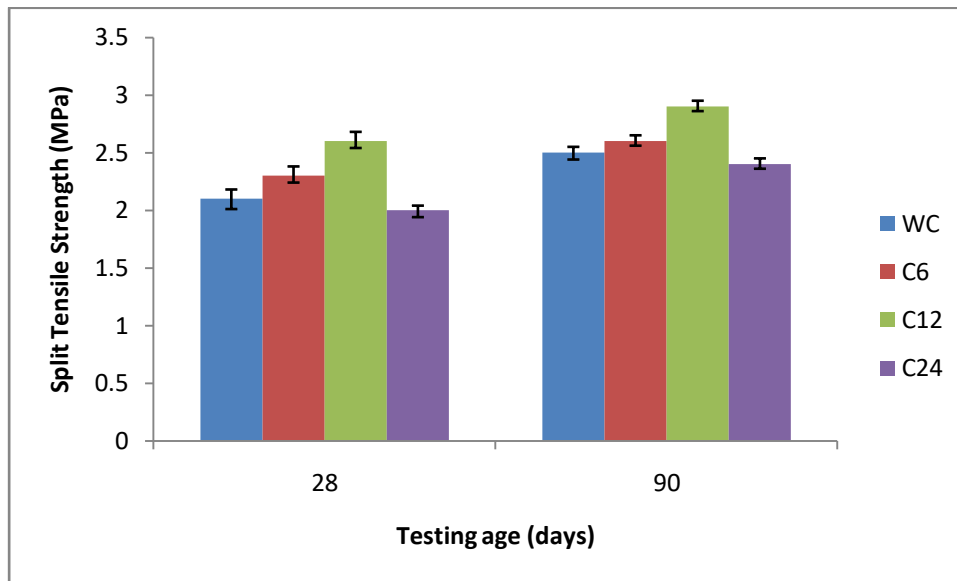


Fig. 5.3: Split tensile strength of concrete subjected to different curing regimes

On comparing the effect of carbonation curing on compressive strength and split tensile strength of concrete, it was observed that at the testing age of 28 days, compressive strength of concrete was improved by 4.8% and 13.1% for 6 hours and 12 hours of carbonation curing respectively; whereas the corresponding improvement in split tensile strength was 9.5% and 23.8% respectively. This indicated that the split tensile strength of concrete was influenced more significantly by carbonation curing. The higher improvement in split tensile strength as compared to the compressive strength can be due to better bonding between particles due to precipitation of CaCO_3 in the pores of concrete. The split tensile strength is known to be more dependent on the quality of the paste in the interstitial transition zone (Singh and Siddique, 2013; Vardhan et al., 2019). The enhancement of characteristics of cement paste in the concrete is clearly evident from the influence of carbonation curing on split tensile strength.

5.2.3 Abrasion Resistance

Abrasion resistance is a measure of mechanical performance of the surface of concrete. Abrasion resistance of concrete is described as its ability to resist the wearing of the surface by rubbing and friction. It is an important durability property of concrete and is particularly important for concrete floors, concrete pavements and concrete dams. The property typically refers to the ability to resist wearing due to frictional movement between the surfaces of different characteristics. In the test, the abrasive particles are made to rub against stationary concrete block. The abrasive particles are provided with relative motion that creates shear force between particles and the concrete surface. The shear force so generated leads to formation of scratches on the surface. Also, a normal load of some value is put on the concrete block so that the abrasive particles penetrate into the concrete block. Both normal force and shear force ultimately leads to wearing away of concrete surface that is noted in terms of weight loss after the required number of revolutions.

In the present study, abrasion resistance was measured in terms of depth of wear, which was also used by earlier researchers (Ghafoori and Sukandar, 1995; Naik et al., 2003; Siddique et al., 2012; Siddique and Khatib, 2010). The test was conducted on specimens of size 35 x 70x 70mm as per the specifications of IS 1237:2012 (IS 1237, 2012). The testing of abrasion resistance was done at the age of 3, 28 and 90 days of casting. At a particular testing age, the specimens were subjected to wear from 20 gm of abrasive powder spread over a grinding machine, which was rotated at 20 rpm. The weight of specimen was measured after each 22 revolutions till the end of 220 revolutions. Two parameters were recorded from the measured data, which includes the progressive variation in depth of wear with each set and the final depth of wear at the end of 220 revolutions. The final depth of wear after 220 revolutions for all the mixes is presented in Fig. 5.4; while the progressive depth of wear of each mix at 3, 28 and 90 days of casting is presented in Figs. 5.5-5.7.

It is evident from the results of abrasion resistance test that the type of curing regime significantly impacts the performance of concrete surface. It can be observed from Fig. 5.4, that the abrasion resistance at an early testing age of 3 days was considerably

improved by the carbonation curing. C6 specimens show 25.2%, C12 specimens show 32% and C24 specimens show 30% better abrasion resistance than the WC specimens. The similar trend was also observed in the compressive strength test results. The conversion of Ca(OH)_2 into CaCO_3 during carbonation was found to improve the surface characteristics of concrete. The precipitation of CaCO_3 in the pores and formation of additional C-S-H gel during the ACC processes provided a densely packed concrete surface that resulted in better abrasion resistance to the external forces.

The effect of duration of ACC on abrasion resistance was not much evident at early ages. However, at the later testing ages of 28 days and 90 days, the duration of ACC was found to have significant impact on the performance of concrete against abrasion. C12 and C6 specimens, owing to sufficient hydration reaction post carbonation, exhibited better resistance to abrasion than the WC specimens at the later testing ages too.

The detrimental effect of higher duration of ACC on the surface characteristics of concrete is evident from the results of abrasion resistance test of C24 specimens at the age of 28 days and 90 days. The poor performance of C24 specimens at the later ages can also be attributed to insufficient hydration post the carbonation period. It can be seen that in the C24 specimens, no significant development in abrasion resistance of concrete was observed as the testing age progressed from 3 days to 28 days. Absence of sufficient hydration reaction in C24 specimens did not allow production of C-S-H in the specimens and hence, the abrasion resistance could not improve with age in C24 specimens as compared to other curing regimes. However, the abrasion resistance of C24 specimens at the age of 28 days was still comparable to the WC specimens. This can be probably attributed to higher content of CaCO_3 produced in the C24 specimens during the early age carbonation. On the contrary to results observed in compressive strength test, it was seen that the values of abrasion resistance at the age of 28 days was still higher for C24 specimens as compared to water cured specimens, whereas, the compressive strength of C24 specimens was found to be lesser than water cured specimens at the testing age of 28 days. This

further confirmed that the effect of ACC was more prominent on the surface characteristics of concrete as compared to the bulk properties.

The progressive depth of wear at the testing age of 3 days, 28 days and 90 days has been depicted in Figs. 5.5, 5.6 and 5.7 respectively. It can be observed that at the testing age of 3 days, the initial slope was higher for all specimens, which got flatter at the later revolutions, indicating greater depth of wear initially. It indicated that the top surface was not uniformly strong. Among all the tested mixes, carbonation cured mixes had lower value of initial slope as compared to WC specimens. This indicated better performance of surface layer in the carbonation cured specimens as compared to water cured specimens. It clearly demonstrated the positive effect of calcium carbonate precipitation in the surface pores during carbonation curing on the concrete surface.

At the later age of testing i.e. at 28 days and 90 days, WC specimens and C24 specimens exhibited similar slopes for the initial revolutions, indicating almost similar surface characteristics of both the specimens; while the slope of C6 and C12 mixes was flatter. It indicated the better surface performance of C6 and C12 specimens than the water cured specimens and C24 specimens. It further confirmed that the lack of hydration negates the performance benefits achieved during carbonation curing; and hence strengthens the importance of carbonation duration and subsequent hydration post carbonation in the ACC procedure.

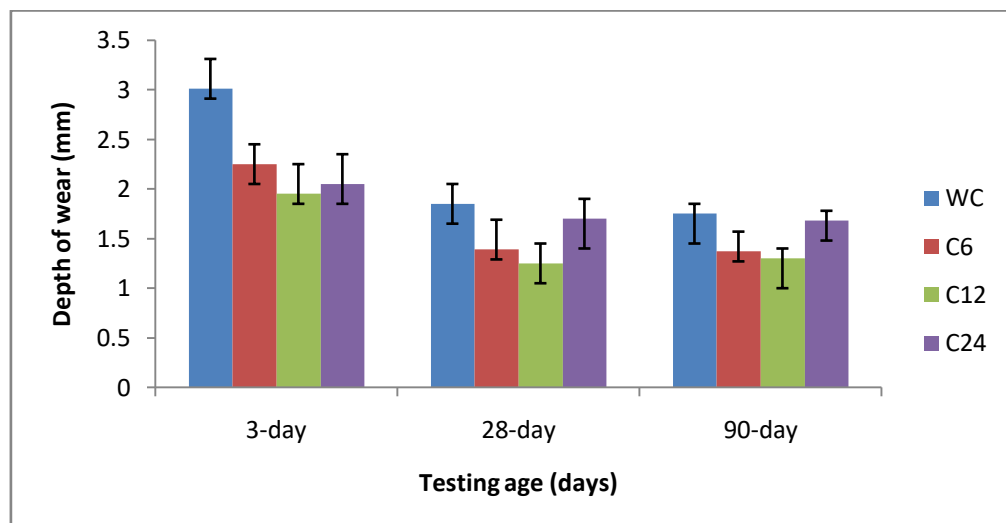


Fig. 5.4: Abrasion resistance of concrete subjected to different curing regimes

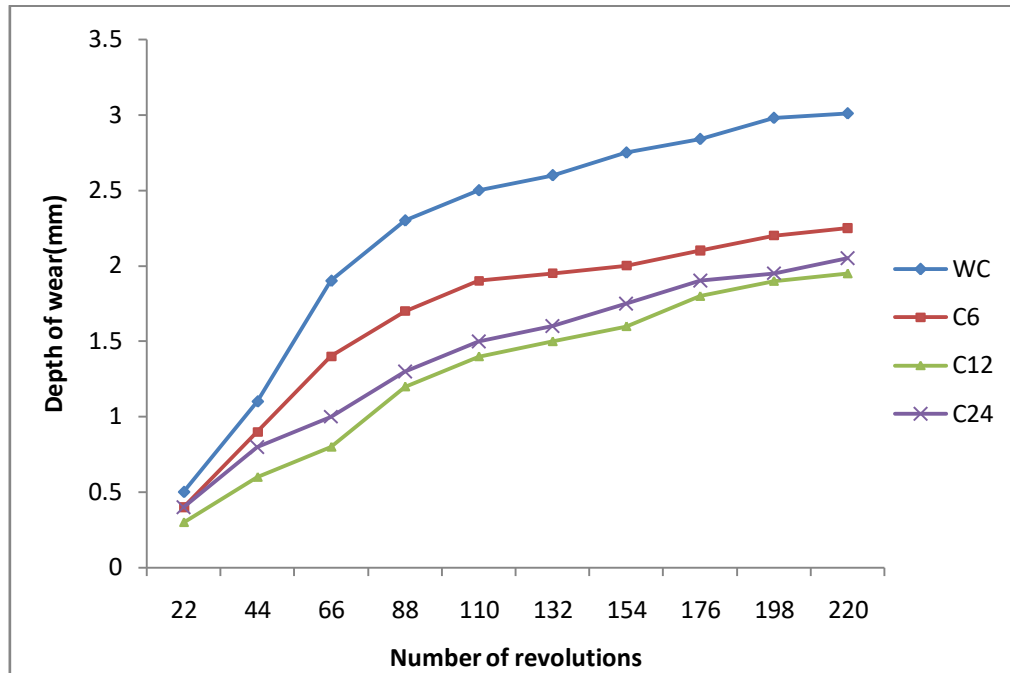


Fig. 5.5: Progressive depth of wear at the testing age of 3 days

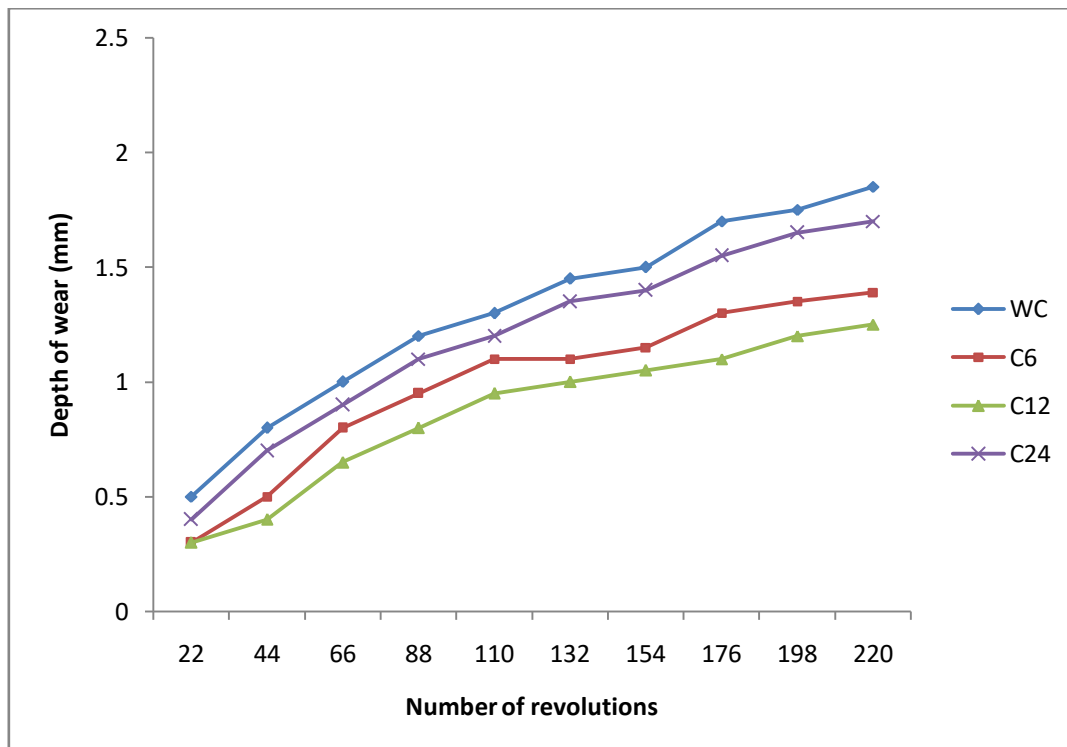


Fig. 5.6: Progressive depth of wear at the testing age of 28 days

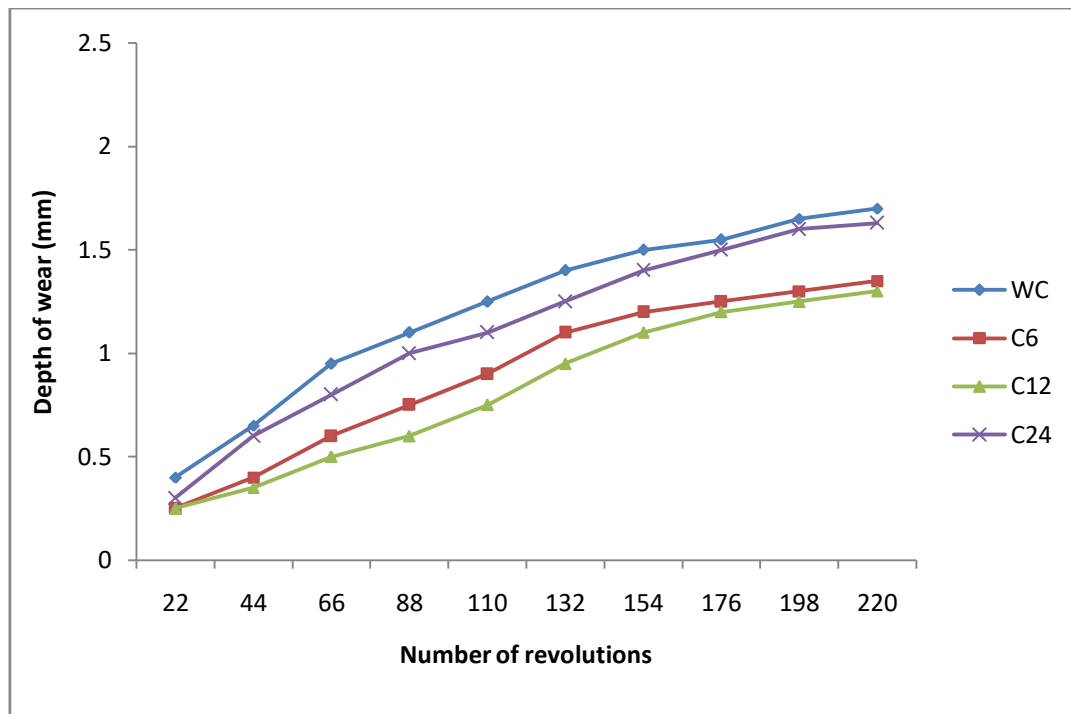
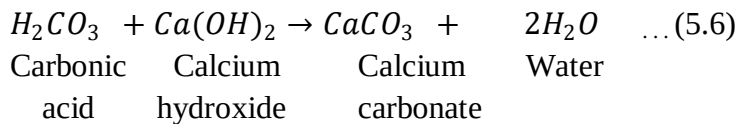
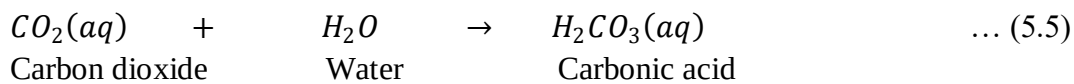


Fig. 5.7: Progressive depth of wear at the testing age of 90 days

5.3 EFFECT OF CARBONATION CURING DURATION ON pH OF CONCRETE

pH is an important parameter in studies related to carbonation. It is due to the already established fact that acidic environment caused by natural carbonation lowers the pH of concrete and hence breaks the passive layer formed around the steel rebar. In dense and good quality concrete, the constituents of concrete provide high alkalinity to the concrete pore solution with pH of the pore solution ranging from 12.5 to 13.5 (Heiyantuduwa et al., 2006; Jamil et al., 2003; Montemor et al., 2002; Pu et al., 2012; Shi and Sun, 2012). When a rebar is embedded in highly alkaline concrete, a protective oxide layer of thickness in nanometers (also known as passive layer) is formed around the rebar spontaneously. This passive layer is composed of hydrated iron oxides with varying degree of ferrous ions (Fe^{+2}) and ferric ions (Fe^{+3}) which protect the rebar from corrosion (Bertolini et al., 2013). In natural weathering carbonation, CO_2 from the environment penetrates the concrete surface and progresses through the capillary pores present in concrete. In the presence of sufficient moisture, CO_2 forms carbonic acid that reacts with $\text{Ca}(\text{OH})_2$ to form CaCO_3 , which causes the

reduction of pH (Neville and Brooks, 2010). The chemical reactions involved in this process are represented in Eq. 5.5 and 5.6. Carbonation causes the pH of the pore solution to drop from its normal values of around pH 13 to values approaching neutrality (Bertolini et al., 2013; Dong et al., 2016; Sisomphon and Franke, 2007). Lowering of the pH of pore solution (from 13.5 to nearly 8) breaks down the passive layer that protects the rebar from corrosion; and hence makes the rebar vulnerable to corrosion.



In order to evaluate any possible effect of carbonation curing in lowering the pH to a level wherein the breakdown of passive layer around the rebar might take place, the pH of all the specimens under different curing regimes was monitored. The pH investigations were carried out on the powdered specimens collected from the cubes crushed during the compressive strength test. The test was carried out at 28 days of casting. In this study, the specimens were collected from two portions of the cube. First specimen was taken from the surface of the cube and the second specimen was obtained from the core of the cube. It is because of the fact that ACC is believed to be a surface curing procedure and is found to have a more prominent effect on the surface of concrete (Rostami et al., 2011).

Suspension method was used for measurement of pH, as is used by various other researchers as well (Manso and Aguado, 2017; Rasanen and Penttala, 2004; Tripathi et al., 2019). For the measurement of pH, the specimens were fine grounded to produce powder specimens. The powdered specimens were then dissolved in 10 ml of distilled water and mixed for 15 minutes. The solution was then filtered and pH of resultant solution was measured using a digital pH meter. The results of the pH test have been presented in Fig. 5.8.

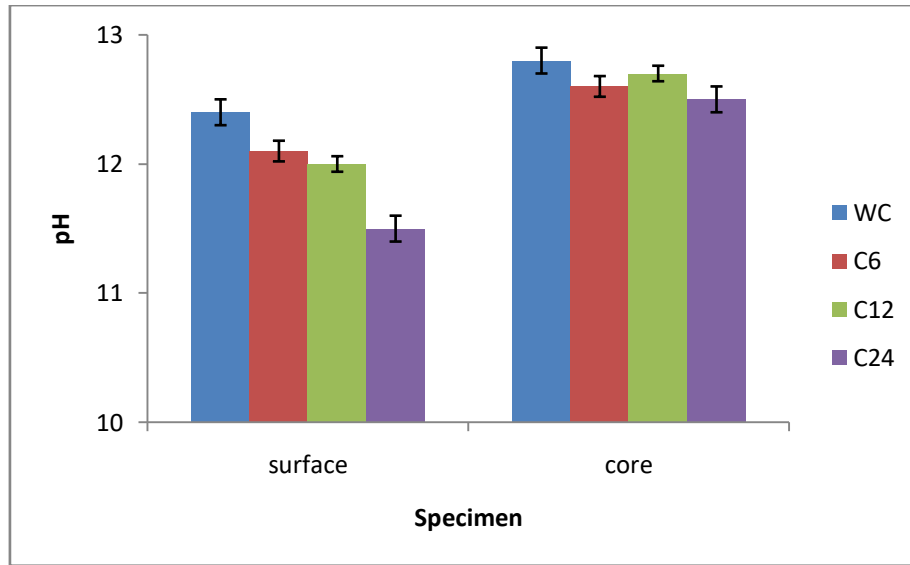


Fig. 5.8: pH of specimens subjected to different types of curing regimes

The results of pH for the specimens obtained from the surface of specimens indicated a drop in pH of surface concrete with the carbonation curing procedure. The pH of concrete reduced from 12.4 in WC specimens to nearly 12.1 and 12 in C6 and C12 mixes respectively; and then reduced further to 11.5 in C24 mix. The drop in pH of carbonation cured concrete was due to conversion of Ca(OH)_2 to CaCO_3 and the carbonation of calcium silicates which produced CaCO_3 instead of Ca(OH)_2 . However, the pH of all the specimens was observed to be well above 11, which is greater than the threshold pH required to de-passivate the protective passive layer on rebar (François et al., 2018). The drop in pH was observed to be directly proportional to the duration of ACC. The C24 specimens exhibited highest drop in pH. This can be attributed to higher extent of carbonation reaction in C24 specimens, due to which large amount of Ca(OH)_2 was converted into CaCO_3 . However, the drop in pH was not significantly low for the C12 and C6 specimens. This can be understood due to the further hydration of concrete during the post conditioning process, which led to formation of sufficient amount of Ca(OH)_2 that compensated the drop in pH of concrete during carbonation. Since, in the case of C24 specimens, sufficient hydration was not available to the specimens post carbonation, the pH was found to be lower in these specimens. The pH of C24 specimens was still significantly alkaline and would not deteriorate the passive layer protecting the rebar.

The second set of specimens was obtained from the core of concrete cubes subjected to specific curing regimes. The results of pH for the specimens from the core of cubes indicated that the change in curing regime did not have any effect on the pH of core concrete. The values of pH of all the ACC specimens were found to be similar to the values obtained for WC specimens. This indicated that the effect of early age carbonation was limited to the surface layer of concrete and did not affect the properties of core concrete. This was also evident from the results of tests conducted for mechanical properties, where the carbonation curing caused greater improvement in abrasion resistance of concrete as compared to compressive strength. It can be inferred from the pH tests that the accelerated carbonation curing would not cause any detrimental effect on the formation of protective passive layer around the steel rebars.

5.4 EFFECT OF ACC DURATION ON PERMEATION PROPERTIES OF CONCRETE

The effect of ACC duration on the permeation properties of concrete has been studied in terms of water absorption and sorptivity. The results of these tests are presented in the following sections.

5.4.1 Water Absorption

The primary permeation characteristics of concrete were assessed with the help of water absorption test. The test was conducted as per ASTM 642: 2008 (ASTM C642-13, 2008a) on cubes of size 100 mm subjected to different curing regimes at the ages of 3 and 28 days of casting. The results for water absorption test are presented in Fig. 5.9. From the results of water absorption test, it is clear that the type of curing regime has a significant effect on permeation characteristics of concrete.

Notably, all ACC specimens showed lesser water absorption at early testing age of three days. At early testing age of 3 days, C12 specimens showed 37% lesser water absorption as compared to WC concrete, C6 specimens exhibited 23.6% lesser water absorption and C24 specimens showed 21% lesser water absorption as compared to WC specimens. The lower water absorption of ACC specimens can be related to the enhanced impermeability of concrete surface layer, primarily due to precipitation of

CaCO_3 in the pores. The precipitation of CaCO_3 crystals restricted the movement of water through the concrete surface.

The variation of water absorption with the duration of ACC can be understood from the intensity of carbonation reaction. At the age of 3 days, C12 specimens exhibited a significant combination of hydration and carbonation products, which provided densification to the mix and resulted in lower permeation. C24 specimens, on the other hand, were found to have higher water absorption among the three durations of ACC. This can be attributed to the higher intensity of carbonation in the C24 specimens, which although produced CaCO_3 , but also resulted in decalcification of C-S-H into weak silica gel (Rostami et al., 2012b). Secondly, the higher intensity of carbonation led to extensive pore water loss from concrete, which not only created internal voids in the mix, but also depleted the available water required for further hydration in concrete. Both these factors led to higher water absorption in the mixes that were subjected to carbonation curing for 24 hours.

The values of water absorption decreased for all the curing regimes from the age of 3 days to 28 days. This is indicative of further hydration reaction in the specimens beyond the age of 3 days. Among all the mixes, the highest decrease in the value of water absorption was observed in the WC specimens, which is a clear result of continuous hydration of these specimens up to the age of 28 days. The ACC specimens also showed decrease in the values of water absorption, with the lowest value of water absorption exhibited by C12 specimens. Comparing the water absorption values of carbonation cured specimens with the reference water cured specimens, it was seen that C12 specimens showed approximately 38% lesser water absorption than the WC specimens. C6 specimens also exhibited approximately 23% lesser absorption than the WC specimens.

The lower water absorption for the C6 and C12 can be attributed to refinement of pore structure of these mixes due to precipitation of CaCO_3 in the pores and formation of additional C-S-H generated from subsequent hydration reactions post carbonation. On the other hand, C24 specimens showed approximately 15% higher water absorption than the WC specimens. It clearly indicates porous structure of C24 mixes, primarily due to lack of subsequent hydration post carbonation. It also indicated the detrimental

effect of increased carbonation curing on both mechanical and permeation properties of the resultant concrete.

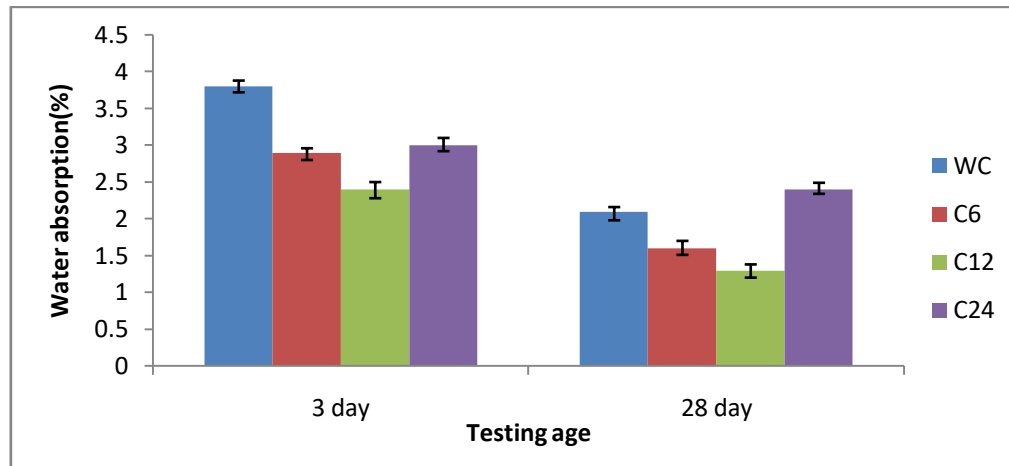


Fig. 5.9: Water absorption of concrete subjected to different curing regimes

5.4.2 Sorptivity

The measure of sorptivity helps to analyze the moisture transport in concrete through capillary action. The test was conducted as per ASTM C1585-2004 (ASTM C1585-13, 2004). In the present study, the testing for sorptivity was done at the age of 3 and 28 days of casting. For obtaining sorptivity of the mix, the specimens were allowed to absorb water through one surface only and the mass gained due to capillary rise of water was noted. The change in mass of the specimen was recorded at 1, 5, 10, 20, 30, 60, 120, 180, 240, 300, 360 minutes and 1, 2, 3, 4, 5, 6, 7 and 8 days of immersion. Figs. 5.10 and 5.11 show the absorption vs square root of time plots for concrete subjected to different curing regimes up to 8 days of testing at the age of 3 days and 28 days respectively. It is observed from the Fig. 5.10 and 5.11 that the absorption increased considerably up to the testing time of 360 minutes, after which the rate of absorption was observed to be consistent for all types of specimens. Similar results for sorptivity of carbonation cured mixes have been reported by Rostami et al. (Rostami et al., 2011). Thus, it can be inferred that the primary sorptivity of the mix varied significantly for different durations of carbonation curing as compared to secondary sorptivity. To analyze the change in primary sorptivity with duration of carbonation curing, a plot was then drawn between the square root of time and volume of the

water absorbed. The slope of the best fitted line obtained by linear regression analysis of data points till 360 minutes is taken as the sorptivity value of the mix. Fig.5.12 represents the values of sorptivity coefficients for different curing regimes at both the testing ages. It is clear from the figure that sorptivity coefficients decreased with time for all specimens, irrespective of the curing regime followed. This indicates a densification in microstructure for all the curing regimes as the age of concrete increased from 3 days to 28 days.

It can be observed from Fig. 5.12 that at an early age of 3 days, WC curing regimes showed highest capillary porosity. ACC specimens showed lesser adsorption at early age as compared to WC specimens, owing to precipitation of CaCO_3 in the pores and production of additional C-S-H gel from combined action of hydration and carbonation processes. The precipitation of CaCO_3 in the pores causes discontinuity in the pore network and results in lesser capillary absorption. Among the three carbonation curing durations, C12 specimens had considerably lower sorptivity value as compared to C24, C6 and WC specimens at three days of curing.

As the testing age progressed, the sorptivity coefficients of all the mixes decreased considerably indicating refinement of pore structure with age due to further hydration. Among all the tested mixes, WC and C6 had almost similar values of sorptivity, while sorptivity value of C12 was little lower. It indicated almost similar capillary porosity of all these mixes. However, C24 specimens exhibited higher sorptivity coefficient as compared to other curing regimes. This is in coherence with the results obtained for mechanical properties where C24 specimens showed weaker abrasion resistance and lower compressive strength at the later ages. This indicated that higher duration of carbonation curing would increase the capillary porosity of the mix.

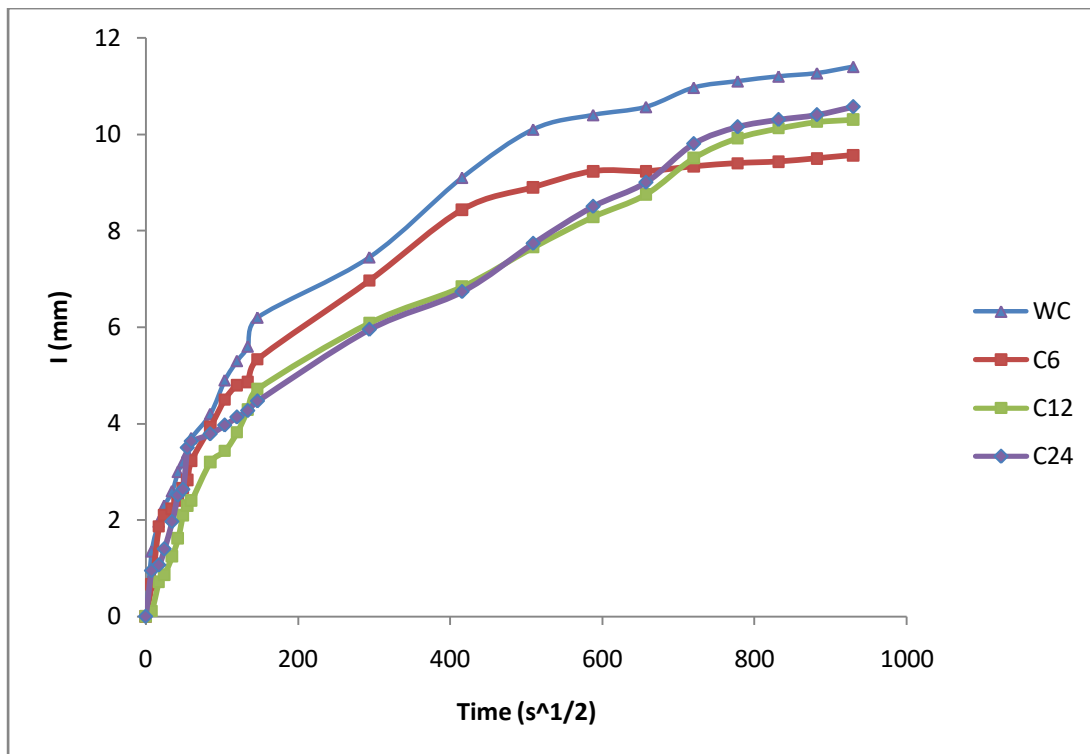


Fig 5.10: Absorption vs square root of time plot at the age of 3 days

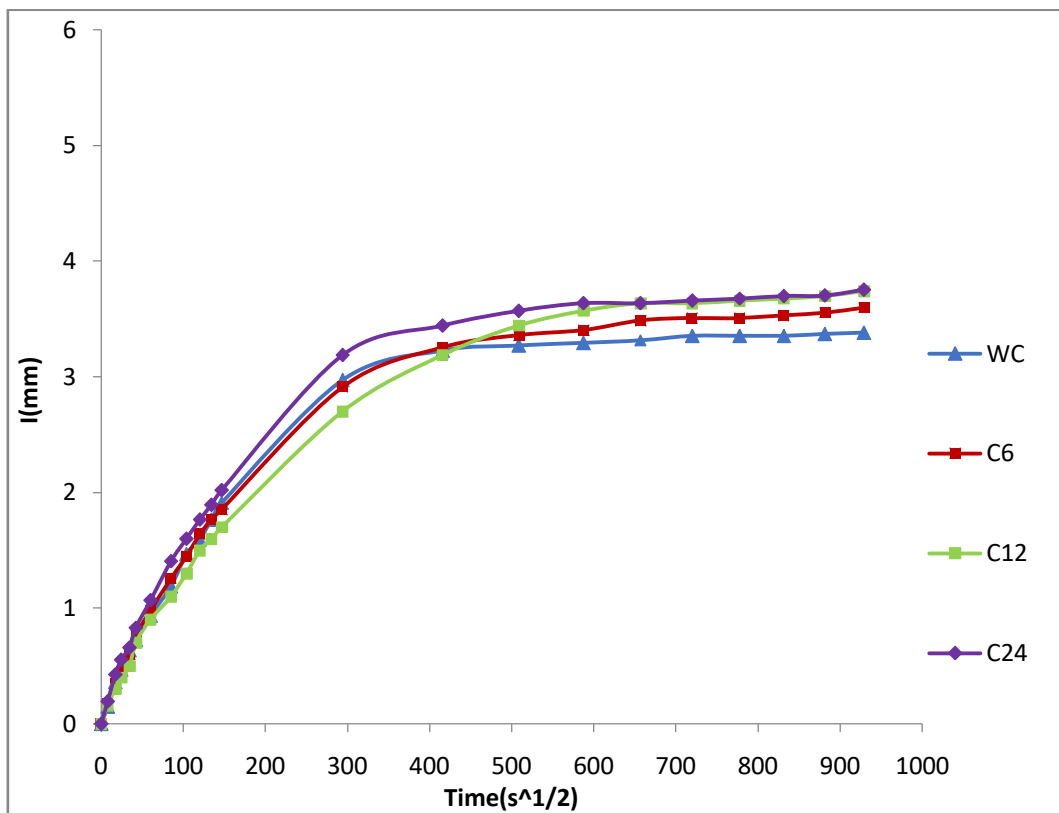


Fig 5.11: Absorption vs square root of time plot at the age of 28 days

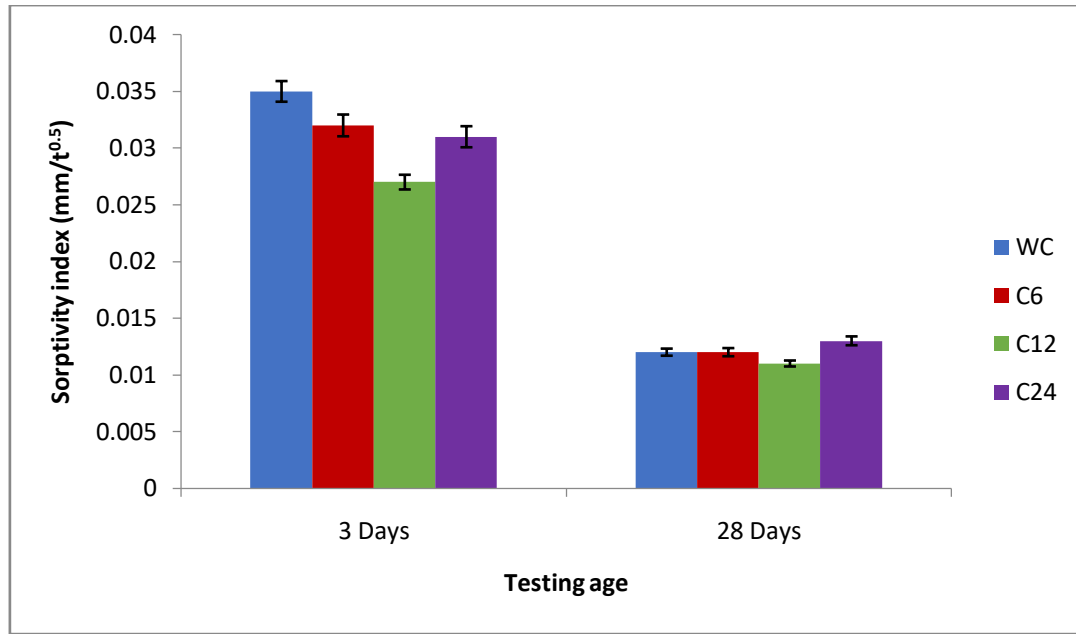


Fig 5.12: Sorptivity coefficients of concrete subjected to different curing regimes

5.5 EFFECT OF ACC DURATION ON MICROSTRUCTURE OF CONCRETE

Curing of concrete is responsible for physiochemical reactions in concrete. Therefore, on varying the curing procedure, microstructure evaluations become necessary to understand these physiochemical changes. In this study, microstructure of concrete was analysed to evaluate the respective changes brought by different curing regimes i.e. WC, C6, C12 and C24. The microstructural study was carried out using X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM)-Energy-dispersive spectrometry (EDS) and Thermogravimetric analysis (TGA). Further porosity of mixes was computed using 2D image analysis of SEM images with the help of Image analysis software ImageJ.

5.5.1 XRD Analysis

XRD analysis was done to analyze different phase changes that occur during curing process. For microstructural analysis, the samples were collected from the top layer of concrete from the specimens that were crushed during compressive strength tests. XRD spectrums of different specimens was observed at three testing durations i.e. just after carbonation and at the age of 3 days and 28 days are presented in stacked form in Fig. 5.13-5.15 respectively. The various peaks and their intensity indicate relative

quantities of certain compounds in the specimen. All the peaks were matched with ICDD reference database using XpertHighscore Plus.

The XRD analysis of WC concrete at the age of 26 hours of casting in Fig.5.13 showed major peaks of silicates of calcium (C_3S and C_2S) accompanied with portlandite ($Ca(OH)_2$) and silica (SiO_2). At an early age just after carbonation, the ACC specimens exhibited additional peaks of calcium carbonate ($CaCO_3$) along with the major hydration products, evidencing the incidence of carbonation reaction and CO_2 uptake. Also, the intensity of portlandite peaks and calcium silicate peaks diminished in ACC specimens owing to the conversion of $Ca(OH)_2$ into $CaCO_3$ and reaction of calcium silicates with CO_2 during accelerated carbonation curing process. Just after the carbonation phase, the strongest calcium carbonate peak was observed for C24 specimens, indicating a higher rate of carbonation with an increased duration of carbonation curing.

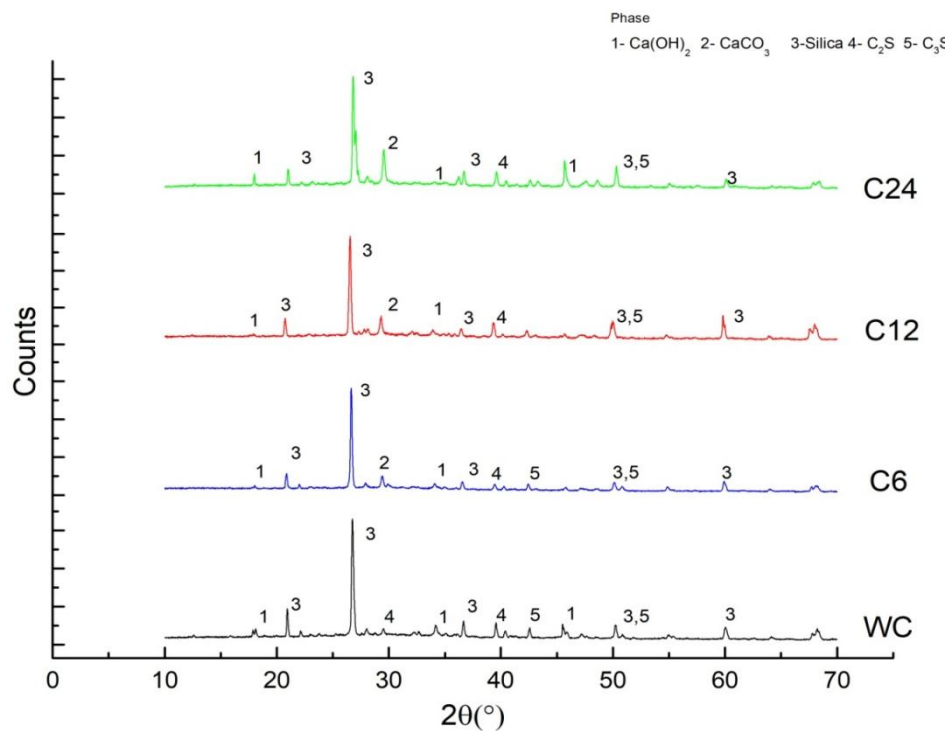


Fig. 5.13: XRD spectrums for different curing regimes after carbonation phase

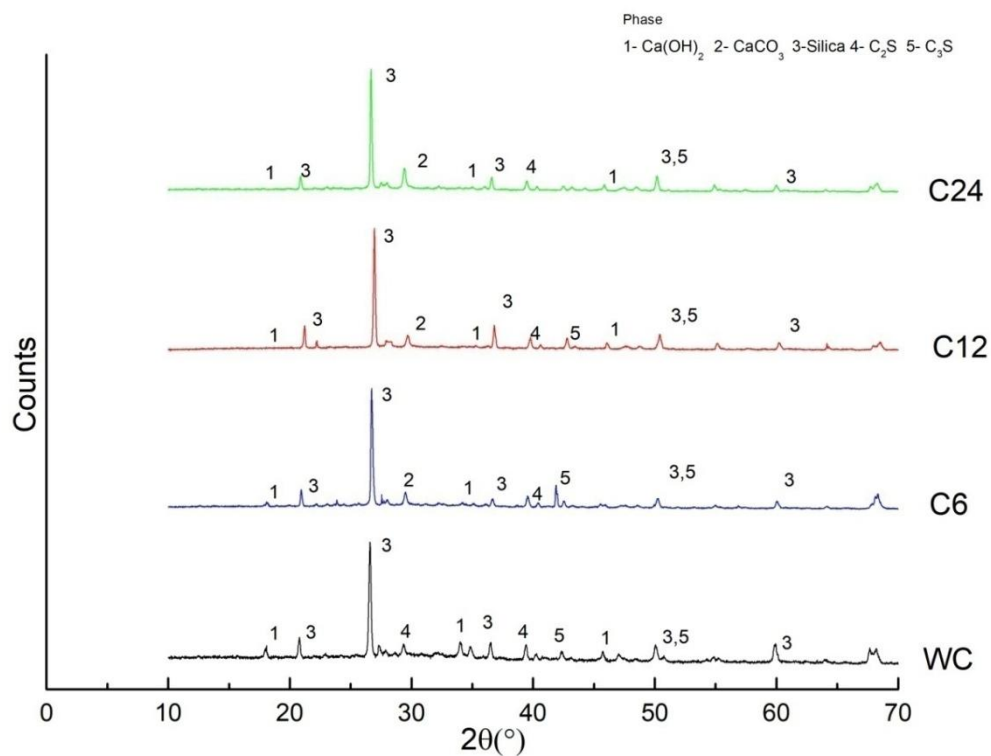


Fig. 5.14: XRD spectrums for different curing regimes at the age of 3 days

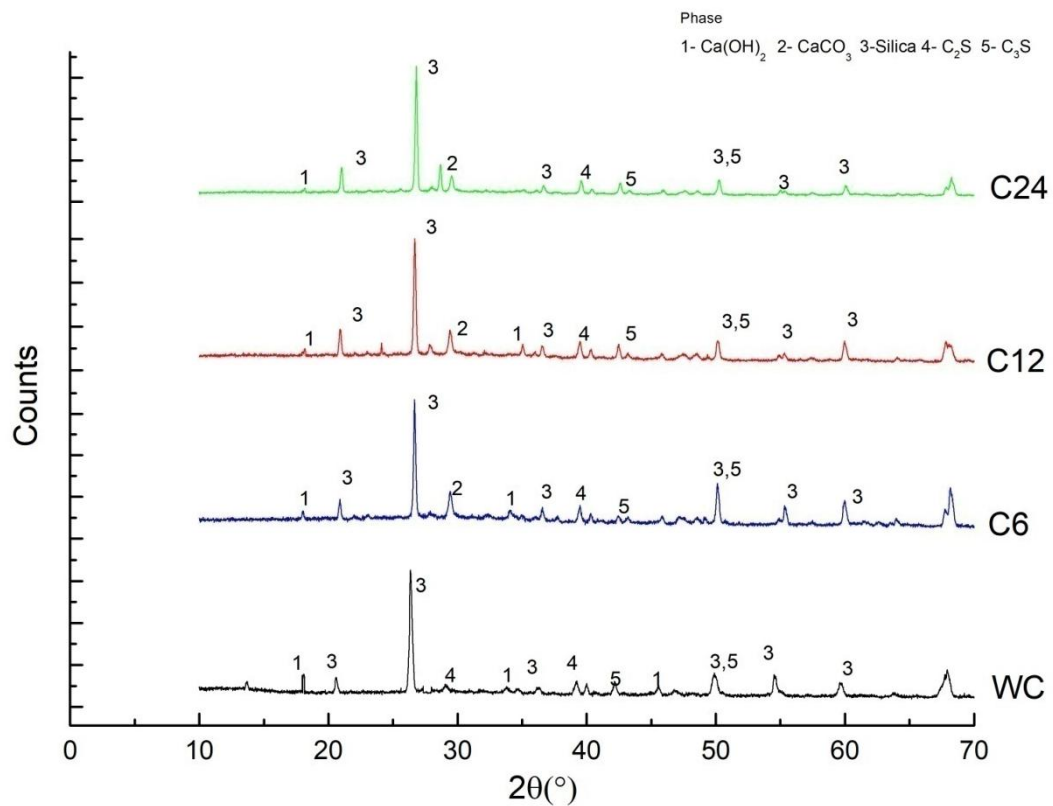


Fig. 5.15: XRD spectrums for different curing regimes at the age of 28 days

At the age of 3 days of casting, the XRD analysis show consistent hydration in the WC specimens as depicted by increased intensity of portlandite peaks and reduced intensity of calcium silicate peaks in Fig. 5.14. In the ACC specimens, a coexistence of hydration and carbonation products was observed, owing to the continuation of hydration with the help of water spray. Strong Ca(OH)_2 peaks were observed in C6 and C12 specimens while the intensity of C_3S and C_2S peaks diminished indicating progression of hydration with time. However, Ca(OH)_2 peaks were observed to be diminished in C24 specimens, indicative of lesser hydration in these specimens as compared to C6 and C12 specimens.

At the age of 28 days of casting as shown in Fig. 5.15, while the WC specimens showed strong peaks of hydration products and diminished peaks of calcium silicates, ACC specimens exhibited CaCO_3 peaks along with the hydration products. This indicated stability of precipitated CaCO_3 in concrete till later ages in carbonation cured concrete. XRD pattern of C24 curing regime exhibit diminished peaks of Ca(OH)_2 as compared to other curing regimes, indicating lesser hydration C24 specimens post carbonation.

5.5.2 SEM- EDS Analysis

The four curing procedures were further analyzed at the microscopic level to understand the changes in the morphology of the resultant mix. Secondary electron imaging mode was used to obtain SEM images and EDS was performed to identify the elemental composition of microstructural crystals. The spot for taking EDS has been marked with (+) on the SEM images. The SEM images along with EDS analysis are shown in Fig 5.16-5.18. The SEM images were obtained for specimens procured at the end of carbonation stage, at the age of 3 days and 28 days of casting. The Si/Ca ratio and C/Ca ratio obtained from EDS analysis of different curing regimes have been depicted in Table 5.3. The SEM images obtained were further analyzed for 2D porosity using ImageJ analysis software as shown in Fig. 5.19 and the results of image analysis are presented in Fig. 5.20.

SEM images obtained just after the carbonation stage for ACC specimens and at the end of 26 hours for the WC specimens are shown in Fig. 5.16. The major products

observed in WC specimens were the hydration products i.e. C-S-H gel and $\text{Ca}(\text{OH})_2$. Along with the major hydration products, ettringite and presence of voids was also clearly seen. In the carbonation cured specimens, presence of CaCO_3 was also observed along with aforementioned hydration products. As seen from Fig. 5.16 (a)-(d), C12 and C24 specimens exhibited denser microstructure than C6 and WC concrete at the early age. The presence of CaCO_3 intermingled with C-S-H gel acted as a composite binder which enhanced the microstructure of the mix. The EDS analysis of WC specimens showed major peaks of Ca and Si, indicating the presence of C-S-H and calcium silicates. In the ACC specimens, EDS analysis shows major peaks of C, Ca and diminished peaks of Si, attributed to formation of CaCO_3 upon carbonation. From the values of each element, Si/Ca ratio and C/Ca ratio for all the curing regimes were calculated. The data is presented in Table 5.3. It can be seen from the table that at the age of 26 hours, C/Ca ratio of the mixes were 0.13, 0.64, 0.7 and 0.82 for WC, C6, C12 and C24 specimens, respectively. On the other hand, Si/Ca ratio was 0.7, 0.45, 0.48 and 0.46 for WC, C6, C12 and C24 specimens respectively. The higher C/Ca ratio of carbonation cured specimens with increase in duration of carbonation indicates a redistribution of Calcium in the mix with higher production of calcium carbonate. The decrease in the Si/Ca ratio in the carbonation curing regimes indicated formation of amorphous gel like phase with Si/Ca ratio lesser than the C-S-H gel produced in the hydration reactions.

At the age of 3 days, further densification of the mix was observed in all types of specimens owing to the subsequent hydration. The post carbonation water curing of carbonation cured specimens provides water to continue the further hydration and also compensate for the water lost during the initial carbonation reactions. At the age of three days, the maximum densification of the mix was observed in C12 specimens, owing to the abundant amount of carbonation and hydration products in the mix. The maximum densification in C12 specimens is indicative of sufficient progression of both the carbonation and hydration processes in this curing regime. On the other hand, while the C6 specimens lack sufficient carbonation, the C24 specimens are deficit of required post carbonation water curing which leads to weak microstructure. This

correlates well with the results observed in compressive strength and split tensile strength results.

From the EDS analysis at the age of 3 days, it is inferred that C/Ca ratio of the mixes were 0.13, 0.6, 0.65 and 0.84 for WC, C6, C12 and C24 specimens respectively. On the other hand, Si/Ca ratio was 0.6, 0.52, 0.54 and 0.49 for WC, C6, C12 and C24 specimens respectively. Higher value of C/Ca ratio in the carbonation cured specimens indicates formation of calcium carbonate. The value of C/Ca increased with increase in carbonation curing duration, indicating a higher degree of carbonation in the specimens cured for higher durations. Also, lower value of Si/Ca in the carbonation cured systems is due to redistribution of calcium in the mix on varying the curing procedure. Further, it was observed that as the age of specimens increased from 26 hours to 3 days, increase in Si/Ca ratio of all the mixes was observed indicating formation of C-S-H gel upon further hydration after the ACC process.

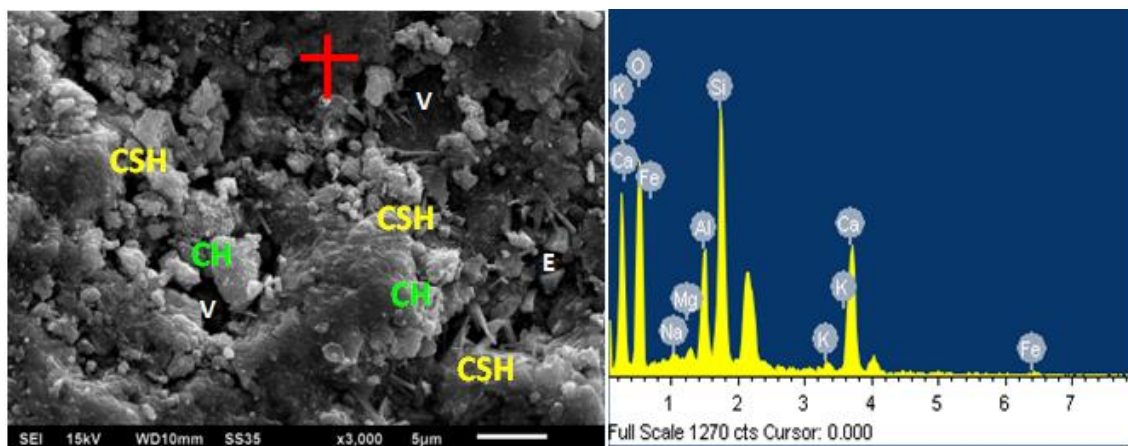
Table 5.3: Si/Ca ratio and C/Ca ratio obtained for different curing regimes

	WC		C6		C12		C24	
	Si/Ca	C/Ca	Si/Ca	C/Ca	Si/Ca	C/Ca	Si/Ca	C/Ca
After carbonation	0.70	0.13	0.45	0.64	0.48	0.70	0.46	0.82
3 days	0.60	0.13	0.52	0.60	0.54	0.65	0.49	0.84
28 days	0.57	0.16	0.55	0.51	0.58	0.56	0.42	0.70

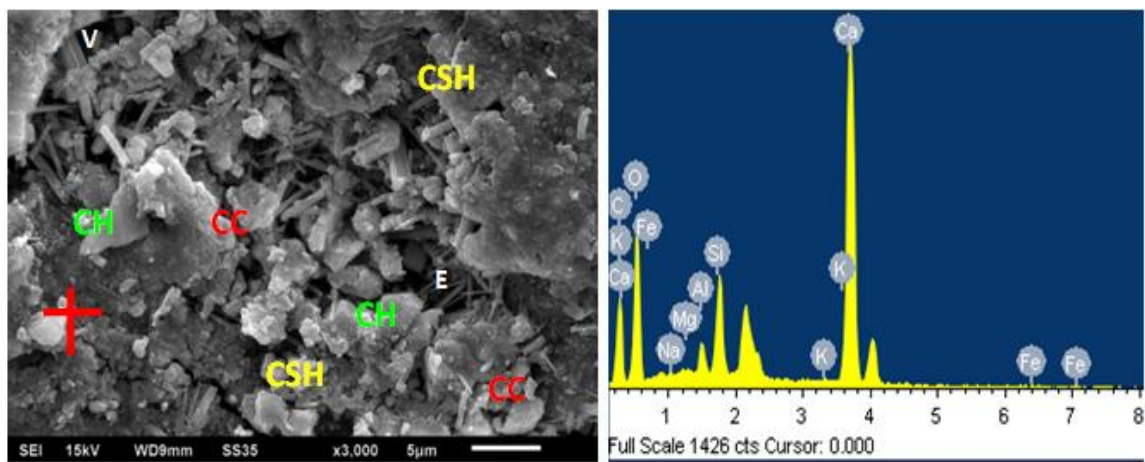
At the age of 28 days, comprehensive amount of hydration products was visible in all curing regimes. The ACC specimens also showed presence of CaCO_3 in the SEM images and EDS plots, indicating the stability of precipitated CaCO_3 till the later ages. The C24 specimens were found to exhibit large voids, which were produced as a result of lower hydration reaction post carbonation, and also higher rate of carbonation tends to disintegrate the C-S-H produced from hydration into weaker silica gel. The EDS analysis of C12 specimens also showed significant peaks of Ca, Si and C, whereas C24 specimens exhibit diminished peaks of Si, indicating insufficient hydration in C24 specimens. At the age of 28 days, C/Ca ratio of the mixes was 0.16, 0.51, 0.56 and 0.7 for WC, C6, C12 and C24 specimens respectively. On the other

hand, Si/Ca ratio was 0.57, 0.55, 0.58 and 0.42 for WC, C6, C12 and C24 specimens respectively. The lowest Si/Ca ratio in the C24 specimens further confirms lack of sufficient hydration in the C24 specimens post ACC.

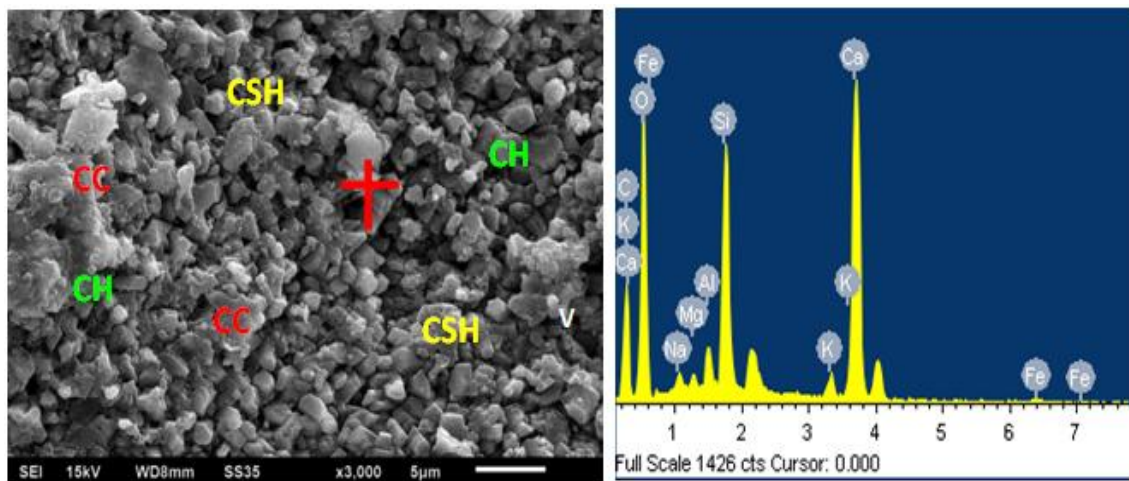
The SEM images were further analyzed using 2-D image analysis software to find surface porosity of the images, and hence of the mixes. The pictures obtained in the software are shown in Fig. 5.19, while the values of porosity obtained are shown in Fig. 5.20. It is observed that lowest values of porosity was exhibited by C24 specimens, followed by C12 specimens and highest value of porosity was seen for WC specimens at the early testing age. C24 specimens have exhibited approximately 36% lesser surface porosity as compared to the WC specimens. The lower values of porosity are attributed to the precipitation of CaCO_3 in pores of concrete, which led to reduction in the void content and provided impermeability to the mix. 2D image analysis at the age of 3 days also showed minimum value of surface porosity for C12 specimens and maximum value for WC specimens. The sufficient hydration in C24 specimens along with presence of carbonation products helped in achieving lower values of surface porosity in C12 specimens. The results of 2D image analysis at the age of 28 days showed the highest porosity values for C24 concrete, which was also observed in the permeation tests. The lowest values of surface porosity were observed for C12 mixes. The C6 specimens and WC specimens indicated the similar levels of porosity at the age of 28 days. While the process of hydration till 28 days of casting produced a dense microstructure in WC concrete, the combined presence of hydration and carbonation products added to the densification of mix in C12 and C6 concrete.



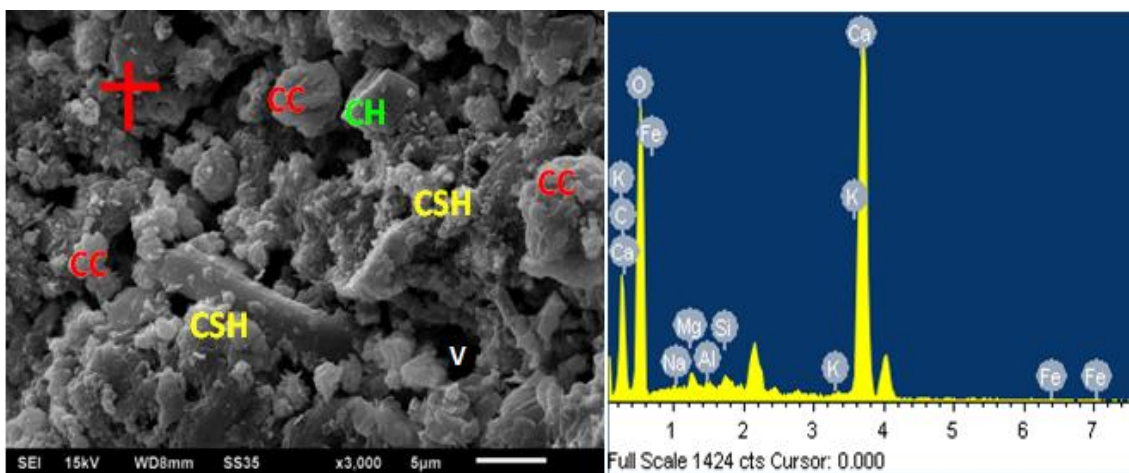
(a) WC specimen



(b) C6 specimen

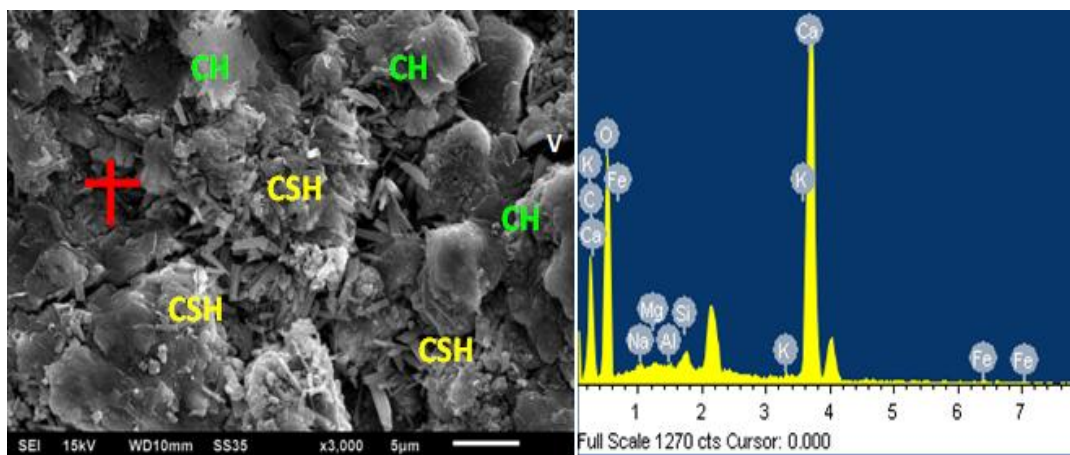


(c) C12 specimen

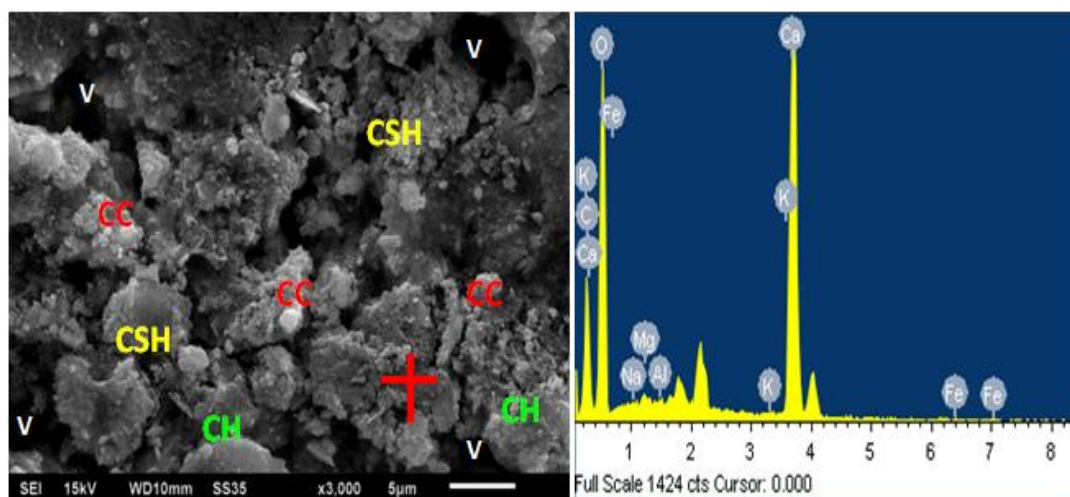


(d) C24 specimen

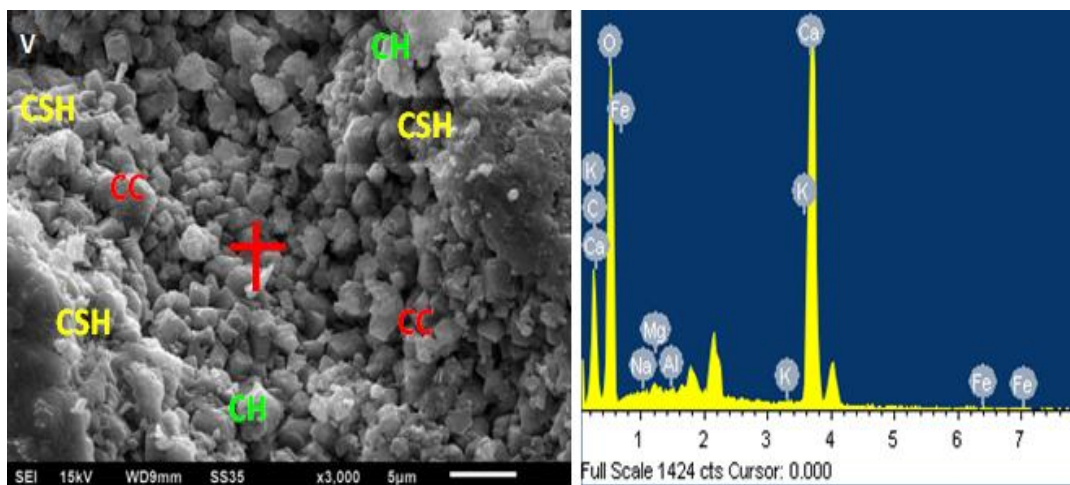
Fig. 5.16: SEM-EDS analysis for different curing regimes just after carbonation



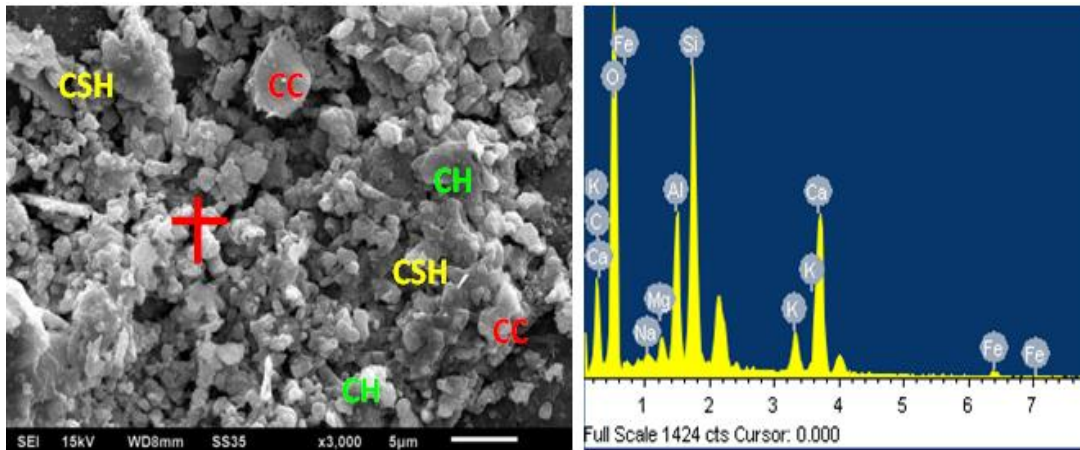
(a)WC specimen



(b) C6 specimen

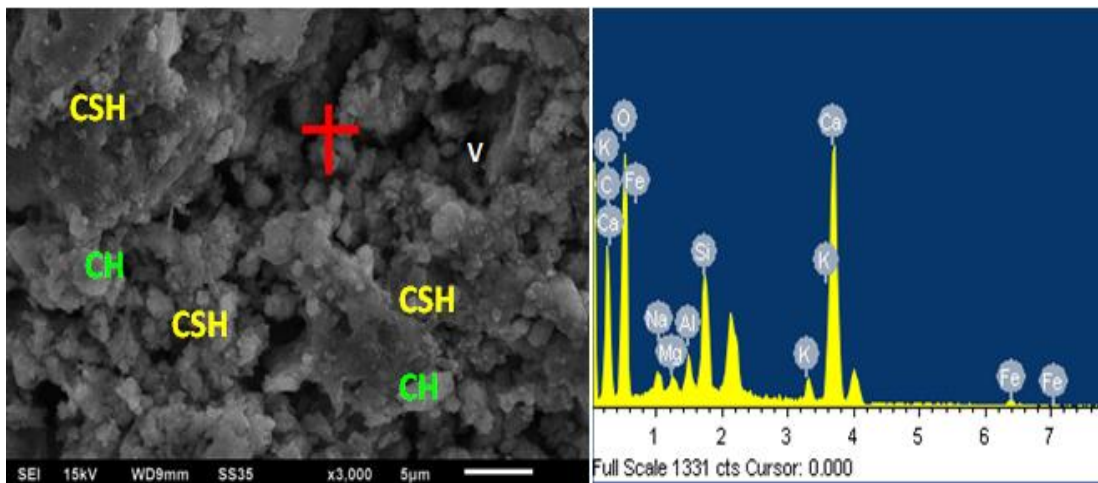


(c) C12 specimen

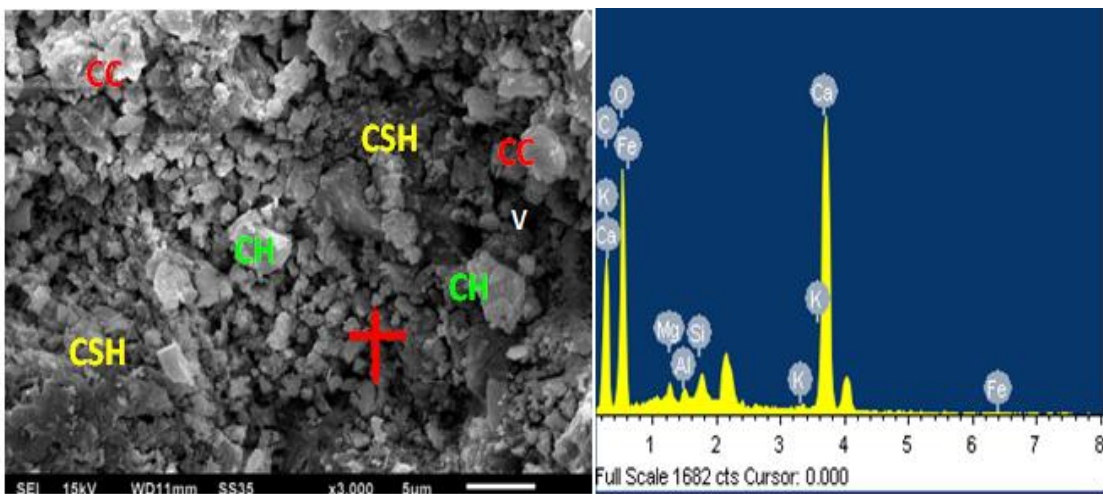


(d) C24 specimen

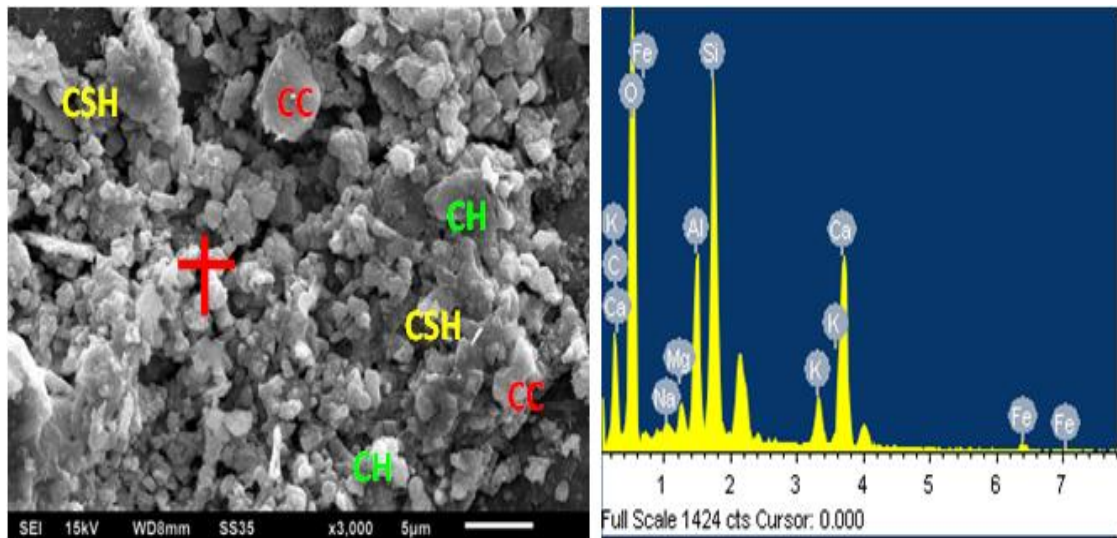
Fig. 5.17: SEM-EDS analysis for different curing regimes at the age of 3 days



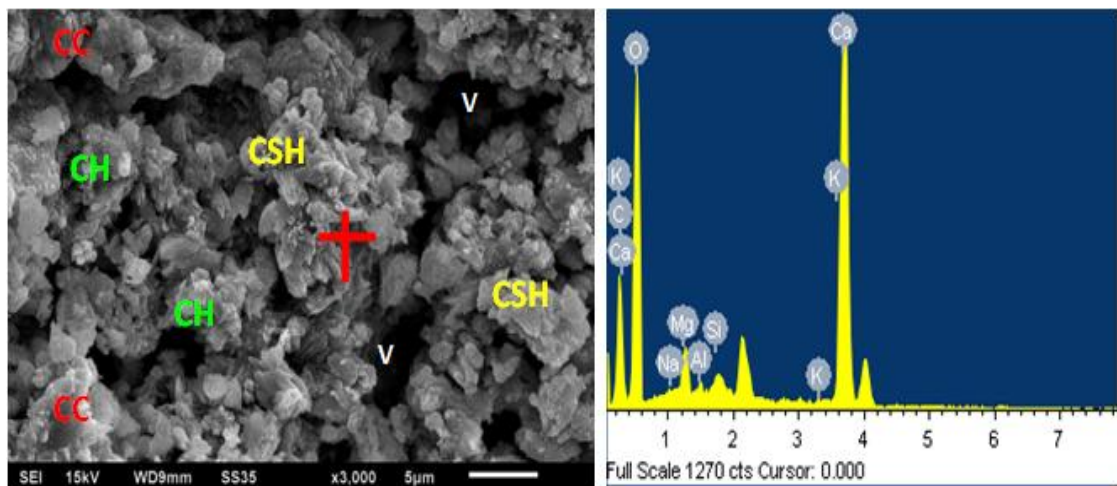
(a)WC specimen



(b) C6 specimen

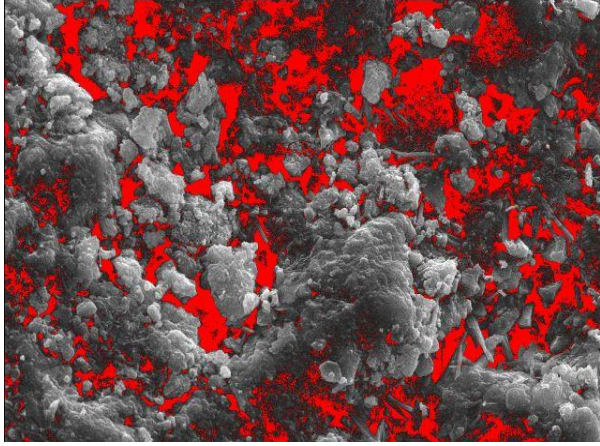


(c) C12 specimen

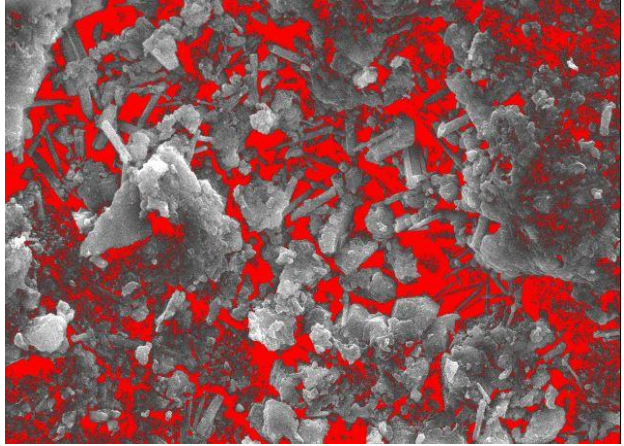


(d)C24 specimen

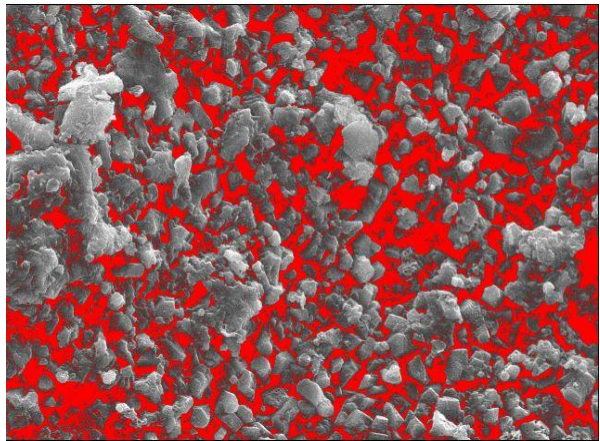
Fig. 5.18: SEM-EDS analysis for different curing regimes at the age of 28 days



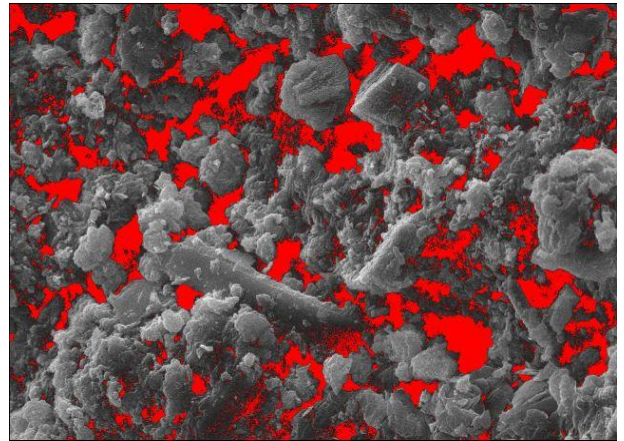
WC



C6

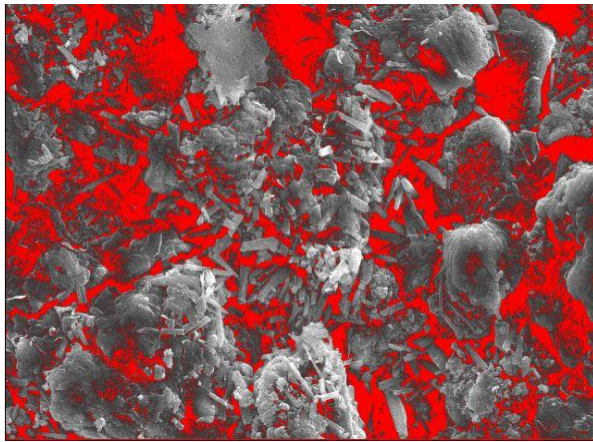


C12

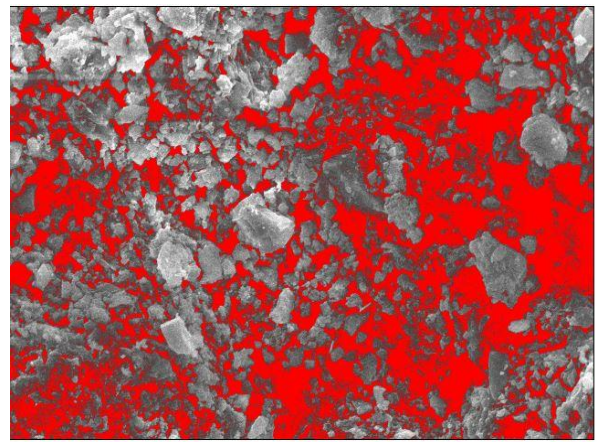


C24

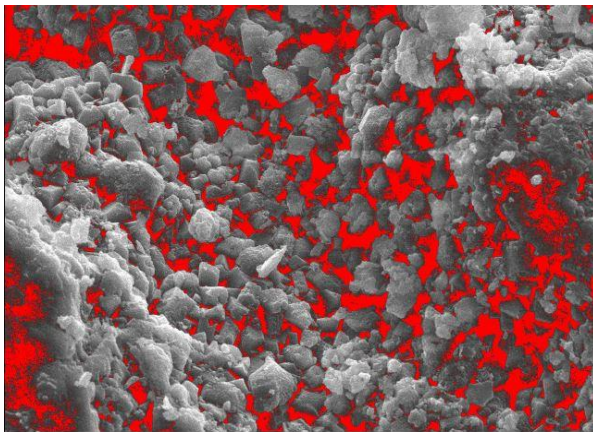
Fig. 5.19(a): 2D image analysis of SEM images just after end of carbonation stage



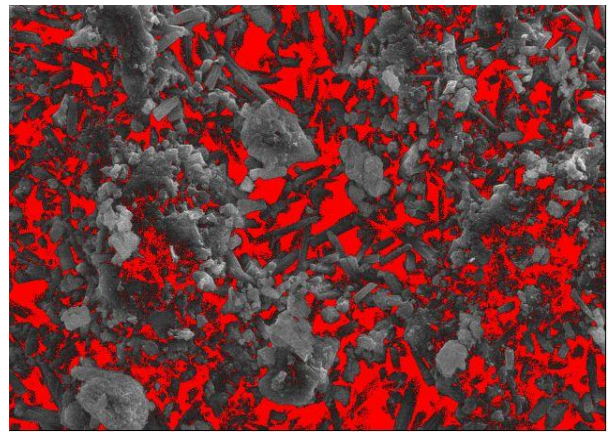
WC



C6

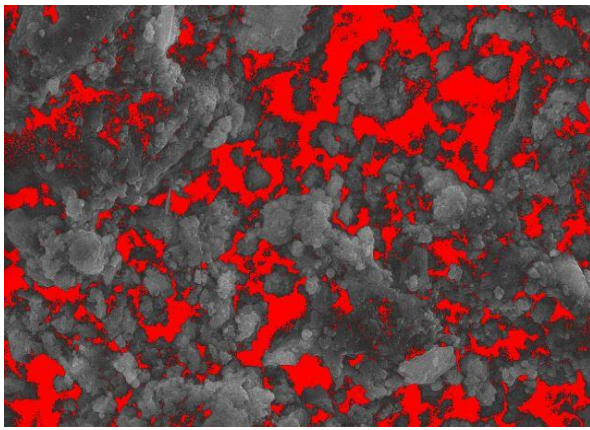


C12

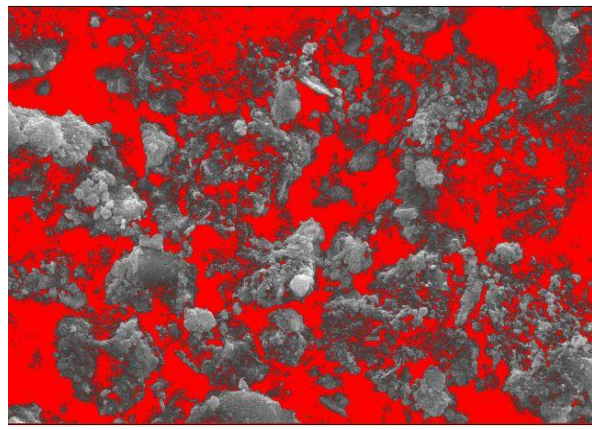


C24

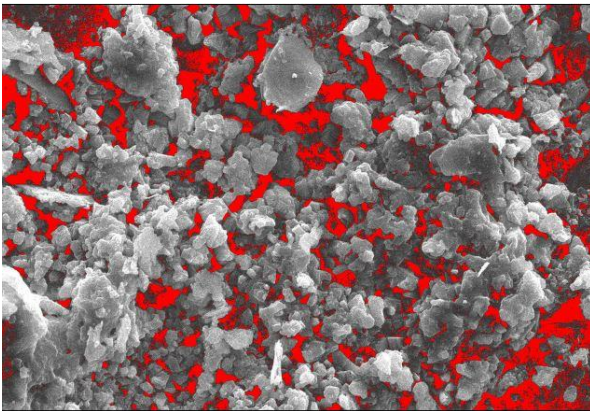
Fig. 5.19 (b): 2D image analysis of SEM images at the age of 3 days



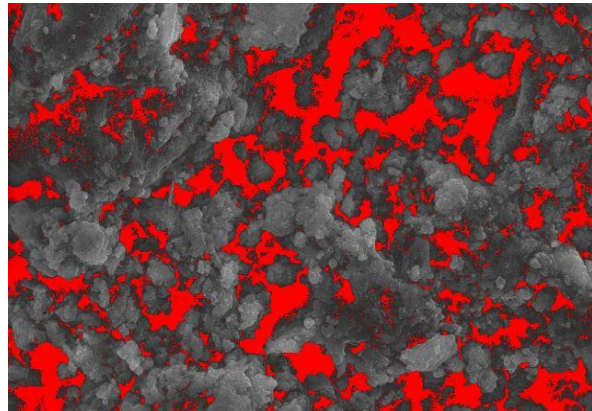
WC



C6



C12



C24

Fig.5.19 (c): 2D image analysis of SEM images at the age of 28 days

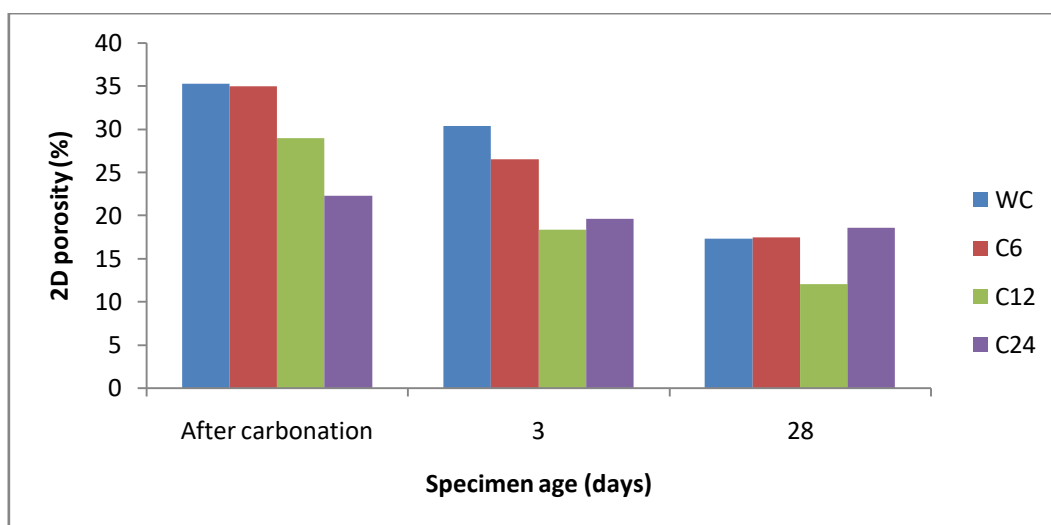


Fig. 5.20: 2D porosity of specimens subjected to different curing regimes

5.5.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of specimens subjected to different curing regimes was done primarily to understand the extent of carbonation that has occurred in different mixes upon subjecting them to ACC of varied durations. For TGA, the specimens were obtained immediately at the end of carbonation stage in ACC specimens (i.e. 26 hours for C6, 32 hours for C12 and 44 hours for C24 mixes); while the representative sample was collected at the age of 26 hours of casting for water cured specimens. To conduct the test, the obtained powdered specimens were heated up to 800°C and the mass loss at regular intervals was measured. The mass loss in a specific temperature range can be correlated to a particular compound formed during curing process. Typically, the TGA plots can be divided into three temperature zones. The mass loss in 100°C - 400°C zone corresponds to the loss of water due to early dehydration of C-S-H. The mass loss in 400°C - 460°C zone is related to the dehydration of lime and gives a quantitative estimate of Ca(OH)₂. The mass loss in 600°C - 800°C corresponds to disintegration of CaCO₃ and estimates the amount of CaCO₃ present in the sample. Some mass loss is observed in the range of 'below 100°C' which is related to loss of pore water.

The results of TGA-DTG for different curing regimes just at the end of carbonation stage are presented in Fig. 5.21. Further, Ca(OH)₂ and CaCO₃ content was quantified from the TGA plots. The content of Ca(OH)₂, CaCO₃ and C-S-H was calculated as per the equations 5.7, 5.8 and 5.9 respectively and Fig. 5.22 is indicative of the C-S-H, Ca(OH)₂ and CaCO₃ contents calculated by using the respective equations for different curing regimes.

$$Ca(OH)_{2,measured} = WL_{Ca(OH)_2} \times \frac{m_{Ca(OH)_2}}{m_{H_2O}} \dots (5.7)$$

$$CaCO_{3,measured} = WL_{CaCO_3} \times \frac{m_{CaCO_3}}{m_{CO_2}} \dots (5.8)$$

$$CSH_{measured} = WL_{CSH} \times \frac{m_{CSH}}{m_{H_2O}} \dots (5.9)$$

where,

$WL_{Ca(OH)_2}$ = Weight loss in the range of 400-460°C

m = molar mass of the compound

WL_{CaCO_3} = Weight loss in the range of 600-800°C

WL_{CSH} = Weight loss in the range of 100-400°C

Comparing the mass losses in TGA plots in the range of 100°C - 400°C for different mixes, it can be seen that the maximum mass loss was observed in C6 and C12 specimens and lowest mass loss was seen in WC specimens. The mass loss in this range corresponds to the loss of water due to dehydration of C-S-H gel. Therefore, higher mass loss in this range indicates higher amount of C-S-H gel in that mix. The values clearly demonstrates formation of higher content of C-S-H gel in C6 and C12 specimens as compared to WC specimens during the initial stages of curing, which also correlates well to the better strength observed in ACC specimens at early age.

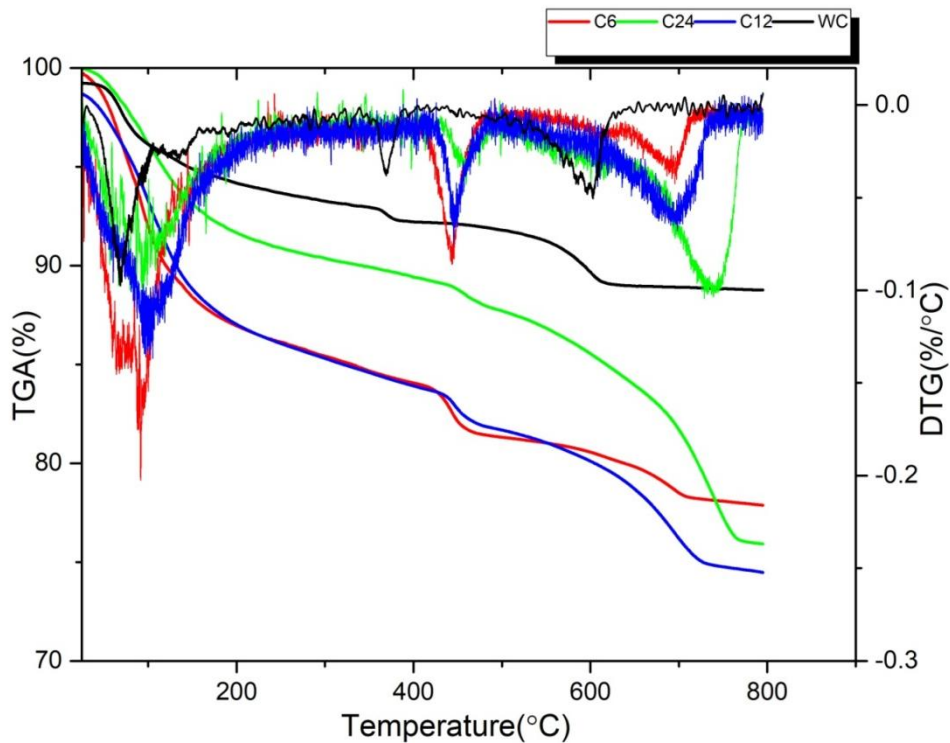


Fig. 5.21: TGA-DTG analysis of concrete for different curing regimes

The mass loss in the range of 400°C - 460°C is indicative of presence of $Ca(OH)_2$. The $Ca(OH)_2$ content calculated by using eq. 5.7 for different curing regimes is depicted in the Fig. 5.22. It can be seen that the maximum content of $Ca(OH)_2$ was achieved for water cured specimens, owing to the hydration reactions which led to production of $Ca(OH)_2$. On the other hand, in the carbonation cured specimens, the reaction of

Ca(OH)_2 with CO_2 led to a reduction in content of Ca(OH)_2 which is also observed from the TGA graphs. The lowest content of Ca(OH)_2 in C24 specimens is indicative of intensive carbonation with an increase in the duration of carbonation.

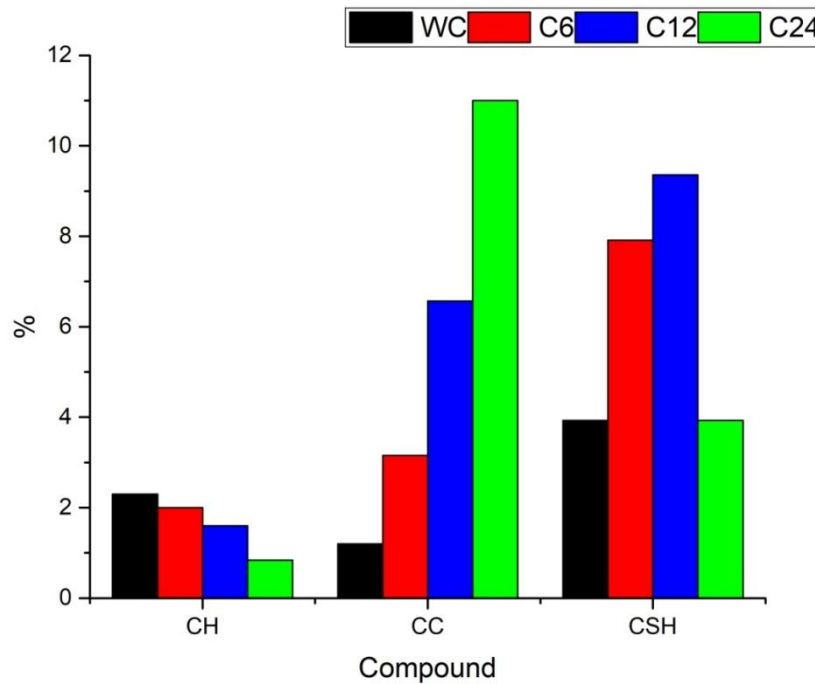


Fig. 5.22: Content of Calcium Hydroxide, Calcium Carbonate and C-S-H calculated from TGA

The range of 600°C - 800°C is indicative of calcium carbonate content in the mix. Carbonation cured specimens show considerable content of CaCO_3 in the mix, while the water cured specimens show negligible amount of CaCO_3 . In this range, maximum weight loss among the carbonation cured specimens was observed in the C24 specimens, which showed the highest content of CaCO_3 in the C24 specimens, in turn indicative of the maximum intensity of carbonation. DTG graphs also show formation of CaCO_3 in the carbonation cured mixes, where large peaks are observed in the temperature range of 600 - 800°C . The drop in DTG peaks was also observed to be highest for the C24 specimens. Also, C12 specimens showed higher content of CaCO_3 than C6 specimens as seen in Fig. 5.22. This indicates a directly proportional relationship between the duration of carbonation in ACC and the extent of carbonation reaction in the mix.

On comparing the content of C-S-H and CaCO₃ from the TGA graphs, it can be observed that the major carbonation product in the C24 specimens resulting from CO₂ uptake is CaCO₃ and the C-S-H content is reduced as compared to other ACC regimes. This indicates that the CO₂ in higher carbonation durations, not only reacts with the unhydrated cement constituents (C₃S, C₂S), but also starts the disintegration of C-S-H gel into the weaker silica gel. The disintegration of C-S-H into silica gel weakens the microstructure of concrete and causes loss of strength. This can also be correlated to lesser compressive strength of C24 specimens as observed from the compressive strength tests. Similar observation related to conversion of C-S-H into weak silica gel was also given by Junior et al. (Junior et al., 2015).

5.6 EFFECT OF ACC DURATION ON CO₂ UPTAKE OF CONCRETE

The major objective of carbonation curing is to serve the dual purpose of improving the performance of concrete and to sequester carbon dioxide. The carbon sequestration ability of the ACC procedure can be judged from the potential of concrete to act as carbon sink, which can be assessed on the basis of CO₂ uptake after the carbonation process. The CO₂ uptake was quantified from the results of Thermogravimetric analysis. For this, the data related to the mass of sample in the range of 600°C - 800°C in the TGA plot was utilized. In the present study, this data was collected from the TGA plots given in Fig. 5.21. The CO₂ uptake was then calculated as per Eq. 5.10. The CO₂ uptake value obtained for different durations of carbonation curing durations is shown in Fig. 5.23.

$$CO_2 \text{ uptake (\%)} = \frac{\text{Sample mass at } 600^\circ\text{C} - \text{sample mass at } 800^\circ\text{C}}{\text{cement mass in original sample}} \times 100 \quad \dots (5.10)$$

The results of CO₂ uptake show a directly proportional relationship between the duration of carbonation and the value of CO₂ uptake. The value of CO₂ uptake is directly indicative of the extent of carbonation reaction in the ACC process. The C6 curing regimes exhibited a CO₂ uptake of approximately 14%, C12 specimens showed a CO₂ uptake of 20% and the C24 specimens showed a CO₂ uptake of 24%. Similar observations of increase in CO₂ uptake with the increase in carbonation duration was made by (Ahmad et al., 2017; Junior et al., 2015). Ahmad et al. varied the

carbonation duration from 1 to 10 hours while Junior et al. used two durations of carbonation; 1 hour and 24 hours in his study. It was observed in both the studies that the CO₂ uptake increased with an increase in the duration of carbonation curing.

The highest CO₂ uptake in C24 specimens clearly showed the highest intensity of carbonation reaction in C24 specimens. However, it was also observed from the TGA curves that due to higher CO₂ uptake in longer duration of carbonation curing, CO₂ not only reacts with calcium silicates and Ca(OH)₂, but also with the C-S-H gel produced from hydration, which led to loss of strength in concrete.

The CO₂ uptake capacity can further be correlated to the carbon sequestration potential in a construction industry. Precast panels are widely used these days in construction practices. Let us consider a typical precast panel of size 2.5m x 1m x 0.15m and the panel is cured using an accelerated carbonation curing of 12 hours. Since the carbonation curing is a surface curing procedure and is expected to affect a depth of 5mm, then total CO₂ sequestering area can be considered as 0.01m³. With expected CO₂ uptake of 20% with carbonation curing, each precast panel can be expected to sequester 0.8 Kg of CO₂ during the process of ACC.

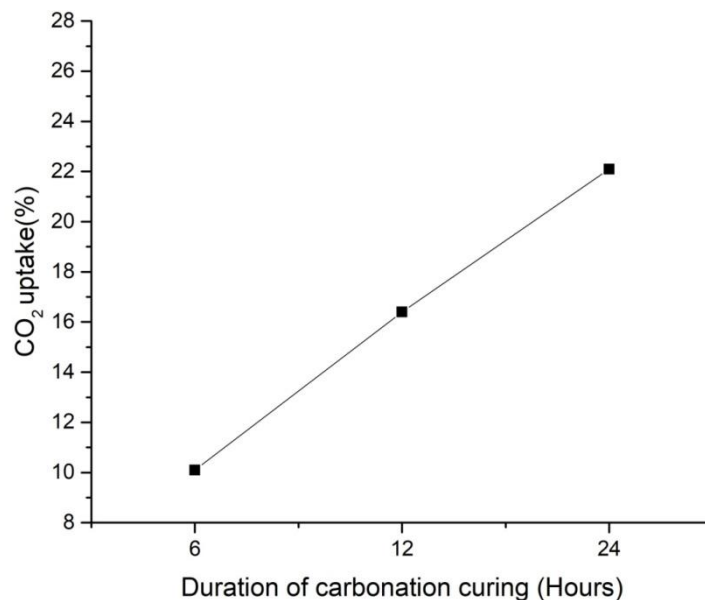


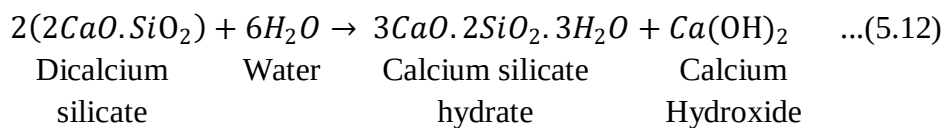
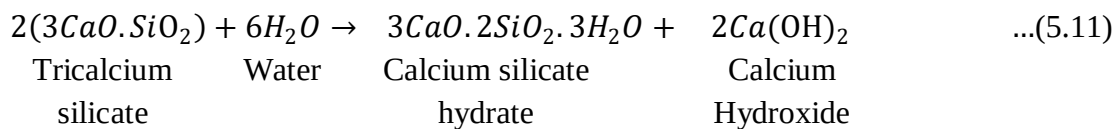
Fig. 5.23: CO₂ uptake from different durations of carbonation curing

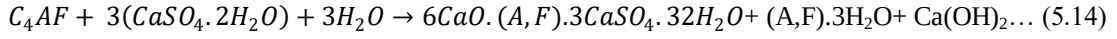
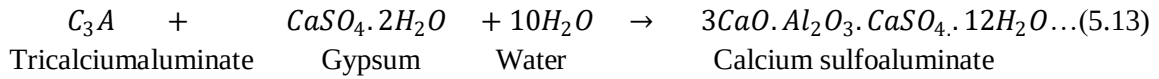
5.7 STOICHIOMETRIC ANALYSIS OF DIFFERENT DURATIONS OF ACC

Carbonation curing is a chemical process which involves reaction of CO₂ with unhydrated cement constituents (majorly C₃S and C₂S) and hydrated cement compounds (C-S-H and Ca(OH)₂). Water curing involves the hydration reaction of cement constituents with water. Since, these chemical reactions are the basis of performance of concrete subjected to different curing regimes, stoichiometric analysis has been done in this section to analyse the net change in phase configurations in these different durations and the result was also compared with stoichiometric analysis of water curing. The stoichiometric analysis was done up to the age of 3 days of casting and the results of stoichiometric analysis have been presented in Fig. 5.24.

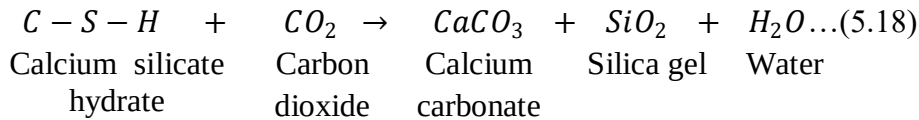
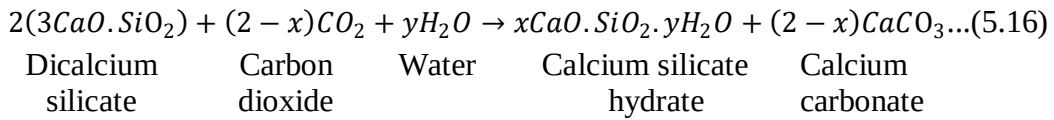
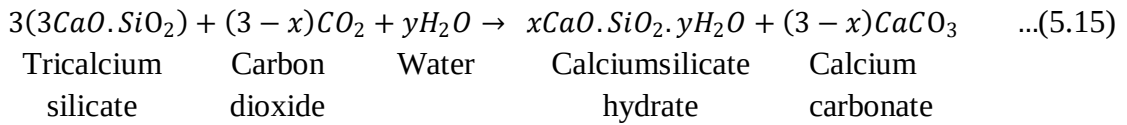
The stoichiometric analysis was done with the help of CO₂ uptake data collected from the TGA graphs and presented in Fig. 5.24 for different duration of carbonation curing; and the reaction mechanism in carbonation and hydration processes. The hydration reactions of cement constituents are depicted in equations 5.11-5.14. It can be seen from the equations that the major compounds formed during hydration reactions of C₂S, C₃S are Ca(OH)₂ and C-S-H gel; whereas hydration of C₃A and C₄AF results in formation of ettringite and calcium sulfoferrite respectively.

For the stoichiometric analysis, ‘C’ amount of cement is considered and the corresponding contents of C₃S, C₂S, C₃A and C₄AF in fractions of ‘C’ are represented in the first block of Fig. 5.24. Initially, all the specimens are allowed to hydrate for 18 hours before the specimens are de-moulded and subjected to specific curing regime. As can be seen from the Fig. 5.24, with progressive hydration, the relative composition of C₃S, C₂S, and C₃A decreased, with the corresponding increase in quantities of Ca(OH)₂ and C-S-H as seen in block 2 of Fig. 5.24.





The analysis for carbonation curing regimes was further carried out using the chemical equations shown in Fig. 5.15-5.18 and values of CO₂ uptake calculated in different duration of carbonation curing with TGA.



The stoichiometric analysis of three durations of ACC clearly indicated formation of highest amount of C-S-H gel at the end of 3 days in the C12 specimens along with considerable formation of CaCO₃. C12 specimens showed 0.39C and 0.225C fractions of C-S-H and CaCO₃ respectively as compared to 0.29C content of C-S-H in the WC specimens. In the C24 specimens, C-S-H gel formation (0.30C) was observed with highest content of CaCO₃ (0.27C) which correlates well with the observation of XRD and SEM-EDS analysis. The combined presence of C-S-H and CaCO₃ observed in different durations of ACC results in production of a dense microstructure and also correlates well with better compressive strength and lower porosity in the C12 and C24 specimens at the age of 3 days. Similar results of better performance of concrete due to amalgamated microstructure composed of both the hydration and carbonation products has been reported by various researchers (Liu et al., 2016; Pan et al., 2019).

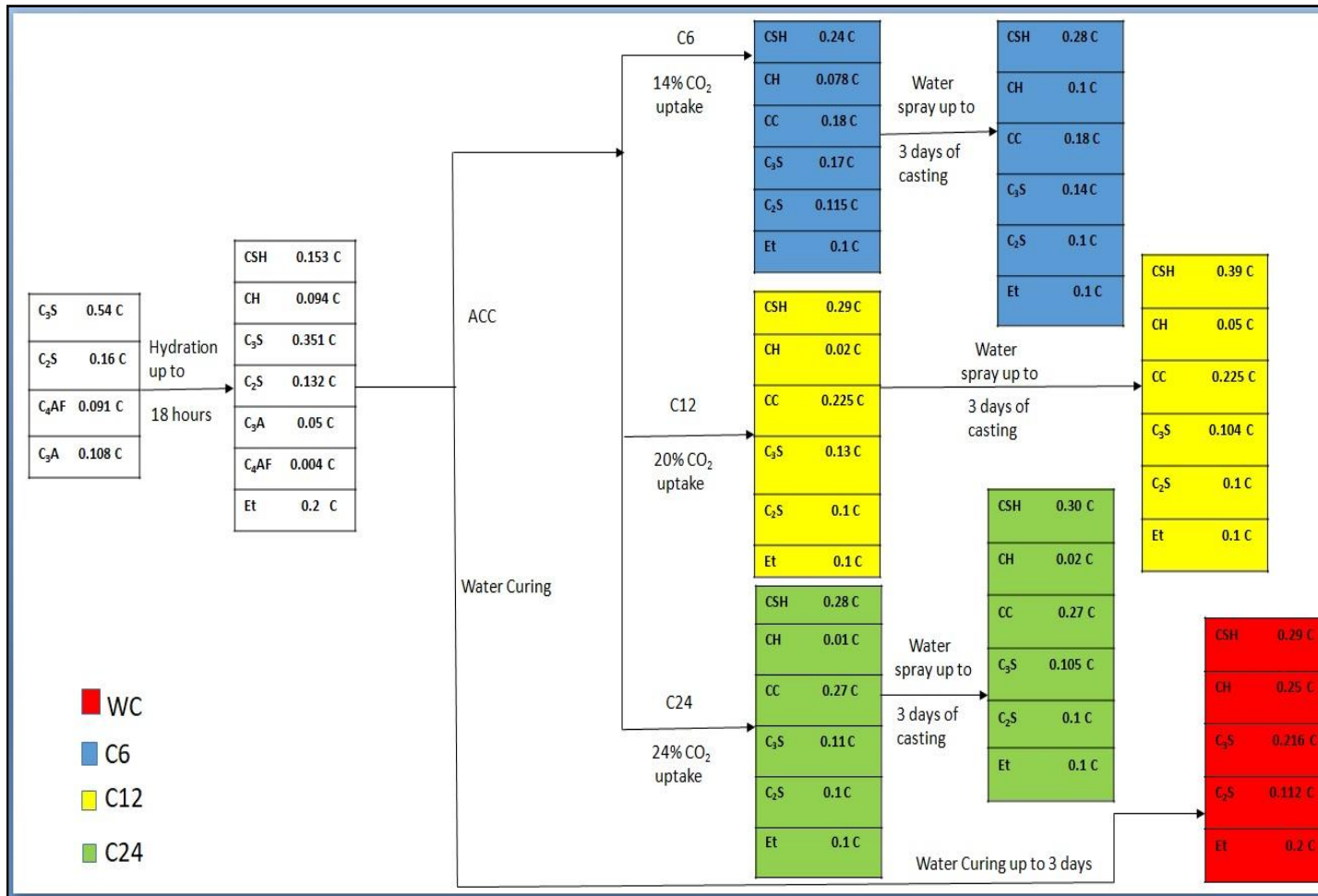


Fig. 5.24: Stoichiometric analysis of different durations of carbonation curing

5.8 STATISTICAL ANALYSIS OF EFFECT OF ACC DURATION ON PROPERTIES OF CONCRETE

From the experimental results in the present study, it is clear that the extent of carbonation curing affects the mechanical properties of the mixes. To determine the significance of carbonation curing in predicting bulk properties (compressive strength and split tensile strength) and surface property (abrasion resistance) of concrete, statistical analysis of variance (ANOVA) was performed by using SPSS software. The results are presented in the following sections.

5.8.1 Analysis of Variance

Statistical analysis of effect of carbonation curing duration on properties of concrete was performed using Analysis of Variance (ANOVA) using software SPSS statistics tool. ANOVA was performed on results obtained for compressive strength, abrasion resistance and split tensile strength. A level of significance of 0.05 was considered for the analysis. The results of ANOVA for compressive strength, abrasion resistance and split tensile strength are presented in Tables 5.4, 5.5 and 5.6 respectively.

In the data obtained, p-value represents significance level of each variable; variables having p-value lower than 0.05 have significant effect on the said property at 95% confidence level (Videla and Aguilar, 2006). The p-value for all the three characteristics was observed to be less than 0.5, which provides an evidence to reject the null hypothesis and to further infer that means vary significantly. This indicated that the duration of carbonation curing was an important parameter that significantly affects the characteristics of concrete. When the ANOVA was performed for different durations of carbonation curing, it was observed that the change in duration of ACC significantly affected both the compressive strength and abrasion resistance. This indicated a comprehensive effect of ACC duration on the surface concrete as well as on bulk concrete.

Table 5.4: Analysis of variance for compressive strength

Parameter		Sum of Squares	df	Mean Square	F	p-value	Significance (Significant if $p < 0.05$)
ANOVA for Compressive strength	Between groups	106.28	3	35.35	15.48	0.001	Significant
	Within groups	18.28	8	2.28			
	Total	124.24	11				

Table 5.5: Analysis of variance for abrasion resistance

Parameter		Sum of Squares	df	Mean Square	F	p-value	Significance (Significant if $p < 0.05$)
ANOVA for abrasion resistance	Between groups	2.03	3	0.68	28.93	0.001	Significant
	Within groups	0.19	8	0.02			
	Total	2.21	11				

Table 5.6: Analysis of variance for split tensile strength

Parameter		Sum of Squares	df	Mean Square	F	p-value	Significance (Significant if $p < 0.05$)
ANOVA for split tensile strength	Between groups	0.66	3	0.22	4.13	0.048	Significant
	Within groups	0.43	8	0.05			
	Total	1.09	11				

5.8.2 Relationship between Abrasion Resistance and Compressive Strength

As observed from the ANOVA results for compressive strength and abrasion resistance, it can be seen that both these parameters vary significantly with change in duration of carbonation in the ACC process. Also, the level of significance is also observed to be same for both these parameters. Therefore, a mathematical relationship can be developed between the abrasion resistance and compressive strength for the

carbonation cured concrete. An attempt has been made to develop a regression equation correlating compressive strength and depth of wear carbonation cured concrete as shown in Fig. 5.25. The correlation equation developed from Fig. 5.25 is as shown in Eq. 5.19:

$$D_w = 4.316e^{-0.02(CS)} \quad \dots (5.19)$$

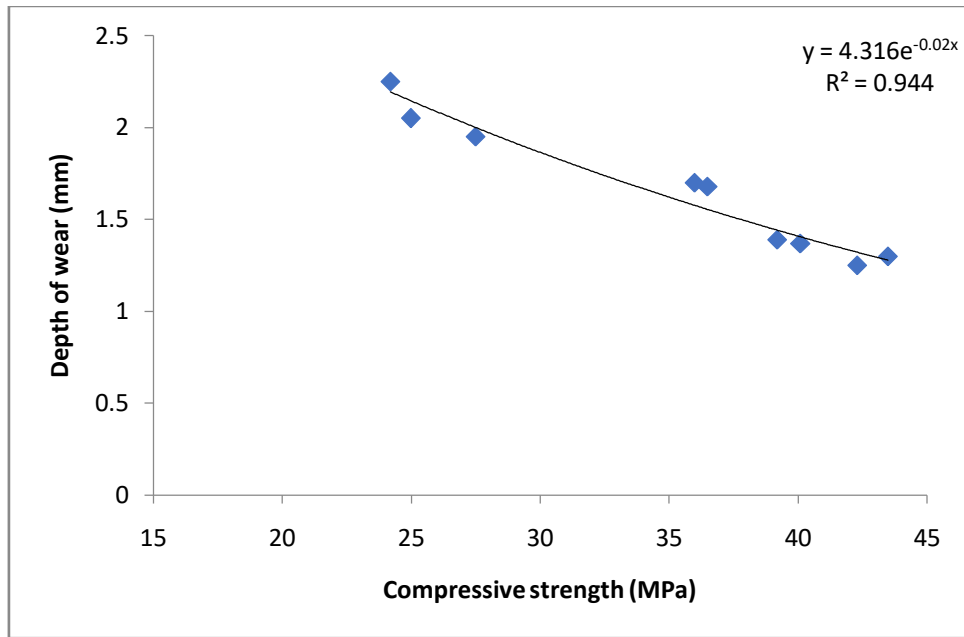


Fig. 5.25: Relationship between depth of wear and compressive strength for carbonation cured specimens

The predicted values of depth of wear based upon the above relationship shown in Eq.5.19 was calculated and plotted against the experimental values in Fig. 5.26. It can be clearly observed that the predicted values are in good agreement with the experimental values and all the points lie within the 95% confidence interval.

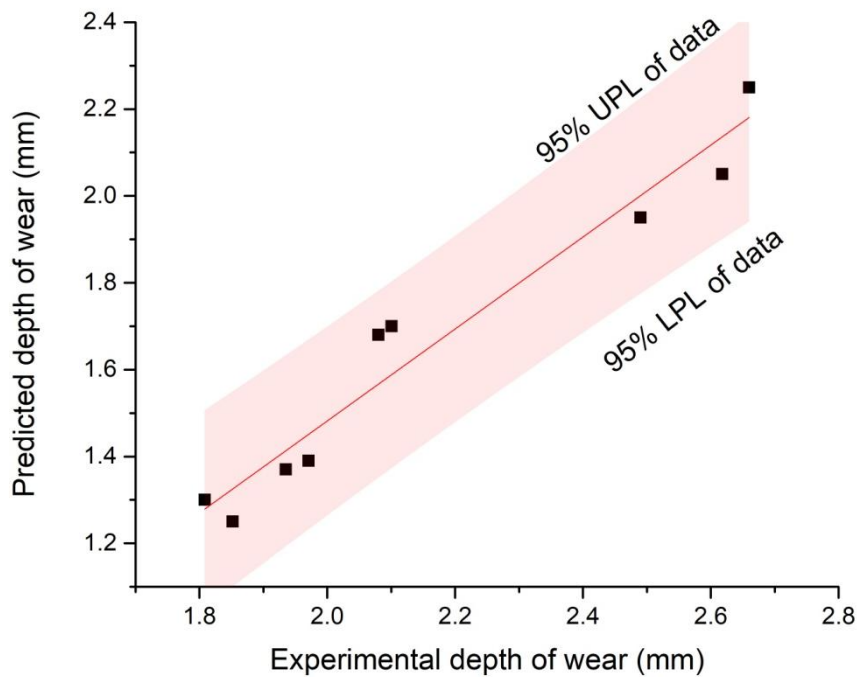


Fig. 5.26: Comparison between observed and predicted depth of wear using developed relationship

5.9 EFFECT OF ACC DURATION ON LONG TERM PERFORMANCE OF CONCRETE

The long term performance of concrete subjected to different durations of carbonation curing was assessed in terms of two major parameters. Firstly, drying shrinkage of carbonation cured concrete was studied. Secondly, the effect of carbonation curing on resistance to weathering carbonation was assessed and the results were also compared with water cured concrete. The test results are resented in the following sections:

5.9.1 Effect of ACC Duration on Drying Shrinkage of Concrete

Drying shrinkage of concrete was measured in terms of unrestrained shrinkage as per the guidelines of ASTM C 157-2017 (ASTM C157, 2017). For this, the specimens were cured for a period of 28 days; i.e. continuous water curing was adopted for WC specimens while a curing in plastic bags after carbonation curing for requisite duration followed by water spray for three days was adopted for carbonation cured specimens. After the initial curing period, all the specimens were subjected to air drying for a period of 9 months in the laboratory environment, with relative humidity between 60 – 80%. The length comparator readings were taken at several intervals

during the drying period, which were used to calculate drying shrinkage strain as per ASTM C157-2017 (ASTM C157, 2017). During the first month of drying, the shrinkage strain was measured at 4, 7, 10, 14, 21 and 28 days of drying. In the subsequent months, as shrinkage slowed down, drying shrinkage readings were taken at 15 days interval and the specimens were monitored up to the drying period of 270 days. The value of shrinkage strain at the drying age of 270 days was referred as ultimate shrinkage strain.

The results of drying shrinkage test have been presented in Fig. 5.27. It can be seen from the figure that ultimate shrinkage strain at the drying age of 270 day was maximum for WC specimens and the lowest ultimate shrinkage strain was observed for concrete carbonation cured for 24 hours. At 270 days of drying, the drying shrinkage strain observed for water cured concrete was $370 \mu\text{ mm/mm}$. The corresponding values for accelerated carbonation cured concrete were 358, 346 and $332 \mu\text{ mm/mm}$ respectively for C6, C12 and C24 mixes. It clearly indicated that water cured concrete had 11 % higher shrinkage than C24 mixes. It clearly indicated that carbonation curing helped in restricting the shrinkage values, which would help in reducing the shrinkage cracks.

It is pertinent to mention that initial drying shrinkage strain was similar for all the carbonation curing regimes up to a drying age of 28 days. However, the initial drying shrinkage strain was higher for water cured specimens as compared to carbonation cured specimens. This can be attributed to initial water loss from the surface of prismatic specimens. The drying shrinkage values for different curing regimes vary significantly as the drying age was increased. At the later age, significant decrease in drying shrinkage was observed in ACC specimens as compared to WC specimens. This can be attributed to two factors. First, the densified microstructure of ACC specimens prevented the water loss from concrete, leading to a decreased value of drying shrinkage strain. Secondly, the major product present in WC concrete after curing is C-S-H gel. C-S-H is a porous product with high specific surface area and therefore was responsible for higher loss of water during drying processes (Shi et al., 2012c). Hence, WC concrete exhibited higher shrinkage of hardened concrete. On the other hand, the major product in ACC specimens along with C-S-H is CaCO_3 , which

is a well crystallized product and possesses excellent dimensional stability. Therefore, the carbonation cured specimens exhibited lesser drying shrinkage as compared to the WC specimens.

On comparing the effect of ACC duration on the shrinkage behaviour of concrete, it was observed that the drying shrinkage of concrete decreased as the duration of ACC was increased. The lower drying shrinkage for higher durations of ACC can be attributed to two major factors. First factor being the presence of CaCO_3 as the major reaction product in ACC specimens and the content of CaCO_3 being greater for higher durations of ACC. CaCO_3 unlike C-S-H gel, did not favour release of water from the surface during the drying process. The second factor being the early age loss of water from the ACC specimens during the initial exothermic carbonation reactions. The loss of water is found to be directly proportional to the extent of carbonation reaction (Rostami et al., 2012a). Therefore, the higher water loss during the initial curing in C12 and C24 specimens also resulted in lesser drying shrinkage in these specimens at later stage.

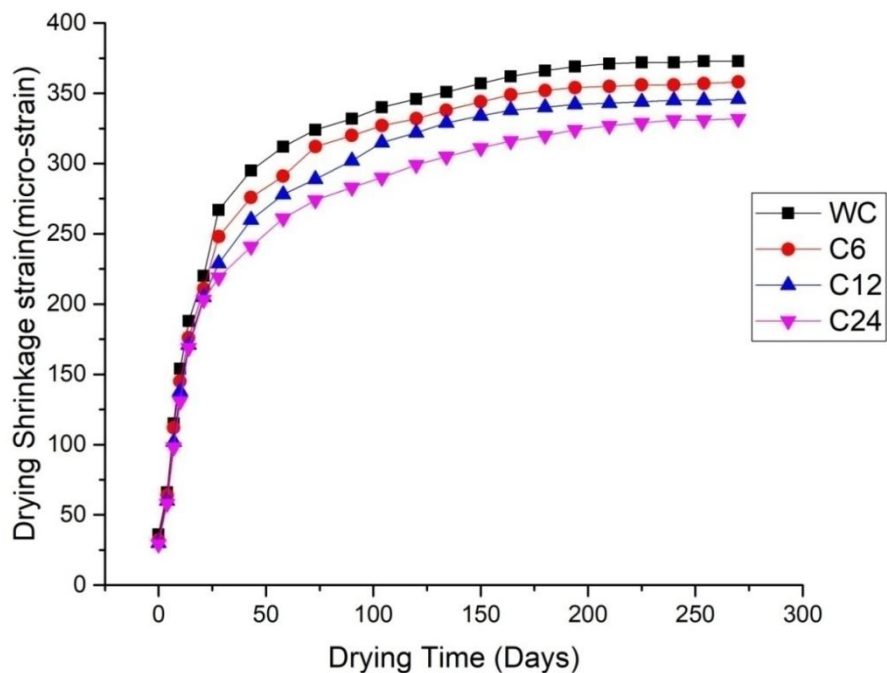


Fig 5.27: Effect of different curing regimes on drying shrinkage of concrete

5.9.2 Effect of ACC Duration on Resistance to Weathering Carbonation

Weathering carbonation is the phenomenon of reaction of concrete to the atmospheric CO_2 over the span of many years. In the presence of sufficient moisture, CO_2 forms carbonic acid that reacts with Ca(OH)_2 to form CaCO_3 , which causes the reduction of pH (Neville and Brooks, 2010). The chemical reactions involved in this process have been shown in Eq. 5.5 and 5.6. Lowering of the pH of pore solution (from 13.5 to nearly 8) breaks down the protective passive layer that protects the rebar from corrosion. As ACC is also a carbonation induced process, it becomes necessary to evaluate the performance of concrete against the adverse environment of weathering carbonation, as ACC is suspected to increase the vulnerability of concrete to carbonation induced corrosion.

In the present study, the performance of concrete against weathering carbonation was assessed using carbonation depth test and measuring corrosion current density using Linear Polarization Resistance test. The specimens after completion of the specific curing regime at the age of 28 days of casting were subjected to 5% CO_2 exposure over a period of 360 days. The testing was initiated at an interval of 30 days from the initial exposure till 360 days of exposure. The test results are presented in the following sections:

5.9.2.1 Carbonation Depth

Carbonation depth was measured on the monthly basis using phenolphthalein indicator method. For this, concrete cubes were cast and were exposed to 5% CO_2 in the environment chamber after the specific curing regime of 28 days. In order to ensure unidirectional flow of CO_2 gas, only one surface was subjected to exposure, while the other five surfaces were sealed with epoxy. At the testing age, the specimens were taken out of the carbonation chamber and were split vertically into two halves along the exposed surface. Immediately after splitting, the exposed surface was cleaned and sprayed with Phenolphthalein indicator. The indicator used was a phenolphthalein 1% ethanol solution with 1g phenolphthalein and 90 ml 95.0 V/V% ethanol diluted in water to 100 ml (Fukushima et al., 1998). Phenolphthalein indicator gives purple-red colour for un-carbonated part; while in carbonated part, no coloration

occurred(Hussain and Ishida, 2009; Talakokula et al., 2016). The depth of colourless region was measured from five points on each split surface using a vernier caliper with least count on 0.02 mm. The average depth so obtained is taken as the representative carbonation depth of the specimen.

The results of carbonation depth test are presented in Fig. 5.28. The carbonation depth obtained at early ages of exposure i.e.30 days and 60 showed the lowest value of carbonation depth for C6; while the highest value of the carbonation depth was observed for C24 specimens.

The higher value of carbonation depth of C24 specimens at the initial ages of exposure can be attributed to the higher intensity of carbonation in these specimens in the initial carbonation reactions during ACC. Also, the C24 specimens suffered due to insufficient hydration reaction after the carbonation stage of ACC. Because of insufficient hydration reaction, large amount of cement compounds (i.e. calcium silicates) remained unreacted and were, therefore, available for reaction with CO_2 at the later stage during weathering carbonation. Therefore, higher value of carbonation depth was observed for C24 specimens at early ages of exposure.

The lower value of carbonation depth in the C6 and C12 specimens can be attributed to densification of microstructure in the near surface of concrete owing to the precipitation of CaCO_3 in the pores of concrete and presence of CSH- CaCO_3 amalgamated microstructure in the near surface that acted as a barrier to the infiltration of CO_2 in concrete. The decreased permeation of CO_2 in concrete resulted in a lower rate of carbonation reaction in the concrete and hence, exhibiting the lower values of carbonation depth in C12 and C6 specimens. The lower value of the carbonation depth in the carbonation cured specimens can also be understood due to lesser availability of Ca(OH)_2 that is the major reactant in the carbonation reaction. Ca(OH)_2 content is considerably reduced in carbonation cured specimens due to reaction with CO_2 in early age carbonation, which has also been observed from the TGA results.

As the age of exposure increases from 60 days to 90 days, a sharp increase is observed in the carbonation depth for all the curing regimes. This can be attributed to

the CO₂ gas crossing the barrier of near surface concrete up to approximate depth of 5mm from the surface of concrete. The near surface concrete provides the initial resistance to penetration of CO₂ inside the concrete. Therefore, after crossing the threshold of 5mm in this test, a considerable increase in the carbonation depth was observed in all the curing regimes.

The value of carbonation depth progressed for all the specimens as the age of CO₂ exposure increases. At the later ages up to the age of 360 days, the maximum value of carbonation depth was observed for the WC specimens and the C24 specimens. This is in coherence with the results of permeation tests also, wherein the maximum porosity was observed for the WC and C24 specimens. The lesser rate of hydration in C24 specimens led to lower production of C-S-H gel in the mix, which made the mix porous. Secondly, a higher intensity of carbonation resulted in disintegration of produced C-S-H into weaker silica gel leading to opening up of pores in the concrete. This facilitated easy penetration of CO₂ in concrete resulting in the higher carbonation depth in C24 specimens. WC specimens also exhibited higher carbonation depth than the C12 and C6 specimens. The considerable production of both the hydration and carbonation products in the C12 and C6 specimens was found to increase their resistance against the deteriorating environmental agents.

It has been reported in the previous studies(Sisomphon and Franke, 2007) that for concrete subjected to conventional water curing, the rate of carbonation reduced with increase in time period of exposure. A typical relationship between carbonation depth and exposure time for the water cured concrete is depicted in Eq. 5.20.

$$X_c = k\sqrt{t} \dots (5.20)$$

where,

X_c = measured carbonation depth (mm)

t = exposure time (days)

k = carbonation coefficient obtained from the regression analysis

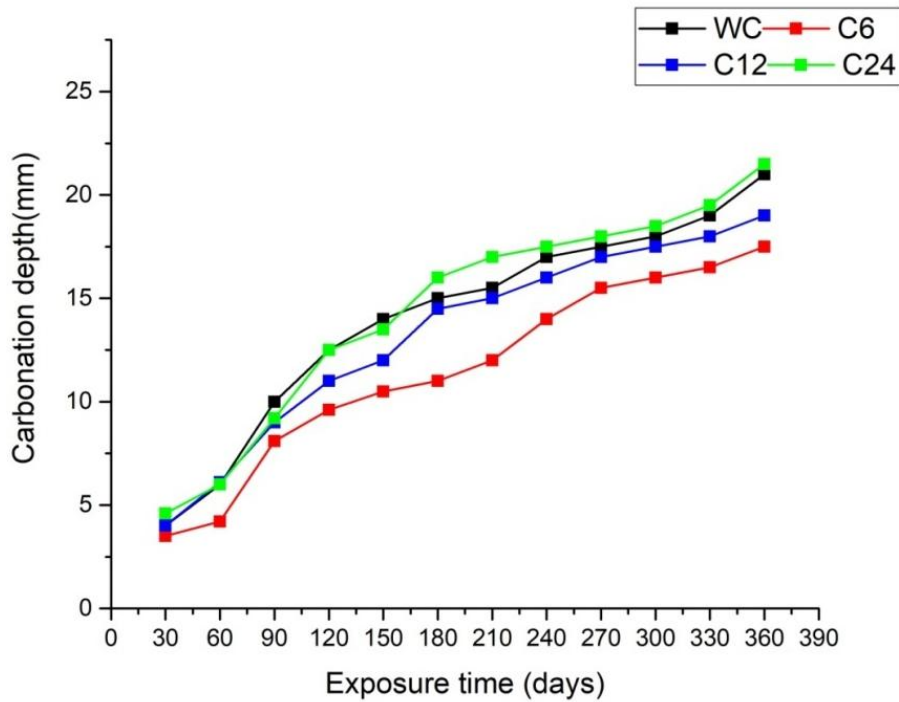


Fig 5.28: Carbonation depth test at different ages of exposure

To investigate that if similar kind of relationship exists in the case of carbonation cured concrete, a graph between the carbonation depth and square root of exposure duration was plotted for all curing regimes, which is presented in Fig. 5.29. The figure confirms that carbonation depth is directly proportional to the square root of exposure duration for accelerated carbonation cured concrete as well. A very high correlation coefficient further strengthens the efficacy of the established relationship. The carbonation coefficient was therefore obtained for all the mixes, and the values are presented in Table 5.7.

Table 5.7: Parameters of the fitted curves with change in curing regime

Type of specimen	Carbonation coefficient (K)	Standard error	R ²	Change in 'K' (%)
WC	1.320	0.851	0.979	-
C6	1.182	0.905	0.971	-10.4%
C12	1.211	0.526	0.990	-8.2%
C24	1.408	0.848	0.982	+6.6%

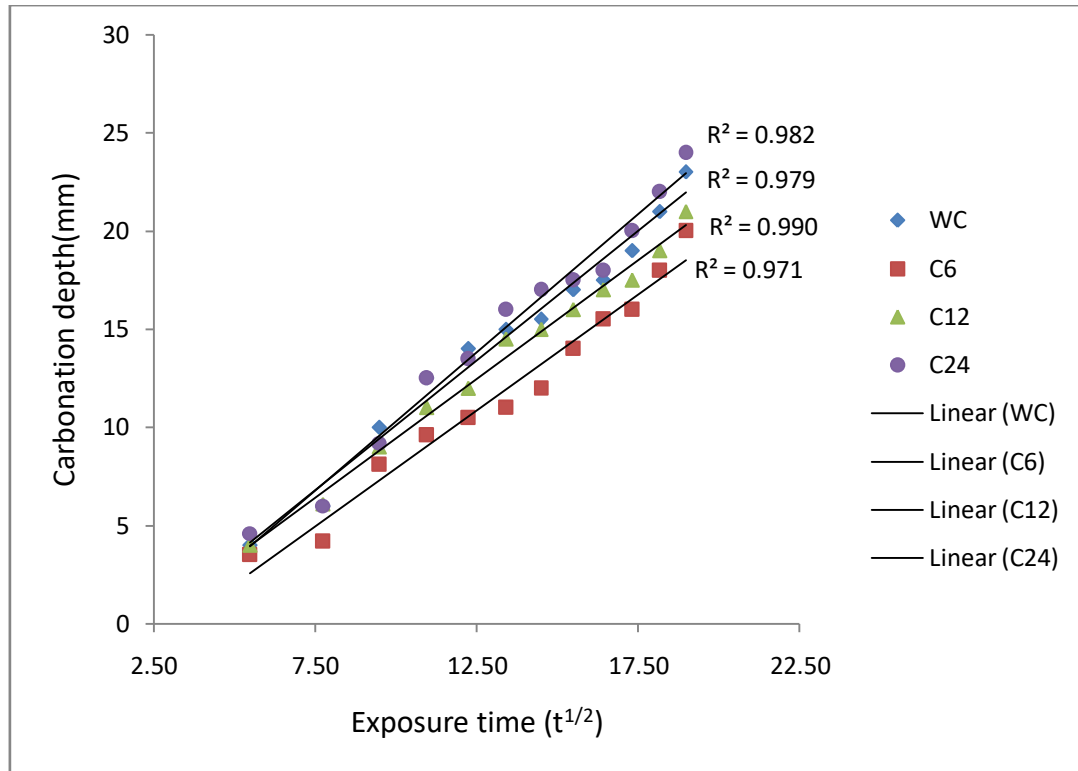


Fig. 5.29: Carbonation depth variation with square root of exposure duration

It can be seen from Table 5.7 that the value of carbonation coefficient ‘K’ was reduced for the C6 and C12 specimens as compared to WC specimens. The value of carbonation coefficient decreased by 10.4% and 8.2 % in C6 and C12 specimens, respectively, as compared to WC specimens. The observed decrease in carbonation coefficient in the C6 and C12 specimens was indicative of concrete pore refinement in these specimens and hence decreased ingress of carbonation front. On the contrary, C24 specimens showed an increase of 6.6% in the carbonation coefficient as compared to water cured concrete, exhibiting a weak resistance to CO₂ ingress in concrete.

5.9.2.2 Corrosion rate measurement by Linear Polarization Resistance technique

The corrosion rate of reinforced concrete subjected to different curing regimes was analysed using Linear Polarization Resistance (LPR) test. LPR test was conducted on reinforced cylindrical specimens of diameter 100mm and length 200 mm. In this test, three-electrode cell system was used for the electrochemical measurements. The reinforcement bar functioned as the working electrode, the steel wire mesh acted as

the auxiliary electrode and the calomel electrode functioned as reference electrode. A typical experimental set up is shown in Fig. 5.30. The corrosion rates of the specimens were measured periodically after every 30 days of exposure till the end of exposure duration of 360 days. For the LPR test, the cylindrical specimens were covered with steel mesh and placed in soap solution and the working electrode was polarized to $\pm 25\text{mV}$ from the equilibrium potential at a sweep rate of 10 mV/min , and the resulting current was plotted against the applied potential as shown in Fig. 5.31. The analysis of LPR results was done using Tafel extrapolation method as shown in Fig. 5.31.

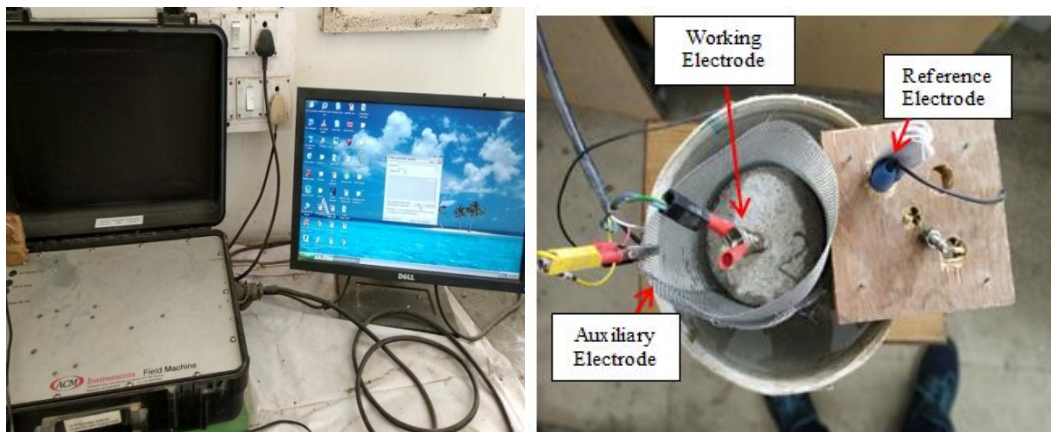


Fig. 5.30: Test setup for corrosion rate measurement using LPR

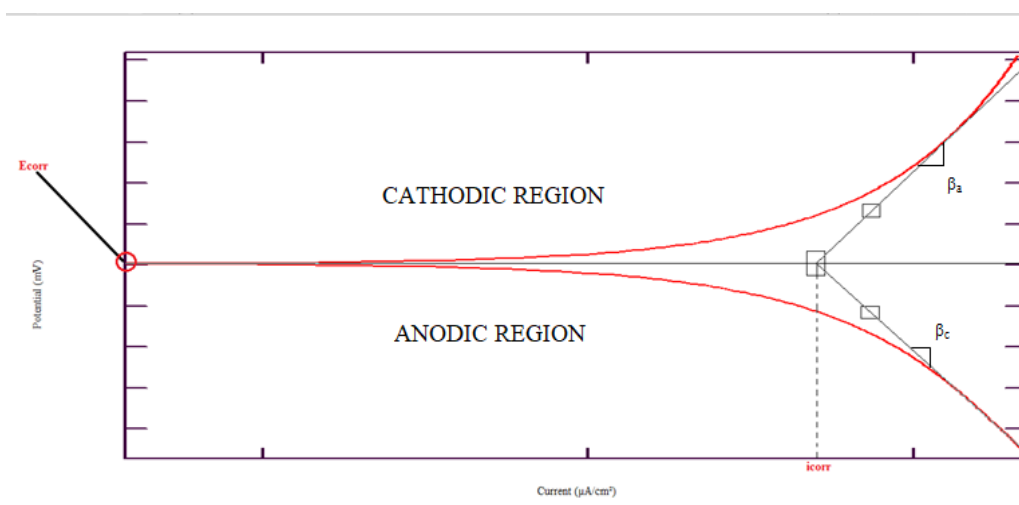


Fig. 5.31: Analysis of LPR results using TAFEL extrapolation method

The plot of corrosion current density (i_{corr}) vs. the age of CO_2 exposure has been shown in Fig. 5.32 for the different curing regimes. At the initial ages of exposure i.e. upto 60 days, the values of i_{corr} were similar for all the curing regimes. The initial exposure to CO_2 acts on the surface of the concrete and does not significantly impact the LPR test. As the age of exposure to CO_2 increases, the values of i_{corr} started to vary notably for different curing regimes. The highest value of i_{corr} was observed in WC specimens, followed closely by C12 and C24 specimens. As observed in the results of permeation properties, ACC reduced the permeability of concrete surface due to precipitation of CaCO_3 in the pores of concrete and production of additional C-S-H gel. The blocking of pores by CaCO_3 in concrete hinders the movement of CO_2 in concrete and as a result, the rate of CO_2 attack was reduced in ACC specimens.

As the exposure to CO_2 increased, the CO_2 gas crosses the surface barrier in the carbonation cured specimens, a considerable increase in the i_{corr} values was observed in these specimens as compared to WC concrete. This increase was more significant in the C24 specimens than the C12 specimens. This can be understood due to insufficient hydration reaction in C24 specimens due to high rate of loss of water during early age carbonation. This insufficient hydration resulted in poor microstructure of bulk concrete in the C24 specimens and hence, facilitated easy movement of CO_2 through the concrete and made the concrete vulnerable to carbonation induced corrosion.

At the age of 365 days, the highest values of i_{corr} were observed for C24 and WC specimens. However, notably the values of i_{corr} lie in the low range of rate of corrosion as per RILEM TC 154-EMC as shown in Table 5.8 (RILEM TC 154-EMC, 2003). Significant difference was observed in the value of i_{corr} in C24 specimens from the other carbonation cured specimens i.e. C12 and C6. In the C6 and C12 specimens, the combination of carbonation and hydration processes provided a stable microstructure to concrete. On the other hand, in the C24 specimens, intense carbonation and insufficient hydration provided a weakened microstructure to the concrete. Also, in the C24 specimens, the major reactant in carbonation reactions i.e. Ca(OH)_2 was already utilised in the early age carbonation. Therefore, when the concrete is subjected to atmospheric carbonation, the major reactant to CO_2 is C-S-H

gel. Reaction of CO_2 with C-S-H gel results in its disintegration into silica gel that further weakens the microstructure of C24 concrete. This infers that duration of ACC plays a significant role in the long term performance of concrete.

However, it is also evident that in comparison to water curing, ACC carried out for 12 hours did not exhibit higher values of i_{corr} . Therefore, it can be inferred that ACC does not increase the vulnerability of concrete to carbonation induced corrosion.

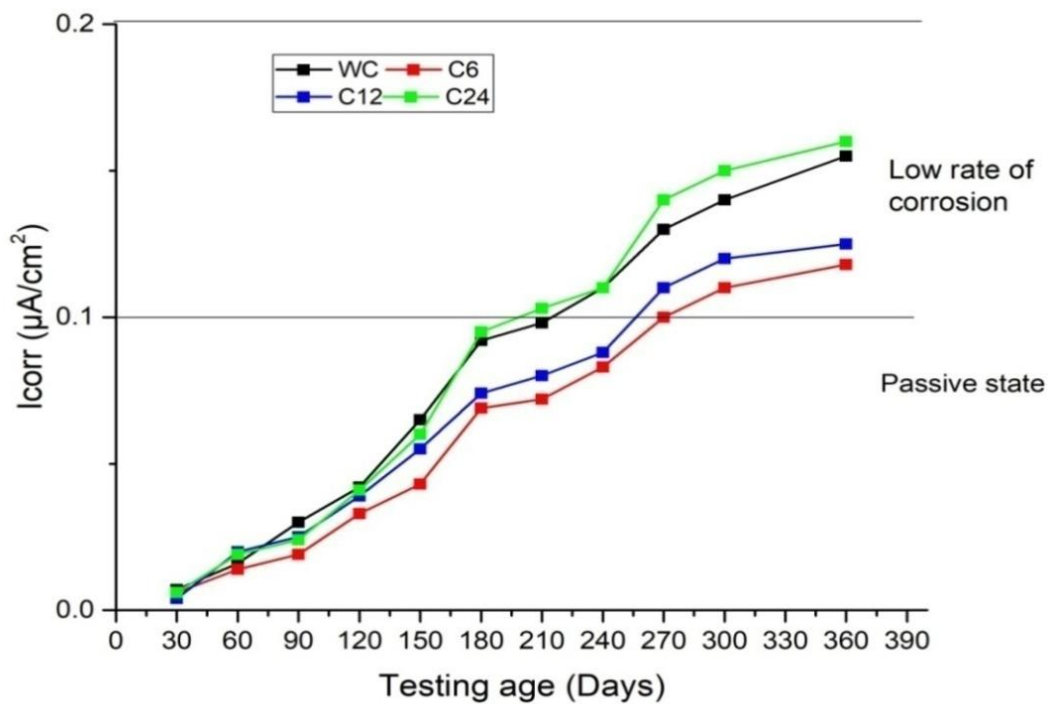


Fig 5.32: Corrosion current density for different curing regimes

Table 5.8: Corrosion activity from LPR as per RILEM TC 154-EMC

S.No.	Threshold($\mu\text{A}/\text{cm}^2$)	Corrosion activity description	Corrosion Activity Levels
1.	$i_{\text{corr}} \leq 0.2$	Corrosion rate is negligible and that the steel is in the passive state.	A
2.	$0.2 \leq i_{\text{corr}} \leq 1$	Corrosion has initiated and is proceeding at a moderate rate	B
3.	$1 \leq i_{\text{corr}}$	High rate of corrosion	C

5.10 CLOSING REMARKS

In this chapter, the effect of different duration of accelerated carbonation curing was studied on various properties of concrete. Long term performance of concrete subjected to different durations of carbonation curing was also examined. Concrete specimens were subjected to 6, 12 and 24 hours of carbonation curing and results were also compared with water cured concrete.

Carbonation cured concrete irrespective of the curing duration exhibited higher early age strength than the water cured concrete. Out of the three durations of carbonation curing, the carbonation curing of 12 hours duration was found to give best results in terms of mechanical strength, durability properties and CO₂ sequestration in concrete. Carbonation curing of 24 hours although provided higher sequestration of CO₂ in concrete, but also proved to be detrimental to the resultant performance of concrete. Concrete carbonation cured for 6 hours was observed to have similar compressive strength to water cured concrete.

The long term performance of concrete was tested in terms of drying shrinkage, carbonation depth and resistance to carbonation induced corrosion. The drying shrinkage of concrete was found to be reduced with carbonation curing and the drying shrinkage was observed to be decreasing on increasing the duration of carbonation curing. The resistance to weathering carbonation of carbonation cured concrete was analysed in terms of carbonation depth and the corrosion rate measurement. Concrete carbonation cured for 6 hours exhibited highest resistance to weathering carbonation and concrete carbonation cured for 24 hours exhibited highest carbonation depths and rate of corrosion, indicating a deteriorated long term performance with higher durations of carbonation curing.

CHAPTER 6

PERFORMANCE OF MINERAL ADMIXTURE BASED CEMENTITIOUS SYSTEMS UNDER ACC

6.1 GENERAL

Cement is the major constituent of concrete, which acts as a binding material and is responsible for imparting strength to concrete. Generally, cement gains strength by the hydration reaction which is the reaction of cement compounds with water. From the basic nature of the reaction, it can be inferred that the chemical composition of cement plays an important role in the proportioning of hydration compounds that ultimately governs the performance of resultant concrete. A typical hydrated cement paste of ordinary Portland cement (OPC) contains approximately 70% C-S-H, 20% calcium hydroxide, 7% of sulfo-aluminate and 3% of secondary phases (Oner and Akyuz, 2007).

Because of the environmental concerns related to the production of OPC, use of mineral admixtures as partial replacement of cement has been recommended. Mineral admixtures are pozzolanas which in itself possess little or no cementation value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementitious properties (Papadakis and Tsimas, 2002). Chemically, they are defined as either siliceous or siliceous - aluminous materials. Due to the presence of mineral admixtures, hydration process is followed by the pozzolanic reaction, which ultimately leads to formation of additional C-S-H gel. Since the siliceous content varies for different mineral admixtures, chemical composition of the mineral admixture will also affect the properties of resultant concrete.

When carbonation curing is introduced in the system, chemical interaction of CO₂ takes place with the constituents of cement and products formed after hydration of cement. Therefore, the chemical reactions become more complicated for ACC of cements containing mineral admixtures. In order to understand the performance of

mineral admixture based cementitious system, a detailed study on such systems is required. In the present investigation, three types of cementitious systems are studied. Firstly, effect of ACC on flyash based cementitious system is studied by using fly ash based PPC (Portland Pozzolana Cement). Secondly, ground granulated blast furnace slag (GGBS) based cementitious system is studied by using GGBS as partial replacement of cement. Thirdly, cement kiln dust (CKD) based cementitious system is studied by using CKD as partial replacement of cement. The chemical composition and physical properties of PPC, CKD and GGBS alongwith OPC is shown in Table 6.1. The detailed test matrix is shown in Fig. 6.1 and the test results are discussed in the following sections.

Table 6.1: Chemical composition and physical properties of OPC, PPC, CKD and GGBS

Chemical Composition				
Constituent	OPC	PPC	CKD	GGBS
SiO ₂	21.25	35.77	15	73.47
CaO	63.49	53.02	39.4	12.4
Fe ₂ O ₃	4.30	0.65	2.3	2.3
MgO	1.02	2.71	1.8	2.18
SO ₃	2.93	2.41	5.7	1
Al ₂ O ₃	4.74	2.59	3.2	4.5
Na ₂ O	0.30	0.22	1.4	0.5
K ₂ O	0.78	0.70	3.1	2.1
TiO ₂	0.36	0.39	0.1	0.2
LOI	2.23	1.5	19	1.35
Physical Properties				
Fineness (m ² /kg)	310	324	460	449
Specific Gravity	3.14	2.88	2.7	2.9

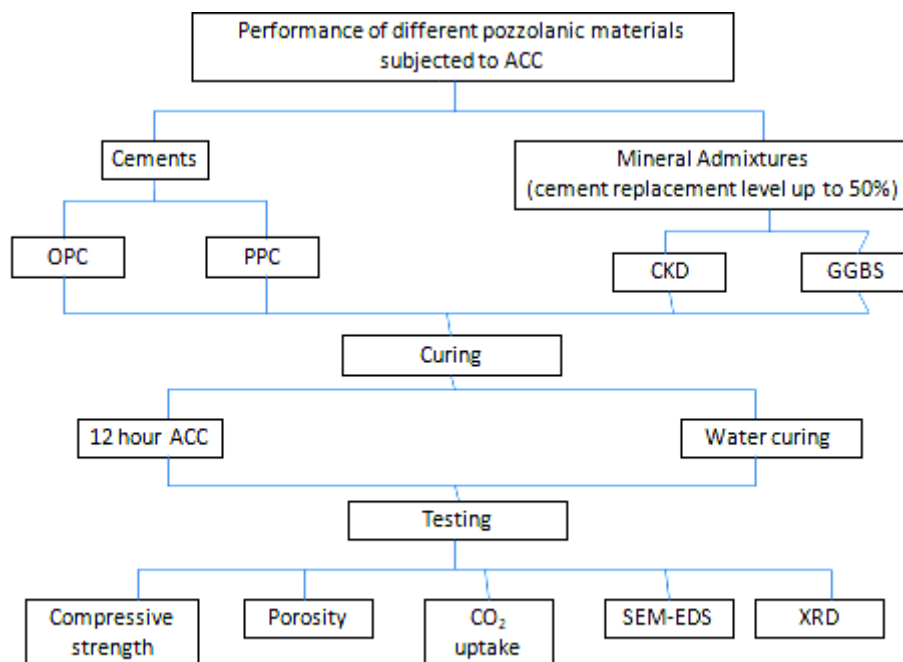


Fig. 6.1: Flowchart for studying the performance of different mineral admixture based cementitious systems under accelerated carbonation curing

6.2 PERFORMANCE OF FLYASH BASED PPC UNDER ACCELERATED CARBONATION CURING

In order to understand the fly ash based cementitious system in accelerated carbonation curing, mortar specimens were prepared using flyash based Portland pozzolana cement (PPC). For comparison, similar set of specimens were prepared with OPC. A comparison of chemical composition of OPC and PPC is presented in Table 6.1. The table clearly shows that OPC has more amount of calcium oxide than PPC; while PPC has more amount of silicon dioxide than OPC.

The mortar samples prepared in this study were de-moulded after 18 hours of casting. After de-moulding, the specimens were separated into three sets. Each set was subjected to different curing regimes. The first set was subjected to water curing till the testing age. The second set was subjected to 12 hours of ACC followed by sealing in plastic bags till the testing age. The third set of specimens was subjected to 12 hours of ACC followed by 3 days of water spray and then sealed in plastic bags till the testing age. The details of the curing regimes along with the mix designation are

shown in Table 6.2. The performance of mortars was evaluated in terms of compressive strength, porosity and microstructural characteristics.

Table 6.2: Details of curing regimes used in this study

Curing Scheme	Details of curing scheme			Mix designation
	Pre Conditioning	Curing	Post Conditioning	
Water curing (WC)	-	Water curing at 27±2°C temperature and 100% RH	-	P-WC (for PPC) O-WC (for OPC) CKD-WC (for CKD) G-WC (for GGBS)
Carbonation curing (CC)	Initial pre conditioning for 2 hours	Carbonation curing for 12 h	Sealed in Plastic Bag	P-CC O-CC CKD-WC (for CKD) G-WC (for GGBS)
Carbonation curing followed by water spray (CS)	Initial pre conditioning for 2 hours	Carbonation curing for 12 h	Water spray for 3 days and then sealed in plastic bag	P-CS O-CS CKD-WC (for CKD) G-WC (for GGBS)

6.2.1 Compressive Strength

The compressive strength of mortar specimens was tested at the age of 3, 7, 28, 90 and 180 days of casting. Compressive strength test was carried out on cubes of size 70.6 mm as per IS 4031 (Part 6): 1988 (IS 4031:Part6, 1988). Three samples of each mix were tested and the average value was considered as the representative compressive strength of the mix. The results for compressive strength test of mortar mixes made with OPC have been presented in Fig. 6.2 and the results for mortar mixes made with PPC have been presented in Fig. 6.3.

It can be observed from the results of compressive strength for OPC mortars that at an early age of testing i.e. 3 days, specimens subjected to carbonation curing exhibited higher strength than the water cured specimens. O-CC mix exhibited 9.5% higher strength than O-WC mix; while the strength gain in O-CS mix was as high as 28.5% as compared to O-WC mix. The higher strength of carbonation cured specimens can be clearly attributed to conversion of Ca(OH)_2 into CaCO_3 and production of additional C-S-H gel from the carbonation reactions. It is also reported that the rate of

carbonation reactions is higher than the hydration reactions (Papadakis et al., 1989). Therefore, rapid formation of C-S-H gel took place in carbonation cured specimens (O-CC and O-CS) as compared to the corresponding water cured (O-WC) specimens. Among the two carbonation cured mixes, higher strength was achieved when the carbonation process was followed by water spray up to 3 days. The water spray post carbonation was useful in replenishing the evaporated water during carbonation and facilitated further hydration of unreacted cement constituents. The similar observations related to the importance of post hydration was made by He et al. and Rostami et al. (He et al., 2016a; Rostami et al., 2012b).

With the increase in testing age, O-CS specimens maintained the advantage of higher initial strength; while O-CC specimens had lower strength development with age thereby achieving lower strength levels than the corresponding O-WC specimens. This clearly indicated the effect of carbonation curing with post carbonation water spray was better than water curing process on the strength development of mortars. It further confirmed the importance of post carbonation in strength development of the mixes. In O-CC specimens, loss of water during the exothermic carbonation reactions could not be replenished due to lack of post carbonation, thereby leading to decrease in the rate of hydration reaction post carbonation. This caused lesser production of C-S-H gel in mortars and hence, a lower strength value was observed in the tests.

At the later ages of 28 days, 90 days and 180 days, O-CS specimens were found to achieve significantly higher strength than both O-WC specimens and O-CC specimens. It clearly indicated that the benefits achieved in early ages by carbonation curing followed by water spray helped in maintaining higher strengths even at later ages. The matrix composed of C-S-H gel amalgamated with CaCO_3 provides a dense mass with higher compressive strength.

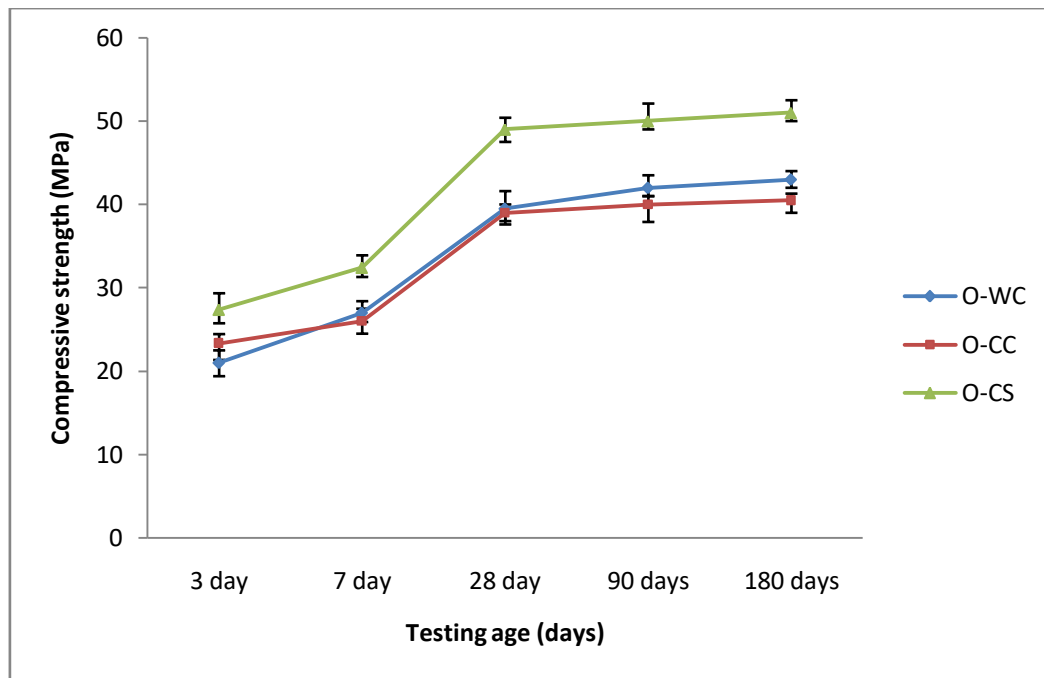


Fig. 6.2: Compressive strength of OPC mortars subjected to different curing regimes

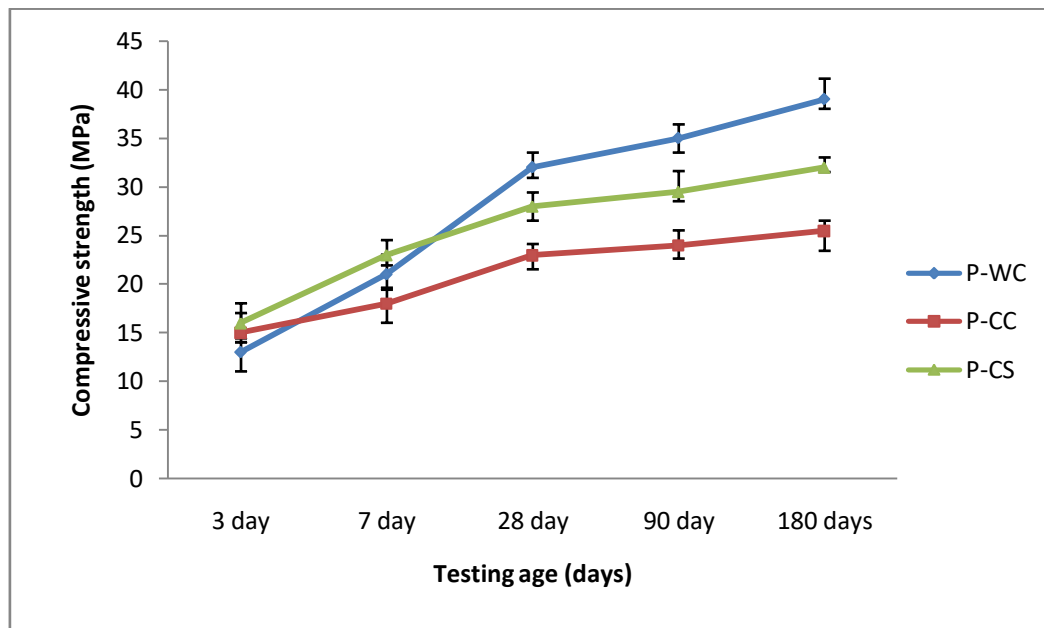
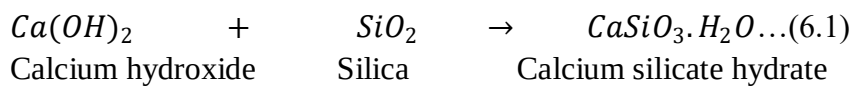


Fig. 6.3: Compressive strength of PPC mortars subjected to different curing regimes

On the other hand, in O-CC specimens, the absence of sufficient hydration post carbonation resulted in poor strength development at later ages. The strength level was even lower than the corresponding water cured specimens. It further highlighted

the importance of proper post carbonation phase. In all, the compressive strength results on mortar mixes made with OPC indicated better performance of carbonation cured concrete with proper post conditioning.

The compressive strength of mortar mixes made with fly ash based-PPC mortars have been presented in Fig. 6.3. It can be observed from Fig. 6.3, that at an early age of 3 days, PPC mortars exhibited gain in strength on subjecting to carbonation curing. P-CS specimens and P-CC specimens exhibited 23% and 15% better compressive strength respectively than the P-WC specimens at the age of 3 days. As the age of mortar increased, higher rate of strength development in P-WC specimens was observed due to combined effect of further hydration and pozzolanic reaction in the PPC mortars. The pozzolanic reaction that is responsible for strength gain in the PPC specimens is shown in Eq. 6.1. The calcium hydroxide produced from the hydration of cement constituents reacts with SiO_2 from the pozzolanic material to produce C-S-H gel, which imparts strength to concrete at the later ages. The strength gain in the P-WC specimens was observed beyond the age of 28 days also i.e. at the age of 90 days and 180 days, implying the pozzolanic activity till later ages in PPC specimens.



However, the strength development of P-CS and P-CC specimens at the later ages was significantly reduced as compared to P-WC specimens. Lower strength development at the later ages in carbonation cured mortar mixes made with PPC was due to the basic nature of carbonation reactions and the pozzolanic reactions. The later age strength development in the pozzolanic based cementitious systems is due to the pozzolanic reaction that require the presence of Ca(OH)_2 as a reactant. However, the carbonation curing procedure consumes most of the Ca(OH)_2 formed at early ages in the carbonation reaction and converts it into calcium carbonate. Due to this, Ca(OH)_2 is not available in the matrix to allow the continuation of the pozzolanic reaction of fly ash. Therefore, the advantage of presence of pozzolanic material could not be achieved in carbonation cured mortars. Among the two carbonation cured processes, it can be observed that lower strength levels were achieved in P-CC mixes, where subsequent hydration post carbonation was not provided. The 180 day strength of

such mixes was 36% lower than the WC mixes and was 22% lower than the P-CS mixes. Due to lack of subsequent hydration, regeneration of Ca(OH)_2 could not take place for P-CC specimens, which could have participated in the pozzolanic reaction. On the other hand, in the P-CS specimens, due to hydration post carbonation, the hydration reaction progressed and generated Ca(OH)_2 which further reacted with SiO_2 to produce C-S-H gel. Therefore, in case of PPC specimens, the strength gain was observed to be higher in P-CS than the P-CC specimens, not only because of subsequent hydration, but also due to pozzolanic reaction at the later ages. The similar observations regarding importance of hydration post carbonation for fly ash based systems was made by Monkman and Shao and Zhang et al. (Monkman and Shao, 2006; Zhang et al., 2016).

On comparing the results of Figs. 6.2 and 6.3 for mortar mixes made with OPC and PPC respectively, it can be observed that the strength development pattern of PPC mixes were different from the OPC mixes. In OPC mixes, most of the strength was achieved within 28 days of casting for all the three curing regimes; while the PPC mixes continued to gain strength even at later ages. Comparing the performance of carbonation cured specimens; it was observed that at the early ages, both cement types had better performance in carbonation curing. However, at later ages, mixes made with PPC showed lower strength when subjected to carbonation curing. Even at the early age of 3 days, lower increase in strength was observed in carbonation cured mixes as compared to water curing regime in case of PPC mortars. This can be understood from the chemical composition of PPC. The chemical composition of PPC indicated lesser content of calcium silicates (C_3S , C_2S) as compared to OPC. Since calcium silicates are the primary reactants in the carbonation reactions, lesser amount of C_3S and C_2S in PPC would mean lower extent of carbonation reaction. Along with the lower rate of carbonation reaction, PPC based mortars had slower rate of hydration reaction of C_3S and C_2S with water, leading to formation of Ca(OH)_2 , which is the major reactant in carbonation reactions. Lesser production of Ca(OH)_2 at an early age further reduced the rate of carbonation reaction which is responsible for conversion of Ca(OH)_2 to CaCO_3 and for improvement in performance of carbonation cured specimens.

At the later ages, due to consumption of Ca(OH)_2 in the carbonation reactions, lesser strength gain is observed in carbonation cured PPC specimens since the strength gain at the later ages is dependent on the pozzolanic reaction. On the other hand, the carbonation cured OPC specimens gain significant strength at later ages owing to the subsequent hydration reactions post carbonation.

6.2.2 Porosity

The porosity of OPC and PPC mortars subjected to different curing regimes was tested at the age of 3 days and 180 days of casting as per the guidelines of ASTM C642-13: 2008 (ASTM C642-13, 2008b). The results of porosity for OPC and PPC mortars have been presented in Fig. 6.4 and 6.5 respectively.

It can be observed from the results of porosity for OPC mortars that the values of porosity were significantly reduced when the specimens were subjected to ACC. At the early age of 3 days, O-CC specimens exhibited 20% lesser porosity as compared to O-WC specimens; while O-CS specimens exhibited 31% lesser values of porosity as compared to WC specimens. This correlated well with the results of compressive strength test, wherein early age compressive strength of concrete was found to be higher for carbonation cured mixes. On comparing the percentage improvements in compressive strength and porosity, it can be seen that higher improvement was observed in porosity results. It indicated that the carbonation curing procedure had more effect on the surface characteristics of the mixes, as compared to the bulk property. The lesser porosity due to ACC is attributed to conversion of Ca(OH)_2 into CaCO_3 during the carbonation reaction. CaCO_3 possesses higher volume than Ca(OH)_2 , which resulted in increase in solid volume of mortars. The CaCO_3 formed precipitates in the pores of mortars and decreases the pore fraction of mortars, thus exhibiting lower values of porosity. The decrease in porosity values was found to be even higher for O-CS specimens, where the process of carbonation was followed by water spray. The formation of additional C-S-H gel due to subsequent hydration further led to densification of the mix and decreased the porosity.

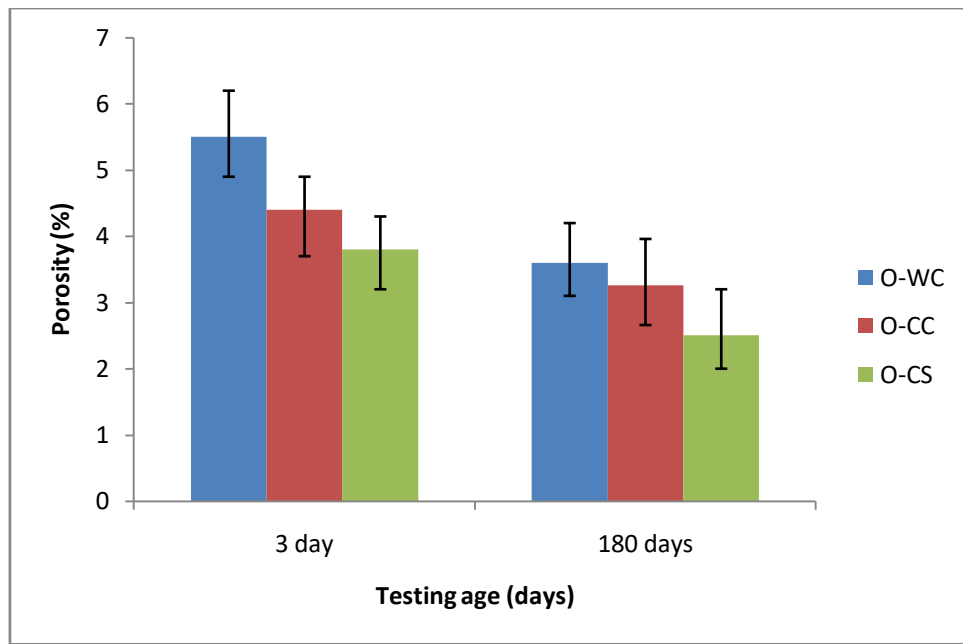


Fig. 6.4: Porosity of OPC based mortars when subjected to different curing regimes

The reduction in porosity at 3 days with ACC has also been observed in PPC mortars as shown in Fig. 6.5. In case of PPC mortars, P-CC specimens exhibited 15.4% lesser porosity than P-WC specimens; while P-CS specimens exhibited 22.5% lesser porosity than P-WC specimens. Similar to results of compressive strength, the decrease in porosity due to ACC was found to be lesser in PPC specimens as compared to the OPC specimens. The decrease in porosity has primarily occurred due to consumption of Ca(OH)_2 in the carbonation reactions and formation of CaCO_3 . Since, the hydration reactions occur at a slower rate in PPC specimens as compared to OPC specimens, therefore, the content of Ca(OH)_2 produced during the hydration reaction was also lesser in PPC specimens. Due to the presence of lesser amount of Ca(OH)_2 , the reduction in porosity of PPC specimens was also limited.

At the age of 180 days, the effect of ACC on OPC and PPC mortars was found to be significantly different. In the OPC specimens subjected to ACC, both O-CS and O-CC exhibited lesser porosity as compared to O-WC specimens. On the other hand, in the PPC specimens, the porosity of ACC mixes (P-CS and P-CC) was observed to be higher than the water cured specimens (P-WC). It further indicated the negative effect of unfavourable conditions for pozzolanic reaction on the performance of the

mixes. Due to lack of pozzolanic action in the ACC specimens, the C-S-H gel could not be produced in sufficient amount and a porous mix was obtained in the carbonation cured PPC based mortars.

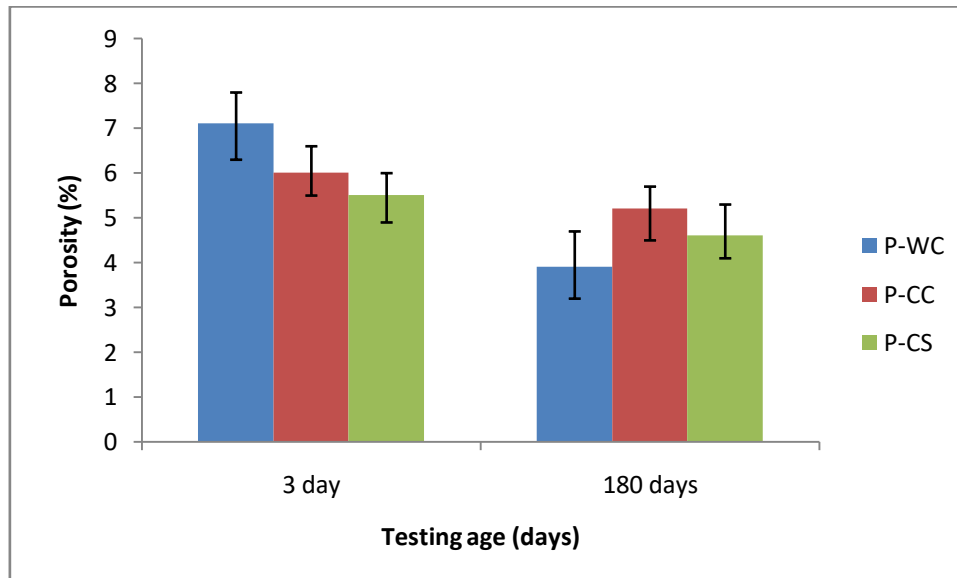


Fig. 6.5: Porosity of PPC based mortar mixes when subjected to different curing regimes

Another observation is made between the compressive strength results and porosity results at the age of 180 days. In OPC based mixes, maximum compressive strength was achieved by O-CS mix, followed by O-WC and O-CC mix. On the other hand, porosity results indicated performance of mixes in descending order as O-CS, followed by O-CC and O-WC mix. It indicated that both the carbonation cured mixes (irrespective of post carbonation procedure) had better performance than water cured mix. It was due to precipitation of CaCO_3 in the surface pores, which had greater effect on porosity results, than on the bulk properties of concrete.

6.2.3 Microstructure

The microstructure of OPC and PPC based mortars subjected to ACC and water curing was analysed using XRD analysis and SEM-EDS. The specimens for XRD and SEM-EDS were obtained from the crushed specimens of compressive strength at the age of 180 days of casting. The results of XRD of OPC and PPC based mortars are presented in Fig. 6.6 and 6.7 respectively.

The XRD analysis of water cured specimens of OPC mortar (O-WC) exhibited peaks of Portlandite (Ca(OH)_2), Calcite (CaCO_3), Tricalcium silicate(C_3S), Dicalcium silicate(C_2S) and Silica (SiO_2). The peaks of these compounds were identified in software XpertHighscore Plus using ICDD reference database. In the water cured OPC specimens, strong peak of Ca(OH)_2 was observed, which was produced as a product of hydration reaction of calcium silicates and water. In the carbonation cured specimens (O-CC and O-CS), additional peaks of calcite were observed along with the peaks corresponding to Portlandite (Ca(OH)_2), Tricalcium silicate(C_3S), Dicalcium silicate (C_2S) and silica (SiO_2), which confirms formation of CaCO_3 during the carbonation reactions of ACC. The conversion of Ca(OH)_2 to CaCO_3 during ACC is evident from diminishing of the Ca(OH)_2 peaks in the O-CC specimens. In the O-CS specimens, where ACC was followed by water spray upto 3 days, strong peaks of Ca(OH)_2 and of CaCO_3 were observed which can be understood due to the hydration of unreacted cement constituent post carbonation, which produced additional Ca(OH)_2 .

The XRD analysis of PPC based mortars subjected to different curing regimes has been depicted in Fig. 6.7. In the XRD analysis of PPC specimens, strong peaks of silica (SiO_2), Tricalcium silicate(C_3S) and Dicalcium silicate(C_2S) were observed in the water cured specimens(WC). Unlike the OPC specimens, water cured PPC specimens did not exhibit the peaks of Ca(OH)_2 . This can be attributed to the pozzolanic reaction that takes place in PPC cement, where SiO_2 reacts with Ca(OH)_2 to form C-S-H gel, as shown in chemical equation 6.1. The absence of Ca(OH)_2 peaks in PPC specimens evidences the pozzolanic activity and also correlates well with the results obtained from the compressive strength tests.

In the ACC specimens of PPC mortars (P-CC and P-CS), peaks of calcite were observed similar to OPC specimens. However, the calcite peaks were weaker in PPC specimens as compared to the OPC specimens. This is possibly due to the lower rate of carbonation in PPC mortars. The rate of early hydration of PPC is lower as compared to OPC, which results in lesser production of Ca(OH)_2 in the early age. Since, Ca(OH)_2 is the major reactant in carbonation reactions, the carbonation rate of PPC is also found to be lower. The ACC specimens of PPC mortars also exhibited negligible peaks of Ca(OH)_2 as compared to OPC specimens. In the PPC mortars,

Ca(OH)_2 is the major reactant for both the carbonation as well as pozzolanic reactions. Therefore, the Ca(OH)_2 produced from the subsequent hydration post carbonation was also consumed in the pozzolanic reaction and hence, the XRD analysis did not exhibit peaks of Ca(OH)_2 .

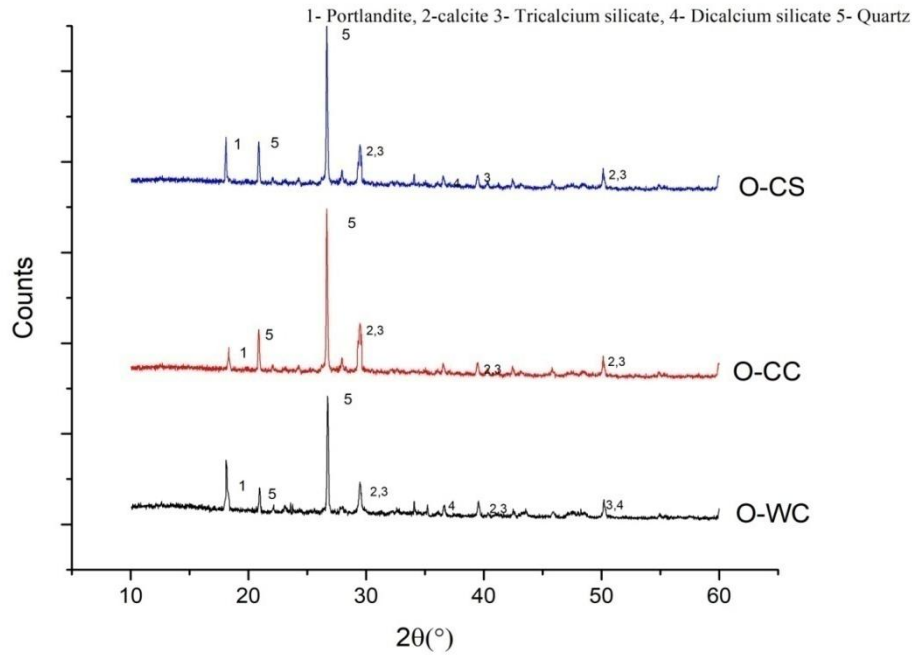


Fig. 6.6: XRD analysis of OPC mortars at the age of 180 days

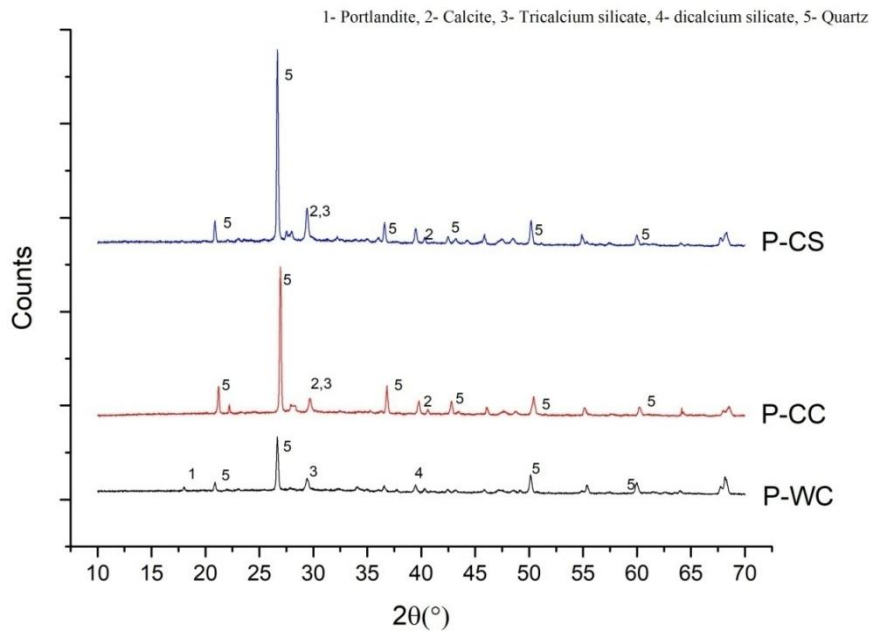


Fig. 6.7: XRD analysis of PPC mortars at the age of 180 days

The SEM-EDS images of OPC mortars subjected to different curing regimes are presented in Fig. 6.8-6.10. The samples for SEM images were obtained from mortars mixes at the age of 180 days of casting. It can be clearly observed from the SEM images that the O-CS curing regime i.e. ACC followed by subsequent water spray led to formation of a dense microstructure. This dense microstructure in O-CS specimens can be attributed to adequate formation of both the carbonation and the hydration products in this curing regime. First, the carbonation curing led to conversion of Ca(OH)_2 to CaCO_3 , which increases the solid volume of mortars. Secondly, the subsequent water curing post carbonation ensures the continuation of hydration reaction in the mortars, which produces the additional C-S-H gel as observed in the SEM images. The presence of CaCO_3 was also observed in the EDS analysis, where the O-CS specimens exhibited a higher C/Ca ratio (0.56) and lower Si/Ca ratio (0.49) as compared to O-WC specimens which exhibited a lower C/Ca ratio (0.16) and higher Si/Ca ratio (0.57). The combined action of hydration and carbonation reactions in O-CS curing regime leads to formation of a dense and compact mix. This is in coherence with the results of compressive strength test, where the highest compressive strength is observed in O-CS specimens at the age of 180 days.

The ACC specimens that were not followed by subsequent water curing i.e. O-CC curing regime exhibited a slightly loose microstructure as compared to the water cured specimens. The Si/Ca ratio (0.42) was also observed to be lesser in the O-CC specimens as compared to O-CS specimens, indicating a lesser degree of hydration in O-CC specimens. This is understood because of the lack of sufficient hydration in O-CC specimens, due to which adequate amount of C-S-H gel was not produced in the specimens post carbonation and a weak and porous microstructure was observed in these specimens.

The SEM-EDS images of PPC mortars subjected to different curing regimes have been presented in Fig. 6.11-6.13. The water cured PPC mortars at the age of 180 days show a compact and dense microstructure owing to the combined action of hydration and pozzolanic reactions. The hydration reaction of cement and pozzolanic reaction between Ca(OH)_2 and SiO_2 forms C-S-H gel, which provides densification to the microstructure. The ACC specimens of PPC were observed to show a weaker

microstructure than WC specimens. This is in sync with the results of compressive strength and porosity tests where the ACC specimens exhibited lower strength and higher porosity. The unavailability of $\text{Ca}(\text{OH})_2$ in the ACC specimens due to carbonation reactions leads to lesser pozzolanic activity, which is responsible for reduced formation of C-S-H gel.

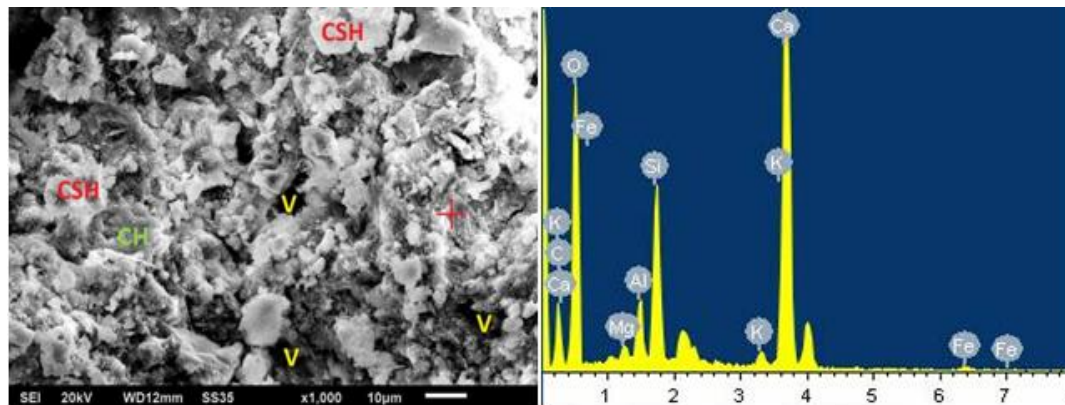


Fig. 6.8: SEM-EDS of water cured OPC mortar at the age of 180 days

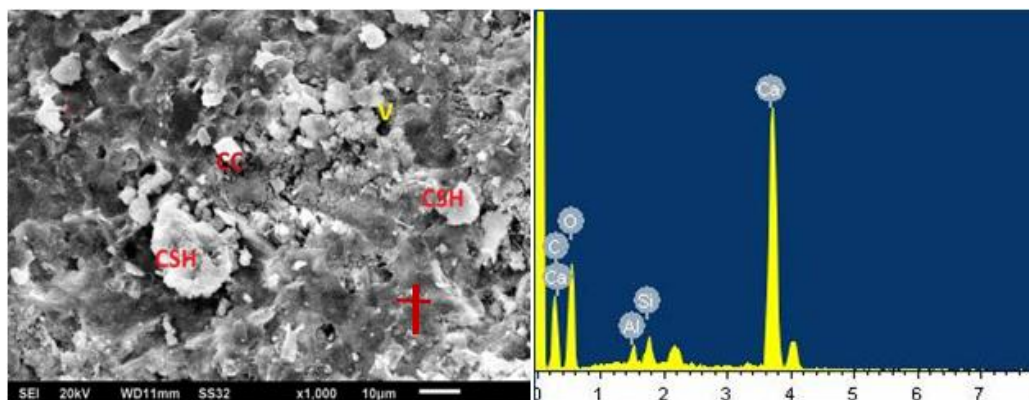


Fig. 6.9: SEM-EDS of carbonation cured (O-CC) OPC mortar at 180 days

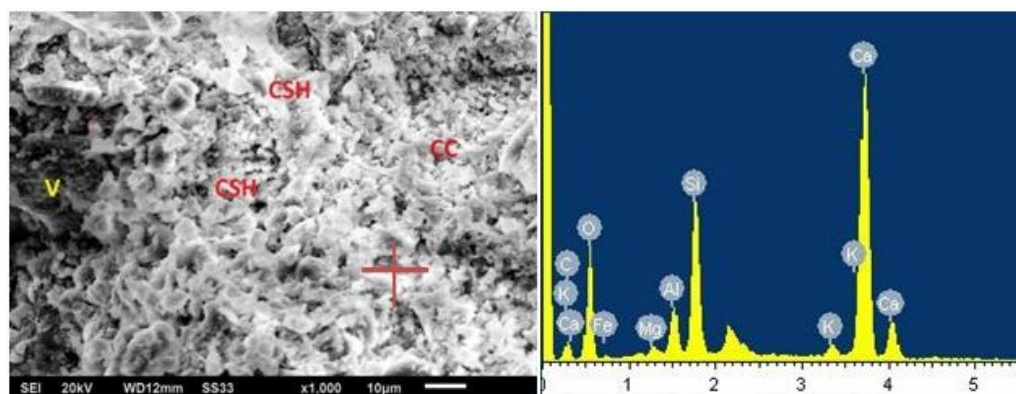


Fig. 6.10: SEM-EDS of carbonation cured (O-CS) OPC mortar at 180 days

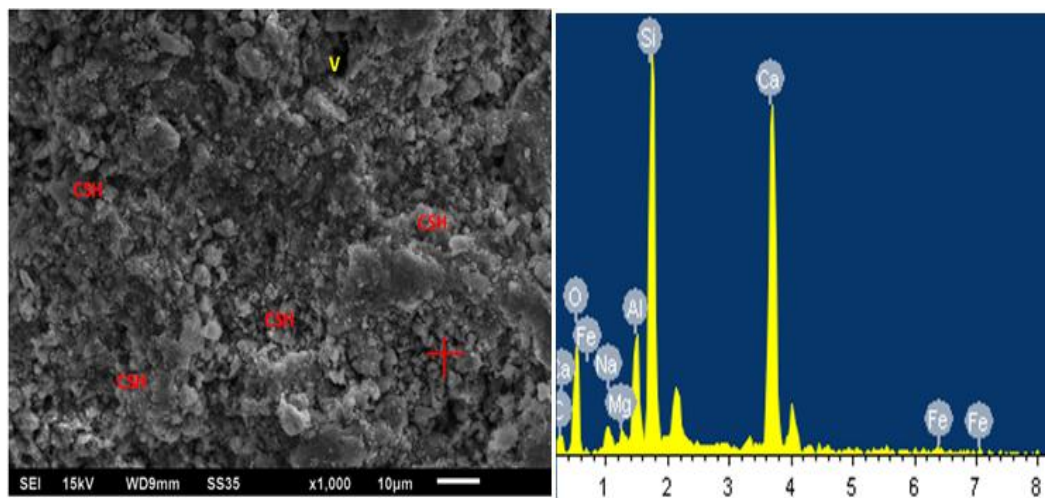


Fig. 6.11: SEM-EDS of water cured PPC mortar at 180 days

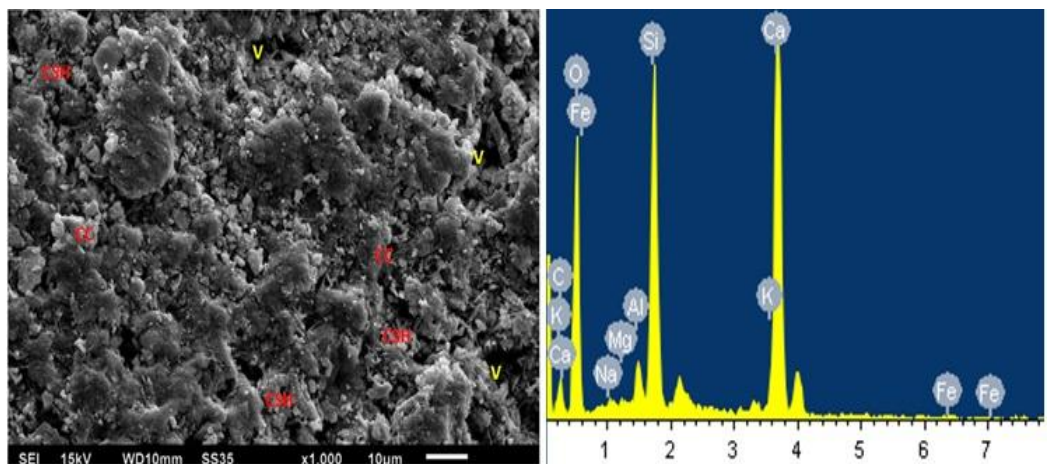


Fig. 6.12: SEM-EDS of carbonation cured (P-CC) PPC mortar at 180 days

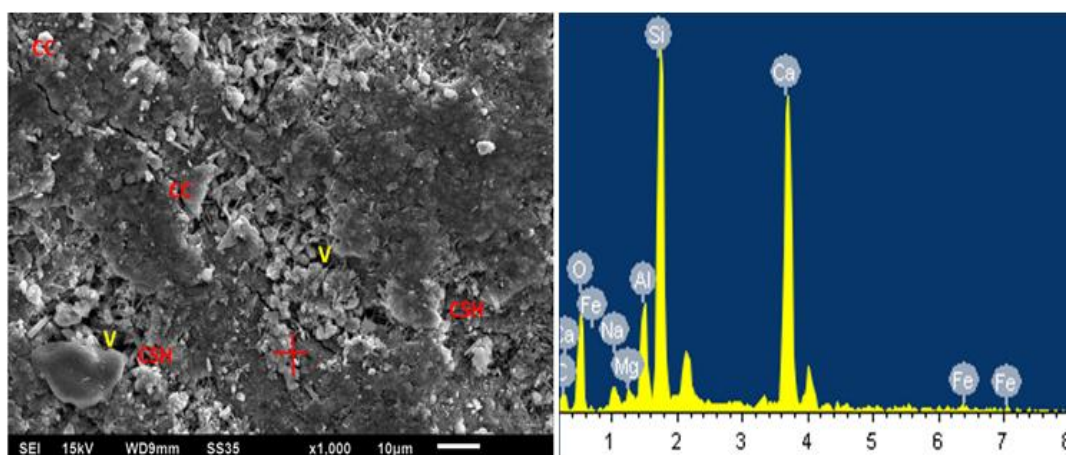


Fig. 6.13: SEM-EDS of carbonation cured (P-CS) PPC mortar at the age of 180 days

6.3 EFFECT OF ACC ON MORTARS INCORPORATING CKD AS PARTIAL REPLACEMENT OF CEMENT

Cement kiln dust is a by-product of cement manufacturing industry and is considered as an industrial waste. In the present study, CKD was used as a partial replacement of cement in mortars and the percentage of CKD in the mix was varied from 0 to 50% by the weight of cement. The chemical composition and physical properties of CKD vis-à-vis OPC have been shown in Table 6.1. It can be observed from Table 6.1 that the major constituent of CKD is CaO, indicating a chemical composition similar to OPC. The prepared mortar specimens were subjected to three types of curing regimes: The first set was subjected to water curing (WC) till the testing age. The second set was subjected to 12 hours of ACC followed by sealing in plastic bags till the testing age (CKD-CC). The third set of specimens was subjected to 12 hours of ACC followed by 3 days of water spray and then sealed in plastic bags till the testing age (CKD-CS). The performance of mortars was examined in terms of compressive strength, porosity and microstructure.

6.3.1 Compressive Strength

The compressive strength of CKD mortars subjected to different curing regimes was tested at the age of 3, 7, 28, 90 and 180 days. The results of compressive strength at the age of 3, 7, 28, 90 and 180 days have been respectively presented in Fig. 6.14 - 6.18. The compressive strength study was based on two parameters. Firstly, the effect of addition of CKD in varying percentages was observed and secondly, the effect of water curing and carbonation curing for the same mix was compared.

On comparing the 3-day compressive strength of mortar mixes for various percentages of CKD, it is observed that at 5% and 10% replacement of cement by CKD, the compressive strength was comparable to compressive strength of the control mix. As the percentage of CKD was increased more than 10%, the compressive strength started decreasing for all types of curing regimes. The lesser strength on increasing the content of CKD is attributed to lesser rate of hydration in mixes with CKD due to reduced cement content of the mix.

On comparing the compressive strength of ACC and WC specimens at the age of 3 days, it is observed that ACC specimens achieved at least 20% higher strength than WC specimens for each mix. The carbonation reaction during ACC causes conversion of products from hydration reaction and unhydrated cement constituents (C_3S and C_2S) into C-S-H gel or $CaCO_3$. The compressive strength of ACC specimens is even higher, if the carbonation process is followed by subsequent hydration of specimens. The subsequent hydration allows formation of additional C-S-H gel that imparts higher strength to concrete. Liu et al. and Panesar and Mo also found in their studies that carbonation curing results in improved early age compressive strength (Liu et al., 2016; Panesar and Mo, 2013). One more significant factor is the increase in compressive strength was greater for higher percentages of CKD in the mix. It might be due to finer particle size of CKD particles and presence of alkali in CKD that can promote the carbonation reaction. Thus, a greater strength gain is achieved at higher percentages of CKD.

The effect of carbonation curing on 7-days and 28-days compressive strength of CKD mortars is different from what was observed for 3-days strength. It can be seen from Fig. 6.15 and 6.16 that the compressive strength for ACC specimens not followed by water spray (CKD-CC) was slightly lower than water cured specimens. Carbonation reaction, which is an exothermic reaction, causes early age water loss from the mix. Since this water loss is not compensated in these specimens, water required for subsequent hydration is not available which slows down the hydration reaction, hence a decrease in compressive strength is observed. However, when the carbonation curing was followed by a water spray, higher compressive strengths were achieved for all mixes. It clearly indicated that water compensation is essential for the later age hydration reaction to continue.

Strength gain is observed in CKD-WC specimens as the age of mortar increases from 28 days to 90 days and 180 days. The strength gain in carbonation cured specimens at the later ages was lower as compared to water cured specimens. This can be attributed to the slight pozzolanic activity in CKD mortars due to presence of silica. The pozzolanic activity was limited in the carbonation cured mortars because of the consumption of $Ca(OH)_2$ in the carbonation reaction. However, the CKD-CS mortars

exhibited the highest strength till the later ages. This can be observed due to the subsequent hydration that is provided in the CKD-CS curing regime post carbonation. The subsequent hydration produces $\text{Ca}(\text{OH})_2$ in the mix which later participates in the pozzolanic reaction and contributes to the strength of CKD-CS specimens.

It can be clearly observed from the results of compressive strength tests that addition of CKD to the mix as a replacement of cement caused loss of strength in mortars. However, it was also observed that the strength of mortars incorporated with higher percentages of CKD has also improved when cured using ACC. This infers that CKD favours the carbonation reaction, which can be understood because of larger surface area of particles and higher alkalinity. Thus, it is evident that ACC can compensate for the loss of strength caused by addition of CKD to the mix.

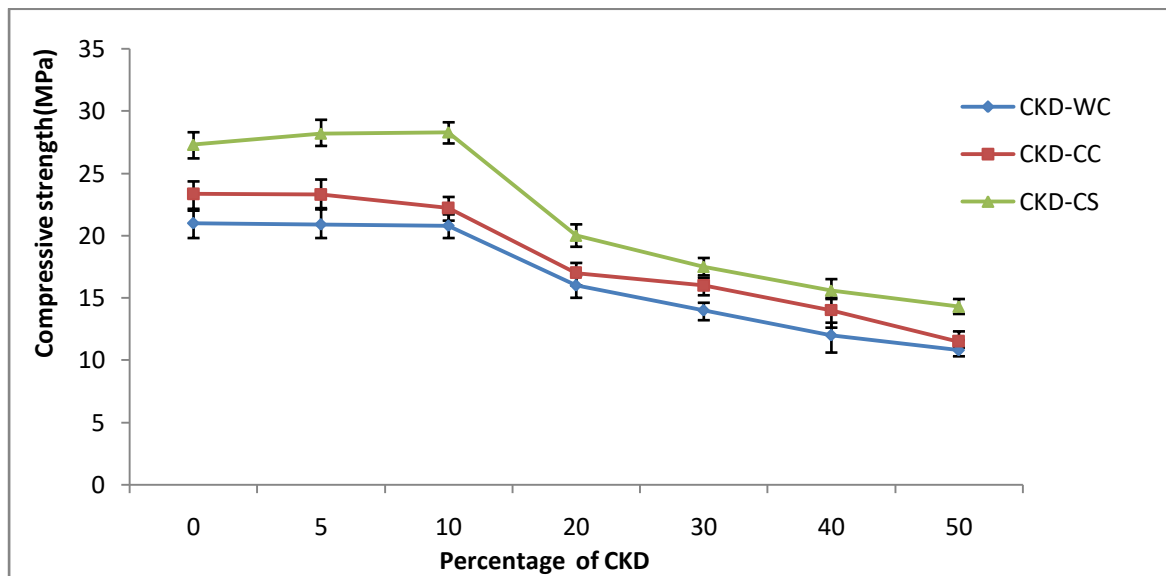


Fig.6.14: Compressive strength of CKD mortars at the age of 3 days

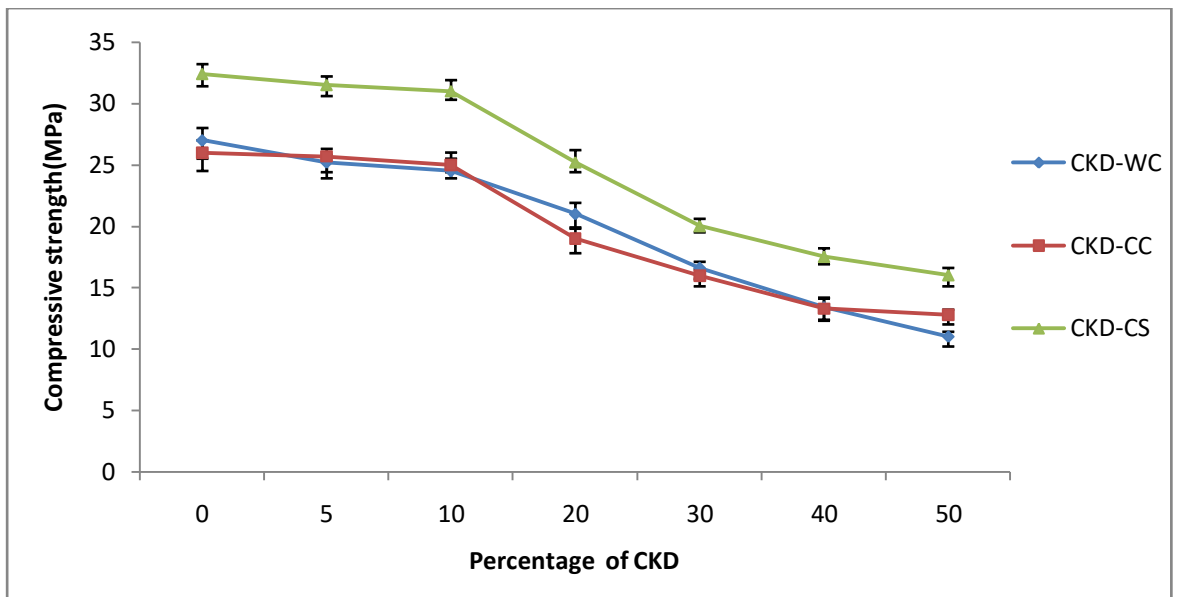


Fig.6.15: Compressive strength of CKD mortars at the age of 7 days

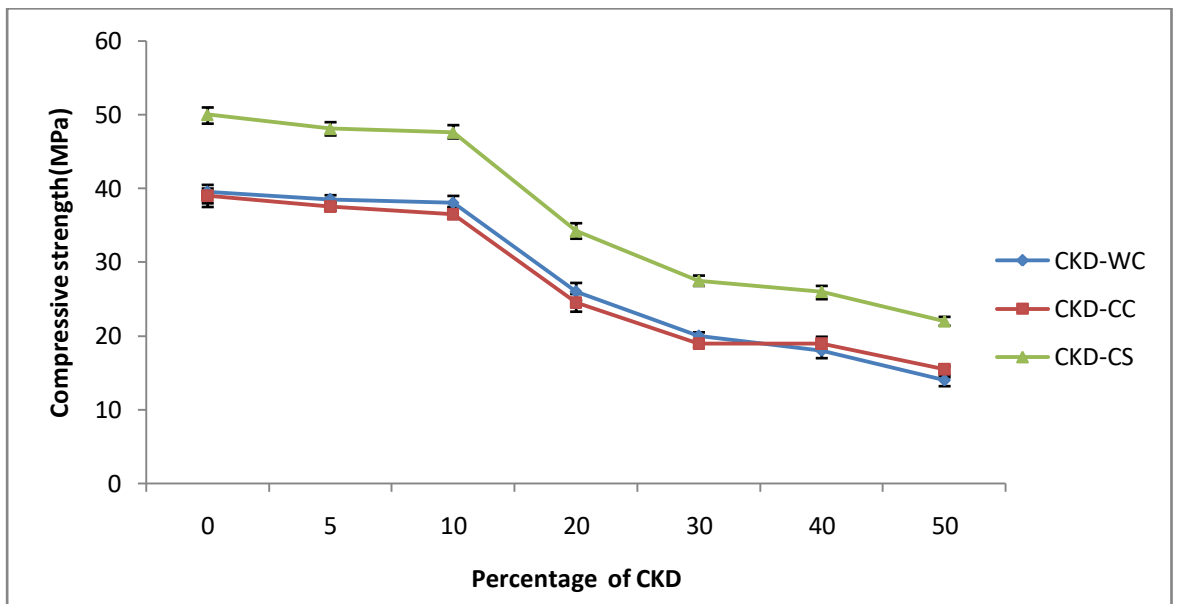


Fig. 6.16: Compressive strength of CKD mortars at the age of 28 days

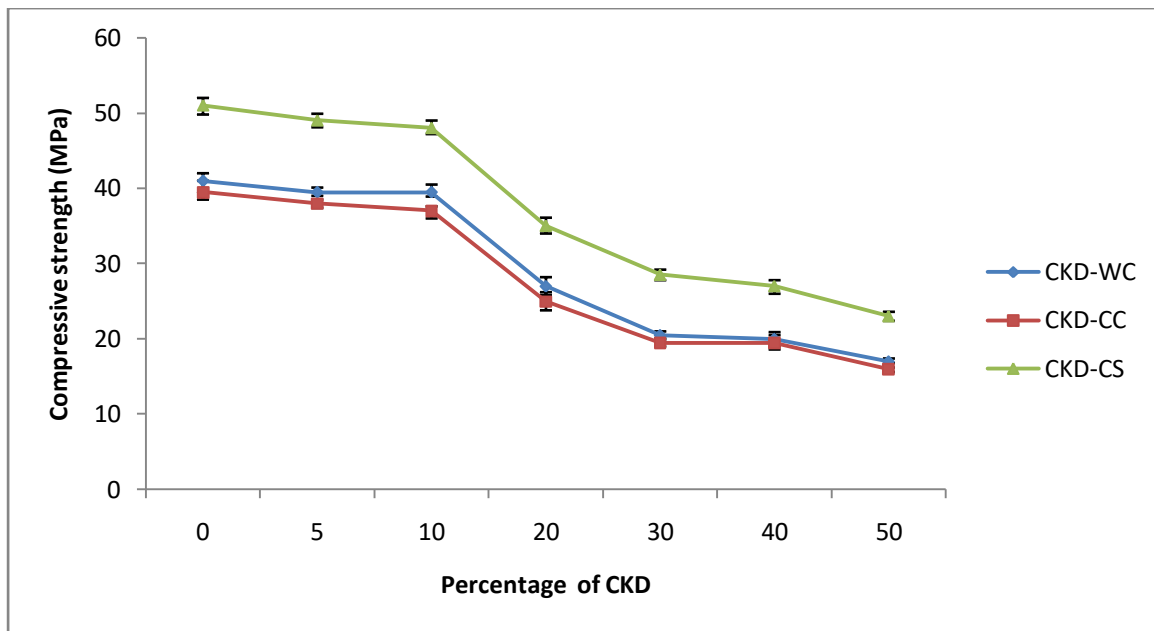


Fig. 6.17: Compressive strength of CKD mortars at the age of 90 days

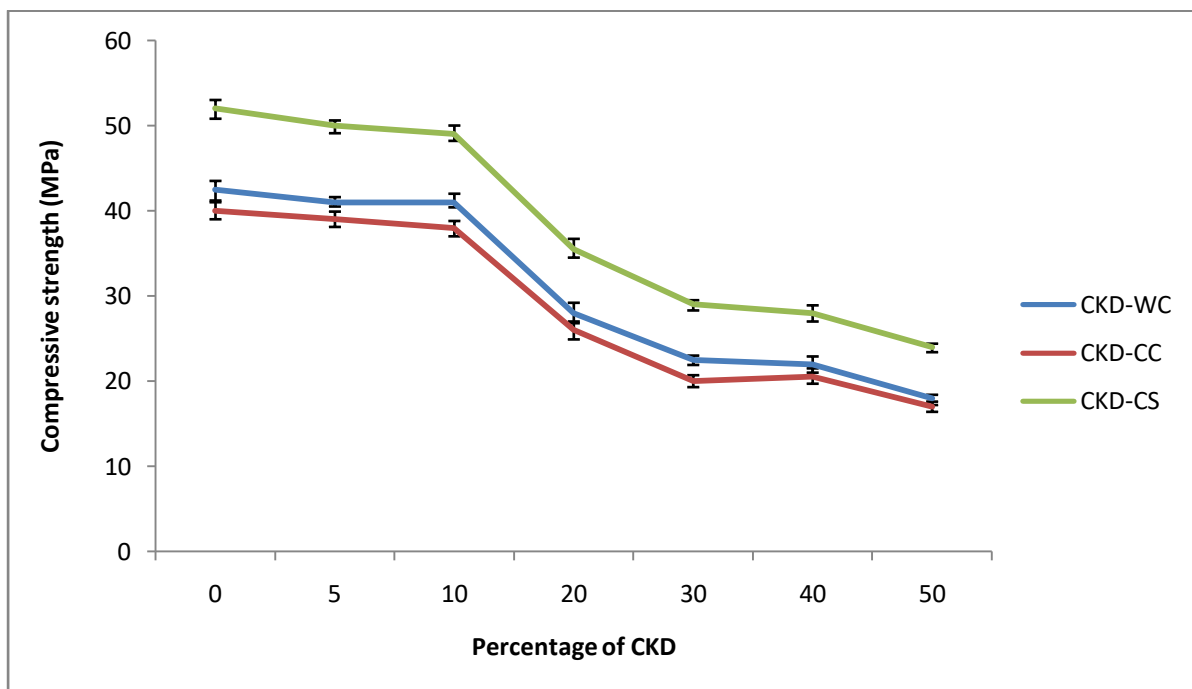


Fig. 6.18: Compressive strength of CKD mortars at the age of 180 days

6.3.2 Porosity of CKD Mortars

Porosity test on CKD mortars subjected to different curing regimes was carried out at the age of 3 days and 180 days and the corresponding results are presented in Figs. 6.19 and 6.20 respectively.

It was observed from the results of porosity test of CKD mortars at both the testing ages that porosity of the mix increased considerably when the content of CKD in the mix was increased beyond 10%. It can be attributed to the decrease in the amount of C-S-H gel because of the lesser cement content in the mix, which makes the mix porous. The increase in chloride content of mixes with higher percentages of CKD also contributes to an increase in porosity(Najim et al., 2014). The excessive chloride content enhances the crystallization of hydration products which causes opening of the pore system(Marku et al., 2012). El-Aleem et al. and Maslehuddin et al. also found similar observations for porosity in their respective research. With increase in the percentage of CKD beyond 10%, the concrete becomes more porous and less durable as compared to the control mix(Maslehuddin et al., 2009, El-Aleem et al., 2005).

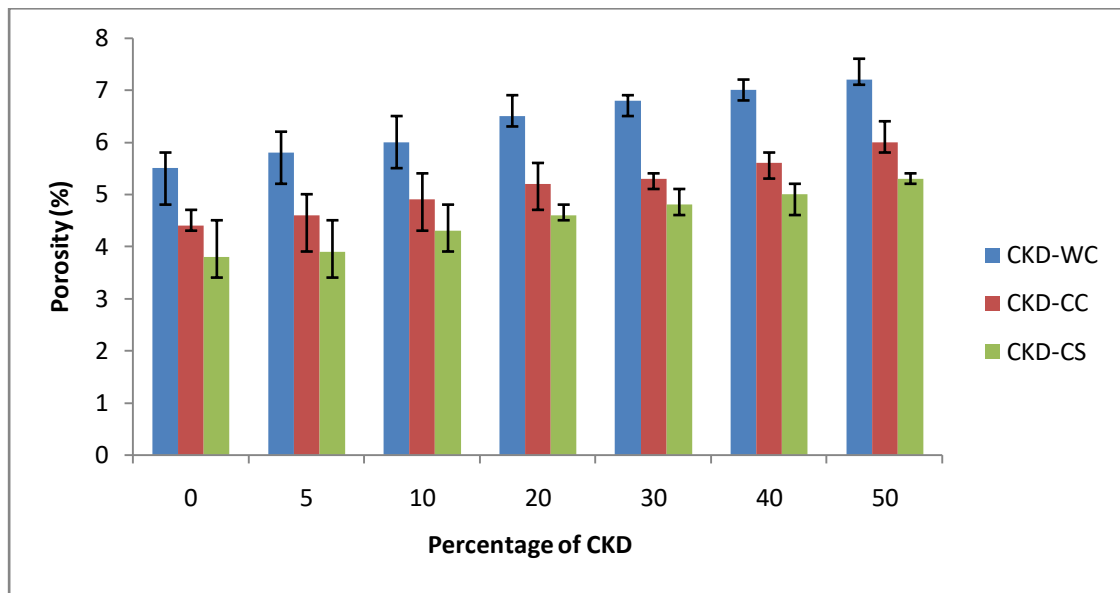


Fig. 6.19: Porosity of CKD mortars at the age of 3 days

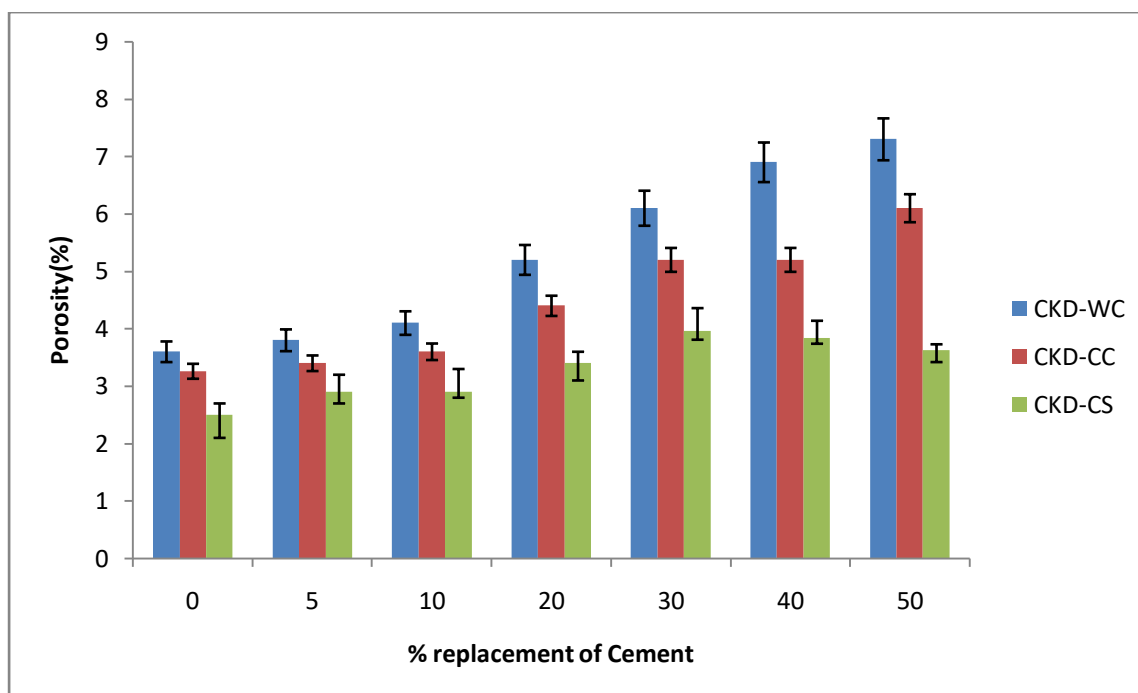


Fig. 6.20: Porosity of CKD mortars at the age of 180 days

When the porosity of ACC and WC specimens was compared, it was observed that ACC specimens exhibited lower porosity as compared to water cured specimens. The reaction of carbon dioxide with the hydration reaction products causes conversion of unstable Ca(OH)_2 into stable CaCO_3 . Frias and Goni and Morandeau et al. obtained similar results for porosity in their respective studies (Frías and Goñi, 2013; Morandeau et al., 2015). The decrease in porosity was even greater when the carbonation curing process was followed by the water spray (CKD-CS). The water spray helps in replenishing the water lost in carbonation reaction, which leads to further hydration of the mix that creates more C-S-H gel and a denser microstructure. Rostami et al. found that the carbonated concretes exhibited lower porosity because concrete pores become less connected and do not easily allow the movement of ions in the concrete (Rostami et al., 2012b). Liu et al. suggested that the CaCO_3 produced after the carbonation reaction creates a micro aggregate effect in concrete decreasing the porosity of concrete considerably (Liu et al., 2016).

In this study, it was observed that decrease in porosity by carbonation was found to be greater for the higher percentages of CKD. This is possibly because the addition of CKD favours the carbonation reaction because of larger surface area of particles and

higher alkalinity. Also, high initial porosity of the mix helps in greater ingress of CO_2 , thus allowing more amount of CaCO_3 formation. Higher CaCO_3 precipitation leads to increased amount of solid phases in the pore system network (Rostami et al. 2011). Carbonation curing process helps enhance the durability of concrete mix by decreasing the porosity. The similar efficiency of carbonation curing in improving compressive strength of the mix was not observed. It can be due to the fact that carbonation curing is a surface phenomenon, and hence affects surface properties like porosity to a larger extent.

6.3.3 Microstructure

The microstructure of CKD mortars was analysed at the age of 180 days of casting using XRD and SEM-EDS. The samples for microstructure analysis were obtained from the broken pieces obtained after performing compressive strength tests. The SEM images of CKD mortars containing 10% CKD as a replacement of cement were obtained for all the three curing regimes. Along with SEM, XRD analysis of mixes with 10% CKD were also carried out.

The XRD results of mixes with 10 % CKD are shown in Fig. 6.21. The XRD analysis of water cured CKD mortars (CKD-WC) shows peaks of Portlandite (Ca(OH)_2), Tricalcium silicate (C_3S), Dicalcium silicate (C_2S) and silica (SiO_2) similar to the OPC mortars. The XRD analysis of carbonation cured CKD mortars (CKD-CC and CKD-CS) showed additional peaks of calcite in addition to the peaks observed in the water cured specimens. The calcite is formed from the carbonation reaction of Ca(OH)_2 which gets converted into CaCO_3 . The effect of ACC on CKD mortars is similar to what was observed for the OPC mortars. In the CKD-CS specimens, the peaks of Ca(OH)_2 were observed clearly; whereas in the CKD-CC specimens, the peak of Ca(OH)_2 are not visible. This indicates the subsequent hydration in case of CKD mortars also, where Ca(OH)_2 peaks re-emerge on account of the progress of hydration reaction post carbonation curing.

The SEM-EDS analysis of CKD mortars subjected to different curing regimes have been shown in Fig. 6.22, 6.23 and 6.24. The SEM images of water cured specimen depicted the presence of C-S-H gel, Ca(OH)_2 and voids in the mix. The formation of

CaCO_3 was also observed in the ACC specimens because of the carbonation reaction. The EDS for ACC specimens followed by water spray (CKD-CS) showed greater Si/Ca (0.22) and C/Ca ratio (0.32) than the reference water cured and only carbonation cured specimens, indicating more C-S-H gel and CaCO_3 formation.

The densest mix was observed in the CKD-CS specimens owing to the CaCO_3 formation and C-S-H gel formed from the hydration reactions. This CaCO_3 produces a micro aggregate effect in the mix, which causes its densification. Therefore, lesser voids were observed in carbonated specimens as compared to the water cured specimen. This also accounts for the decrease in porosity which was also observed in the porosity tests. The CKD-CC specimens on the other hand showed a porous mix as compared to the CKD-WC specimens, which can be attributed to lack of sufficient hydration post ACC. This was also observed in the compressive strength tests where CKD-CS specimens depicted higher strength than the CKD-WC specimens and the CKD-CC specimens showed slightly lesser strength than the WC specimens.

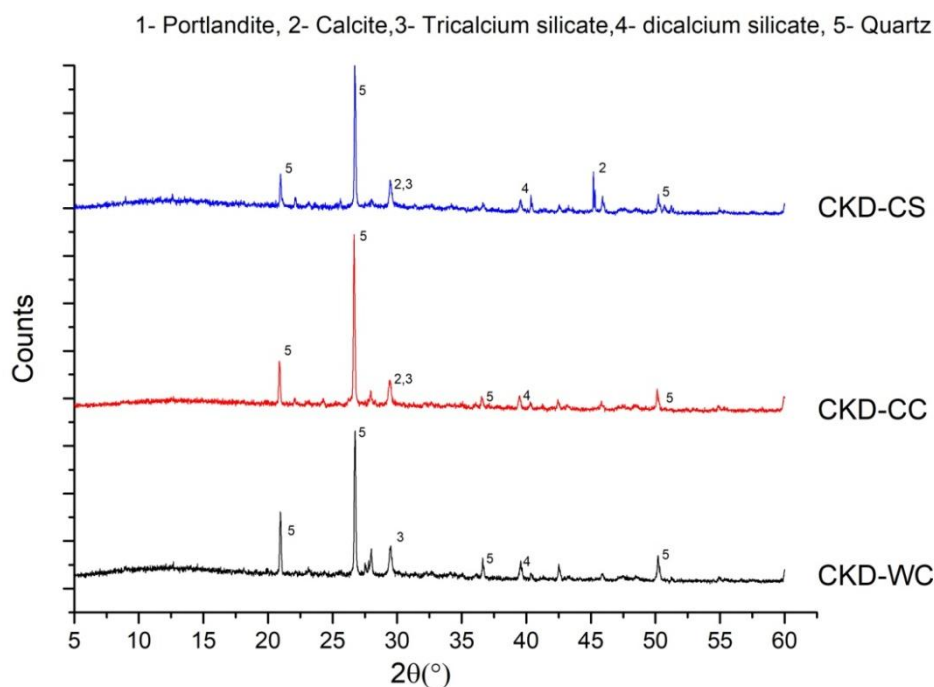


Fig. 6.21: XRD analysis of CKD mortars at the age of 180 days

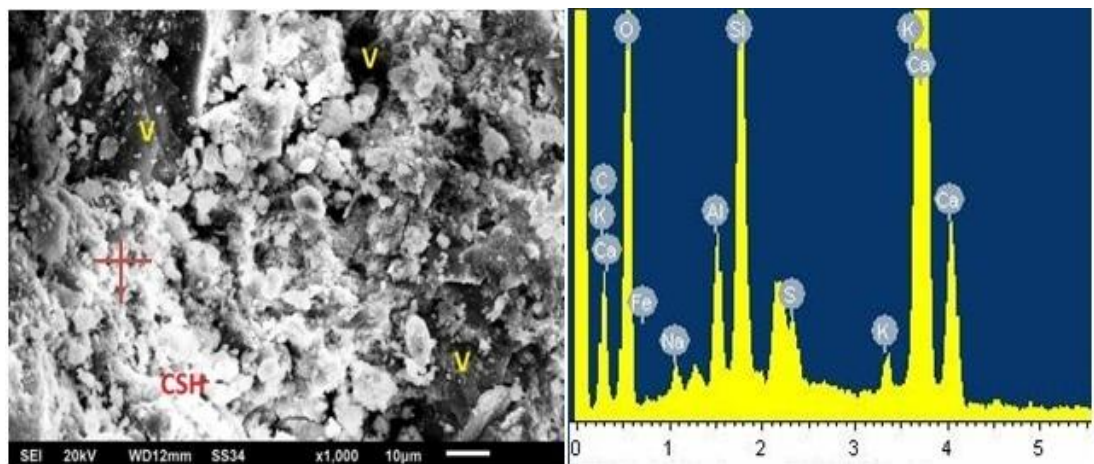


Fig. 6.22: SEM-EDS of Water cured CKD mortars at 180 days

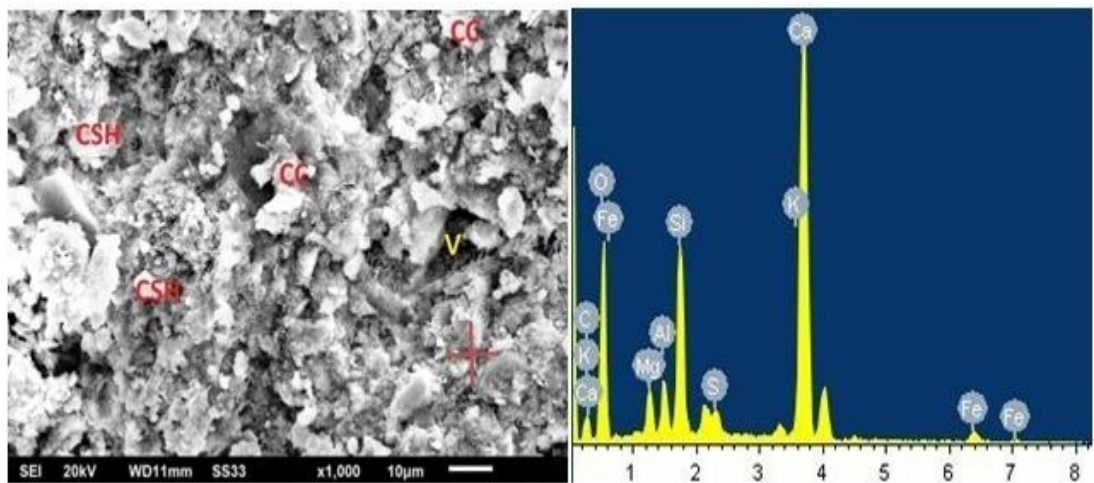


Fig. 6.23: SEM-EDS of carbonation cured (CC) CKD mortars at 180 days

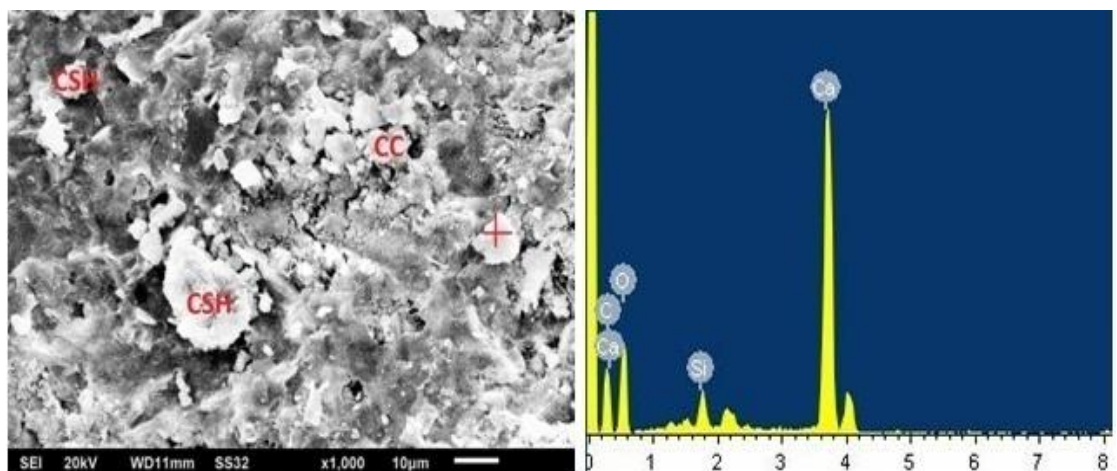


Fig. 6.24: SEM-EDS of carbonation cured (CS) CKD mortars at 180 days

6.4 EFFECT OF ACC ON MORTARS INCORPORATING GGBS AS PARTIAL REPLACEMENT OF CEMENT

GGBS is an industrial waste produced from the blast furnaces of iron industry. In this study, GGBS was used as a partial replacement of cement in mortars in varying percentages of 0-50%. The chemical composition of GGBS and physical properties of GGBS have been compared with OPC in Table 6.1. It can be seen from Table 6.1 that the major constituent in the GGBS is SiO_2 . The prepared mortars were subjected to three types of curing regimes: The first set was subjected to water curing (G-WC) till the testing age. The second set was subjected to 12 hours of ACC followed by sealing in plastic bags till the testing age (G-CC). The third set of specimens was subjected to 12 hours of ACC followed by 3 days of water spray and then sealed in plastic bags till the testing age (G-CS). The performance of mortars was examined in terms of compressive strength, porosity and microstructure.

6.4.1 Compressive Strength

The compressive strength of mortars prepared with GGBS was tested at the age of 3, 7, 28, 90 and 180 days of testing and the corresponding results are presented in Fig.6.25-6.29 respectively. The compressive strength of GGBS mortars at the age of 3 days indicated that irrespective of the curing regime, the strength of mortars decreased on replacing cement with GGBS. The loss of strength can be attributed to two major factors. Firstly, the lesser cement content in GGBS mortars, which causes a reduction in rate of hydration and production of lesser C-S-H gel in the mix. The loss of strength was observed to be directly proportional to content of GGBS in the mix. Secondly, the slower reaction rate of GGBS also led to delay in strength gain of concrete.

On comparing the effect of different curing regimes on compressive strength of GGBS mortars, it was observed that the carbonation cured specimens, both G-CC and G-CS specimens exhibited higher strength than the G-WC specimens. The enhancement in strength was observed for all the mixes. However, the extent of increase in strength due to ACC was observed to be inversely proportional to the GGBS content in the mix. This can be understood due to the change in composition of

mix due to addition of GGBS. The major constituent of GGBS is SiO_2 , which does not show high reactivity to CO_2 . Therefore, addition of higher content of GGBS to the mix leads to higher content of SiO_2 instead of CO_2 reactive constituents like C_3S and C_2S . This limits the impact of carbonation curing in mixes containing higher percentages of GGBS. The initial strength of ACC mixes is found to be even higher for the G-CS specimens, where the carbonation is followed by water spray. Similar to OPC mortars, the hydration of GGBS mortars post carbonation also produced additional C-S-H gel in the mix which provides a higher compressive strength.

The compressive strength of GGBS mortars at the age of 7 days and 28 days has been shown in Fig. 6.26 and 6.27 respectively. It can be observed that the strength of water cured GGBS mortars at the age of 28 days increased on addition of GGBS to the mix and the maximum strength was observed at replacement level of 30%. The higher strength of GGBS mixes is attributed to pozzolanic reaction due to presence of SiO_2 in the GGBS. SiO_2 reacts with Ca(OH)_2 from the hydration reactions to produce additional C-S-H gel, which provides compressive strength at the later ages to the mix. At the later testing ages of 90 days and 180 days as shown in Fig. 6.28 and 6.29 respectively, significant gain of strength is observed in the water cured GGBS mortars owing to the late pozzolanic reaction. The strength gain is observed to be increasing as the content of GGBS is increased in the mix and the highest strength is observed for mixes prepared with 30% content of GGBS.

It was observed that for the carbonation cured GGBS mortars that the strength of carbonation cured mortars at the later ages decreased with the increase in content of GGBS in the mix. This can be attributed to the fact that the strength gain in GGBS mortars is mainly dependent on the pozzolanic reaction at later ages of mortar. In case of carbonation cured mortars, the pozzolanic activity gets hindered due to consumption of Ca(OH)_2 in the early carbonation reactions and lesser production of Ca(OH)_2 later on as compared to water cured specimens. However, on comparing the two types of carbonation curing regimes, the strength gain of G-CS specimens was observed to be better in GGBS mortars which can also be attributed to the production of Ca(OH)_2 in the subsequent hydration process which aids the pozzolanic reaction.

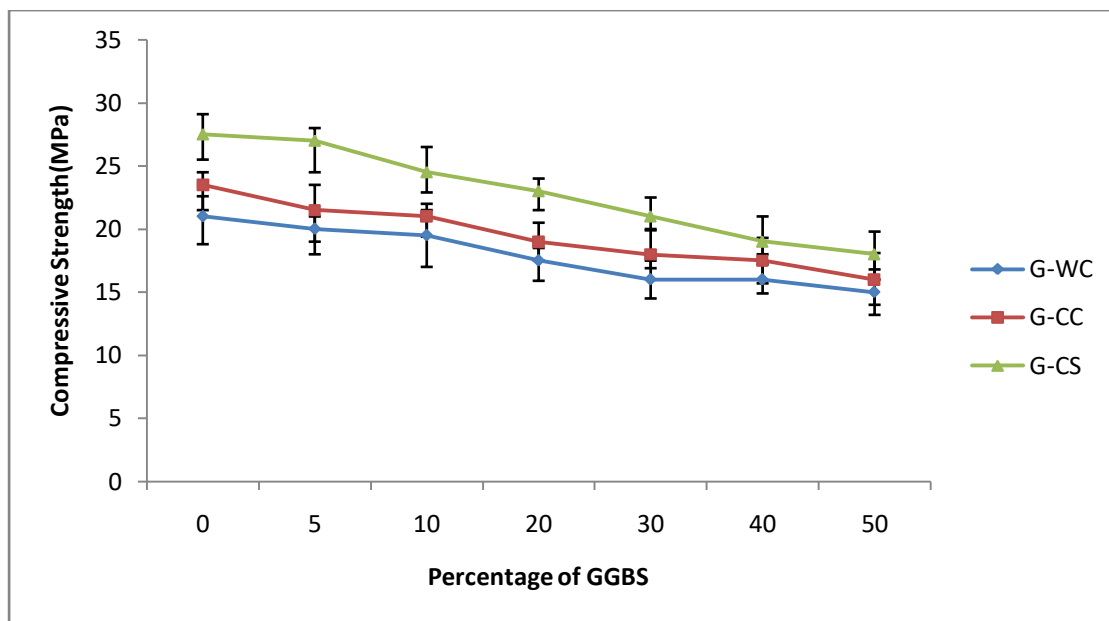


Fig. 6.25: Compressive strength of GGBS mortars at the age of 3 days

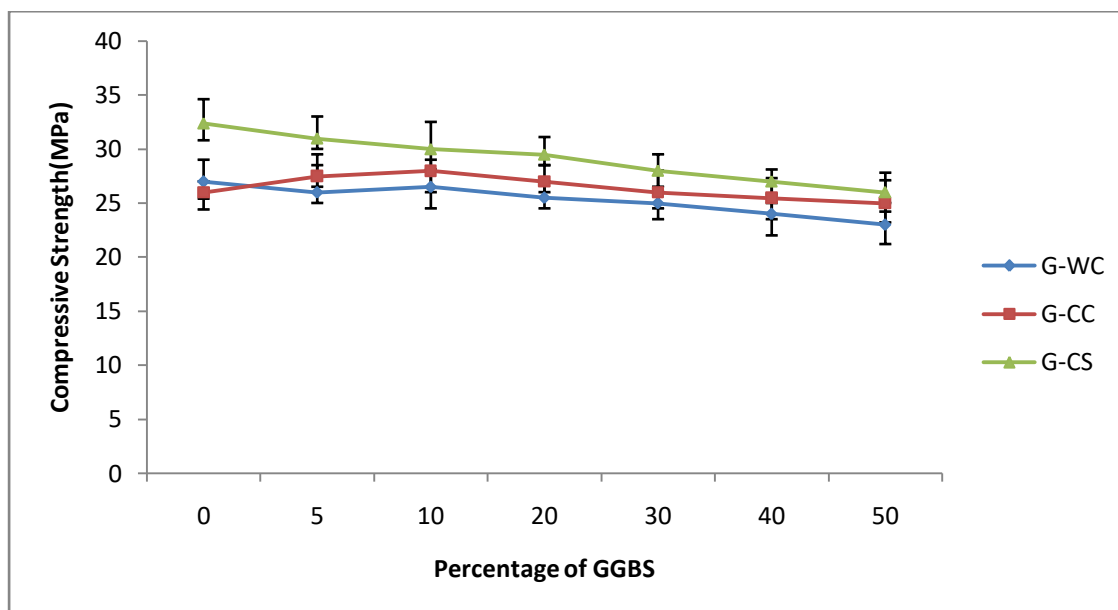


Fig. 6.26: Compressive strength of GGBS mortars at the age of 7 days

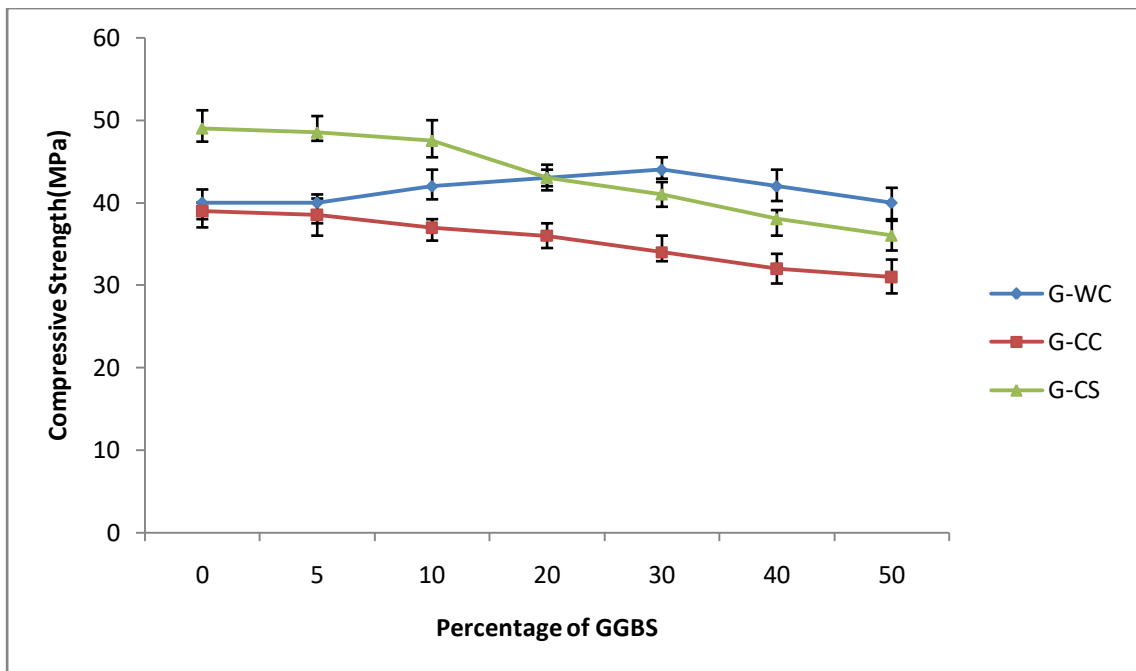


Fig. 6.27: Compressive strength of GGBS mortars at the age of 28 days

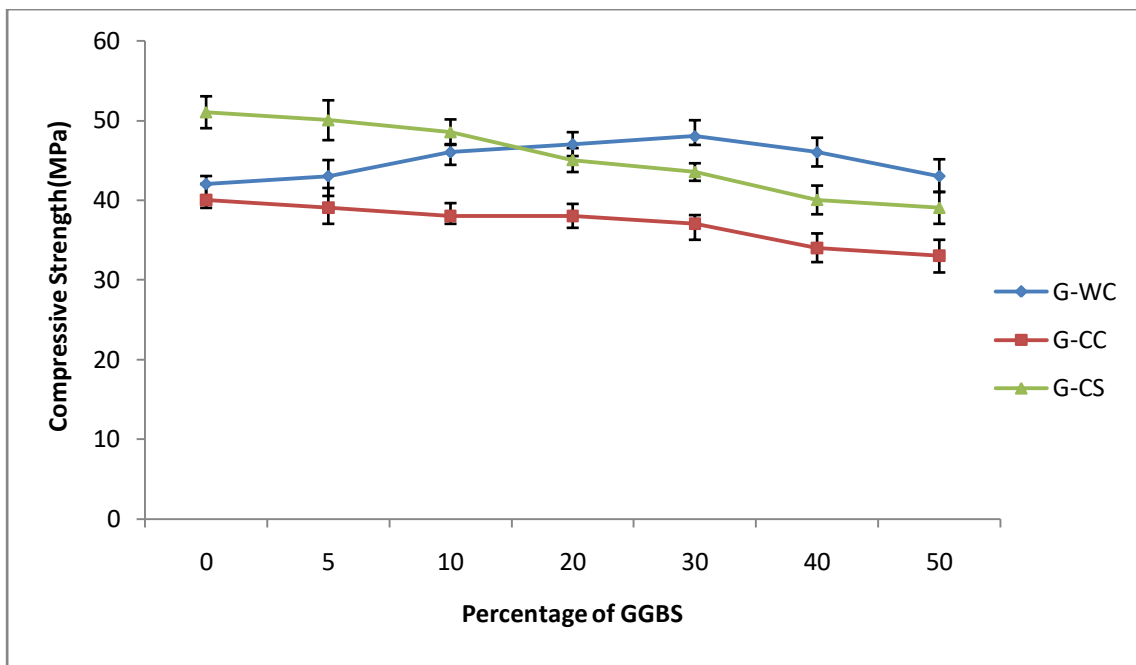


Fig. 6.28: Compressive strength of GGBS mortars at the age of 90 days

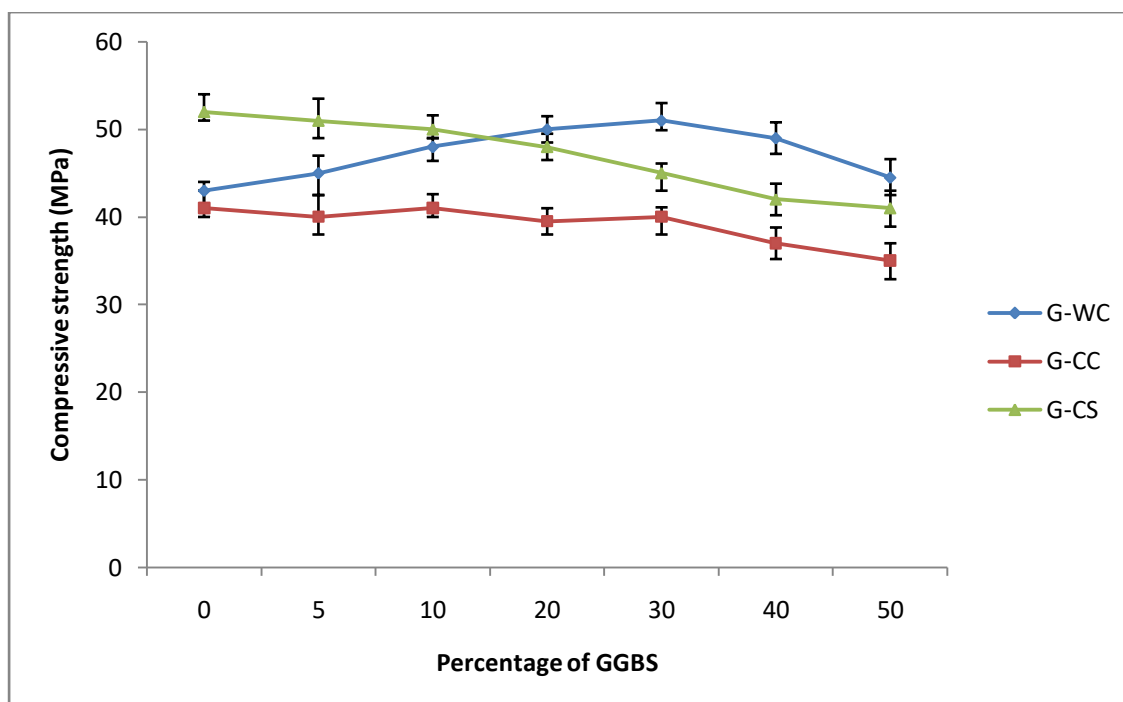


Fig. 6.29: Compressive strength of GGBS mortars at the age of 180 days

6.4.2 Porosity of GGBS Mortars

The porosity of GGBS mortars subjected to different curing regimes was tested at the age of 3 days and 180 days of casting and the corresponding results are depicted in Fig. 6.30 and 6.31 respectively. It can be observed from the results of porosity at the age of 3 days that the value of porosity gradually increased irrespective of the curing regime, when the content of GGBS was increased in the mix. The increase in porosity at the early age can be understood due to the decrease in cement content on adding GGBS to the mix. Decreased cement content reduces the hydration rate of mortars and results in production of a porous mix. This also correlates to the results observed for the compressive strength tests of GGBS mortars.

The ACC specimens showed lesser values of porosity than the water cured specimens. The conversion of Ca(OH)_2 to CaCO_3 upon carbonation is responsible for the observed decrease in values of porosity. The decrease in porosity was observed to be even greater when the process of ACC was followed by water curing which results in production of additional C-S-H gel that also contributes to reduction in porosity. However, the decrease in porosity of GGBS mortars with ACC was lesser when

compared to OPC or CKD mortars. This can be attributed to the lesser content of Ca(OH)_2 in GGBS mortars at an early age owing to the lesser rate of hydration reaction. Since, conversion of Ca(OH)_2 to CaCO_3 is the major factor resulting in decrease in porosity of mortars, a lesser extent of reduction was observed in case of GGBS mortars.

At the later age of 180 days as shown in Fig. 6.31, the porosity of water cured GGBS mortars was observed to decrease when the replacement level of GGBS was increased in the mix and the lowest value of porosity was observed at 30% replacement level. The decreased porosity with increase in content of GGBS can be understood as a result of pozzolanic reaction of SiO_2 present in GGBS. The pozzolanic activity of GGBS produces C-S-H gel at later stages that causes reduction in porosity. However, the decrease in porosity was not observed in the ACC specimens. This is because of lack of Ca(OH)_2 in the ACC specimens which does not allow the sufficient pozzolanic reaction of SiO_2 and production of C-S-H gel. However, the ACC specimens followed by water spray exhibited lesser porosity than the G-CC specimens, owing to both the subsequent hydration which produces additional C-S-H gel which reduces the porosity of the mix.

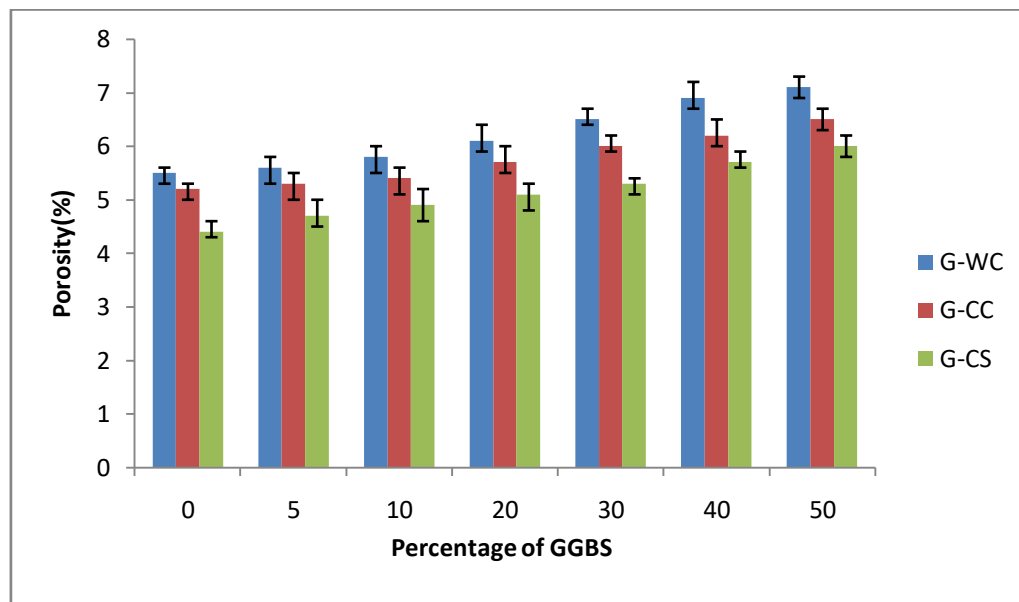


Fig. 6.30: Porosity of GGBS mortars at the age of 3 days

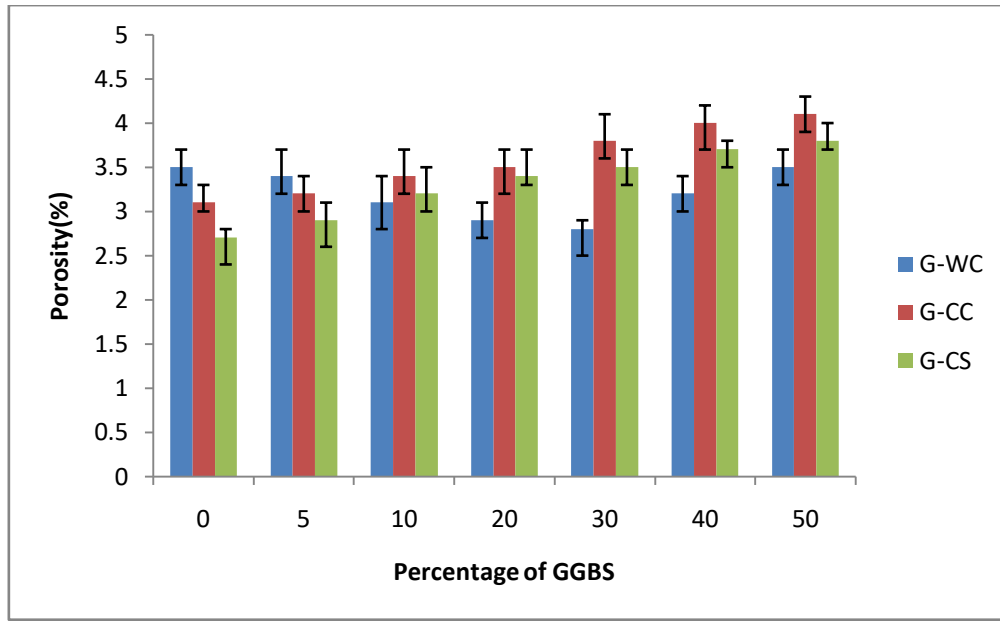


Fig. 6.31: Porosity of GGBS mortars at the age of 180 days

6.4.3 Microstructure of GGBS Mortars

The microstructure of GGBS mortars containing 30% GGBS as a replacement of cement was analysed at the age of 180 days of casting with the help of XRD analysis and SEM-EDS images. The samples for microstructure analysis were obtained from the crushed mortar specimens from the compressive strength test. The results of XRD analysis of GGBS mortars subjected to different curing regimes have been presented in Fig. 6.32.

The XRD analysis of water cured GGBS mortars showed strongest peaks of silica (SiO_2), along with peaks of tricalcium silicate (C_3S) and dicalcium silicate (C_2S). In the XRD analysis of ACC specimens, G-CC and G-CS, peaks of calcite (CaCO_3) are also observed, which evidences the formation of CaCO_3 in GGBS mortars during ACC. Notably, unlike OPC and CKD mortars, the peaks of Ca(OH)_2 were not observed in the GGBS mortars. The absence of Ca(OH)_2 peaks can be attributed to the pozzolanic reaction of Ca(OH)_2 with SiO_2 in the water cured GGBS mortars. In the carbonation cured GGBS mortars, the absence of Ca(OH)_2 peaks can be correlated to consumption of Ca(OH)_2 in both the carbonation as well as pozzolanic reactions. Also, the peaks of SiO_2 are observed to be stronger for the ACC specimens, which can be attributed to the higher SiO_2 content of GGBS mortars. In the water cured

GGBS mortars, SiO_2 reacts with Ca(OH)_2 to form C-S-H, which causes reduced peaks of SiO_2 . However, in case of ACC specimens, due to lesser availability of Ca(OH)_2 for the pozzolanic reactions, SiO_2 remains unreacted and hence, strong peaks of SiO_2 were observed in ACC specimens.

The SEM-EDS analysis of GGBS mortars subjected to different curing regimes has been shown in Fig. 6.33, 6.34 and 6.35. The effect of different curing regimes on GGBS mortars can be clearly observed from the SEM images obtained at the age of 180 days of casting. The water cured GGBS specimens showed the densest microstructure among the three curing regimes. The water cured GGBS mortars showed presence of C-S-H gel, voids and slight presence of Ca(OH)_2 . The dense and compact microstructure of water cured GGBS mortars can be attributed to the pozzolanic activity of GGBS which results in production of C-S-H gel in the mix. On the other hand, the carbonation cured specimens exhibited a comparatively weaker microstructure than the water cured specimens in case of GGBS mortars. This correlates well with the lower compressive strength observed in GGBS mortars when subjected to ACC. The most porous microstructure was observed in the G-CC specimens of GGBS mortars, owing to the lack of both the sufficient hydration and pozzolanic reactions in these specimens.

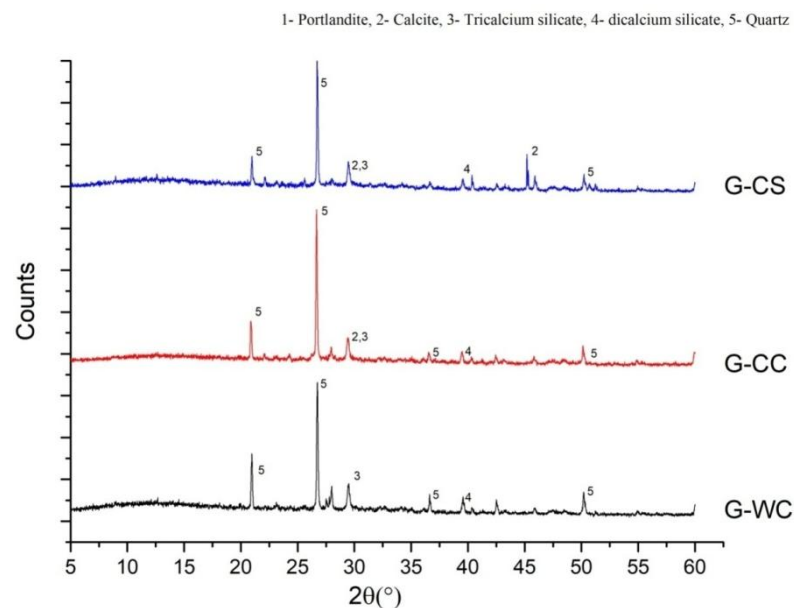


Fig. 6.32: XRD analysis of GGBS mortars at 180 days

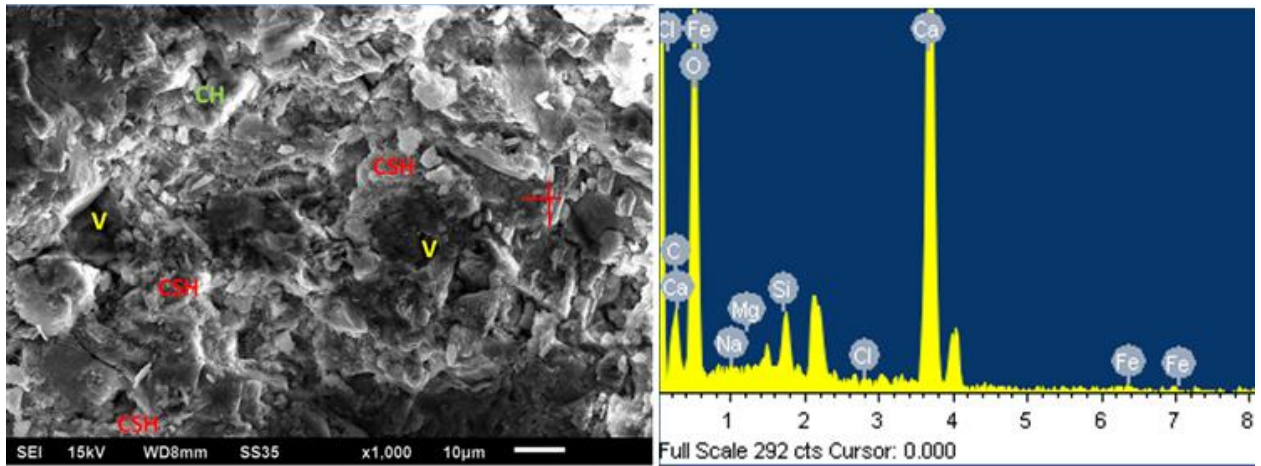


Fig. 6.33: SEM-EDS of Water cured GGBS mortars at 180 days

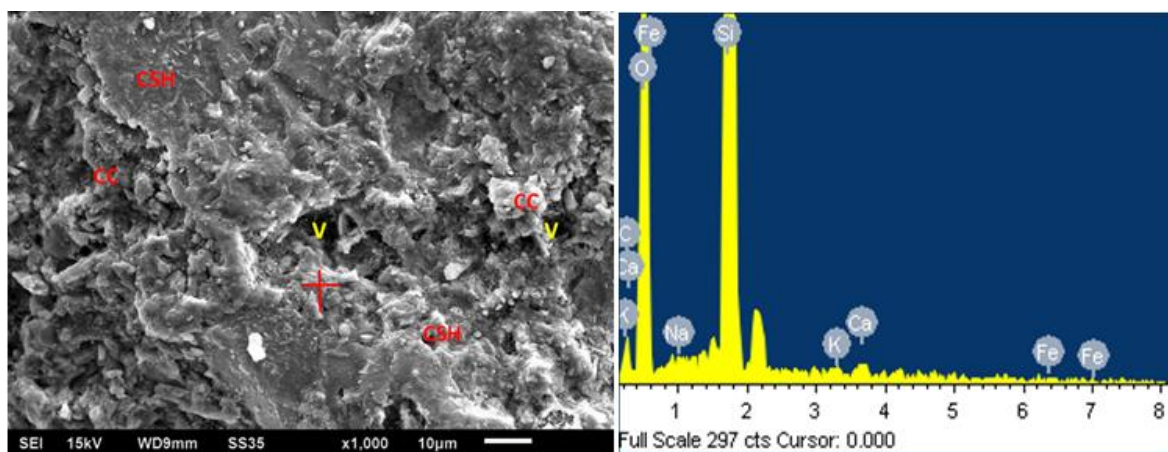


Fig. 6.34: SEM-EDS of carbonation cured (G-CC) GGBS mortars at 180 days

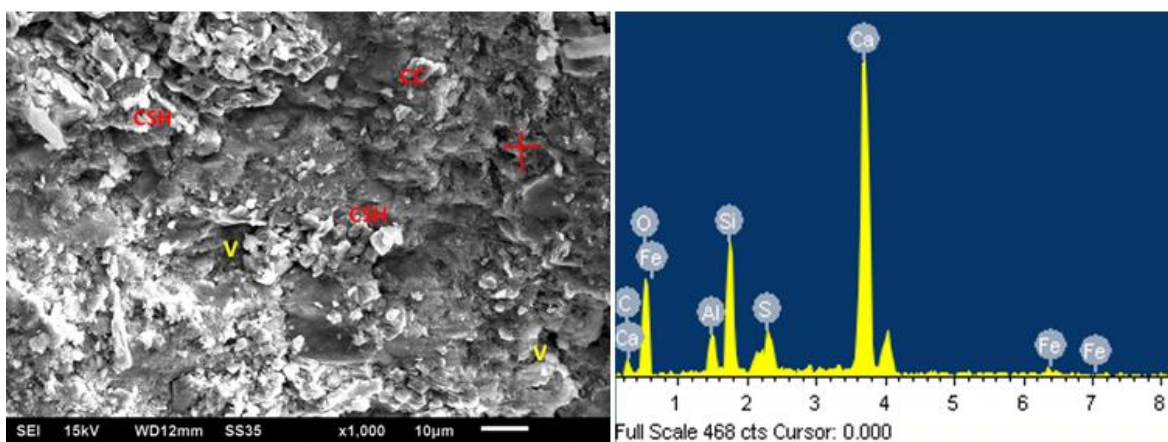


Fig. 6.35: SEM-EDS of carbonation cured (G-CS) GGBS mortars at 180 days

6.5 CO₂ SEQUESTRATION ABILITY

The primary purpose of ACC is to sequester CO₂ in the construction materials. Therefore, the materials used in this study; OPC, PPC, CKD and GGBS were also tested for their respective CO₂ sequestration capability. For this, the CO₂ uptake of these materials was calculated with the help of Thermogravimetric Analysis (TGA). The specimens for TGA were procured from respective mortars right at the end of carbonation period of ACC. The specimen of CKD was procured from the mix containing 10% CKD as a replacement of cement and the specimen for GGBS was taken from the mix containing 30% GGBS as replacement of cement. These mixes were selected for their better performance in the compressive strength tests. For TGA, the specimens were heated from room temperature up to a temperature of 900°C and corresponding weight loss of each sample was recorded. The result of TGA for these materials subjected to ACC is presented in Fig. 6.36. The calculation of CO₂ uptake of these materials was done based on Eq. 6.2.

$$CO_2 \text{ uptake (\%)} = \frac{\text{Sample mass at } 600^\circ C - \text{sample mass at } 800^\circ C}{\text{cement mass in original sample}} \times 100 \quad (6.2)$$

The calculation of CO₂ uptake from the TGA-DTG analysis indicated a CO₂ uptake of 20% for CKD specimen, 18% for OPC specimen, 15 % for PPC specimen and 12% for GGBS specimen. This indicated that the highest CO₂ uptake is achieved by CKD specimens followed by OPC and PPC specimens respectively. The higher CO₂ uptake of CKD indicates a greater reactivity of CKD mix to CO₂. The higher reactivity of CKD to CO₂ can be attributed to larger surface area of CKD particles and higher alkalinity of the CKD mixes.

The lower value of CO₂ uptake in PPC and GGBS mixes can be attributed to the higher content of SiO₂ in these mixes instead of calcium silicates which react actively with CO₂. On the other hand, SiO₂ possesses minimal or no reactivity to CO₂ (Zhang et al., 2017). Another major reason for lesser CO₂ uptake in PPC and GGBS mixes is the lower rate of hydration of these materials as compared to OPC. The lower rate of hydration results in production of lesser amount of Ca(OH)₂, which is the primary reactant in carbonation reactions of ACC. Thus it can be inferred that the pozzolanic

materials with high content of SiO_2 cannot be considered feasible for the purpose of CO_2 sequestration.

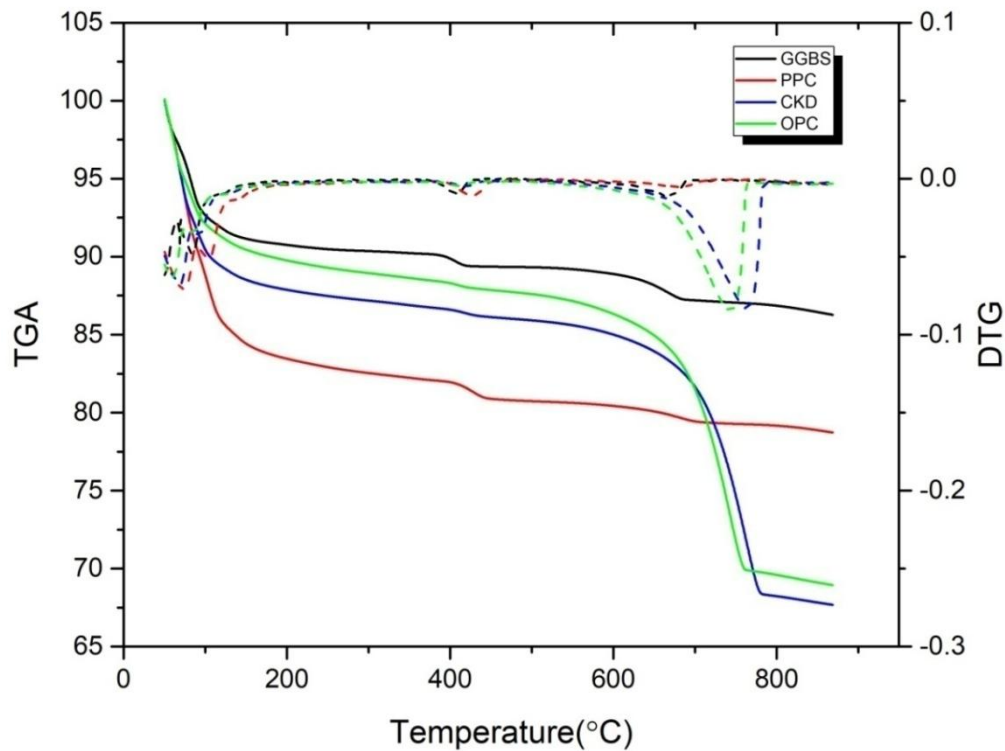


Fig. 6.36: Results of TGA-DTG for different materials subjected to ACC

6.6 CLOSING REMARKS

In this chapter, effect of ACC was studied on cementitious systems made with mineral admixtures. Firstly, effect of ACC was studied on performance of mortars made with flyash based portland pozzolana cement and comparison was made with OPC based mortars subjected to ACC. The effect of ACC was also examined on mortars prepared with GGBS slag and CKD, incorporated as partial replacement of cement.

The early age compressive strength of both the OPC and PPC mortars was observed to be enhanced when subjected to carbonation curing regime. However, the strength of carbonation cured PPC mortars reduced at the later ages as compared to water cured PPC mortars. Mortar specimens prepared with GGBS as a partial replacement of cement under ACC showed the performance similar to the mixes made with fly ash based PPC. The key finding from this study is that the process of carbonation curing

hindered the pozzolanic activity in PPC mortars which is majorly responsible for strength gain in PPC specimens.

In mortar specimens prepared by incorporating CKD as a replacement of cement, it was observed that for water curing regime, compressive strength of mixes decreased with increase in content of CKD. However, CKD mortars subjected to ACC exhibited at least 20% higher early age compressive strength than WC specimens in each mix. CKD was observed to favour the carbonation reaction, which can be understood because of larger surface area of CKD particles and its chemical composition.

The CO₂ sequestration ability of various materials was analyzed with the help of CO₂ uptake. The calculation of CO₂ uptake from the TGA-DTG analysis revealed a CO₂ uptake of 20% for CKD, 18% for OPC, 15 % for PPC and 12% for GGBS. The higher CO₂ uptake of CKD indicated a greater reactivity of CKD mix to CO₂. The lower value of CO₂ uptake in PPC and GGBS mixes indicated a lower reactivity of pozzolanic materials to CO₂ and hence, lesser CO₂ sequestration ability. It is evident from the test results that the pozzolanic materials does not exhibit sequestration potential when subjected to ACC.

CHAPTER 7

CONCLUSIONS

7.1 GENERAL

The objective of this research work is to evaluate the performance of concrete when subjected to accelerated carbonation curing (ACC). The effect of accelerated carbonation curing on the strength, permeation, durability and microstructural characteristics of concrete has been investigated and is compared with the conventional water curing. Special emphasis has been laid on surface characteristics of concrete. The role of duration of carbonation curing on various properties of concrete has been thoroughly investigated. Further, the performance of mineral admixture based cementitious system when subjected to accelerated carbonation curing has been investigated on mortar mixes. Based on the various tests and analysis conducted in this study, the following conclusions can be drawn.

7.2 EFFECT OF ACC VIS-À-VIS WATER CURING ON PROPERTIES OF CONCRETE

In the first phase of this study, the effect of ACC on various properties of concrete has been analysed and the results have been compared with water curing. The major focus of this part of the study is to access the two curing regimes in terms of surface characteristics. The concrete specimens were subjected to 6 hours of ACC, followed by three days of water spraying. The major conclusions drawn are:

1. The mechanical performance of concrete is considerably enhanced by ACC. Both abrasion resistance and compressive strength showed considerable improvement till the age of 3 days as compared to water curing regime. However, benefit of ACC on later ages was more pronounced on the surface strength, with substantial improvement in abrasion resistance of concrete at 28-days as compared to compressive strength. ACC specimens showed 26% and 29% lesser depth of wear than the water cured specimens at the age of 3 days and 28 days respectively. The corresponding improvement in compressive strength was 30%

and 5% respectively. Analysis of variance further confirmed more significant effect of ACC on surface properties than on bulk properties.

2. The water permeation characteristics, measured with the help of sorptivity test and water absorption test, indicated pore refinement of the surface layer of concrete when subjected to ACC. Lower values of water absorption and sorptivity were observed in the carbonation cured specimens as compared to water cured specimens. CaCO_3 precipitated from the carbonation reactions of ACC occupies the void spaces in concrete surface and acts as a barrier to passage of water. This led to pore refinement and better performance of ACC mixes.
3. The SEM-EDS analysis confirmed a densified microstructure of ACC specimens. SEM micrographs showed the presence of C-S-H gel, calcium hydroxide and ettringite in water cured mixes, whereas precipitation of calcium carbonate were observed in the carbonation cured mixes along with other major hydration products. A considerably densified microstructure was observed in SEM images owing to the precipitation of CaCO_3 in the pores of concrete and also production of additional CSH gel in the process of ACC. EDS analysis showed higher C/Ca ratio in ACC specimens as compared to water curing procedure, indicating a redistribution of calcium in the mix with production of CaCO_3 .
4. The XRD analysis of specimens subjected to water curing showed major peaks of calcium silicates, portlandite and silica. The XRD analysis of ACC specimens at early age showed additional peaks of calcite, diminished peaks of portlandite and calcium silicates as compared to water cured specimens. The XRD analysis of ACC specimens at the later ages showed development of portlandite peaks alongwith stable calcite peaks and diminished peaks of calcium silicates, indicating sufficient hydration post carbonation.
5. Thermogravimetric analysis of ACC specimens exhibited considerable mass loss in the temperature range of 600°C - 800°C indicating CO_2 uptake by concrete and presence of CaCO_3 in concrete. TGA of water cured specimens showed presence

of higher content of Ca(OH)_2 as compared to ACC specimens. ACC specimens exhibited a CO_2 uptake of 14.8% as calculated from the TGA plots.

6. Stoichiometric analysis was performed for ACC and water curing process based on the chemical reactions involved and the CO_2 uptake data of present study. The results obtained from Stoichiometric analysis indicated formation of higher content of CSH gel in ACC specimens and considerable formation of CaCO_3 .
7. Analysis of variance performed for the mechanical properties compressive strength and abrasion resistance revealed significant variation in these properties with varying the curing process. Analysis of variance further confirmed more significant effect of ACC on surface properties than on bulk properties.

7.3 EFFECT OF DURATION OF ACC ON PROPERTIES OF CONCRETE

In order to study the effect of duration for which the carbonation curing is provided to the specimens, ACC duration was varied as 6 hours, 12 hours or 24 hours. The consequent effects of ACC duration on properties of concrete are examined and are also compared with water curing regime.

1. The mechanical performance of concrete indicated higher early age performance of ACC concrete than the water cured concrete, irrespective of the ACC duration. However, at later ages, highest strengths and abrasion resistance was achieved in the mixes that were subjected to 12 hours of ACC. Concrete cured with 24 hours of ACC achieved lesser strength than the water cured specimens at later ages, while concrete cured with 6 hours of ACC achieved comparable strength to the water cured specimens.
2. Out of the three durations of carbonation curing, the carbonation curing of 12 hours duration was found to give optimal results in terms of mechanical strength and durability properties of concrete. The better performance of C12 mixes is due to an optimal combination of hydration and carbonation products, which provided densification to the mix and resulted in improvement of properties. Higher extent

of carbonation curing in C24 mixes proved to be detrimental to the properties of concrete. Higher carbonation helped in production of higher amount of CaCO_3 , but also resulted in decalcification of C-S-H into weak silica gel. Also, higher intensity of carbonation led to extensive pore water loss from concrete, which not only created internal voids in the mix, but also depleted the available water required for further hydration in concrete.

3. ACC specimens exhibited a slight drop in pH at the surface of specimens. The extent of drop in pH is directly proportional to the duration of ACC. However, the pH of concrete of all mixes is observed to be greater than the threshold pH of around 9, which is responsible for depletion of the passive layer that protects the rebar from corrosion.
4. ACC specimens exhibited lower values of drying shrinkage as compared to water cured specimens. Shrinkage strain is found to be decreasing with the increase in duration of carbonation in the ACC, with the ACC specimens cured for 24 hours showing lowest values of shrinkage strain. It is due to the formation of CaCO_3 during ACC, which did not favour release of water from the surface during the drying process, and hence lowers the shrinkage strain of the mixes.
5. All the mixes were exposed to natural carbonation in an environment chamber and the carbonation depth was measured till 360 days of exposure. The maximum value of carbonation depth was observed for the water cured specimens and mixes that were carbonation cured for 24 hours. This is in coherence with the results of permeation tests also, wherein the maximum porosity was observed in these mixes. The lesser rate of hydration in C24 specimens led to lower production of C-S-H gel in the mix, which made the mix porous. Secondly, a higher intensity of carbonation resulted in disintegration of produced CSH into weaker silica gel leading to opening up of pores in the concrete. This facilitated easy penetration of CO_2 in concrete resulting in the higher carbonation depth in C24 specimens. On the other hand, considerable production of both the hydration and carbonation

products in the C12 and C6 specimens helped in better performance of these mixes in the adverse environment of weathering carbonation.

6. The carbon sequestration ability of the ACC procedure was assessed on the basis of CO₂ uptake after the carbonation process. The CO₂ uptake was observed to be directly proportional with the duration of ACC specimens. The CO₂ uptake of approximately 14%, 20% and 24% were obtained for C6, C12 and C24 mixes, respectively. The highest CO₂ uptake in C24 specimens clearly showed the highest intensity of carbonation reaction in C24 specimens. However, it was also observed from the TGA curves that due to higher CO₂ uptake in longer duration of carbonation curing, CO₂ not only reacts with calcium silicates and Ca(OH)₂, but also with the C-S-H gel produced from hydration, which led to loss of strength in concrete.
7. Statistical analysis of effect of carbonation curing duration on properties of concrete was performed using Analysis of Variance (ANOVA) using software SPSS statistics tool. When the ANOVA was performed for different durations of carbonation curing, it was observed that the change in duration of ACC significantly affected both the compressive strength and abrasion resistance. Therefore, a mathematical relationship can be developed between the abrasion resistance and compressive strength for the carbonation cured concrete. The values of depth of wear predicted by using the developed relation lie within the 95% confidence level, indicating high accuracy of the model.

7.4 PERFORMANCE OF MINERAL ADMIXTURE BASED CEMENTITIOUS SYSTEM UNDER ACC

The effect of ACC is studied on cementitious systems made with mineral admixtures; which included fly ash based Portland pozzolana cement, ground granulated blast furnace slag and cement kiln dust both incorporated as partial replacement of cement. The test results indicated:

1. The early age compressive strength of both the OPC and PPC mortars is observed to be enhanced when subjected to carbonation curing regime. However, the strength of carbonation cured PPC mortars at the later ages reduced as compared to water cured PPC mortars. Lower strength development at the later ages in carbonation cured mortar mixes made with PPC is due to the fact that the pozzolanic reaction require the presence of Ca(OH)_2 as a reactant. However, the carbonation curing procedure consumes most of the Ca(OH)_2 formed at early ages in the carbonation reaction and converts it into calcium carbonate. Due to this, Ca(OH)_2 is not available in the matrix to allow the continuation of the pozzolanic reaction of fly ash. Therefore, the advantage of presence of pozzolanic material could not be achieved in carbonation cured mortars.
2. Mortar specimens prepared with GGBS as a partial replacement of cement under ACC showed the performance similar to the mixes made with fly ash based PPC. The carbonation cured GGBS mortars on the other hand exhibited better early age performance for all the mixes as compared to water curing. However, the later age performance of GGBS mortars subjected to carbonation curing was found to be deteriorating as compared to water cured mortars, inferring a decreased rate of pozzolanic reaction in GGBS mortars when subjected to carbonation curing.
3. Accelerated carbonation curing increases the compressive strength of mixes containing CKD, both at early and later ages, owing to the production of additional C-S-H gel and CaCO_3 upon carbonation. The porosity of the mortar decreased upon carbonation curing, because of densification of mix caused by conversion of Ca(OH)_2 into CaCO_3 . The porosity reduction by using ACC on mixes containing CKD was more than the corresponding effect on mixes without CKD. This is attributed to better ingress of CO_2 facilitated by porous microstructure of mixes containing CKD. CKD was observed to favour the carbonation reaction, which can be understood because of cementitious nature of CKD and the finer particle size.

4. The CO₂ sequestration ability of various materials was analyzed with the help of CO₂ uptake. The calculation of CO₂ uptake from the TGA-DTG analysis revealed a CO₂ uptake of 20% for CKD, 18% for OPC, 15 % for PPC and 12% for GGBS. The higher CO₂ uptake of CKD indicated a greater reactivity of CKD mix to CO₂. The lower value of CO₂ uptake in PPC and GGBS mixes indicated a lower reactivity of pozzolanic materials to CO₂ and hence, lesser CO₂ sequestration ability.

7.5 SCOPE FOR FUTURE WORK

1. The work can be extended to study the impact of ACC on larger sized precast specimens to evaluate the application of carbonation curing in the field.
2. An integrated approach for carbon dioxide capture and sequestration can be attempted using ACC to further economise the process of CO₂ sequestration.
3. The performance of actual reinforced concrete elements under ACC will give a further insight into the viability of this procedure in actual practice.
4. The work can also be extended to study the impact of factors like Relative Humidity, depth of CO₂ penetration and temperature. Also, Life Cycle Analysis can be carried out to compare the CO₂ sequestered against actual amount of CO₂ produced during the process.

REFERENCES

- Abdullahi, M., Odigure, J.O., Kovo, A.S., Abdulkareem, A.S., 2016. Characterization and predictive reaction model for cement-sand-kaolin composite for CO₂ sequestration. *J. CO₂ Util.* <https://doi.org/10.1016/j.jcou.2016.06.008>
- Ahmad, S., 2018. Accelerated carbon dioxide sequestration, *Carbon Dioxide Sequestration in Cementitious Construction Materials*. Elsevier Ltd. <https://doi.org/10.1016/B978-0-08-102444-7.00005-8>
- Ahmad, S., 2003. Reinforcement corrosion in concrete structures, its monitoring and service life prediction - A review. *Cem. Concr. Compos.* [https://doi.org/10.1016/S0958-9465\(02\)00086-0](https://doi.org/10.1016/S0958-9465(02)00086-0)
- Ahmad, S., Assaggaf, R.A., Maslehuddin, M., Al-Amoudi, O.S.B., Adekunle, S.K., Ali, S.I., 2017. Effects of carbonation pressure and duration on strength evolution of concrete subjected to accelerated carbonation curing. *Constr. Build. Mater.* 136, 565–573. <https://doi.org/10.1016/j.conbuildmat.2017.01.069>
- Al-Harthy, A.S., Taha, R., Al-Maamary, F., 2003. Effect of cement kiln dust (CKD) on mortar and concrete mixtures. *Constr. Build. Mater.* 17, 353–360. [https://doi.org/10.1016/S0950-0618\(02\)00120-4](https://doi.org/10.1016/S0950-0618(02)00120-4)
- Alonso, C., Andrade, C., Argiz, C., Malric, B., 1996. Na₂PO₃F as inhibitor of corroding reinforcement in carbonated concrete. *Cem. Concr. Res.* [https://doi.org/10.1016/S0008-8846\(96\)85028-9](https://doi.org/10.1016/S0008-8846(96)85028-9)
- Andrew, R.M., 2018. Global CO₂ emissions from cement production 195–217.
- Ashraf, W., Olek, J., 2016. Carbonation behavior of hydraulic and non-hydraulic calcium silicates: potential of utilizing low-lime calcium silicates in cement-based materials. *J. Mater. Sci.* <https://doi.org/10.1007/s10853-016-9909-4>
- ASTM C1202, 2012. Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration. ASTM Int. West Conshohocken, PA, 2017 1–8. <https://doi.org/10.1520/C1202-12.2>

- ASTM C150, 2011. Standard Specification for Portland Cement. ASTM Stand.
<https://doi.org/10.1002/jbm.b.31853>
- ASTM C157, 2017. Standard Test Method for Length Change of Hardened Hydraulic-Cement Mortar and Concrete. ASTM Int. West Conshohocken, PA, 2017.
- ASTM C1585-13, 2004. Standard test method for measurement of rate of absorption of water by hydraulic cement concretes. ASTM Int. West Conshohocken, PA, 2017. <https://doi.org/10.1520/C1585-13.2>
- ASTM C642-13, 2008a. Standard Test Method for Density, Absorption, and Voids in Hardened Concrete. <https://doi.org/10.1520/C0642-13.5>.
- ASTM C642-13, 2008b. Standard Test Method for Density, Absorption, and Voids in Hardened Concrete. ASTM Int. West Conshohocken, PA, 2017 11–13.
<https://doi.org/10.1520/C0642-13>
- ASTM G 109-13, 2013. Standard Test Method for Determining the Effects of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete, ASTM International.
- Babu, K.G., Kumar, V.S.R., 2000. Efficiency of GGBS in concrete. *Cem. Concr. Res.* 30, 1031–1036.
- Belda Revert, A., De Weerd, K., Hornbostel, K., Geiker, M.R., 2018. Carbonation-induced corrosion: Investigation of the corrosion onset. *Constr. Build. Mater.* <https://doi.org/10.1016/j.conbuildmat.2017.12.066>
- Berger, R.L., 1979. Stabilization of silicate structures by carbonation. *Cem. Concr. Res.* [https://doi.org/10.1016/0008-8846\(79\)90150-9](https://doi.org/10.1016/0008-8846(79)90150-9)
- Berger, R.L., Klemm, W.A., 1972. Accelerated curing of cementitious systems by carbon dioxide. Part II. Hydraulic calcium silicates and aluminates. *Cem. Concr. Res.* [https://doi.org/10.1016/0008-8846\(72\)90002-6](https://doi.org/10.1016/0008-8846(72)90002-6)
- Berger, R.L., Young, J.F., Leung, K., 1972. Acceleration of Hydration of Calcium

- Silicates by Carbon Dioxide Treatment. *Nat. Phys. Sci.*
<https://doi.org/10.1038/physci240016a0>
- Bertolini, L., Elsener, B., Pedferri, P., Redaelli, E., Polder, R.B., 2013. Carbonation-Induced Corrosion, in: *Corrosion of Steel in Concrete*.
<https://doi.org/10.1002/9783527651696.ch5>
- Böhni, H., 2005. Corrosion in Reinforced Concrete Structures, *Corrosion in Reinforced Concrete Structures*. <https://doi.org/10.1533/9781845690434>
- Bondar, D., Coakley, E., 2014. Use of gypsum and CKD to enhance early age strength of High Volume Fly Ash (HVFA) pastes. *Constr. Build. Mater.* 71, 93–108. <https://doi.org/10.1016/j.conbuildmat.2014.08.015>
- Bonenfant, D., Kharoune, L., Sauvé, S., Hausler, R., Niquette, P., Mimeault, M., Kharoune, M., 2008. CO₂ sequestration potential of steel slags at ambient pressure and temperature. *Ind. Eng. Chem. Res.*
<https://doi.org/10.1021/ie701721j>
- Broomfield, J.P., Davies, K., Hladky, K., 2002. The use of permanent corrosion monitoring in new and existing reinforced concrete structures. *Cem. Concr. Compos.* [https://doi.org/10.1016/S0958-9465\(01\)00024-5](https://doi.org/10.1016/S0958-9465(01)00024-5)
- Bukowski, J.M., Berger, R.L., 1979. Reactivity and strength development of CO₂ activated non-hydraulic calcium silicates. *Cem. Concr. Res.* 9, 57–68.
[https://doi.org/10.1016/0008-8846\(79\)90095-4](https://doi.org/10.1016/0008-8846(79)90095-4)
- Cabrera, J.G., 1996. Deterioration of concrete due to reinforcement steel corrosion. *Cem. Concr. Compos.* [https://doi.org/10.1016/0958-9465\(95\)00043-7](https://doi.org/10.1016/0958-9465(95)00043-7)
- Chabannes, M., Garcia-Diaz, E., Clerc, L., Bénézet, J.C., 2015. Studying the hardening and mechanical performances of rice husk and hemp-based building materials cured under natural and accelerated carbonation. *Constr. Build. Mater.* 94, 105–115. <https://doi.org/10.1016/j.conbuildmat.2015.06.032>
- Chang, J., Fang, Y., Shang, X., 2016. The role of β -C₂S and γ -C₂S in carbon capture

- and strength development. *Mater. Struct. Constr.* <https://doi.org/10.1617/s11527-016-0797-5>
- Cheng, A., Huang, R., Wu, J., Chen, C., 2005. Influence of GGBS on durability and corrosion behavior of reinforced concrete 93, 404–411.
<https://doi.org/10.1016/j.matchemphys.2005.03.043>
- De Silva, P., Bucea, L., Sirivivatnanon, V., 2009. Chemical, microstructural and strength development of calcium and magnesium carbonate binders. *Cem. Concr. Res.* <https://doi.org/10.1016/j.cemconres.2009.02.003>
- Dias, W.P.S., 2000. Reduction of concrete sorptivity with age through carbonation. *Cem. Concr. Res.* 30, 1255–1261.
- Dong, B., Qiu, Q., Gu, Z., Xiang, J., Huang, C., Fang, Y., Xing, F., Liu, W., 2016. Characterization of carbonation behavior of fly ash blended cement materials by the electrochemical impedance spectroscopy method. *Cem. Concr. Compos.* <https://doi.org/10.1016/j.cemconcomp.2015.10.006>
- El-Hassan, H., Shao, Y., 2015. Early carbonation curing of concrete masonry units with Portland limestone cement. *Cem. Concr. Compos.* 62, 168–177.
<https://doi.org/10.1016/j.cemconcomp.2015.07.004>
- El-Hassan, H., Shao, Y., 2014. Dynamic carbonation curing of fresh lightweight concrete. *Mag. Concr. Res.* <https://doi.org/10.1680/mac.13.00222>
- El-Hassan, H., Shao, Y., Ghouleh, Z., 2014. Effect of Initial Curing on Carbonation of Lightweight Concrete Masonry Units. *ACI Mater. J.* 441–450.
- El-Hassan, H., Shao, Y., Ghouleh, Z., 2013. Reaction products in carbonation-cured lightweight concrete. *J. Mater. Civ. Eng.* [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000638](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000638)
- Fang, Y., Chang, J., 2017. Rapid hardening β -C₂S mineral and microstructure changes activated by accelerated carbonation curing. *J. Therm. Anal. Calorim.* <https://doi.org/10.1007/s10973-017-6165-z>

- Farnam, Y., Villani, C., Washington, T., Spence, M., Jain, J., Jason Weiss, W., 2016. Performance of carbonated calcium silicate based cement pastes and mortars exposed to NaCl and MgCl₂ deicing salt. *Constr. Build. Mater.* <https://doi.org/10.1016/j.conbuildmat.2016.02.098>
- Fernández-Carrasco, L., Rius, J., Miravittles, C., 2008. Supercritical carbonation of calcium aluminate cement. *Cem. Concr. Res.* <https://doi.org/10.1016/j.cemconres.2008.02.013>
- François, R., Laurens, S., Deby, F., 2018. Steel Corrosion in Reinforced Concrete, in: *Corrosion and Its Consequences for Reinforced Concrete Structures*. Elsevier, pp. 1–41. <https://doi.org/10.1016/b978-1-78548-234-2.50001-9>
- Frías, M., Goñi, S., 2013. Accelerated carbonation effect on behaviour of ternary Portland cements. *Compos. Part B Eng.* 48, 122–128. <https://doi.org/10.1016/j.compositesb.2012.12.008>
- Fukushima, T., Yoshizaki, Y., Tomosawa, F., Takahashi, K., 1998. Relationship Between Neutralization Depth and Concentration Distribution of CaCO₃ - Ca(OH)₂ in Carbonated Concrete. *Adv. Concr. Technol.*
- García-González, C.A., el Grouh, N., Hidalgo, A., Fraile, J., López-Periago, A.M., Andrade, C., Domingo, C., 2008. New insights on the use of supercritical carbon dioxide for the accelerated carbonation of cement pastes. *J. Supercrit. Fluids.* <https://doi.org/10.1016/j.supflu.2007.07.018>
- Ghafoori, N., Sukandar, B.M., 1995. Abrasion resistance of concrete block pavers. *ACI Mater. J.* <https://doi.org/10.14359/1174>
- Goodbrake, C.J., Young, J.F., Berger, R.L., 1979a. Reaction of Hydraulic Calcium Silicates with Carbon Dioxide and Water. *J. Am. Ceram. Soc.* <https://doi.org/10.1111/j.1151-2916.1979.tb19112.x>
- Goodbrake, C.J., Young, J.F., Berger, R.L., 1979b. Reaction of Beta-Dicalcium Silicate and Tricalcium Silicate with Carbon Dioxide and Water Vapor. *J. Am. Ceram. Soc.* <https://doi.org/10.1111/j.1151-2916.1979.tb19046.x>

- Goto, S., Suenaga, K., Kado, T., Fukuhara, M., 1995. Calcium Silicate Carbonation Products. *J. Am. Ceram. Soc.* <https://doi.org/10.1111/j.1151-2916.1995.tb09057.x>
- Grounds, T., G Midgley, H., V Novell, D., 1988. Carbonation of ettringite by atmospheric carbon dioxide. *Thermochim. Acta.* [https://doi.org/10.1016/0040-6031\(88\)87407-0](https://doi.org/10.1016/0040-6031(88)87407-0)
- Guan, X., Liu, S., Feng, C., Qiu, M., 2016. The hardening behavior of γ -C2S binder using accelerated carbonation. *Constr. Build. Mater.* <https://doi.org/10.1016/j.conbuildmat.2016.03.208>
- Habashi, F., 2017. Principles of extractive metallurgy, Principles of Extractive Metallurgy. <https://doi.org/10.1201/9780203742112>
- Hargis, C.W., Lothenbach, B., Müller, C.J., Winnefeld, F., 2017. Carbonation of calcium sulfoaluminate mortars. *Cem. Concr. Compos.* <https://doi.org/10.1016/j.cemconcomp.2017.03.003>
- He, P., Shi, C., Tu, Z., Poon, C.S., Zhang, J., 2016a. Effect of further water curing on compressive strength and microstructure of CO₂-cured concrete. *Cem. Concr. Compos.* 72, 80–88. <https://doi.org/10.1016/j.cemconcomp.2016.05.026>
- He, P., Shi, C., Tu, Z., Sun, C., Zhang, J., 2016b. Effect of further water curing on compressive strength and microstructure of CO₂-cured concrete Effect of further water curing on compressive strength and microstructure of CO₂-cured concrete. *Cem. Concr. Compos.* 72, 80–88. <https://doi.org/10.1016/j.cemconcomp.2016.05.026>
- He, Z., Yang, H., Shao, Y., Liu, M., 2013. Early carbonation behaviour of no-clinker steel slag binder. *Adv. Cem. Res.* <https://doi.org/10.1680/adcr.12.00054>
- Heiyantuduwa, R., Alexander, M.G., Mackechnie, J.R., 2006. Performance of a Penetrating Corrosion Inhibitor in Concrete Affected by Carbonation-Induced Corrosion. *J. Mater. Civ. Eng.* [https://doi.org/10.1061/\(asce\)0899-1561\(2006\)18:6\(842\)](https://doi.org/10.1061/(asce)0899-1561(2006)18:6(842))

- Hobbs, D.W., 2001. Concrete deterioration: Causes, diagnosis, and minimising risk. *Int. Mater. Rev.* <https://doi.org/10.1179/095066001101528420>
- Huang, R., Chang, J.J., Wu, J.K., 1996. Correlation between corrosion potential and polarization resistance of rebar in concrete. *Mater. Lett.* [https://doi.org/10.1016/0167-577X\(96\)00099-7](https://doi.org/10.1016/0167-577X(96)00099-7)
- Huijgen, W.J.J., Comans, R.N.J., 2006. Carbonation of steel slag for CO₂ sequestration: Leaching of products and reaction mechanisms. *Environ. Sci. Technol.* <https://doi.org/10.1021/es052534b>
- Huijgen, W.J.J., Witkamp, G.J., Comans, R.N.J., 2006. Mechanisms of aqueous wollastonite carbonation as a possible CO₂ sequestration process. *Chem. Eng. Sci.* <https://doi.org/10.1016/j.ces.2006.01.048>
- Huijgen, W.J.J., Witkamp, G.J., Comans, R.N.J., 2005. Mineral CO₂ sequestration by steel slag carbonation. *Environ. Sci. Technol.* <https://doi.org/10.1021/es050795f>
- Hussain, R.R., Ishida, T., 2009. Critical carbonation depth for initiation of steel corrosion in fully carbonated concrete and development of electrochemical carbonation induced corrosion model. *Int. J. Electrochem. Sci.*
- IEA, 2018. Emissions [WWW Document]. URL <https://www.iea.org/geco/emissions/> (accessed 10.13.19).
- IPCC, 2005. Special Report on Carbon Dioxide Capture and Storage.
- IS:10262, 2009. Concrete mix proportioning- guidelines. Bur. Indian Stand.
- IS 1237, 2012. Cement Concrete Flooring Tiles — Specification. Bur. Indian Stand. New Delhi.
- IS 1489, 1991. Portland-Pozzolana Cement Specification. Bur. Indian Stand.
- IS 1786, 2008. High strength deformed steel bars and wires for concrete reinforcement. Bur. Indian Stand.
- IS 383, 2016. Coarse and Fine Aggregate for Concrete - Specification. Bur. Indian

Stand.

IS 4031:Part6, 1988. Methods Of Physical Tests For Hydraulic Cement. Bur. Indian Stand. New Delhi.

IS 516, 2004. Method of Tests for Strength of Concrete. Bur. Indian Stand. New Delhi.

IS 5816, 1999. Method of Test Splitting tensile strength of concrete. Bur. Indian Stand.

IS 8112, 2013. Ordinary Portland cement, 43 grade-Specification. Bur. Indian Stand. New Delhi.

Ismail, M., Muhammad, B., Ismail, M.E.G., 2010. Compressive strength loss and reinforcement degradations of reinforced concrete structure due to long-term exposure. *Constr. Build. Mater.*
<https://doi.org/10.1016/j.conbuildmat.2009.12.003>

Jamil, H.E., Montemor, M.F., Boulif, R., Shrir, A., Ferreira, M.G.S., 2003. An electrochemical and analytical approach to the inhibition mechanism of an amino-alcohol-based corrosion inhibitor for reinforced concrete. *Electrochim. Acta.* [https://doi.org/10.1016/S0013-4686\(03\)00472-9](https://doi.org/10.1016/S0013-4686(03)00472-9)

Jang, J.G., Lee, H.K., 2016. Microstructural densification and CO₂ uptake promoted by the carbonation curing of belite-rich Portland cement. *Cem. Concr. Res.* 82, 50–57. <https://doi.org/10.1016/j.cemconres.2016.01.001>

Jauffret, G., Morrison, J., Glasser, F.P., 2015. On the thermal decomposition of nesquehonite. *J. Therm. Anal. Calorim.* <https://doi.org/10.1007/s10973-015-4756-0>

Jia, Y., 2012. Natural and accelerated carbonation of concrete containing fly ash and GGBS after different initial curing period. *Mag. Concr. Res.* 64, 143–150.

Johnson, D.C., Macleod, C.L., Carey, P.J., Hills, C.D., 2003. Solidification of stainless steel slag by accelerated carbonation. *Environ. Technol.* (United

Kingdom). <https://doi.org/10.1080/09593330309385602>

- Junior, A.N., Dias, R., Filho, T., Moraes, E. De, Fairbairn, R., Dweck, J., Neves Junior, A., Toledo Filho, R.D., De Moraes Rego Fairbairn, E., Dweck, J., 2015. The effects of the early carbonation curing on the mechanical and porosity properties of high initial strength Portland cement pastes. *Constr. Build. Mater.* 77, 448–454. <https://doi.org/10.1016/j.conbuildmat.2014.12.072>
- Kashef-Haghighi, S., Ghoshal, S., 2010. CO₂ sequestration in concrete through accelerated carbonation curing in a flow-through reactor, in: *Industrial and Engineering Chemistry Research*. pp. 1143–1149. <https://doi.org/10.1021/ie900703d>
- Kashef-haghighi, S., Shao, Y., Ghoshal, S., 2015. Mathematical modeling of CO₂ uptake by concrete during accelerated carbonation curing. *Cem. Concr. Res.* 67, 1–10. <https://doi.org/10.1016/j.cemconres.2014.07.020>
- Khan, M.I., Siddique, R., 2011. Utilization of silica fume in concrete: Review of durability properties. *Resour. Conserv. Recycl.* <https://doi.org/10.1016/j.resconrec.2011.09.016>
- Khatib, J.M., Mangat, P.S., 1995. Absorption characteristics of concrete as a function of location relative to casting position. *Cem. Concr. Res.* [https://doi.org/10.1016/0008-8846\(95\)00095-T](https://doi.org/10.1016/0008-8846(95)00095-T)
- Khoshnazar, R., Shao, Y., 2018. Characterization of carbonation-cured cement paste using X-ray photoelectron spectroscopy. *Constr. Build. Mater.* <https://doi.org/10.1016/j.conbuildmat.2018.02.175>
- Klemm, W.A., Berger, R.L., 1972. Accelerated curing of cementitious systems by carbon dioxide. Part I. Portland cement. *Cem. Concr. Res.* 2, 567–576. [https://doi.org/10.1016/0008-8846\(72\)90111-1](https://doi.org/10.1016/0008-8846(72)90111-1)
- Köliö, A., Honkanen, M., Lahdensivu, J., Vippola, M., Pentti, M., 2015. Corrosion products of carbonation induced corrosion in existing reinforced concrete facades. *Cem. Concr. Res.* <https://doi.org/10.1016/j.cemconres.2015.07.009>

- Kollar, K.L., Macauley, P., 1980. Water requirements for industrial development. *Am. Water Work. Assoc. J.* 72, 2–9. <https://doi.org/10.1002/j.1551-8833.1980.tb04456.x>
- Kunal, Siddique, R., Rajor, A., Kunal, P., Siddique, R., Rajor, A., 2012. Use of cement kiln dust in cement concrete and its leachate characteristics. *Resour. Conserv. Recycl.* <https://doi.org/10.1016/j.resconrec.2012.01.006>
- Limbachiya, M.C., Roberts, J.J., 2004. Hardened properties of recycled aggregate concrete prepared with fly ash. *Proc. Int. Conf. Sustain. waste Manag. Recycl. challenges Oppor.* Thomas Telford, London, UK 189–197.
- Liu, Q., Liu, J., Qi, L., 2016. Effects of temperature and carbonation curing on the mechanical properties of steel slag-cement binding materials. *Constr. Build. Mater.* 124, 999–1006. <https://doi.org/10.1016/j.conbuildmat.2016.08.131>
- Long, A.E., Henderson, G.D., Montgomery, F.R., 2001. Why assess the properties of near-surface concrete? *Constr. Build. Mater.* 15, 65–79. [https://doi.org/10.1016/S0950-0618\(00\)00056-8](https://doi.org/10.1016/S0950-0618(00)00056-8)
- Lothenbach, B., Scrivener, K., Hooton, R.D., 2011. Supplementary cementitious materials. *Cem. Concr. Res.* <https://doi.org/10.1016/j.cemconres.2010.12.001>
- MacMaster, D., Tavares, O., 2015. Carbon sequestration of concrete masonry units. *ACI Mater. J.* <https://doi.org/10.14359/51688069>
- Mahoutian, M., Shao, Y., 2016. Production of cement-free construction blocks from industry wastes. *J. Clean. Prod.* 137, 1339–1346. <https://doi.org/10.1016/j.jclepro.2016.08.012>
- Manso, S., Aguado, A., 2017. A review of sample preparation and its influence on pH determination in concrete samples. *Mater. Construcción* 67, 1–10. <https://doi.org/10.3989/mc.2017.08515>
- Marku, J., Dumi, I., Liço, E., Dilo, T., Çakaj, O., 2012. The characterization and the utilization of cement kiln dust (CKD) as partial replacement of Portland cement

- in mortar and concrete production. *Zaštita Mater.* 53, 334–344.
- Maslehuddin, M., Al-Amoudi, O.S.B., Rahman, M.K., Ali, M.R., Barry, M.S., 2009. Properties of cement kiln dust concrete. *Constr. Build. Mater.* 23, 2357–2361. <https://doi.org/10.1016/j.conbuildmat.2008.11.002>
- masterbuilder.com [WWW Document], 2018. URL <https://www.masterbuilder.co.in/technologies-water-cement-concrete>
- McCarter, W.J., 1993. INFLUENCE OF SURFACE FINISH ON SORPTIVITY ON CONCRETE. *J. Mater. Civ. Eng.* 5, 130–136.
- Mikulčić, H., Vujanović, M., Markovska, N., Filkoski, R. V., Ban, M., Duić, N., 2013. CO₂ emission reduction in the cement industry. *Chem. Eng. Trans.* 35, 703–708. <https://doi.org/10.3303/CET1335117>
- Mo, L., Panesar, D.K., 2013. Accelerated carbonation - A potential approach to sequester CO₂ in cement paste containing slag and reactive MgO. *Cem. Concr. Compos.* <https://doi.org/10.1016/j.cemconcomp.2013.07.001>
- Mo, L., Panesar, D.K., 2012. Effects of accelerated carbonation on the microstructure of Portland cement pastes containing reactive MgO. *Cem. Concr. Res.* <https://doi.org/10.1016/j.cemconres.2012.02.017>
- Mo, L., Zhang, F., Deng, M., 2016a. Mechanical performance and microstructure of the calcium carbonate binders produced by carbonating steel slag paste under CO₂ curing. *Cem. Concr. Res.* 88, 217–226. <https://doi.org/10.1016/j.cemconres.2016.05.013>
- Mo, L., Zhang, F., Deng, M., Panesar, D.K., 2016b. Effectiveness of using CO₂ pressure to enhance the carbonation of Portland cement-fly ash-MgO mortars. *Cem. Concr. Compos.* <https://doi.org/10.1016/j.cemconcomp.2016.03.013>
- Monkman, S., Kenward, P.A., Dipple, G., MacDonald, M., Raudsepp, M., 2018. Activation of cement hydration with carbon dioxide. *J. Sustain. Cem. Mater.* <https://doi.org/10.1080/21650373.2018.1443854>

- Monkman, S., MacDonald, M., Hooton, R.D., Sandberg, P., 2016. Properties and durability of concrete produced using CO₂ as an accelerating admixture. *Cem. Concr. Compos.* 74, 218–224.
<https://doi.org/10.1016/j.cemconcomp.2016.10.007>
- Monkman, S., Shao, Y., 2010a. Integration of carbon sequestration into curing process of precast concrete. *Can. J. Civ. Eng.* <https://doi.org/10.1139/L09-140>
- Monkman, S., Shao, Y., 2010b. Carbonation curing of slag-cement concrete for binding CO₂ and improving performance. *J. Mater. Civ. Eng.*
[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000018](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000018)
- Monkman, S., Shao, Y., 2006. Assessing the Carbonation Behavior of Cementitious Materials. *J. Mater. Civ. Eng.* 18, 768–776.
[https://doi.org/10.1061/\(ASCE\)0899-1561\(2006\)18:6\(768\)](https://doi.org/10.1061/(ASCE)0899-1561(2006)18:6(768))
- Montemor, M.F., Cunha, M.P., Ferreira, M.G., Simões, A.M., 2002. Corrosion behaviour of rebars in fly ash mortar exposed to carbon dioxide and chlorides. *Cem. Concr. Compos.* [https://doi.org/10.1016/S0958-9465\(01\)00025-7](https://doi.org/10.1016/S0958-9465(01)00025-7)
- Morandea, A., Thiery, M., Dangla, P., 2015. Impact of accelerated carbonation on OPC cement paste blended with fly ash. *Cem. Concr. Res.* 67, 226–236.
<https://doi.org/10.1016/j.cemconres.2014.10.003>
- Naik, T.R., Kraus, R.N., Siddique, R., 2003. Controlled low-strength materials containing mixtures of coal ash and new pozzolanic material. *ACI Mater. J.* 100, 208–215. <https://doi.org/10.14359/12621>
- Najim, K.B., Mahmood, Z.S., Atea, A.K.M., 2014. Experimental investigation on using Cement Kiln Dust (CKD) as a cement replacement material in producing modified cement mortar. *Constr. Build. Mater.* 55, 5–12.
<https://doi.org/10.1016/j.conbuildmat.2014.01.015>
- National Public Radio, 2011. What Countries Are Doing To Tackle Climate Change [WWW Document]. URL <https://www.npr.org/2011/12/07/143302823/what-countries-are-doing-to-tackle-climate-change>

- Neville, A.M., Brooks, J.J., 2010. Concrete Technology, Building and Environment. [https://doi.org/10.1016/0360-1323\(76\)90009-3](https://doi.org/10.1016/0360-1323(76)90009-3)
- Nishikawa, T., Suzuki, K., Ito, S., Sato, K., Takebe, T., 1992. Decomposition of synthesized ettringite by carbonation. *Cem. Concr. Res.* [https://doi.org/10.1016/0008-8846\(92\)90130-N](https://doi.org/10.1016/0008-8846(92)90130-N)
- Nochaiya, T., Wongkeo, W., Chaipanich, A., 2010. Utilization of fly ash with silica fume and properties of Portland cement-fly ash-silica fume concrete. *Fuel*. <https://doi.org/10.1016/j.fuel.2009.10.003>
- Oner, A., Akyuz, S., 2007. An experimental study on optimum usage of GGBS for the compressive strength of concrete 29, 505–514. <https://doi.org/10.1016/j.cemconcomp.2007.01.001>
- Pan, X., Shi, C., Farzadnia, N., Hu, X., Zheng, J., 2019. Properties and microstructure of CO₂ surface treated cement mortars with subsequent lime-saturated water curing. *Cem. Concr. Compos.* 99, 89–99. <https://doi.org/10.1016/j.cemconcomp.2019.03.006>
- Pan, X., Shi, C., Hu, X., Ou, Z., 2017. Effects of CO₂ surface treatment on strength and permeability of one-day-aged cement mortar. *Constr. Build. Mater.* 154, 1087–1095. <https://doi.org/10.1016/j.conbuildmat.2017.07.216>
- Panesar, D.K., Mo, L., 2013. Properties of binary and ternary reactive MgO mortar blends subjected to CO₂ curing. *Cem. Concr. Compos.* 38, 40–49. <https://doi.org/10.1016/j.cemconcomp.2013.03.009>
- Papadakis, V.G., Tsimas, S., 2002. Supplementary cementing materials in concrete: Part I. Efficiency and design. *Cem. Concr. Res.* [https://doi.org/10.1016/S0008-8846\(02\)00827-X](https://doi.org/10.1016/S0008-8846(02)00827-X)
- Papadakis, V.G., Vayenas, C.G., Fardis, M.N., 1989. A reaction engineering approach to the problem of concrete carbonation. *AIChE J.* 35, 1639–1650. <https://doi.org/10.1002/aic.690351008>

- Peethamparan, S., Wong, S.F., Wee, T.H., Swaddiwudhipong, S., 2003. Carbonation of concrete containing mineral admixtures. *J. Mater. Civ. Eng.*
[https://doi.org/10.1061/\(ASCE\)0899-1561\(2003\)15:2\(134\)](https://doi.org/10.1061/(ASCE)0899-1561(2003)15:2(134))
- Plessis, A., Olawuyi, B.J., Boshoff, W.P., Roux, S.G., 2014. Simple and fast porosity analysis of concrete using X-ray computed tomography. *Mater. Struct.*
<https://doi.org/10.1617/s11527-014-0519-9>
- Pu, L., Unluer, C., 2016. Investigation of carbonation depth and its influence on the performance and microstructure of MgO cement and PC mixes. *Constr. Build. Mater.* <https://doi.org/10.1016/j.conbuildmat.2016.05.067>
- Pu, Q., Jiang, L., Xu, J., Chu, H., Xu, Y., Zhang, Y., 2012. Evolution of pH and chemical composition of pore solution in carbonated concrete. *Constr. Build. Mater.* <https://doi.org/10.1016/j.conbuildmat.2011.09.006>
- Qian, L., Jiexiang, L., Liqian, Q., 2016. Effects of temperature and carbonation curing on the mechanical properties of steel slag-cement binding materials. *Constr. Build. Mater.* 124, 999–1006. <https://doi.org/10.1016/j.conbuildmat.2016.08.131>
- Rasanen, V., Penttala, V., 2004. The pH measurement of concrete and smoothing mortar using a concrete powder suspension. *Cem. Concr. Res.* 34, 813–820.
<https://doi.org/10.1016/j.cemconres.2003.09.017>
- RILEM TC 154-EMC, 2003. Recommendations of RILEM TC 154-EMC: 'Electrochemical Techniques for Measuring Metallic Corrosion'- Half-cell potential measurements-Potential mapping on reinforced concrete structures. *Mater. Struct.*
- Rostami, V., Shao, Y., Boyd, A.J., 2012a. Carbonation Curing versus Steam Curing for Precast Concrete Production. *J. Mater. Civ. Eng.* 24, 1221–1229.
[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000462](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000462).
- Rostami, V., Shao, Y., Boyd, A.J., 2011. Durability of concrete pipes subjected to combined steam and carbonation curing. *Constr. Build. Mater.* 25, 3345–3355.
<https://doi.org/10.1016/j.conbuildmat.2011.03.025>

- Rostami, V., Shao, Y., Boyd, A.J., He, Z., 2012b. Microstructure of cement paste subject to early carbonation curing. *Cem. Concr. Res.* 42, 186–193.
<https://doi.org/10.1016/j.cemconres.2011.09.010>
- Roy, S.K., Poh, K.B., Northwood, D.O., 1999. Durability of concrete - Accelerated carbonation and weathering studies. *Build. Environ.*
[https://doi.org/10.1016/S0360-1323\(98\)00042-0](https://doi.org/10.1016/S0360-1323(98)00042-0)
- Sadek, D.M., El-Attar, M.M., Ali, A.M., 2017. Physico-mechanical and durability characteristics of concrete paving blocks incorporating cement kiln dust. *Constr. Build. Mater.* 157, 300–312. <https://doi.org/10.1016/j.conbuildmat.2017.09.107>
- Saraswathy, V., Song, H.W., 2007. Improving the durability of concrete by using inhibitors. *Build. Environ.* <https://doi.org/10.1016/j.buildenv.2005.08.003>
- Scrivener, K., Snellings, R., Lothenbach, B., 2016. A Practical Guide to Microstructural Analysis of Cementitious Materials. CRC Press, Taylor and Francis Group.
- Shao, Y., El-Hassan, H., 2013. CO₂ utilization in concrete, in: *Sustainable Construction Materials and Technologies*.
- Shao, Y., Mirza, M.S., Wu, X., 2006a. CO₂ sequestration using calcium-silicate concrete 1 776–784. <https://doi.org/10.1139/L05-105>
- Shao, Y., Mirza, M.S., Wu, X., 2006b. CO₂ sequestration using calcium-silicate concrete. *Can. J. Civ. Eng.* <https://doi.org/10.1139/L05-105>
- Shao, Y., Rostami, V., He, Z., Boyd, A.A., 2014a. Accelerated carbonation of portland limestone cement. *J. Mater. Civ. Eng.*
[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000773](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000773)
- Shao, Y., Rostami, V., Jia, Y., Hu, L., 2014b. Feasibility Study on Replacing Steam by Carbon Dioxide for Concrete Masonry Units Curing, in: *Masonry 2014*.
<https://doi.org/10.1520/stp157720130134>
- Shao, Y., Shi, C., 2006. Carbonation curing for making concrete products – an old

- concept and a renewed interest, in: Proceedings of the 6th International Symposium on Cement and Concrete, Xian, China, pp. 823–30.
- Shao, Y., Xudong, Z., Monkman, S., Shao, Y., Zhou, X., Monkman, S., 2006c. A new CO₂ sequestration process via concrete products production, in: 2006 IEEE EIC Climate Change Technology Conference, EICCCC 2006.
<https://doi.org/10.1109/EICCCC.2006.277189>
- Shi, C., He, F., Wu, Y., 2012a. Effect of pre-conditioning on CO₂ curing of lightweight concrete blocks mixtures. *Constr. Build. Mater.* 26, 257–267.
<https://doi.org/10.1016/j.conbuildmat.2011.06.020>
- Shi, C., Liu, M., He, P., Ou, Z., 2012b. Factors affecting kinetics of CO₂ curing of concrete. *J. Sustain. Cem. Mater.* <https://doi.org/10.1080/21650373.2012.727321>
- Shi, C., Wang, D., He, F., Liu, M., 2012c. Weathering properties of CO₂-cured concrete blocks. *Resour. Conserv. Recycl.* 65, 11–17.
<https://doi.org/10.1016/j.resconrec.2012.04.005>
- Shi, C., Wu, Y., 2008. Studies on some factors affecting CO₂ curing of lightweight concrete products. *Resour. , Conserv. Recycl.* 52, 1087–1092.
<https://doi.org/10.1016/j.resconrec.2008.05.002>
- Shi, J.J., Sun, W., 2012. Electrochemical and analytical characterization of three corrosion inhibitors of steel in simulated concrete pore solutions. *Int. J. Miner. Metall. Mater.* <https://doi.org/10.1007/s12613-012-0512-7>
- Shtepenko, O., Hills, C., Brough, A., Thomas, M., 2006. The effect of carbon dioxide on β -dicalcium silicate and Portland cement. *Chem. Eng. J.*
<https://doi.org/10.1016/j.cej.2006.02.005>
- Siddique, R., 2011. Utilization of silica fume in concrete: Review of hardened properties. *Resour. Conserv. Recycl.*
<https://doi.org/10.1016/j.resconrec.2011.06.012>
- Siddique, R., 2006. Utilization of cement kiln dust (CKD) in cement mortar and

- concrete-an overview. *Resour. Conserv. Recycl.*
<https://doi.org/10.1016/j.resconrec.2006.03.010>
- Siddique, R., Bennacer, R., 2012. Use of iron and steel industry by-product (GGBS) in cement paste and mortar. *Resour. Conserv. Recycl.* 69, 29–34.
<https://doi.org/10.1016/j.resconrec.2012.09.002>
- Siddique, R., Kapoor, K., Kadri, E.H., Bennacer, R., 2012. Effect of polyester fibres on the compressive strength and abrasion resistance of HVFA concrete. *Constr. Build. Mater.* <https://doi.org/10.1016/j.conbuildmat.2011.09.011>
- Siddique, R., Kaur, A., 2011. Effect of metakaolin on the near surface characteristics of concrete. *Mater. Struct. Constr.* 44, 77–88. <https://doi.org/10.1617/s11527-010-9610-z>
- Siddique, R., Khatib, J.M., 2010. Abrasion resistance and mechanical properties of high-volume fly ash concrete. *Mater. Struct. Constr.*
<https://doi.org/10.1617/s11527-009-9523-x>
- Singh, M., Siddique, R., 2013. Effect of coal bottom ash as partial replacement of sand on properties of concrete. *Resour. Conserv. Recycl.*
<https://doi.org/10.1016/j.resconrec.2012.12.006>
- Sisomphon, K., Franke, L., 2007. Carbonation rates of concretes containing high volume of pozzolanic materials. *Cem. Concr. Res.*
<https://doi.org/10.1016/j.cemconres.2007.08.014>
- Song, G., 2000. Equivalent circuit model for AC electrochemical impedance spectroscopy of concrete. *Cem. Concr. Res.* [https://doi.org/10.1016/S0008-8846\(00\)00400-2](https://doi.org/10.1016/S0008-8846(00)00400-2)
- Song, H.W., Kwon, S.J., 2007. Permeability characteristics of carbonated concrete considering capillary pore structure. *Cem. Concr. Res.*
<https://doi.org/10.1016/j.cemconres.2007.03.011>
- Stutzman, P.E., Feng, P., Bullard, J.W., 2016. Phase Analysis of Portland Cement by

- Combined Quantitative X-Ray Powder Diffraction and Scanning Electron Microscopy. *J. Res. Natl. Inst. Stand. Technol.* 121, 47.
<https://doi.org/10.6028/jres.121.004>
- Talakokula, V., Bhalla, S., Ball, R.J., Bowen, C.R., Pesce, G.L., Kurchania, R., Bhattacharjee, B., Gupta, A., Paine, K., 2016. Diagnosis of carbonation induced corrosion initiation and progression in reinforced concrete structures using piezo-impedance transducers. *Sensors Actuators, A Phys.*
<https://doi.org/10.1016/j.sna.2016.02.033>
- Tonoli, G.H.D., Santos, S.F., Savastano, H., Delvasto, S., Mejía De Gutiérrez, R., Lopez De Murphy, M.D.M., 2011. Effects of natural weathering on microstructure and mineral composition of cementitious roofing tiles reinforced with fique fibre. *Cem. Concr. Compos.*
<https://doi.org/10.1016/j.cemconcomp.2010.10.013>
- Torgal, F.P., Shi, C., Palomo, A. (Eds.), 2018. Carbon Dioxide Sequestration in Cementitious Construction Materials, 1st ed. Woodhead Publishing.
- Toutanji, H., Delatte, N., Aggoun, S., Duval, R., Danson, A., 2004. Effect of supplementary cementitious materials on the compressive strength and durability of short-term cured concrete. *Cem. Concr. Res.*
<https://doi.org/10.1016/j.cemconres.2003.08.017>
- Tripathi, E., Anand, K., Goyal, S., Reddy, M.S., 2019. Bacterial based admixed or spray treatment to improve properties of concrete. *Sadhana - Acad. Proc. Eng. Sci.* <https://doi.org/10.1007/s12046-018-0999-3>
- Ukwattage, N.L., Ranjith, P.G., Li, X., 2017. Steel-making slag for mineral sequestration of carbon dioxide by accelerated carbonation. *Meas. J. Int. Meas. Confed.* <https://doi.org/10.1016/j.measurement.2016.10.057>
- Unluer, C., 2018. Carbon dioxide sequestration in magnesium-based binders, in: *Carbon Dioxide Sequestration in Cementitious Construction Materials.*
<https://doi.org/10.1016/b978-0-08-102444-7.00007-1>

- Unluer, C., Al-Tabbaa, A., 2014. Enhancing the carbonation of MgO cement porous blocks through improved curing conditions. *Cem. Concr. Res.*
<https://doi.org/10.1016/j.cemconres.2014.02.005>
- Vandeperre, L.J., Al-Tabbaa, A., 2007. Accelerated carbonation of reactive MgO cements. *Adv. Cem. Res.* <https://doi.org/10.1680/adcr.2007.19.2.67>
- Vardhan, K., Siddique, R., Goyal, S., 2019. Strength, permeation and micro-structural characteristics of concrete incorporating waste marble. *Constr. Build. Mater.*
<https://doi.org/10.1016/j.conbuildmat.2019.01.079>
- Videla, C., Aguilar, C., 2006. An updated look at drying shrinkage of Portland and blended Portland cement concretes. *Mag. Concr. Res.* 58, 459–476.
<https://doi.org/10.1006/exnr.2000.7527>
- Wang, S., Mazzotti, M., Carlos, J., Allam, R., Lackner, K.S., Meunier, F., Rubin, E.M., Sanchez, J.C., Yogo, K., Zevenhoven, R., Wu, Y., Peng, K., 2007. Carbonation of cement-based products with pure carbon dioxide and flue gas. *Jom.* <https://doi.org/10.1007/s11837-018-2827-y>
- World Water Development Report 2018 | UN-Water [WWW Document], 2018. URL <https://www.unwater.org/publications/world-water-development-report-2018/> (accessed 2.12.21).
- Xuan, D., Zhan, B., Poon, C.S., 2016. Development of a new generation of eco-friendly concrete blocks by accelerated mineral carbonation. *J. Clean. Prod.*
<https://doi.org/10.1016/j.jclepro.2016.06.062>
- Young, J.F., Berger, R.L., Breese, J., 1974. Accelerated Curing of Compacted Calcium Silicate Mortars on Exposure to CO₂. *J. Am. Ceram. Soc.* 57, 394–397.
<https://doi.org/10.1111/j.1151-2916.1974.tb11420.x>
- Zhan, B., Poon, C., Shi, C., Baojian, Z., Chisun, P., Caijun, S., 2013a. CO₂ curing for improving the properties of concrete blocks containing recycled aggregates. *Cem. Concr. Compos.* 42, 1–8.
<https://doi.org/10.1016/j.cemconcomp.2013.04.013>

- Zhan, B., Sun, C., Liu, Q., Kou, S., Shi, C., 2013b. Experimental study on CO₂ curing for enhancement of recycled aggregate properties. *Constr. Build. Mater.* 7–11. <https://doi.org/10.1016/j.conbuildmat.2013.09.008>
- Zhan, B.J., Poon, C., Shi, C., 2016. Materials characteristics affecting CO₂ curing of concrete blocks containing recycled aggregates. *Cem. Concr. Compos.* 67, 50–59. <https://doi.org/10.1016/j.cemconcomp.2015.12.003>
- Zhang, D., Asce, S.M., Cai, X., Shao, Y., 2016. Carbonation Curing of Precast Fly Ash Concrete. *ASCE J. Mater. Civ. Eng.* 28, 1–9. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0001649](https://doi.org/10.1061/(ASCE)MT.1943-5533.0001649).
- Zhang, D., Ghoulah, Z., Shao, Y., 2017. Review on carbonation curing of cement-based materials. *J. CO₂ Util.* 21, 119–131. <https://doi.org/10.1016/j.jcou.2017.07.003>
- Zhang, D., Shao, Y., 2018. Surface scaling of CO₂-cured concrete exposed to freeze-thaw cycles. *J. CO₂ Util.* <https://doi.org/10.1016/j.jcou.2018.07.012>
- Zhang, D., Shao, Y., 2016a. Early age carbonation curing for precast reinforced concretes. *Constr. Build. Mater.* 113, 134–143. <https://doi.org/10.1016/j.conbuildmat.2016.03.048>
- Zhang, D., Shao, Y., 2016b. Effect of early carbonation curing on chloride penetration and weathering carbonation in concrete. *Constr. Build. Mater.* 123, 516–526. <https://doi.org/10.1016/j.conbuildmat.2016.07.041>
- Zhang, J., Scherer, G.W., 2011. Comparison of methods for arresting hydration of cement. *Cem. Concr. Res.* 41, 1024–1036. <https://doi.org/10.1016/j.cemconres.2011.06.003>
- Zhang, R., Panesar, D.K., 2018. Water absorption of carbonated reactive MgO concrete and its correlation with the pore structure. *J. CO₂ Util.* 24, 350–360. <https://doi.org/10.1016/j.jcou.2018.01.026>
- Zhao, Y., Jin, W., 2016. Steel Corrosion in Concrete, in: *Steel Corrosion-Induced*

Concrete Cracking. <https://doi.org/10.1016/b978-0-12-809197-5.00002-5>

Zheng, L., Xuehua, C., Mingshu, T., 1991. MgO-type delayed expansive cement. Cem. Concr. Res. [https://doi.org/10.1016/0008-8846\(91\)90065-P](https://doi.org/10.1016/0008-8846(91)90065-P)