

Corrosion mechanisms of steel reinforcement in fly ash/slag based powder form of geopolymer concrete

by TRAN HUYEN VU

Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Dr Nadarajah Gowripalan,
Professor Vute Sirivivatnanon and Associate Professor Pre
De Silva

University of Technology Sydney
Faculty of Engineering and Information Technology

September 2021

This page is intentionally left blank

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, *Tran Huyen Vu*, declare that this thesis, is submitted in fulfilment of the requirements for the award of *Doctor of Philosophy*, in the *School of Civil and Environmental Engineering/Faculty of Engineering & Information Technology* at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This research is supported by the Australian Government Research Training Program.

Signature:

Production Note:
Signature removed prior to publication.

Date: 28/09/2021

This page is intentionally left blank

ACKNOWLEDGEMENTS

Thank God for keeping me and my family healthy. I would like to dedicate this dissertation to my sons and my family for always loving me no matter what I treated them. I am enormously grateful to Dr Nadarajah Gowripalan, Professor Vute Sirivivatnanon and Associate Professor Pre De Silva, whose unfailing support and valuable advice, have encouraged and improved my work. Also, I would like to express my gratitude to Professor Tuan Van Nguyen who generously served as a mentor. Thank you, my friends who I have known and have not known for standing by my side in the worst times and forgiving my mistakes. Thank you, Sydney and Australia.

This study would not be able to be performed without the generous supports and involvements of Cement Australia and Australian Research Council Research Hub - Nanoscience Based Construction Materials Manufacturing.

I would love to express my sincere gratitude to Mulugheta Hailu, Rami Haddad, Peter Brown, Lam Dinh Nguyen, Habib Rasouli, Ann Yan and other staffs at Tech-lab for kindly supporting me when I was working there.

I should also mention my debt to Professor Arnaud Caste (School of Civil and Environmental Engineering- UTS), Dr. Quang Dieu Nguyen (School of Civil and Environmental Engineering- UTS), Dr. Md Abu Hasan Johir (Environmental Engineering Laboratories - UTS), Dr. Herbert Yuan (MAU-UTS), Dr. Mark Lockre (MAU-UTS), Dr. Katie McBean (MAU-UTS), Dr. Igor Shikhov (Research Associate, University of New South Wales), Dr. Duy Nguyen (Cement Concrete & Aggregates Australia), Dr. Amin Noushini (Rocla), Mr. Bede Harrington (Rocla) and Josephine Delacruz (Rocla) who generously helped and shared their knowledge and time to support my study.

I would love to acknowledge the help of people who I have forgotten mentioning here and request your forgiveness for my bad memory.

ABSTRACT

Investigation of the durability related aspects of geopolymer concrete has been increasingly conducted worldwide. The suitability of geopolymer concretes in structural applications, still, has not been well proven because of the lack of information on service history and durability performance. Further, the conventional production techniques of geopolymer binders requiring the handling of highly alkaline liquids that are dangerous. Therefore, one-part geopolymer, a new way of producing geopolymer, is introduced to deal with such a safety issue. However, one-part geopolymer invariably has an issue related to a short setting time. To promote the use of geopolymer materials in structure applications, this study aimed to investigate on carbonation and chloride resistance of one-part fly ash/slag geopolymer concretes, which have been deemed as the durability issues attributed to corrosion of steel reinforcement in geopolymer materials. Additionally, the possibility of using a sodium-based set retarder to address the issue of short setting time was included in the investigation.

The investigation of carbonation focused on changes of carbonation depth and pH under both accelerated and natural carbonation conditions. The influence of carbonation on porosity and pore size characteristics of one-part fly ash/slag geopolymer mortar was also investigated by using neutron tomography and mercury intrusion porosimetry (MIP). For assessing chloride resistance, accelerated chloride diffusion, rapid chloride permeability test (RCPT), and the movements of ions in RCPT were performed. A brief examination of chloride diffusion at seawater concentration was also carried out. To explore how the set retarder affects the setting time and other early age properties of one-part geopolymer concrete, changes of setting time, heat released, and compressive strength when different amounts of retarder

applied were thoroughly examined. Scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS) was also performed in order to supplement the findings of the other tests.

The key findings indicated that using the set retarder mentioned above prolonged the setting time of one-part geopolymer binders and reduced the heat released by activation reactions. The compressive strength, however, was decreased when increasing the percentage of retarder. This problem could be avoided by using the retarder with an amount of 2-6%. The results obtained also showed that carbonation alone might not lead to steel corrosion in one-part geopolymer concrete investigated because the pH in carbonated parts was always higher than 10. For assessing chloride resistance of one-part fly ash/slag geopolymer concretes in an accelerated test in 16.5% NaCl solution, 40% fly ash/ 60% slag geopolymer concrete had a lower chloride resistance than OPC concretes, while chloride resistance of 60% fly ash/ 40% slag geopolymer concrete was worse. Due to the presence of both fly ash and slag in the precursor, chloride ions were physically and chemically bound when penetrating in the one-part geopolymer concretes. Regarding RCPT, using 60 voltage, advocated in ASTM C1202, caused the issue of overheating. RCPT performed at 30 voltage was highly suggested because it was well correlated with the accelerated chloride diffusion test. However, it was difficult to distinguish the ability of chloride resistance between different one-part geopolymer concretes based on the charge passed obtained in RCPT. It was because the charge passed was contributed by the movement of all ions present, not by only Cl⁻.

CONTENTS

List of tables.....	ix
List of figures.....	x
Publications.....	xiv
Chapter 1: General Introduction	1
1.1 Introduction	1
1.2 Initial questions	4
1.3. Research objectives	7
1.4 Significance of the study	8
1.5. Organisation of the thesis	9
CHAPTER 2: Literature Review	11
2.1 Introduction	11
2.2 Steel reinforcement corrosion due to carbonation and chloride ions	11
2.3 Comparison of carbonation induced corrosion in geopolymer and Portland cement concretes	15
2.3.1 Carbonation in fly ash geopolymer.....	15
2.3.2 Carbonation in fly ash/slag blended geopolymer	17
2.4 Comparison of chloride induced corrosion of steel reinforcement in geopolymer concrete and Portland cement-based concrete.....	18
2.4.1 Chloride induced corrosion in fly ash geopolymer.....	19
2.4.2 Chloride induced corrosion in fly ash/slag geopolymer	24
2.5 Factors affecting carbonation induce corrosion in geopolymer concrete.....	26
2.5.1 Synthesis condition	26
2.5.2 Carbonation condition.....	28

2.5.3 Factors affecting chloride induced corrosion geopolymer.....	28
2.5.4 Conclusions.....	30
CHAPTER 3: Influence of Set Retarder on Early Age Properties of Fly ash/Slag Geopolymer Pastes and Mortars	32
3.1 Introduction	32
3.2 Experimental program.....	33
3.2.1 Materials and mix proportions	33
3.2.2 Experimental procedure	35
3.3 Results and discussion.....	38
3.3.1 Influence of retarder on setting time	38
3.3.2 Influence of set retarder on geopolymerisation process	39
3.3.3 Influence of set retarder on heat evolution	48
3.3.4 Influence of set retarder on workability	50
3.3.5 Influence of set retarder content and curing conditions on compressive strength development	51
3.4 Conclusions	56
CHAPTER 4: Carbonation in Fly Ash/Slag Geopolymer Mortar and Concrete	57
4.1 Introduction	57
4.2 Experimental program.....	58
4.2.1 Material and mix proportions.....	58
4.2.2 Preparation of specimens	59
4.2.3 Carbonation testing for mortar and concrete	59
4.2.4 Measurement of compressive strength	60
4.2.5 Measurement of carbonation depth.....	60
4.2.6 Measurement of pH profile of mortar specimens	60

4.2.7 Porosity analysis and visualisation	61
4.3. Results and discussion.....	62
4.3.1 Carbonation depth of mortar over time.....	62
4.3.2 Change in pH during carbonation	64
4.3.3 Carbonation depth of geopolymer concrete.....	70
4.3.4 Influence of carbonation on compressive strength of one-part fly ash/ slag geopolymer concrete	72
4.3.5 Influence of carbonation on porosity and pore size distribution in one-part fly ash/ slag geopolymer mortars.....	74
4. 4 Conclusions	90
CHAPTER 5: Chloride Penetration in One-part Fly Ash/Slag Geopolymer Concrete	92
5.1 Introduction	92
5.2 Methodology	94
5.2.1 Materials and concrete mix proportions	94
5.2.2 Preparation of specimens	95
5.2.3 Rapid chloride permeability test as per ASTM C1202 and modified rapid chloride permeability tests	96
5.2.5 Investigation of ion movements in rapid chloride permeability test (RCPT).....	97
5.2.6 Chloride bulk diffusion test as per ASTM C1556 and determination of acid soluble chloride as per ASTM C1152	98
5.3 Results and discussions	99
5.3.1 Charge passed in rapid chloride permeability test.....	99
5.3.2 Chloride profiles and apparent chloride diffusion coefficient in one-part fly ash/slag geopolymer concrete	102

5.3.3 Chloride diffusion test in 3.5% NaCl.....	107
5.3.4 Movement of ions in one-part fly ash/slag geopolymer concrete under the electrical field applied in RCPT.....	111
5.4 Conclusions	115
CHAPTER 6: Conclusions and Recommendations.....	117
6.1 Conclusions	117
6.2 Recommendations for future research.....	119
References.....	121

LIST OF TABLES

Table 1.1 Requirement for durability of culvert headwalls, headwall extensions and cut-off walls.....	5
Table 3.1 Chemical compositions of fly ash and ground granulated blast furnace slag.....	34
Table 3.2 Mix proportions (by weight) of Geo 1 and Geo 2 binders.....	34
Table 3.3 Setting time of Geo 1 pastes with different amounts of retarder	39
Table 3.4 Setting time of Geo 2 pastes with different amounts of retarder	39
Table 4.1 Mix proportion of concretes	59
Table 4.2 Carbonation depth under accelerated & natural carbonation conditions.....	63
Table 4.3 Carbonation depth in concrete after 6 month exposure to carbonation	71
Table 5.1 Mix proportion of concretes	94
Table 5.2. Charge passed in RCPT at 60V, 30V and 10 V.....	100
Table 5.3 Chloride penetration related properties of concretes investigated.....	105
Table 5.4 Changes in concentrations of ion and cation in Geo 1 concrete in rapid chloride permeability test	113
Table 5.5 Changes in concentrations of ion and cation in OPC concrete in rapid chloride permeability test	114

LIST OF FIGURES

Figure 2.1	Volume of corrosion products relative to that of iron	12
Figure 2.2	Chloride diffusion coefficients after 1 year of exposure, compressive strength at 28 days and porosity before exposure for fly ash geopolymer concretes and OPC concrete.....	21
Figure 2.3	Corrosion rate and time to failure of steel reinforcement in OPC concrete and in geopolymer concrete T4, T7 and T10	22
Figure 2.4	The relationship of CaO/SiO ₂ of fly ash and porosity of resulting geopolymer concrete.	27
Figure 3.1	TG/DTG curves of (a) fly ash and (b) ground granulated blast slag.....	34
Figure 3.2	Particle size distribution of Geo 1 and Geo 2 binders	35
Figure 3.3	Hobart mixer and mortar flow test	36
Figure 3.4	XRD results of Geo 1 with 2% retarder	41
Figure 3.5	XRD results of Geo 2 with 4% retarder	42
Figure 3.6	XRD results of silicate mineral in activator	42
Figure 3.7	SEM/EDS results of NaX-type zeolite in Geo 1 paste	43
Figure 3.8	SEM/EDS results of NaX-type zeolite in Geo 2 paste	44
Figure 3.9	SEM/EDS results of N-(C)-A-S-H gels in Geo 1 paste	45
Figure 3.10	SEM/EDS results of N-(C)-A-S-H gels in Geo 2 paste	46
Figure 3.11	XRD results of Geo 2 with 0% retarder	47
Figure 3.12	XRD results of Geo 2 with 8% retarder	48
Figure 3.13	Heat evolution of Geo 1 and Geo 2 paster	49
Figure 3.14	Flow of Geo 1 and Geo 2 mortars	51
Figure 3.15	Compressive strength development of Geo 1 mortar under sealed curing and sealed & heat curing	54

Figure 3.16 Compressive strength development of Geo 2 mortar under sealed curing and sealed & heat curing	55
Figure 4.1 Carbonation depth of Geo 1 and Geo 2 mortars after 8 months in atmosphere.....	63
Figure 4.2 Carbonation depth of Geo 1 and Geo 2 mortars after 18 months in atmosphere.....	64
Figure 4.3 Change in pH of Geo 2 mortar after 3 months and 8 months under accelerated carbonation	65
Figure 4.4 Change in pH of Geo1 and Geo 2 mortars after 8 months under natural carbonation	66
Figure 4.5. Steel reinforcement in Geo 1 concrete after 6 months under accelerated carbonation	663
Figure 4.6 Steel reinforcement in Geo 2 concrete after 6 months under accelerated carbonation	664
Figure 4.7 Carbonation depth of Geo 1 concrete, indicated by Phenolphthalein and Alizarine Yellow R.....	70
Figure 4.8 Carbonation depth of Geo 2 concrete, indicated by Phenolphthalein and Alizarine Yellow R.....	71
Figure 4.9 Change in compressive strength of concretes over 6 month exposure to natural carbonation conditions	73
Figure 4.10 Change in compressive strength of concretes over 6 month exposure to accelerated carbonation conditions.....	73
Figure 4.11 Specimens of carbonated Geo 1 and carbonated Geo 2 mortars used for neutron tomography experiments	739

Figure 4.12 Tomographic reconstruction of carbonated Geo 1 mortar in the shape of a 25 mm cube	73
Figure 4.13 Tomographic reconstruction of carbonated Geo 2 mortar in the shape of a 25 mm cube	76
Figure 4.14 Pore size distribution of carbonated Geo 1 and Geo 2 mortars	77
Figure 4.15 Porosity analysis of different portions in 25 mm cubes of Geo 1 mortar and Geo 2 mortar.....	80
Figure 4.16 Tomographic reconstructions of 5 x 5 x 5mm, 7 x 7 x 7mm, 10 x 10 x 10mm and 15 x 15 x 15mm in volumes	82
Figure 4.17. Selected mapping area of a region on the surface of a carbonated Geo 2 mortar and compositional maps for Na, Ca and C	83
Figure 4.18 Tomographic reconstruction of a noncarbonated portion in the centre of a specimen.....	84
Figure 4.19 Tomographic reconstruction of carbonated portion at the surface of a specimen.....	86
Figure 4.20 Pore size distribution of noncarbonated and carbonated portions of Geo 1 mortar in the ranged 15-2000 μ m and in the range 15-500 μ m	87
Figure 4.21 Pore size distribution of noncarbonated and carbonated portions of Geo 2 mortar in the ranged 15-2000 μ m and in the range 15-500 μ m	88
Figure 4.22 Pore size distribution of non-carbonated and carbonated portions of Geo 1 mortar using MIP.....	89
Figure 4.23 Pore size distribution of non-carbonated and carbonated portions of Geo 2 mortar using MIP.....	90
Figure 5.1 Three portions sliced from one concrete specimen	95

Figure 5.2 Preparation of test specimens for chloride penetration in concrete by rapid chloride permeability and chloride diffusion	96
Figure 5.3. A test cell in RCPT test	97
Figure 5.4. Charge passed in RCPT at 30V	101
Figure 5.5 Charge passed in RCPT at 10V	102
Figure 5.6 Total chloride profile in concretes.....	104
Figure 5.7 Chloride profile of four types of concrete	1049
Figure 5.8 Steel reinforcement and chloride depth in Geo 1 concrete after 6 months exposure in a 3.5% NaCl solution	109
Figure 5.9 Steel reinforcement and chloride depth in Geo 2 concrete after 6 months exposure in a 3.5% NaCl solution	110
Figure 5.10 Steel reinforcement and chloride depth in Geo 2 concrete after 6 months exposure in a 3.5% NaCl solution.....	111
Figure 5.11 Movements of ions and cations in rapid chloride permeability test.....	113

PUBLICATIONS

Vu, T.H., Gowripalan, N., de Silva, P., Kidd, P. & Sirivivatnanon, V. 2020, „Investigating chloride resistance of one-part fly ash/slag geopolymer concrete“ - About to submit to Cement and Concrete Research.

Vu, T.H., Gowripalan, N., de Silva, P., Kidd, P. & Sirivivatnanon, V. 2020, „Influence of set retarder on early age properties of one-part fly ash/ slag geopolymer pastes and mortars“ - Under review of Construction and Building Materials.

Vu, T.H., Gowripalan, N., de Silva, P., Kidd, P. & Sirivivatnanon, V. 2020, „Assessing carbonation in one-part fly ash/slag geopolymer mortar: Change in pore characteristics using the state-of-the-art technique neutron tomography“, Cement and Concrete Composites, 114:103759.

Vu, T.H., Gowripalan, N., de Silva, P., Kidd, P. & Sirivivatnanon, V. 2019, „Influence of curing and retarder on early-age properties of dry powder geopolymer concrete“, Concrete in Australia 45(2):41-46.

Vu, T.H., Gowripalan, N., de Silva, P., Kidd, P. & Sirivivatnanon, V. 2019, „Assessing corrosion resistance of powder form of geopolymer concrete“. Proceedings of Concrete 2019, Sydney, Australia, 9-12 September 2019.

Vu, T.H., Gowripalan, N. 2018, „Mechanism of heavy metal immobilisation using geopolymerization techniques – A review“, Journal of Advanced Concrete Technology 16(3):124-135.

Vu, T.H., Gowripalan, N., de Silva, P., Kidd, P. & Sirivivatnanon, V. 2018, „Carbonation and Chloride Induced Steel Corrosion Related Aspects in Fly Ash/Slag Based Geopolymers - A Critical Review“. Proceedings of the 5th International fib Congress 2018, Melbourne, Australia, 7-11 October 2018.