Performance and Mechanism of Autogenous Self-healing in Cementitious Composites Materials

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DOCTOR OF PHILOSOPHY

under the supervision of

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, ***Caihong Xue***, 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 and 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 document has not been submitted for qualifications at any other academic institution.

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List of Publications

- Effect of chloride ingress on self-healing recovery of smart cementitious composite incorporating crystalline admixture and MgO expansive agent, ***Cement and Concrete Research***, vol. 139.

- Numerical investigation on interface crack initiation and propagation behaviour of self-healing cementitious materials, ***Cement and Concrete Research,*** vol. 122.

- Self-healing efficiency and crack closure of smart cementitious composite with crystalline admixture and structural polyurethane, ***Construction and Building Materials***, vol. 260.

- Novel experimental and numerical investigation on bonding behaviour of crack interface in smart self-healing concrete, ***Smart Materials and Structures***, vol. 29.

- Effect of incompatibility between healing agent and cement matrix on self-healing performance of intelligent cementitious composite, ***Smart Materials and Structures***, vol. 29.

- A review study on encapsulation‐based self-healing for cementitious materials, ***Structural Concrete***, vol. 20.

- Self-healing performance of cementitious composite in marine environments-A prospect in Australia ***Concrete in Australia***, vol. 46.

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List of Abbreviations

AE	Acoustic Emission Analysis
ASTM	American Society for Testing and Materials
BSE	Backscattered Electron
BN	Expansive Bentonite
CT	X-ray computed tomography
CA-α	Notation for one of the used crystalline admixtures
CA-β	Notation for one of the used crystalline admixtures
Cl-1	The 0.545 mol/L sodium chloride solution
Cl-2	The 2 mol/L sodium chloride solution
DIC	Digital Image Correlation
DTT	Uniaxial Direct Tensile Test
DTG	Derivative Thermogravimetry
EGC	Engineered Geopolymer Composites
ECC	Engineered cementitious composites
EDS	Energy Dispersive-X-ray Analysis
EPMA	Electron Probe Micro-Analysis
FRC	Fiber Reinforced Concrete
FTIR	Fourier Transform Infrared Spectroscopy

GP	General Purpures Cement
GGBFS	Ground Granulate Blast Furnace Slag
HPFRC	High Performance Fiber Reinforced Concrete
HPFRCC	High Performance Fibre Reinforced Cementitious Composites
HPC	High Performance Concrete
HMCs	Hydrated Magnesium Carbonates
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IC	Ion Chromatography
L	Lime
LVDTs	Linear Variable Displacement Transducers
NMR	Nuclear Magnetic Resonance
NSC	Normal Strength Concrete
OM	Optical Microscope
RCPT	Rapid Chloride Permeability Test
RMC	Magnesium-based Concrete
PLC	Portland Limestone Cement
PVA	Polyvinyl Alcohol
SDT	Stiffness Damage Test
SCMs	Supplementary cementitious materials

SHCCMs	Self-healing cementitious composites materials
SF	Silica fume
T	Temperature
TEM	Transmission Electron Microscopy
TG	Thermogravimetry
TGA	Thermogravimetry Analysis
TRF	Transverse Resonant Frequency
UHC	Unhydrated Cement Particles
UHPC	Ultra-High-Performance-Concrete
UMGs	Unhydrated MgO Grains
w/d	Wet/dry cycles
w	Wetting
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

Cement chemistry

Al_2O_3	Aluminium oxide
AH_3	Aluminium hydroxide ($Al(OH)_3$)
AFm	Aluminate ferrite monosulfate
AFt	Al_2O_3-Fe_2O_3-trisulfate

B	Brucite
C	Calcite
Ca^{2+}	Calcium ions
C-A-S-H	Calcium aluminium silicon hydrate
CAs	Crystalline additives
C_4AF	Tetracalcium aluminoferrite
CaO	Calcium oxide
Cc	Calcium carbonates ($CaCO_3$)
CH	Calcium hydroxide ($Ca(OH)_2$)
CO_3^{2-}	Carbonate
CO_2	Carbon dioxide
CSA	Sulfoaluminate-based expansive additive
C_2S	Belite
C_3S	Alite
C-S-H	Calcium silicate hydrates
Cl	Chloride
Cl^-	Chloride ions
E	Ettringite
Fs	Friedel's salt

G	Gypsum
Hc	Hemicarboaluminate
HNO_3	Nitric acid
K	Potassium
K_2O	Potassium oxide
Mc	Monocarboaluminate
Mg	Magnesium
MgO	Magnesium oxide
MH	Brucite ($Mg(OH)_2$)
M-S-H	Magnesium Silicate Hydrate
Ms	Monosulfoaluminate
MK	Metakaolin
Na	Sodium
Na_2CO_3	Sodium Carbonates
$NaHCO_3$	Sodium bicarbonate
Na_2O	Sodium oxide
Na_2SO_4-H_2O	Sodium sulfate salt
Na_2SO_4	Sodium sulfate
$Na_2SO_4{\cdot}10H_2O$	Mirabilite

P	Portlandite
Q	Quartz (SiO_2)
S	Sulfur
SO_3	Sulfur trioxide
SiO_2	Sulfur oxide
SO_4^{2-}	Sulfate
T	Thenardite (Na_2SO_4)

Roman symbols (lowercase)

a	Area of the specimen
c	Crack closing ratio
d	Density of the water
f_{peak_virgin}	Peak flexural strength of the virgin specimen
$f_{peak\_self\text{-}healed}$	Peak flexural strength of the self-healed specimen
f_c	Compressive strength
$f_{c\_original}$	Compressive strength of the original specimen
$f_{c\_cracked}$	Compressive strength of the cracked specimen
$f_{c\_self\text{-}healed}$	Compressive strength of the self-healed specimen
m_i	Mass change in grams
t	Self-healing duration

w_i	Width of a crack before self-healing
w_t	Width of the crack after self-healing

Roman symbols (uppercase)

A_i	Area of crack mouth before self-healing
A_t	Area of crack mouth after self-healing
$E_{original}$	Elastic modulus of the original specimen
$E_{cracked}$	Elastic modulus of the cracked specimen
ERI	Compressive elastic modulus recovery index
I	Slope of the best fit line for water absorption
IDaRUPV	Stiffness/damage recovery measured by UPV
ISR	Index of flexural strength recovery
$ISR_{pre\text{-}peak}$	*ISR* for pre-peak cracked specimens
$ISR_{post\text{-}peak}$	*ISR* for post-peak cracked specimens
COD	Crack Opening Displacement
$K_{cracked}$	Gas permeability coefficient of the cracked specimen
$K_{self\text{-}healed}$	Gas permeability coefficient of the self-healed specimen
$K_{flexural\_self\text{-}healed}$	Slope of $P_{flexural}$-*COD* for the self-healed specimen
$K_{flexural\_cracked}$	Slope of $P_{flexural}$-*COD* for the cracked specimen
$K_{flexural\_original}$	Slope of $P_{flexural}$-*COD* for the original specimen

$K_{split\_self\text{-}healed}$	Slope of P_{split}-COD for the self-healed specimen
$K_{split\_cracked}$	Slope of P_{split}-COD for the cracked specimen
$K_{split\_original}$	Slope of P_{split}-COD for the original specimen
P_{split}	Splitting tensile load
$P_{split\_unloading}$	Unloading splitting tensile load
$P_{split\_max\_principal}$	Principle peak splitting tensile load of the original specimen
$P_{split\_max\_secondary}$	Secondary peak splitting tensile load of the original specimen
$P_{split\_max\_self\text{-}healed}$	Maximum splitting tensile load of the self-healed specimen
$P_{split\_cracking\_original}$	Splitting tensile cracking load of the original specimen
$P_{split\_cracking\_self\text{-}healed}$	Splitting tensile cracking load of the self-healed specimen
$PRI_{splitting}$	Splitting tensile load capacity recovery
$P_{self\text{-}healed}$	Water permeability of the self-healed specimen
$P_{cracked}$	Water permeability of the cracked specimen
$P_{flexural\_max\_original}$	Maximum flexural load of the original specimen
$P_{flexural\_unloading}$	Unloading flexural load
$P_{flexural\_max\_cracked}$	Maximum flexural load of the cracked specimen
PDI	Plastic damage index
PRI	Plastic damage recovery index
$PRI_{flexural}$	Recovery of the flexural load capacity

R_p	Relative water permeability
S_i	Initial water sorptivity
$S_{i,wet/dry,self\text{-}healed}$	Initial sorptivity of the self-healed specimen
$S_{i,wet/dry,original}$	Initial sorptivity of the original specimen
S_s	Secondary water sorptivity
$S_{s,wet/dry,uncracked}$	Secondary sorptivity of the self-healed specimen
$S_{s,wet/dry,original}$	Secondary sorptivity of the original specimen
SDI	Stiffness damage index
$SDI_{cracked}$	Stiffness damage index of the cracked specimen
$SDI_{self\text{-}healed}$	Stiffness damage index of the self-healed specimen
$SDI_{original}$	Stiffness damage index of the original specimen
$SDI_{strength}$	Compressive strength reduction index
$SRI_{c\_stiffness}$	Compressive stiffness reduction recovery index
$SRI_{c\_strength}$	Compressive strength recovery index
$SRI_{flexural,stiffness}$	Flexural stiffness recovery index
$SRI_{splitting,stiffness}$	Splitting tensile stiffness recovery
$UPV_{self\text{-}healed}$	Ultrasonic pulse velocity of the self-healed specimen
$UPV_{cracked}$	Ultrasonic pulse velocity of the cracked specimen
UPV_{virgin}	Ultrasonic pulse velocity of the virgin specimen

Creek symbols

σ_c	Compressive stress
σ_N	Nominal flexural stress
σ_{N_loss}	Nominal flexural strength loss due to cracking
$\sigma_{N\_Inherent}$	Inherent nominal flexural strength regain
$\sigma_{N\_unloading\_virgin}$	Unloading nominal flexural strength of virgin specimen
$\sigma_{N\_unloading\_cracking}$	Unloading nominal flexural strength during cracking
η_{gas}	Recovery of the gas permeability of the cracked specimen

Abstract

The mechanical properties and durability of concrete structures can be seriously impaired by cracks. The need to reduce the risk of cracking and repair the damage caused by concrete cracks led to the development of self-healing cementitious composite materials (SHCCMs). SHCCMs are able to heal cracks without human intervention and can generally be classified into either autogenous self-healing or autonomous self-healing. In comparison with autonomous self-healing, autogenous self-healing is more cost effective and easier to implement in full-scale application, while it is limited to healing crack widths of about 100-150 μm.

Supplementary cementitious materials (SCMs), expansive minerals and crystalline admixtures (CAs) are used to promote the autogenous self-healing of cementitious composite materials and develop SHCCMs. However, the absence of standardized test procedure and performance assessment criteria for self-healing resulted in disagreement with regard to the effectiveness of stimulated autogenous self-healing in concrete. The benefit of SHCCMs to durability of cracked concrete in chloride solutions and marine environments is not well understood. Moreover, in order to tailor self-healing reactions of SHCCMs for better performance, it is necessary to understand the mechanisms of stimulated autogenous self-healing. Currently, these issues are hindering the application and development of SHCCMs.

In this study, the methodology for evaluating the influence of autogenous self-healing on the mechanical properties and durability performance of concrete was developed and validated. Cracked specimens with and without CAs were exposed to water, sodium chloride solutions and seawater to facilitate self-healing. Afterwards, the effect of self-

healing on the compressive, flexural and splitting tensile properties, water absorptivity as well as chloride penetration of cracked materials was assessed. The mineralogy of self-healing products was also characterized to reveal the mechanism of autogenous self-healing. Furthermore, the influence of CAs on the hydration and leaching behaviour of cement was investigated, in order to explore factors that can help improve the autogenous self-healing of cementitious composites materials.

With regards to mechanical properties, autogenous self-healing improves the stiffness but barely affects the load capacity of cracked specimens under compressive, flexural and splitting tensile loading. Indexes that are related to stiffness are recommended for self-healing performance assessment. The results also highlight that exposure environments affect self-healing mechanisms (reaction) and subsequently, self-healing performance. The rate of crack closure is fastest in seawater followed by NaCl solutions and water, which results in the lower chloride penetration into self-healed cracked specimens from seawater than NaCl solution. The rapid precipitation of $Mg(OH)_2$ in cracks dominates the self-healing in seawater. Compared to water, NaCl solutions accelerate self-healing by promoting the precipitation of $CaCO_3$ in cracks. This suggests that a faster rate of self-healing helps improve the durability of cracked structures more than the type of products that form during self-healing. Moreover, the hydration and leaching behaviour of cement incorporating CAs indicates that a higher pH of the pore solution and a reasonable degree of carbonation could benefit the self-healing of cementitious composite materials.