# NONDESTRUCTIVE EVALUATION OF THE CONCRETE INFRASTRUCTURE USING NUCLEAR MAGNETIC RESONANCE RELAXOMETRY

Ву

Iman Harsini

## A DISSERTATION

Submitted to Michigan State University in partial fulfilment of the requirements for the degree of

Civil Engineering – Doctor of Philosophy

#### ABSTRACT

## NONDESTRUCTIVE EVALUATION OF THE CONCRETE INFRASTRUCTURE USING NUCLEAR MAGNETIC RESONANCE RELAXOMETRY

### By

#### Iman Harsini

Management of the nation's aging transportation infrastructure constitutes a growing financial burden. Limited resources are available for inspection, maintenance, repair, rehabilitation and replacement of the deteriorating infrastructure. More efficient management of the aging concrete-based transportation infrastructure would allow for effective use of available resources to maintain a viable transportation system.

Development of compact, lightweight and economically viable equipment for implementing some analytical chemistry methods have facilitated their growing semi-destructive or nondestructive field applications (e.g., in the field of geology). Initial efforts to make direct use of these methods for semi- or non-destructive field evaluation of concrete, however, have encountered challenges associated with the heterogeneity of concrete structure, and the complexity of concrete structure and deterioration mechanisms. Nuclear Magnetic Resonance (NMR) spectroscopy and relaxometry provide means of resolving and quantifying the chemistry of chemical compounds in various materials. Advances have been made in recent years towards applications of NMR for nondestructive inspection in the fields of manufacturing, arts and health sciences. These advances open the prospects for nondestructive evaluation of the concretebased infrastructure with portable NMR systems. In this research for the first time a comprehensive experimental approach is adopted to investigate the effects of various deterioration mechanisms of concrete on the NMR relaxation signals of water confined in concrete pore network using a portable NMR device. The relaxation parameters such as transverse and longitudinal relaxation times and self-diffusion coefficients are obtained for concrete exposed to accelerated aging conditions. These parameters are obtained on the surface and in the depth of concrete at various stages of deterioration. At the same time, corroborative measurements are obtained using UPV and elastic modulus tests, as well as the microscopy observations. In case needed, other tests such as XRD, XRF and other analytical techniques are utilized to further investigate the structure of concrete. Moreover, field data is obtained by testing the existing concrete structures with unknown caused of the damage. The obtained data are compared with established trends of concrete specimens. In this work, the NMR trends of associated with various concrete deterioration mechanisms are identified and discussed. These trends are established over time at different depths of concrete exposed to various deterioration mechanisms. Moreover, a numerical study is performed to estimate the porosity and permeability of concrete using a numerical model that receives NMR relaxation data and predicts the properties of porous materials. In this model the NMR-derived fractional volumes of free and bound fluid, logarithmic mean values of relaxation times and empirically determined constant which depends on the surface relaxivity are incorporated. Results from this study will help engineers to identify the cause and extent of damage in existing concrete infrastructure. Additionally, it helps the researchers to study and characterize the damage to concrete structure caused by various deterioration mechanisms from a fresh perspective.

This research is dedicated to my parents and my teachers.

#### ACKNOWLEDGEMENTS

I would like to express my deep gratitude for my advisor's support, Professor Parviz Soroushian throughout the course of my study at Michigan State University.

I treasure the training and service I received at Michigan State University under his supervision. In additional, I would like to express my appreciation to my PhD committee members, Prof. Venkatesh Kodur, Prof. Rouzbeh Daragazany and Prof. Mohsen Zayernouri for their time and providing valuable guidance on improving this research. Moreover, I would like to thank Dr. James Kirkpatrick valuable inputs on my work.

Undoubtedly, the support and encouragement of my parents helped me a great deal to overcome the obstacles in the path of Ph.D. studies.

My ultimate regards go to Dr. Dan Holmes for his valuable support during the experimental program in this research. I would like to thank Dr. Richard Staples and the personnel of the Crystallographer lab, Composite Materials and Structures Center, MSU department of geography, personnel of MDOT material laboratory.

I would like to extend my thanks to Ms. Laura Post, Ms. Margaret Conner, Ms. Laura Taylor, for their hard work and splendid support during the past 5 years.

I would also like to express my gratitude to Dr. Anagi Balachandra, Saqib Abideen, Weerasiri Rankothge, Nalin Daranasiri and Nastaran Rafizadeh.

Finally, I would like to express my deepest gratitude to Mr. Faridazar and FHWA Turner-Fairbank Highway Research Center for supporting this project financially and technically.

# TABLE OF CONTENTS

LIST OF TABLES	xi
LIST OF FIGURES	xiii
KEY TO ABBREVIATIONS	xxvi
1 INTRODUCTION 1.1 General	
1.2 Role of NMR in Condition Assessment of Concrete	2
1.3.1 Directly compared to non-destructive inspection techniques	
1.3.2 Indirectly competing / complementary non-destructive inspection technique 1.4 Deterioration Mechanisms of Concrete Infrastructure	es 6
1.5 Research Objectives	
1.6  Anticipated Research Impact    1.7  Scope and Outline	12 12
2 STATE-OF-THE-ART REVIEW	15
2.1 General	15
2.2 NMR: A Novel Tool to Study Materials	
2.3 Basics of NMR	19
2.3.1 Polarization	19
2.3.2 Pulse tipping and free induction decay	20
2.3.3 Relaxation mechanisms in porous media	22
2.3.4 T <sub>2</sub> measurements	25
2.3.5 T <sub>1</sub> measurements	
2.4 Experimental Studies	29
2.4.1 Cement-based materials	30
2.4.2 Concrete Materials	
2.5 Numerical and Analytical Studies	
2.5.1 NMR models for permeability predication	43
2.5.2 Permeability and size distribution	45
2.5.3 Molecular dynamics modeling	48
2.6 Standard and Specifications	50
2.7 Knowledge Gap	54
3 MATERIALS and SPECIMEN PREPARATION	57
2.2 Aggregator	
3.2 Aggregales	
5.2.1 Faiticle shape and surface texture	

3.2.2	Grading (sieve analysis)	68
3.2.3	Specific gravity and absorption capacity	
3.2.4	Bulk density and voids in aggregates	
3.2.5	Los Angeles abrasion	74
3.2.6	Chemical composition of aggregates	
3.2.7	SEM – EDS of aggregates	
3.2.8	Ultrasonic pulse velocity	
3.2.9	Rate of absorption	101
3.2.10	X-Ray diffraction analysis of aggregates	103
3.2.11	Soundness of aggregates	108
3.2.12	X-ray μCT of aggregates	114
3.2.13	Visual inspection of damaged aggregates	119
3.3 C	ementitious Binders	124
3.3.1	X-Ray diffraction analysis of cementitious materials	124
4 INVES	TIGATION OF CONCRETE USING NMR	129
4.1 U	Inderstanding Relaxation Parameters	129
4.1.1	Longitudinal relaxation time (T <sub>1</sub> )	129
4.1.2	Transverse relaxation time (T <sub>2</sub> )	132
4.1.3	Self-diffusion coefficient (D)	
4.2 S <sup>-</sup>	tudying Different Phases of Concrete	137
4.2.1	NMR relaxometry of aggregates	
4.3 R	ole of Water in Concrete Deterioration	
4.4 V	Vater Content Measurements	150
4.5 V	Vater Distribution in Cement Paste	154
5 PORTA	ABLE NMR SYSTEM COMPONENTS AND OPERATION	157
5.1 N	IMR Probe	158
5.1.1	Magnets	159
5.1.2	RF coil	160
5.1.3	Spectrometer	160
5.2 D	vevice Specifications	160
5.3 S	ignal-to-Noise Ratio and Ways to Improve	
5.4 S	oftware Preparation and Execution	162
5.4.1	Pulse sequences	162
5.4.2	Software Integration	174
6 NOND	ESTRUCTIVE NMR EVALUATION OF THE DAMAGING EFFECTS OF A	ALKALI-SILICA
REACTION	ON CONCRETE	177
6.1 G	ieneral	177
6.2 Ir	ntroduction	178
6.3 N	Naterials and Methods	182
6.4 R	esults and Discussion	185
6.4.1	ASR susceptibility of aggregates	185

6.4	2 XRD results	187
6.4	3 NMR test results	190
6.4	4 Corroborative tests	201
6.5	Conclusions	204
7 NO	NDESTRUCTIVE EVALUATION OF FREEZE-THAW DAMAGE USING PORTABLE	E NMR 206
7.1	General	206
7.2	Introduction	207
7.3	Experimental Program	209
7.4	Results and Discussion	210
7.4	1 Visual observations	210
7.4	2 NMR relaxometry	211
7.4	3 Ultrasound Pulse Velocity (UPV) and Dynamic Elastic Modulus	223
7.4	4 Scanning Electron Microscopy	224
7.5	Nondestructive NMR Testing at the Michigan Department of Transportat	ion 226
7.6	Conclusions	234
о NO		
8 NO	NDESTRUCTIVE NMR EVALUATION OF THE DAMAGING EFFECTS OF CARB	UNATION ON
CONCRE	1E	
8.1	Abstract	
8.2	Carbonation of Concrete	
8.3	Materials and Methods	
8.4	Results and Discussions	
8.4	1 NMR relaxometry	242
8.4	2 UPV and dynamic modulus	254
8.4	3 Scanning electron microscopy	255
8.5	Conclusions	256
۵ <u>د</u> ۱۱۱		250
9 JUL	Abstract	
9.1	Sulfate Attack in Concrete Structures	
9.2	Materials and Methods	
9.5	Experimental Program	
9.4	Experimental Program	
9.5	LIDV and dynamic modulus of electicity	
9.0	Conclusions	
9.7		270
10 NO	NDESTRUCTIVE NMR EVALUATION OF THE CHLORIDE ION DIFFUSION ANI	D BINDING IN
CONCRE		272
10.1	Abstract	
10.1	Chloride Ion Diffusion and Binding	272
10.2	Materials and Methods	275
10.5	Experimental Program	
10.4	Results and Discussions	

10.5.1 UPV and Elastic Modulus Measurements
10.5.2 Scanning Electron Microscopy
10.6 Conclusions
11 NUMERICAL AND ANALYTICAL STUDIES 289
11.1 Indirect Measurements of Concrete Porosity 289
11.1.1 Porosity measurements
11.1.2 Experimental investigations 291
11.2 NMR Data Interpretation Software 298
11.2.1 Structural Inputs
11.2.2 Climate/Weather Inputs
11.2.3 Surface Appearance
11.2.4 Relaxation Results
11.2.5 Damage Analysis and Condition Rating
11.3 Conclusion
12 FIELD OPERATION OF PORTABLE NMR
12.1 General
12.2 Operating of Portable NMR 306
12.3 NMR Field Testing
12.3.1 Testing at Michigan DOT
12.3.2 Various structures 319
12.3.3 Corroborative SEM and XRD Investigations
12.4 Measurements in the Presence of Reinforcing Bars
12.5 Field testing: Mapping and Sampling Methods 342
12.6 Conclusions
13 CONCLUSION AND RECOMMENDATIONS
13.1 General
13.2 Key Findings
13.3 Research Impact and Practical Implications
13.4 Recommendations for Future Research
REFERENCES

## LIST OF TABLES

Table 1. Mix designs to be evaluated without accelerated aging, and the corresponding testmethods.60
Table 2. Mix designs, accelerated aging conditions, and test methods (total of 303 specimens).
Table 3. Mix proportion for normal- and high-strength concrete
Table 4. The measured values of aggregate specific gravity and absorption capacity
Table 5. Measured values of bulk density (compacted) and voids in aggregates.    74
Table 6. LA abrasion test results. 75
Table 7. Summary of the aggregate physical test results
Table 8. Chemical composition of aggregates. 77
Table 9. Measured values of ultrasonic pulse travel time and velocity through packed aggregateparticles
Table 10. Sample mass requirement for coarse aggregates.    109
Table 11. Sample mass requirement for fine aggregates.    109
Table 12. Sieve used to determine loss after test.    110
Table 13. Summary of soundness results for basalt    112
Table 14. Summary of soundness results for chert.    112
Table 15. Summary of soundness results for dolomite.    112
Table 16. Summary of soundness results for flint.    112
Table 17. Summary of soundness results for granite.    113
Table 18. Summary of soundness results for gravel. 113
Table 19. Summary of soundness results for limestone
Table 20. Summary of soundness results for sandstone 113

Table 21. Summary of soundness results for sand
Table 22. Chemical composition of cementitious materials.    124
Table 23. CPMG pulse sequence parameters.    151
Table 24. Maximum signal intensity and water content.    154
Table 25. Area measurements. 156
Table 26. Settings and performance parameters for different measurement depths
Table 27. Concrete mix designs. 183
Table 28. Chemical compositions of aggregates and cement (weight percent).    183
Table 29. Summary of the titration data for aggregates.    186
Table 30. Concrete mix designs. 209
Table 31. Summary of T <sub>1</sub> measurements 216
Table 43. Outcomes of the analysis of variance of the short component of $T_2$ measured after different numbers of freeze-thaw cycles
Table 33. Outcomes of the analysis of variance performed at different levels of freeze-thaw damage on the long component of $T_2$
Table 34. The concrete mix proportions used in the carbonation experiments
Table 35. Two-sample paired t-test Table.    253
Table 36. Concrete mix designs considered in sulfate attack tests.    263
Table 37. Mix designs and curing conditions considered in the chloride diffusion tests 277
Table 38. List of concrete cores obtained from different locations of US-23 by MDOT
Table 39 Values of the Correction Factor

## LIST OF FIGURES

Figure 1. Net magnetization ( $M_0$ ) resulting from the precession of proton spins about an external magnetic field [44]
Figure 2. Nuclear magnetization M can be rotated away from the direction of $B_0$ . The angle $\theta$ between the z-axis and the magnetization is called 'flip angle' [45]
Figure 3. After application of a 90° rf pulse, the proton spins dephase, and a free induction decay (FID) signal can be detected [44]
Figure 4. Hahn echo decay pulse sequence for measurement of $T_2$ ; FID is the free induction decay, $\tau$ between the two pulses, and $t_E$ is the inter-echo spacing used in the pulse-sequence.
Figure 5. CPMG sequence for detection of the signal decay by the NMR core-scanners; FID is the free induction decay, $t_E$ echo time and $T_2$ transverse relaxation time [45]
Figure 6. CPMG echo envelope measured on a water-saturated sediment sample (left) and corresponding frequency distribution of $T_2$ obtained by regularized inverse Laplace transformation with the UPEN program [55]
Figure 7. Saturation recovery pulse sequence to measure the longitudinal relaxation time $T_1$ which is the recovery time of the longitudinal component of the magnetization $M_z$ to the equilibrium value $M_0(1-1/e)$ ; $\tau_1$ is recovery time and $t_E$ echo time [45]
Figure 8. $T_1$ contour plots and $T_1$ distribution profiles vs hydration time for 3 specimens [59] 32
Figure 9. Comparison of NMR and MIP distribution profiles at selected hydration times for two specimens [60]
Figure 10. T <sub>1</sub> –T <sub>2</sub> two-dimensional relaxation correlation spectra of cement samples measured over 7days
Figure 11. Top left: A schematic of the water in the gel pores of an "as-prepared" paste. op right: The hydrate after sufficient drying to remove almost all the water from the gel pores [64] 36
Figure 12. T2 values at various depths from the surface on the left and specimens treated with phenolphthalein on the right [65]
Figure 13. Maximum of the FID-amplitude as a function of moisture content [67]

Figure 14. Pore water distribution of mortar determined from relaxation measurements [68]. 39

Figure 15. Application of the portable NMR on buildings. The device senses the composition of the substrate at the point where the magnetic field lines of the magnet and of the RF coil cross each other [70]
Figure 16. a) Water content during freeze-thaw deicing salt exposure in the near surface b) Gravimetric determined solution uptake. c) Inverse Laplace transformation of the T <sub>2</sub> nAE d) IL transformation of the T <sub>2</sub> decay measured in the outer zone AE
Figure 17. Simple model for porous media with smooth capillaries of radius r <sub>eff</sub> [79] 46
Figure 18. Simple model for porous media with smooth spheres of radius r <sub>por</sub>
Figure 19. Image showing a porous media (rock) according to the fractal pore space model composed of geometrical pores and hydraulic capillaries with effective radius r <sub>eff</sub> [79]
Figure 20. MD simulation snapshot of the tobermorite, $Ca_5Si_6O_{16}(OH)_2$ , interface with 0.25MKCl aqueous solution [82]
Figure 21. At top, a model quasi-two-dimensional pore shows fluid (gray) confined by walls (black) [83]
Figure 22. Molds used for casting of specimens
Figure 23. Visual appearance and description of aggregates
Figure 24. Sieve shaker
Figure 25. Gradation of (a) coarse aggregates, and (b) fine aggregate
Figure 26. Measure and rod for bulk density measurements
Figure 27. The LA abrasion drum steel
Figure 28. The SEM- EDS system
Figure 29. SEM- EDS samples: (a) examples of polished and unpolished gravel; (b) different aggregate particles
Figure 30. Natural surface of limestone
Figure 31. Polished surface of limestone
Figure 32. BES images of basalt at different magnifications for a) natural surface, b) polished surface of aggregate particles

Figure 33. BES images of chert at different magnifications for a) natural surface, b) polished surface of aggregate particles
Figure 34. BES images of dolomite at different magnifications for a) natural surface, b) polished surface of aggregate particles
Figure 35. BES images of flint at different magnifications for a) natural surface, b) polished surface of aggregate particles
Figure 36. BES images of granite at different magnifications for a) natural surface, b) polished surface of aggregate particles
Figure 37. BES images of gravel at different magnifications for a) natural surface, b) polished surface of aggregate particles
Figure 38. BES images of sandstone at different magnifications for a) natural surface, b) polished surface of aggregate particles
Figure 39. BES images of natural sand at different magnifications
Figure 40. EDS spectra of a) natural surface b) polished surface of limestone
Figure 41. EDS graph of basalt for a) natural surface and b) polished surface
Figure 42. EDS graph of chert for a) natural surface and b) polished surface
Figure 43. EDS graph of dolomite for a) natural surface and b) polished surface
Figure 44. EDS graph of flint for a) natural surface and b) polished surface
Figure 45. EDS graph of granite for a) natural surface and b) polished surface
Figure 46. EDS graph of gravel for a) natural surface and b) polished surface
Figure 47. EDS graph of limestone for a) natural surface and b) polished surface
Figure 48. EDS graph of sandstone for a) natural surface and b) polished surface
Figure 49. EDS graph of natural sand
Figure 50. UPV instrument
Figure 51. UPV test sample 100
Figure 52. Percent of 24-hr absorption versus time for aggregates
Figure 53. The Bruker Davinci Diffractometer

Figure 54. XRD spectrum of basalt	
Figure 55. XRD spectrum of chert	105
Figure 56. XRD spectrum of dolomite	105
Figure 57. XRD spectrum of limestone.	106
Figure 58. XRD spectrum of flint	
Figure 59. XRD spectrum of granite	107
Figure 60. XRD spectrum of sandstone	107
Figure 61. XRD spectrum of sand	
Figure 62. Summary of soundness test	111
Figure 63. Aggregate specimen used for X-ray μCT	115
Figure 64. Layered images of the aggregate X-ray scans at 46µm resolution	116
Figure 65. Layered images of the aggregate X-ray scans at $27\mu m$ resolution	116
Figure 66. X-ray $\mu$ CT of basalt aggregates at 46 $\mu$ m resolution	117
Figure 67. X-ray $\mu$ CT of basalt aggregates at 27 $\mu$ m resolution	
Figure 68. X-ray $\mu$ CT of (natural) gravel particles at 27 $\mu$ m resolution	119
Figure 69. SEM micrographs of basalt aggregates	120
Figure 70. SEM micrographs of chert aggregates	120
Figure 71. SEM micrographs of dolomite aggregates	
Figure 72. SEM micrographs of flint aggregates	
Figure 73. SEM micrographs of granite aggregates	
Figure 74. SEM micrographs of natural gravel aggregates	
Figure 75. SEM micrographs of limestone aggregates.	123
Figure 76. SEM micrographs of sandstone aggregates	123
Figure 77. SEM micrographs of natural sand	123

Figure 78. XRD spectrum of Type I cement
Figure 79. XRD spectrum of Type I/II cement126
Figure 80. XRD spectrum of Class C fly ash126
Figure 81. XRD spectrum of Class F fly ash 127
Figure 82. XRD spectrum of silica fume 127
Figure 83. XRD spectrum of slag
Figure 84. Physical principles of Nuclear Magnetic Resonance. (1) Static magnetic field B <sub>0</sub> , (2) RF magnetic field B <sub>1</sub> , (3) NMR signal, (4) Spin-spin interactions, (5) spin-lattice interactions [101].
Figure 85. $T_1$ saturation recovery pulse sequence. In the first part of the sequence, net magnetization is destroyed. During the recovery time, magnetization is restored and read out with a CPMG sequence [32]
Figure 86. The T <sub>1</sub> saturation recovery user interface
Figure 87. The CPMG pulse sequence. The echo envelope decays with time constant $T_2$ [32]. 133
Figure 88. The T <sub>1</sub> saturation recovery user interface
Figure 89. A schematical representaiton of an isolated pore and a moving water molecule [68].
Figure 164. Stimulated spin echo [102] sequence [32].
Figure 91. Stimulated spin echo
Figure 92. Moisture conditions of aggregates [103]138
Figure 93. Pore size distribution of test aggregates [104]138
Figure 94. Throat pore volume measured following the PDC-MIP testing sequence [105] 139
Figure 95. Incremental porosity distribution of pure cement paste w/c= 0.4 and cement paste of mortar (3 months old). A new porous volume in excess for the pores bounded by 0.045 and 0.1 $\mu$ m may be observed [109]
Figure 96. Selected rocks for testing via portable NMR
Figure 97. Testing a rock sample by the portable NMR equipment

Figure 98 $T_1$ longitudinal relaxation curves for (a) cement paste, and (b) concrete 143
Figure 99 CPMGFast program settings for (a) paste and (b) concrete specimens stored in water. 144
Figure 100 $T_2$ relaxation curves for (a) paste and (b) concrete specimens stored in water 144
Figure 101. The $T_1$ longitudinal relaxation curves for (a) paste and (b) concrete specimens stored in water
Figure 102. $T_2$ relaxation curves for (a) paste and (b) concrete specimens stored in water 145
Figure 103. T <sub>1</sub> relaxation curves for saturated rocks
Figure 104. T <sub>2</sub> relaxation curves for saturated rocks148
Figure 105. Test setup for water content measurements151
Figure 106. Signal intensity of paste cube at (a) 2.5mm and (b) 5mm from the surface
Figure 107. Signal intensity of bulk water at (a) 2.5mm and (b) 5mm from the surface
Figure 108. Four-point back-tracked extrapolation of signal amplitude for (a) water and (b) cement paste
Figure 109. (a) T2 decay of a saturated paste sample. (b) Bi-exponential fit. (c) Inverse Laplace. 154
Figure 110. Inverse Laplace transformation of cement paste at (a) 2.5mm and (b) 5mm depth
Figure 111. Main components of the portable NMR157
Figure 112. The sensor and lift assembly157
Figure 113. The spectrometer and laptop assembly
Figure 114. The Prospa interface
Figure 115. (a) Magnets and coil configuration (b) probe and lift [116]
Figure 116 The FID signal [1]163
Figure 117 The CPMP pulse sequence164
Figure 118 Hahn Echo sequence ( <i>encoding period</i> ) followed by a CPMG detection train ( <i>detection period</i> )

Figure 119 Saturation recovering + Hahn Echo sequence (encoding period) followed by CPMG detection train (detection period)167
Figure 120. Testing of cubic paste (left) and cylindrical concrete (right) specimens with the portable NMR system
Figure 121. $T_1$ longitudinal relaxation curves for (a) cement paste, and (b) concrete 169
Figure 80. $T_2$ relaxation curves for (a) paste and (b) concrete specimens stored in water 170
Figure 81. The $T_1$ longitudinal relaxation curves for (a) paste and (b) concrete specimens stored in water
Figure 82. $T_2$ relaxation curves for (a) paste and (b) concrete specimens stored in water 171
Figure 125. $T_1$ relaxation curves for saturated rocks
Figure 126. T <sub>2</sub> relaxation curves for saturated rocks
Figure 127. Microstructure and mineralogy at aggregate-paste interfaces in concrete undergoing ASR [134]
Figure 128. Measured values of expansion versus time
Figure 129. XRD spectrum of limestone
Figure 130. XRD spectrum of flint
Figure 131. XRD spectrum of Chert
Figure 132. XRD spectrum of MI sand 189
Figure 133. XRD spectrum of TX sand190
Figure 134. Statistical evaluation of the measured values of T <sub>1</sub>
Figure 135. T <sub>2</sub> decays (left) and the T <sub>2</sub> distributions obtained from inverse Laplace transformation (right) of Mixes M1 (a,b), M2 (c,d) and M3 (e, f)
Figure 136. The $T_2$ distribution peak fitting for the specimen M25A1 (a) in unaged conditions, and (b) after early stages of exposure to accelerated ASR condition
Figure 137. Moisture content of concrete specimens as a function of the accelerated aging duration
Figure 138. Effects of accelerated ASR aging on the short component of T <sub>2</sub> for three different concrete mixtures

Figure 139. Ultrasound pulse velocity (UPV) of specimens prior to and after aging 202
Figure 140. Dynamic elastic modulus of specimens prior to and after aging 203
Figure 141. Uranyl-acetate treated cross section of concrete (a) mix M1 (made of chert) and (b) mix M2 (made of flint)
Figure 142. Test specimens after exposure to 450 cycles of freezing and thawing: (a) Mix M1; (b) Mix M11; (c) Mix M14; and (d) Mix M23
Figure 143. Relaxation decay curves of different concrete materials prior to and after accelerated freeze-thaw aging
Figure 144. Relative change of amplitude with depth for: (a) Mix M1; (b) Mix M11; (c) Mix M14; and (d) Mix M23
Figure 145. T <sub>1</sub> values measured for concrete specimens (a) M23FT1, (b) M23FT2, (c) M23FT3.
Figure 146. Two-sample t-test graph for measured values of $T_1$ prior to and after deterioration under freeze-thaw cycles
Figure 147. Relaxation time distributions 218
Figure 148. The relative change in the short and long components of $T_2$ for different concrete mixtures. 220
Figure 149. Effects of the number of freeze-thaw cycles on the short component of $T_2$ (considering all three specimens and measurements made at different depths) 221
Figure 150. Effects of freeze-thaw damage on the long component of T <sub>2</sub> 222
Figure 151. Effects of freeze-thaw cycles on UPV and dynamic elastic modulus
Figure 152. SEM images of different concrete materials after exposure to 450 freeze-thaw cycles
Figure 153. The beams subjected to freeze-thaw cycles by the Michigan DOT 226
Figure 154. NMR testing of freeze-thaw beams at the MDOT facility
Figure 155. Relaxation decay curves of the beams subjected to freeze-thaw cycles 228
Figure 156. Relaxation time distributions of the freeze-thaw beams
Figure 157. Relative changes in the short and long components of $T_2$ with depth 231

Figure 158. Self-diffusion coefficient for beams subjected to freeze-thaw cycles
Figure 159. Measured values of dilation, and average values of the short and long components of T <sub>2</sub>
Figure 160. Carbonation test chamber 240
Figure 161. Schematics of the accelerated carbonation test set-up [156]
Figure 162. Relaxation decay curves of concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19.
Figure 163. Relative change of amplitude versus depth for concrete mixtures (a) M1, (b) M11, (c) M16, and (d) M19
Figure 164. The relaxation time distributions for concrete mixtures (a) M1, (b) M11, (c) M16, and (d) M19248
Figure 165. Relative changes of short $T_2$ with accelerated carbonation and with age for concrete mixes (a) M1, (b)M11, (c) M16, and (d) M19
Figure 166. Lesat squares means of short T <sub>2</sub> 251
Figure 167. Lesat squares means of long T <sub>2</sub> values 251
Figure 167. Lesat squares means of long $T_2$ values
Figure 167. Lesat squares means of long $T_2$ values.251Figure 168. Relative change on $T_1$ (a) M1, (b)M11, (c) M16 and (d)M19.252Figure 169. Normal distribution and box plot of $T_1$ values.253
Figure 167. Lesat squares means of long T2 values.251Figure 168. Relative change on T1 (a) M1, (b)M11, (c) M16 and (d)M19.252Figure 169. Normal distribution and box plot of T1 values.253Figure 170. Relative change of self-diffusion coefficient (D) with respect to depth prior to and after accelerated carbonation for concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19 254
Figure 167. Lesat squares means of long T2 values.251Figure 168. Relative change on T1 (a) M1, (b)M11, (c) M16 and (d)M19.252Figure 169. Normal distribution and box plot of T1 values.253Figure 170. Relative change of self-diffusion coefficient (D) with respect to depth prior to and after accelerated carbonation for concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19 254Figure 171. (a)Ultrasound pulse velocity (UPV) and (b) dynamic elastic modulus test results for different concrete materials exposed to various periods of accelerated carbonation.
Figure 167. Lesat squares means of long T2 values.251Figure 168. Relative change on T1 (a) M1, (b)M11, (c) M16 and (d)M19.252Figure 169. Normal distribution and box plot of T1 values.253Figure 170. Relative change of self-diffusion coefficient (D) with respect to depth prior to and after accelerated carbonation for concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19 254Figure 171. (a)Ultrasound pulse velocity (UPV) and (b) dynamic elastic modulus test results for different concrete materials exposed to various periods of accelerated carbonation.255Figure 172. SEM images of the high-strength concrete mix M19 (a) control, (b) carbonated, and normal-strength concrete mix M1 (c) control and (d) carbonated.256
Figure 167. Lesat squares means of long T2 values.251Figure 168. Relative change on T1 (a) M1, (b)M11, (c) M16 and (d)M19.252Figure 169. Normal distribution and box plot of T1 values.253Figure 170. Relative change of self-diffusion coefficient (D) with respect to depth prior to and after accelerated carbonation for concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19 254Figure 171. (a)Ultrasound pulse velocity (UPV) and (b) dynamic elastic modulus test results for different concrete materials exposed to various periods of accelerated carbonation.Figure 172. SEM images of the high-strength concrete mix M19 (a) control, (b) carbonated, and normal-strength concrete mix M1 (c) control and (d) carbonated.256Figure 173. Schematics of the pH-controlled accelerated sulfate attack test apparatus [22] 262
Figure 167. Lesat squares means of long T2 values.251Figure 168. Relative change on T1 (a) M1, (b)M11, (c) M16 and (d)M19.252Figure 169. Normal distribution and box plot of T1 values.253Figure 170. Relative change of self-diffusion coefficient (D) with respect to depth prior to and after accelerated carbonation for concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19.254Figure 171. (a)Ultrasound pulse velocity (UPV) and (b) dynamic elastic modulus test results for different concrete materials exposed to various periods of accelerated carbonation.255Figure 172. SEM images of the high-strength concrete mix M19 (a) control, (b) carbonated, and normal-strength concrete mix M1 (c) control and (d) carbonated.256Figure 173. Schematics of the pH-controlled accelerated sulfate attack test apparatus [22].262Figure 174. Relaxation time distributions of concrete mixtures M1 (a,b) and M11 (c,d).266
Figure 167. Lesat squares means of long T2 values.251Figure 168. Relative change on T1 (a) M1, (b)M11, (c) M16 and (d)M19.252Figure 169. Normal distribution and box plot of T1 values.253Figure 170. Relative change of self-diffusion coefficient (D) with respect to depth prior to and after accelerated carbonation for concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19.254Figure 171. (a)Ultrasound pulse velocity (UPV) and (b) dynamic elastic modulus test results for different concrete materials exposed to various periods of accelerated carbonation.255Figure 172. SEM images of the high-strength concrete mix M19 (a) control, (b) carbonated, and normal-strength concrete mix M1 (c) control and (d) carbonated.256Figure 173. Schematics of the pH-controlled accelerated sulfate attack test apparatus [22].262Figure 174. Relaxation time distributions of concrete mixtures M1 (a,b) and M11 (c,d).266Figure 175. Relaxation decay curves of concrete mixtures M1 (a,b) and M11 (c,d).267

Figure 177. Measured values of short T <sub>2</sub> versus depth for concrete mixtures M1 (a) and M11 (b).
Figure 178. Measured values of long $T_2$ versus depth for concrete mixtures M1 (a) and M11 (b)
Figure 179. UPV (a) and dynamic modulus (b) data for concrete mixtures M1 and M11, measured at different stages of sulfate attack
Figure 180. AASHTO T259 test setup [203] 276
Figure 181. Nordtest setup [203] 277
Figure 182. Relaxation decay curves for concrete mixtures M1 (a, b), M11 (c, d), M16 (e, f), M19 (g, h)
Figure 183. Relative change of amplitude with depth for concrete mixtures (a)M1, (b)M11, (c)M16 and (d)M19
Figure 184. Relaxation time distribution of (a) M1, (b) M11, (c) M16 and (d)M19281
Figure 185. Relative change of short $T_2$ for concrete mixtures (a) M1, (b)M11, (c) M16 and (d)M19 at different states of exposure to chloride solution
Figure 186. Relative change of the measured values of long $T_2$ for concrete mixtures (a) M1, (b)M11, (c) M16 and (d)M19 prior to and after exposure to chloride solution
Figure 187. Relative change of $T_1$ for concrete mixtures (a) M1, (b)M11, (c) M16 and (d)M19 prior to and after exposure to chloride solution
Figure 188. (a)UPV and (b) elastic modulus of carbonation mixes
Figure 189. SEM images of the concrete mix M1 (a) prior to and (b) after exposure to chloride solution
Figure 190. Sorptivity and sorption measurement test setup
Figure 191. Correlation of the concrete porosities determined with the portable NMR instrument $(\Phi_{NMR})$ versus the method involving moisture sorption measurement
Figure 192. Porosity measurements via NMR relaxometry for concrete materials prior to and after exposure to accelerated freeze-thaw cycling and carbonation
Figure 193. Magnetic susceptibility values of concrete materials
Figure 194. Correlation of the permeability coefficients measured with the NMR instrument and sorptivity measurements per ASTM C1585

Figure 195. Estimated permeability values based on NMR measurements for concrete prior to and after accelerated aging via freeze-thaw cycling or carbonation	materials 297
Figure 196. NMR Relaxation Software layout	299
Figure 197. NMR Relaxation software – Structural Input	300
Figure 198. NMR Relaxation software – Climate/Weather input	301
Figure 199. NMR Relaxation software – Surface appearance input	302
Figure 200. NMR Relaxation software – Relaxation input	303
Figure 201. NMR Relaxation software – Analysis output.	304
Figure 182. (a) Portable NMR components, (b) spectrometer and	307
Figure 203. Portable NMR testing and processing sequence	308
Figure 204. (a) Rock A and (b) nondestructive NMR testing	309
Figure 205. Relaxation decay curves of Rock A	311
Figure 206. Relative change in NMR amplitude with respect to surface, reflecting the moisture content for Rock A	change in 312
Figure 207. Relaxation time distribution of Rock A at various depths.	313
Figure 208. The self-diffusion coefficent of Rock A at various depths.	313
Figure 209. (a) Rock B and (b) NMR testing	314
Figure 210. Relaxation decay curves at different depths of Rock B.	315
Figure 211. Relative change in NMR amplitude with respect to surface, reflecting the moisture content for Rock B.	change in 315
Figure 212. Relaxation decay of rock B	316
Figure 213. The self-diffusion coefficient of Rock B at different depths	317
Figure 214. Rock C	317
Figure 215. NMR testing of a freeze-thaw prismatic specimen at Michigan DOT	318
Figure 216. NMR testing of cores taken from US-23	319
Figure 217. Pictures of structure I in (a) undamaged and (b) damaged condition	320

Figure 218. Change of short $T_2$ in intact and cracked locations
Figure 219. SEM images of concrete structure I
Figure 220. Pictures of structure II in (a) damaged and (b) damaged condition
Figure 221. The trends observed in the NMR data generated for the $T_2$ values (a) and the percent change in decay amplitude with respect to depth
Figure 222. SEM images of concrete structure II
Figure 223. XRD patterns of (a) structure III and (b) structure IV
Figure 224. The NMR software analysis of Structure III (a), and Structure IV (b)
Figure 225. Pictures of the intact (a) and deteriorated (b) regions of Structure III
Figure 226. Pictures of the intact (a) and deteriorated (b) regions of Structure IV
Figure 227. The trends in the transverse relaxation time $(T_2)$ and amplitude change with depth for the undamaged and damaged regions of Structure III
Figure 228. The trends in the transverse relaxation time $(T_2)$ and decay amplitude change with depth for the undamaged and damaged regions of Structure IV
Figure 229. Typical SEM image of Structure III
Figure 230. Typical SEM image of Structure IV
Figure 231. XRD patterns of Structures III and IV
Figure 232. Prismatic specimens with different number of rebars (6 in clear cover over reinforcement)
Figure 233. The effect of steel reinforcement with 6 in clear cover on NMR signal of concrete at (a) 2mm, (b) 4mm, and (c) 6mm from surface
Figure 234. Prismatic beams and number of rebars in NMR testing with 4 in clear cover over reinforcing bars
Figure 235. The effect of rebars with 4 in clear cover on the NMR signal of concrete at (a) 2mm, (b) 4mm and (c) 6mm from surface
Figure 236. Prismatic beams simulating 1.7 in clear cover over reinforcement, and the number of rebars used in NMR testing

Figure 237. The effect of reinforcing bars with 1.7 in clear cover on the NMR signal of concrete at (a) 2mm, (b) 4mm and (c) 6mm from surface
Figure 238. Visual representation of magnetic field lines around a bar magnet
Figure 239. Comparison between Monte Carlo and LHS simulations: (a) Entire domain; (b) Monte Carlo; and (c) LHS
Figure 240. Example of sampling in LHS method
Figure 241. Example of a randomly generated test spots using the LHS rules

### **KEY TO ABBREVIATIONS**

- NMR: Nuclear Magnetic Resonance
- NDT: Nondestructive Testing
- NDE: Nondestructive Evaluation
- SNMR: Surface NMR
- W/C: Water-to-Cement Ratio
- **ITZ: Interfacial Transition Zone**
- C-S-H: Calcium-Silicate-Hydrate
- *T*<sub>1</sub>: Longitudinal relaxation time (or spin-spin relaxation time)
- *T*<sub>2</sub>: Transverse relaxation time (or spin-lattice relaxation time)
- D: Self-diffusion coefficient
- M: Magnetization
- *B*<sub>0</sub>: Static magnetic field
- B<sub>1</sub>: Magnetic field
- *f*: Frequency
- $\gamma$ : gyromagnetic ratio
- $M_{0xy}$ : Magnitude of transverse magnetization
- $M_{z}(t)$ : Magnitude of magnetization in z direction at time t
- $\boldsymbol{\theta} \colon \mathrm{Tip} \; \mathrm{angle}$
- $\rho_{\rm 1}$  ,  $\,\rho_{\rm 2}$  : Surface relaxivity values corresponding to T\_1 and T\_2
- S/V: Surface-to-volume ratio

G: Gradient of the magnetic field

- $t_E$ : Inter-echo spacing
- *¢*: Porosity
- k: permeability

## **1** INTRODUCTION

## 1.1 General

Management of the nation's aging transportation infrastructure constitutes a growing financial burden. Limited resources are available for inspection, maintenance, repair, rehabilitation and replacement of the deteriorating infrastructure. More efficient management of the aging concrete-based transportation infrastructure, enabled by thorough and practical condition assessment techniques, would allow for effective use of available resources to maintain a viable transportation system. Condition assessment of the vast concrete-based transportation infrastructure is challenged by the complex structure and deterioration mechanisms of concrete, and the complicating effects of surface treatments.

Development of compact, lightweight and economically viable equipment for implementing some analytical chemistry methods (e.g., x-ray diffractometry, nuclear magnetic resonance, Xray fluorescence spectroscopy, Fourier-transform infrared spectroscopy) have facilitated their growing semi-destructive or nondestructive field applications (e.g., in the field of geology). Initial efforts to make direct use of these methods for semi- or non-destructive field evaluation of concrete, however, have encountered challenges associated with the heterogeneity of concrete structure, and the complexity of concrete structure and deterioration mechanisms. Nuclear Magnetic Resonance (NMR) spectroscopy and relaxometry provide means of resolving and quantifying the chemistry of chemical compounds in various materials. Advances have been made in recent years towards applications of NMR for nondestructive inspection in the fields of

manufacturing, arts and health sciences. These advances open the prospects for nondestructive evaluation of the concrete-based infrastructure with portable NMR systems.

Concrete comprises different elementary phases: cement hydrates, anhydrous cement, unreacted pozzolans, water, and aggregates. Water resides within the pore system of concrete (which covers a broad size range) in different binding conditions. Various processes of concrete deterioration produce complex changes in the chemistry and structure of concrete.

### 1.2 Role of NMR in Condition Assessment of Concrete

NMR spectroscopy and relaxometry offer means of investigating the chemistry and microstructure of cement-based materials, partly because they can resolve local structures of materials [1].<sup>29</sup>Si NMR spectroscopy provides quantitative information on the fractions of silicon present in different tetrahedral environments in silicates as cementitious materials evolve during hydration and pozzolanic reactions, and undergo various processes of deterioration (e.g., alkali-silica reaction).<sup>29</sup>Si NMR spectroscopy also reflects the structure of aggregates and their deterioration conditions (e.g., due to alkali-silica reactions).<sup>27</sup>Al NMR spectroscopy is also helpful for investigating the aluminum-bearing compounds in cement-based materials, which reflect the progress of hydration and different aging mechanisms (e.g., sulfate attack and chloride ion diffusion). <sup>1</sup>H NMR magnetization relaxation offers tools for studying the pore (and crack) systems covering broad size and connectivity conditions, which reflect upon the progress of hydration and pozzolanic reactions, the quality of concrete, and the chemical and physical processes of deterioration [2].

### 1.3 Nondestructive Methods of Concrete Inspection

Non-destructive inspection of the damage and deterioration conditions of concrete is challenged by the heterogeneous structure and the complex physical and chemical manifestations of concrete deterioration in service conditions.

The portable <sup>1</sup>H NMR system can produce quantitative information on: (i) the spatial distribution and concentration, morphology, and size distribution of concrete cracks and pores; (ii) the concentration and spatial distribution of concrete moisture, distinguishing between different binding states and mobility conditions of moisture; and (iii) manifestations and states of chemical deterioration mechanisms.

The more advanced (existing or emerging) techniques for non-destructive condition assessment of concrete, against which the portable NMR system should be compared to more directly, include: (i) ultrasonic pulse velocity (indirect transmission method); (ii) impact (sonic-echo) method; (iii) ground penetrating (short pulse) radar; (iv) infrared thermography; and [2] x-ray computed tomography.

Other concrete non-destructive inspection techniques do not provide information that are similar to those provided by portable above-mentioned methods but could still be compared with or complement the portable NMR system. These techniques include: (vi) surface hardness methods; (vii) penetration resistance techniques; (viii) pull-out tests; [3] maturity method; (x) absorption and permeability tests; (xi) surface wave methods; (xii) acoustic emission; (xiii) electrical resistivity; (xiv) electrochemical methods (corrosion potential, polarization resistance,

electrochemical impedance spectroscopy); and (xv) electromagnetic (covermeter) method; and (xvi) backscattering microwave tomography.

### 1.3.1 Directly compared to non-destructive inspection techniques

1. Ultrasonic Pulse Velocity (Indirect Transmission Method): Indirect transmission of ultrasound pulse allows for detection of the layers formed parallel to the surface of concrete exposed to aggressive environments. The ultrasonic wave velocities of these layers vary as a function of their microcracking, porosity, moisture and aging conditions. Assuming distinct wave velocities for these layers, the method can provide information on the heights of layers [4]. Deterioration of concrete, however, does not generally produce layers with sharp wave velocity contrasts. Microcracking, porosity, aging and moisture conditions (which affect wave velocity) tend to vary gradually as a function of depth; this compromises the accuracy of calculations based on the assumption of layers with distinct wave velocities. The indirect transmission method lacks the capability to identify the specific factors (microcracking, porosity, aging, moisture content) which are responsible for the wave velocity gradient normal to the surface. The portable NMR system, on the other hand, can potentially account for the gradual variation of concrete damage/deterioration conditions, distinguish between different physical manifestations of concrete aging (microcracking, pore system characteristics, moisture content and mobility), and quantify these damage/deterioration effects (using its relaxometry features). The ability of portable NMR to resolve the 3D variation of damage and deterioration phenomena, and to provide insight into the chemical mechanisms of

concrete deterioration further distinguish it from the indirect transmission method of ultrasound pulse velocity.

- 2. Impact (Sonic-Echo) Method: The sonic-echo method of impact testing, when accompanied with analysis of the waveforms in frequency domain (using a fast Fourier transform technique), can yield information on the location of defects (e.g., cracks) within the concrete depth. This method lacks the resolution to identify finer defects (e.g., microcrack) which tend to be prevalent in deteriorating concrete, cannot provide detailed information on defect (e.g., crack) morphology (shape) or type (crack versus void) [5]. The portable NMR system, on the other hand, can yield information on the size distribution of microcracks and voids, and further provide information on the chemical mechanisms of concrete deterioration.
- 3. Ground Penetrating (Short Pulse) Radar: This method has been used to detect voids and cracking in concrete structures. Research is in progress to employ the short pulse radar method to assess the water content of concrete, its degree of hydration, and the presence of chlorides [6]. Short pulse radar can detect cracks too. Moreover, short pulse radar can produce indirect information on the porosity and nature of water (bulk versus adsorbed), but falls short to yield quantitative information on the size characteristics and spatial distribution of the pore system as well, and to distinguish between different states of water with various degrees of constraint.
- 4. Infrared Thermography: This method can be used to produce qualitative information on the presence of large cracks or areas of high porosity near the concrete surface. The

results are subject to relatively large variations depending on weathering conditions (e.g., wind speed) [7-9].

- 5. X-Ray Computed Tomography: This method, when implemented in laboratory where a concrete specimen can be x-rayed from every angle around it, is a powerful means of 3D mapping of void and crack systems at high resolution. Field applications generally allow for limited angle access to the concrete structure, which challenges the ability of reconstruction algorithms to produce high-resolution images of concrete cracks and voids. Other drawback of this method relate to its high cost and limited depth of penetration, and restricted mobility [10].
- 1.3.2 Indirectly competing / complementary non-destructive inspection techniques
  - 1. Surface Hardness Methods: Schmidt rebound hammer, as a surface harness method, is used to estimate the strength of concrete, and the planar uniformity of concrete strength. This method does not provide any insight into the structure or the physical and chemical manifestations of concrete deterioration [11]. The correlation between rebound and strength in this test method is influenced by the aggregate type, curing condition of concrete, moisture and carbonation conditions of concrete, and location of the plunger with respect to the aggregates occurring near surface. These effects limit the reliability of this method in field applications.
  - 2. Penetration Resistance Techniques: Windsor probe is a common variation of this method, which is used to estimate the strength of concrete. The results, however, are highly sensitive to aggregate type. This method, like Schmidt rebound hammer, does not provide any insight into the structure or the physical and chemical manifestations of concrete

deterioration. This method suits monitoring of the early-age strength development of concrete to help decide on removing formwork or opening the concrete system to traffic.

- 3. Pull-Out Tests: This semi-destructive test method is used to estimate the strength of concrete. The results are influenced by the specifics of concrete mix design. Pull-out tests must be planned in advance. Like penetration resistance, pull-out tests suit monitoring of early-age strength development over time [12]. This method does not provide any insight into the structure or the physical and chemical manifestations of concrete deterioration.
- 4. Maturity Method: This method correlates development of concrete strength with its temperature time-history. It needs prior calibration for a particular mix under consideration. The maturity method neglects the important effects of humidity on strength development, and oversimplifies the effects of temperature at very early age on long-term strength development. It does not provide any insight into the structure or the physical and chemical manifestations of concrete deterioration.
- 5. Absorption and Permeability Tests: The non-destructive initial surface absorption test and the semi-destructive Figg test assess the concrete quality and potential durability based on its water absorption/air permeability attributes. These methods are sensitive to moisture conditions of concrete, which cannot be fully tailored in field conditions. They do not provide any insight into the structure or the physical and chemical manifestations of concrete deterioration.
- 6. Surface Wave Methods: This method can be used to determine the existence of layers with different elastic properties in concrete, which may be a result of poor compaction or

of exposure to aggressive environments [13]. The method, however, cannot identify the reason these layers form.

- 7. Acoustic Emission: This method, which has a history of use with metals, is being researched for studying fracture processes in concrete associated with corrosion of reinforcing steel, alkali-silica reaction and freeze-thaw cycles. Applications of acoustic emission for non-destructive inspection of concrete are challenged by the fact that concrete is a dispersive medium, and many of the theoretical and analytical tools available for metals are not necessarily valid for the acoustic emission signals from concrete. In addition, quantitative analysis of acoustic emission in concrete is difficult because the actual exact source mechanisms are not known or fully characterized beforehand, and the propagating medium is not a homogeneous, isotropic, and elastic field; material properties can change by an order of magnitude over short distances. While acoustic emission could offer indications of some deterioration phenomena in concrete, it does not seem to offer the potential for reliable identification and quantitative assessment of different mechanisms of concrete deterioration based on their physical and chemical manifestations [10, 14].
- 8. Electrical Resistivity: This method provides information relevant to the susceptibility and state of steel corrosion in concrete. Electrical resistivity measurements are sensitive to the moisture condition of concrete, which is difficult to control in field conditions [15]. Electrical resistivity measurements could complement the data generated using the mobile NMR system; the two methods could be used together to gain further insight into the mechanisms and state of concrete deterioration.

- Electrochemical Methods (corrosion potential, polarization resistance, electrochemical impedance spectroscopy): These methods provide information on the state and rate of corrosion of steel in concrete. They do not overlap, but complement the information generated by mobile NMR [16, 17].
- Electromagnetic (covermeter) Method: This method is commonly used for locating reinforcing bars and estimating the thickness of concrete cover over steel reinforcement [18]. This limited data could complement the comprehensive information generated by mobile NMR.
- 11. Backscattering Microwave Tomography: This method can be used to estimate the size and location of steel bars in complex reinforcing concrete structures, produce tomographic images of reinforcing bars [19, 20]. This limited information can complement the data generated by mobile NMR on concrete structure, deterioration mechanisms and health condition.

## 1.4 Deterioration Mechanisms of Concrete Infrastructure

During the service life of a concrete structure, concrete material undergoes various physical and mechanical alterations. The following deterioration mechanisms are considered in this research to study their effect on concrete using the portable NMR system: (i) alkali-silica reaction, (ii) freeze-thaw, (iii) carbonation, (iv) sulfate attack and (v) chloride ion diffusion. While the effects of these mechanisms on concrete is still being studied, there is a growing need to identify and quantify the extent of damage to the integrity and health of concrete caused by them.

## 1.5 Research Objectives

Based on above discussion, there is clearly a need for understanding of the field damage and measuring the extent of damage caused by various deterioration mechanisms of concrete. The main aim of this research is to develop fundamental understanding on the effects of various deterioration mechanism on concrete. The knowledge gap described briefly before and more extensively in the following section will be filled by pursuing following objectives

The focus of this research will be on performance of more comprehensive field and laboratory investigations towards development, validation and refinement of the NMR system and operation procedures, and development of data analysis methods and software for identification and quantification of concrete deterioration conditions. The experimental work of this research will cover representative concrete materials, deterioration mechanisms, states of deterioration, and coating conditions. The objectives to be accomplished in this research are listed below.

- <u>Objective 1.</u> Carry out detailed state-out-the-art review on the application of NMR relaxometry on porous materials.
- <u>Objective 2.</u> Conduct NMR relaxometry and spectroscopy and parallel analytical chemistry experiments on aggregates and cementitious materials as well as concrete materials of different compositions and coating conditions, undergoing various types and states of deterioration, and devise methods for operation of the NMR system and analysis of the output data for spatially resolved quantitative evaluation of the concrete structure and deterioration conditions.
- <u>Objective 3.</u> Validate the NMR hardware, operation methods and data analysis software through nondestructive field and corroborating laboratory evaluations of the concrete-based transportation infrastructure with representative materials, deterioration mechanisms and health conditions.
- <u>Objective 4.</u> Developing a data analysis software dedicated to receiving the relaxation data to interpret them with respect to laboratory and field testing data.
- <u>Objective 5.</u> Conduct field investigations and corroborating laboratory studies using the NMR hardware, operation procedures and data analysis software as well as conventional NMR and broader analytical chemistry methods in applications covering representative concrete materials, transportation infrastructure systems, protective coatings, and deterioration conditions.
- <u>Objective 6.</u> Verify and further refine the NMR hardware, operation procedures and data analysis software through evaluation of all NMR and corroborating analytical chemistry data generated in the research.
- <u>Objective 7.</u> Apply the final system towards identification and spatially resolved quantification of the type and extent of deterioration in bridge structures and pavements with unknown health conditions, and subsequently validate the outcomes through performance of corroborative analytical chemistry methods.
- <u>Objective 8.</u> Perform a numerical study towards characterization of concrete using the available NMR models.

#### 1.6 Anticipated Research Impact

Existing capabilities for non-destructive condition assessment of the deteriorating concretebased infrastructure are limited. These non-destructive test methods are limited in terms of: (i) identification and spatially resolved quantification of concrete deterioration processes and health condition; (ii) monitoring of the (moisture, chloride) transport in concrete, and assessment of concrete sorptivity/permeability; (iii) quantitative and spatially resolved evaluation of the concrete pore system characteristics and microcrack conditions; and (iv) identification of the concrete raw materials and estimations of mix proportions.

The proposed Ph.D. research aims to produce two main results. First, the proposed experimentalnumerical approach initiates the application of portable NMR in evaluating concrete undergoing various deterioration mechanisms. Second, since proposed study aims to identify the impact of various deterioration mechanisms on NMR signals, the outcomes of research can also be useful for those researchers who are attempting to rectify the drawbacks associated with current destructive or nondestructive methods of concrete analysis.

# 1.7 Scope and Outline

The current research is carried out to achieve the above objectives, results of which are presented in thirteen chapters in this dissertation.

The dissertation consists of the following chapters:

Chapter 1 provides the basic background with deterioration mechanisms of concrete and how the portable NMR can potentially help with studying these mechanisms in the lab as well as identifying them in the field. This chapter enumerates the challenges in non-destructive testing

(NDT) of concrete infrastructure. The merits of the proposed NDT approach (NMR) are presented and compared with the majority of the current or former NDT methods. The objectives and scope of this research towards development and implementation of the NMR test method are also included in this chapter.

Chapter 2 details the state-of-the-art research on the application of NMR relaxometry on porous materials. This chapter outlines the previous efforts towards instrumentation and application of portable NMR. The experimental and analytical/numerical studies of NMR relaxometry applied to porous materials are documented and reviewed in this chapter. Moreover, the fundamental physics of NMR is explained briefly to acquaint the reader with the basics of the NMR concept and terminology. The governing equations and parameters presented in this section will be frequently used in the latter part of this chapter which is devoted to design of the portable NMR system. Additionally, the standards and specifications used in this research are listed in this chapter. The knowledge gap is underlined in this section.

Chapter 3 includes the experimental program devised and followed throughout this research. Moreover, the NMR main components are described in this chapter: magnets, rf coil, spectrometer and digital hardware and their functionality.

Chapter 4 explains that how NMR relaxometry could be useful in analysis of concrete. The role of water in concrete, water content measurements and water distribution in concrete is explained in this chapter.

Chapter 5 describes the portable NMR machine used in this research. The type of magnets, RF coil and spectrometer and the device specifications are included in this chapter.

Chapters 6 through 10 study the effects of alkali-silica reaction, freeze-thaw, carbonation, sulfate attack and chloride ion diffusion on concrete using portable NMR. The NMR trends associated with each deterioration mechanism is investigated. The corroborative tests are performed to compliment the NMR test results on control and aged concrete specimens. This chapter explains the relaxation parameters (such as transverse and longitudinal relaxation times), role of ware in concrete deterioration and measurements of water, porosity and permeability in concrete using portable NMR.

Chapter 11 describes the portable NMR specification and software preparation and execution. This chapter includes the results of a numerical study towards estimating the concrete surface porosity and permeability using the NMR relaxation data.

Chapter 12 summarizes our efforts towards field application of portable NMR.

Finally, chapter 13 summarized the major outcomes of this research and outlines the future potential research areas.

# 2 STATE-OF-THE-ART REVIEW

# 2.1 General

Non-destructive inspection of the damage and deterioration conditions of concrete is challenged by the heterogeneous structure and the complex physical and chemical manifestations of concrete deterioration in service conditions. The portable NMR system provides unique capabilities for non-destructive condition assessment of concrete, which cannot be matched by competing (existing or emerging) technologies. These unique capabilities are outlined below, followed by competitive evaluation of the portable NMR system against each of the competing technologies.

The portable NMR system can produce quantitative information on: (i) the spatial distribution and concentration, morphology, and size distribution of concrete cracks and pores at different length scales; (ii) the concentration and spatial distribution of concrete moisture, distinguishing between different binding states and mobility conditions of moisture; and (iii) manifestations and states of chemical deterioration mechanisms. Streamlined data analysis procedures will be developed for convenient interpretation of the mobile NMR test data towards quantitative assessment of the concrete structure, and identification of the prevalent cause and the state of progress of concrete deterioration. Portable NMR offers a relatively high resolution, and complements these capabilities with a viable cost structure, moderate depth of penetration, and convenient and versatile operation.

The more advanced (existing or emerging) techniques for non-destructive condition assessment of concrete, against which the portable NMR system should compete more directly, include: (i)

ultrasonic pulse velocity (indirect transmission method); (ii) impact (sonic-echo) method; (iii) ground penetrating (short pulse) radar; (iv) infrared thermography; and [2] x-ray computed tomography. Advantages of the portable NMR over these systems are outlined below. Other concrete non-destructive inspection techniques do not provide information that are similar to those provided by portable NMR, but could still compete with or complement the portable NMR system. These techniques include: (vi) surface hardness methods; (vii) penetration resistance techniques; (viii) pull-out tests; [3] maturity method; (x) absorption and permeability tests; (xi) surface wave methods; (xii) acoustic emission; (xiii) electrical resistivity; (xiv) electrochemical methods (corrosion potential, polarization resistance, electrochemical impedance spectroscopy); and (xv) electromagnetic (covermeter) method; and (xvi) backscattering microwave tomography. The distinctions of portable NMR from these techniques are also outlined below.

# 2.2 NMR: A Novel Tool to Study Materials

Since its discovery in mid 40's, NMR has become a valuable tool in various fields of science and engineering, especially in materials science. The unique feature of NMR is the non-destructive nature of approach. The most well-known application of NMR is medical magnetic resonance imaging (MRI), although NMR is also routinely applied in analytical chemistry for elucidating chemical structures, investigating molecular structures, resolving pore systems, quality control of food products, inspection of polymers, and many more applications of NMR spectroscopy [21-28]. In geophysics, the NMR technique is used well logging [29]; surface NMR (SNMR) is an emerging method of groundwater exploration [30, 31]. Application of NMR in concrete is new, and mostly pertains to measurement of moisture content [32, 33], thickness of concrete coating [34-36], and water transport phenomena during freeze-thaw effects [37].

NMR can be an effective NDT tool if the correct magnet and coil configuration are employed. This method can non-invasively penetrate into objects, and provide spatial maps of different material properties. Although NMR provides insight into the material microstructure, it does not require the occurrence of any chemical reactions, does not use any ionizing radiation, and is thus a completely nondestructive method. Nondestructive NMR operates based on direct sensitivity to H<sub>2</sub>O molecules (either chemically bound or in bulk state). Hydrogen nuclei in fluids of porous minerals are excited with radio frequency (rf) pulses. The nuclei can be perceived as bar magnets. When subjected to a magnetic field, hydrogen nuclei tend to align their magnetic moments parallel to the field, producing a net nuclear magnetization. In the NMR method the angle of magnetization with respect to the magnetic field is changed by the rf pulse. Once the pulse has faded, it regains its original orientation by relaxation. In a saturated porous medium (concrete in our case) this relaxation time depends on the fluid, the medium and the interaction between the medium and the magnetic moments. Hence, study of the relaxation time can provide information on structural parameters as porosity, pore size distribution or permeability of the porous material.

In the past 2 decades, researchers have tried to implement this technique to gain more insight into the structure of various materials. These efforts have covered various materials including soft solids like elastomers, semi-crystalline polymers, paintings, cultural heritage, and concrete. Furthermore, the possibility of refining single-sided NMR to realize high spatial resolution is explored in different applications, namely characterization of multilayered structures, detection

of deterioration and failure mechanisms, and monitoring of the solvent ingress into polymer materials [38].

Perhaps the greatest weakness of NMR relates to the complexity of designing the experiments and analyzing the results. One subset of NMR investigations which overcome this drawback resort to NMR relaxometry. Despite its relative simplicity, NMR relaxometry can provide valuable insight into many physical and chemical processes and structures.

The main motivation for development and implementation of the new NMR platform for concrete is to make NMR more accessible to laboratory and field investigations by lowering the complexity of the procedure and cost while still offering high performance and flexibility. The platform allows for a wide variety of applications enabled by the use of different magnetic field strengths, and magnet and coil geometries. For the purpose of field applications, the system needs to be designed optimally so that it is compact, lightweight and portable to suit convenient field applications. The platform should be used preferably with its own battery, and compatible with a large variety of different magnet and coil designs that are customized for relaxometry applications. The magnetic field generated within the constraints of unilateral NMR relaxometry tends to be inhomogeneous, requiring the use of special acquisition techniques which ensure that the required signals are received with high sensitivity.

This chapter presents the basics of NMR and summarized the previous studies on application of NMR on materials.

## 2.3 Basics of NMR

Pulsed NMR measures the magnetization (M) and relaxation of nuclei (e.g., hydrogen) contained in pore fluids. The magnetization is proportional to the number of (hydrogen) nuclei in the sensitive region of the sensor, and can be scaled to yield NMR data which, in the case of hydrogen, correlate with (saturated) porosity [39, 40]. In principle, the NMR porosity responds directly to the hydrogen content of the material, and is thus unaffected by the lithology effects in density and neutron logging [41].

The size distribution of fluid-filled pores is another essential information on porous samples which can be obtained from low-field NMR engaging hydrogen nuclei [42]. The theoretical principles for deriving relationships relevant to these measurements are outlined below.

#### 2.3.1 Polarization

In a static magnetic field ( $B_0$ ), protons tend to align themselves with the field, and the nuclei spins will start to precess about the direction of the magnetic field. The Larmor Equation [1] expresses the relationship between the strength of the magnetic field ( $B_0$ ) and the precessional frequency (f) of an individual spin:

$$f = \frac{\gamma B_0}{2\pi} \tag{1}$$

where,  $\gamma$  is the gyromagnetic ratio, which is a measure of the strength of the nuclear magnetism. When a large number of spins are precessing about  $B_0$ , most spins adopt the parallel rather than the antiparallel state. Hence, the net magnetization  $M_0$  is in the direction of the  $B_0$  field. The alignment of spins, which is called polarization, gradually increases with a time constant which is the longitudinal relaxation time  $T_1$  [43]:

$$M_{z}(t) = \frac{M_{0}(e^{\frac{t}{T_{1}}} - 1)}{e^{\frac{t}{T_{1}}}}T_{1}$$
[2]

where, t is the time that the spins are exposed to the  $B_0$  field,  $M_z(t)$  is the magnitude of magnetization at time t, when the direction of  $B_0$  is taken along the z-axis, and  $M_0$  equals the asymptotic and maximum magnetization in a given magnetic field.  $T_1$  is also known as the spinlattice relaxation time and characterizes the alignment of spins with the external static magnetic field (Figure 1).



# Figure 1. Net magnetization ( $^{M_0}$ ) resulting from the precession of proton spins about an external magnetic field [44]

2.3.2 Pulse tipping and free induction decay

After the spins are polarized, the next step is to tip the aligned proton spins from the longitudinal

direction to a transverse plane by transmitting an oscillating radio frequency magnetic field ( $B_1$ 

), perpendicular to the direction of the static magnetic field ( $B_0$ ). The frequency of  $B_1$  needs to be equal to the precessing frequency of the spins in order to ensure effective tipping. This frequency is called Larmor frequency which is the resonance frequency of the magnetic nuclei. Application of the oscillating magnetic field ( $B_1$ ) moves the spins to a higher energy level and makes them precess in phase with each other. This process is called Nuclear Magnetic Resonance. The angle through which the magnetization has rotated away from the z-axis (see Figure 2) is known as 'flip angle' or 'tip angle', and is given by:

$$\theta = \gamma B_1 \tau \tag{3}$$

where,  $\theta$  is the tip angle (degrees),  $B_1$  is the amplitude of an oscillating field, and  $\tau$  is the time over which the oscillating field is applied (pulse length of the NMR experiment). The strength and duration of  $B_1$  determine the amount of energy available to achieve spin transitions between parallel and anti-parallel states. Thus, the flip angle is proportional to the strength and the duration of  $B_1$  [44].



Figure 2. Nuclear magnetization M can be rotated away from the direction of B<sub>0</sub>. The angle θ between the z-axis and the magnetization is called 'flip angle' [45].

In NMR tools, the net magnetization is normally tipped at angles of  $\theta = 90^{\circ}$  and  $\theta = 180^{\circ}$ . When a 90° pulse is applied, the polarized proton spins start to precess in phase in a transverse plane. But after the  $B_1$  field has been turned off, the spins dephase over a time  $T_2$  which characterizes the loss of phase coherence due to interactions between the spins. Hence,  $T_2$  is also known as spin-spin relaxation time. The amplitude of the spin-echo train at time t, which is the amplitude of the transverse magnetization  $M_{xy}(t)$ , is given by:

$$M_{xy}(t) = M_{0xy} e^{\frac{-t}{T_2}}$$
 [4]

where,  $M_{0,xy}$  is the magnitude of the transverse magnetization at t = 0 (the time at which the 90° pulse ceases). During dephasing, the net magnetization decreases. Such a reduction in magnetization (decay) is usually exponential and is called Free Induction Decay (FID) (Figure 3).

#### 2.3.3 Relaxation mechanisms in porous media

For fluids in a porous media (say, concrete), three different mechanisms acting in parallel are involved in relaxation [44]:

$$\frac{1}{T_{1A}} = \frac{1}{T_{1F}} + \frac{1}{T_{1S}}$$
[5]

$$\frac{1}{T_{2A}} = \frac{1}{T_{2F}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}$$
[6]



Figure 3. After application of a 90° rf pulse, the proton spins dephase, and a free induction decay (FID) signal can be detected [44].

where, subscripts A, F, S and D denote apparent, free fluid, surface-induced, and diffusioninduced mechanisms, respectively. The free fluid relaxation time (about 3 seconds) is a property of the fluid only, and affects both  $T_1$  and  $T_2$  relaxation. In contrast, water in the pore space of concrete has apparent  $T_1$  and  $T_2$  relaxation times typically varying from one to several hundred milliseconds [46]. Therefore, the contribution from the free fluid in Equations [5] and [6] can be neglected. The surface-induced relaxation which affects both  $T_1$  and  $T_2$  relaxation is due to interaction between the fluid and the solid surface. In contrast, the diffusion-related relaxation which affects only the  $T_2$  relaxation arises from internal magnetic field gradients due to magnetic susceptibility contrast between grains and pore fluid or from inhomogeneities in the applied B<sub>0</sub> field. The surface and diffusion-induced relaxation rates are given by [47]:

$$\frac{1}{T_{1S}} = \rho_1 \frac{S}{V}$$
<sup>[7]</sup>

$$\frac{1}{T_{2S}} = \rho_2 \frac{S}{V}$$
[8]

$$\frac{1}{T_{2D}} = \frac{\left\lfloor \left(\gamma G t_E\right)^2 D_0 \right\rfloor}{12}$$
[9]

where,  $\rho_1$  and  $\rho_2$  are the surface relaxivity values corresponding to  $T_1$  and  $T_2$ , respectively. Surface relaxivity is a measure of how quickly proton spins lose orientation or phase coherence due to magnetic interactions at the fluid-solid interface. It is dominated by paramagnetic ions in the grain surfaces [48]. Surface relaxation falls in the range of approximately 1 µm/s to 50 µm/s for clastics, and is smaller for carbonates [49]. S/V is the surface-to-volume ratio. For spherical pores S/V = 6/d, where d is the pore diameter, G is the gradient of the magnetic field (T/m),  $\gamma$  the gyromagnetic ratio,  $t_E$  the inter-echo spacing used in the pulse sequence, and  $D_0$  the selfdiffusion coefficient of the liquid (m<sup>2</sup>/s).

Cement paste and concrete in general belong to the 'fast-diffusion' relaxation regime [50], in which the relaxation at the surface is slower than the transport of the hydrogen nuclei to the surface. Thus, the spins experience a rapid exchange of environments so that the local fields in each region of a pore are averaged to their mean value. As a consequence, a single exponential decay is observed for a given pore, and the rate of magnetization decay depends on surface to volume ratio only [48]. In the 'slow diffusion' limit, in contrast, the magnetization decay is multi-exponential and depends on the pore geometry. For low magnetic field strength (and thus small *G*) and at short  $t_E$  [51], the contribution to  $T_2$  decay times provided by the diffusion in the inhomogeneous local magnetic fields is negligible compared to that by surface relaxation. Therefore, the measured  $T_1$  and  $T_2$  values can be approximated as:

$$\frac{1}{T_{1A}} = \rho_1 \frac{S}{V}$$
[10]

$$\frac{1}{T_{2A}} = \rho_2 \frac{S}{V}$$
[11]

Equations [10] and [11] form the basis of NMR sample analysis:  $T_1$  and  $T_2$  are proportional to V/S, which in turn is proportional to pore size. This means that relaxation is faster in small pores than in large pores

## 2.3.4 T<sub>2</sub> measurements

Both  $T_1$  and  $T_2$  are important in characterization of concrete microstructure. It is more practical to measure  $T_2$  relaxation because it can be obtained quicker than  $T_1$ . Thus, it provides smaller bed boundary effects and a better vertical resolution. Besides, higher measurements repetition rates increase the signal-to-noise ratio [41].

The increase in the measured transverse magnetization signal induced by repeated rf pulses is noted as a phenomenon which is called spin echo. It was first discovered by Hahn in 1950 [52]. The Hahn echo decay is the basic spin echo sequence to measure  $T_2$  (Figure 4). It consists of a 90° pulse followed by a 180° pulse after the delay time. When hydrogen spins are tipped 90° from the direction of the magnetic field, they precess and dephase due to the inhomogeneity of the magnetic field. The spins can be refocussed by transmission of a 180° pulse. As the spins rephase, they generate a signal in a receiver coil – a spin echo.  $T_2$  can be measured by performing successive measurements for different values of  $\tau$ .



Figure 4. Hahn echo decay pulse sequence for measurement of  $T_2$ ; FID is the free induction decay,  $\tau$  between the two pulses, and  $t_E$  is the inter-echo spacing used in the pulse-sequence. Another pulse sequence to measure transverse magnetization is the CPMG sequence [53] which was used in this study (Figure 5). It consists of one 90° pulse followed by a series of 180° pulses after the delay time interval between two 180° pulses is the echo time  $t_E$  which is equal to  $2\tau$ . The time between two sequences is the recovery time  $t_R$ ; it must be sufficiently long so that magnetization has decayed completely to equilibrium. The advantage of the CPMG pulse sequence is the much shorter time required to measure at multiple echo times as the 180° pulses can be applied repeatedly to produce a series of echo trains. With the Hahn sequence, in contrast, only one echo can be measured. Therefore, much more sequences are needed to get the same amount of echoes [45].



Figure 5. CPMG sequence for detection of the signal decay by the NMR core-scanners; FID is the free induction decay,  $t_E$  echo time and  $T_2$  transverse relaxation time [45].

In the fast diffusion limit and for a sample with a distribution of N different pore sizes, the transient variations of the transverse magnetization  $M_{xy}(t)$  can be expressed as a sum of exponentials:

$$M_{xy}(t) = \sum_{i=1}^{N} M_{xy,i} e^{-\frac{t}{T_{2,i}}}$$
[12]

The above equation shows that the overall decay is the sum of the individual decays. For a vanishing magnetic field gradient, i.e. G = 0, the spectrum or distribution  $P(T_{2i})$  of relaxation times  $T_{2i}$  is a direct map of the pore size distribution P(d) with  $T_2 \sim V/S \sim d$ , where the distribution functions P represent probability densities. Proper fitting routines are used to fit a sum of decay exponents (each with a different decay constant) to the envelope of the echo trains from core samples. All of the decay constants make up the decay time spectrum or the relaxation time distribution [54] (Figure 6). A regularized inverse Laplace transformation based on the UPEN program [55] will be used in this study to obtain the distribution of transverse relaxation times  $T_2$ . A nonlinear least square routine will be used to fit the simulated decay time spectrum to the original data points. Thus, the model parameters (standard deviation and expected values of the

lognormal distributions) will be obtained that yield the curve closest to the data points. This method has the advantage that reliable results can even be obtained when measurements are performed with a low signal to noise ratio.



Figure 6. CPMG echo envelope measured on a water-saturated sediment sample (left) and corresponding frequency distribution of  $T_2$  obtained by regularized inverse Laplace transformation with the UPEN program [55].

2.3.5 T<sub>1</sub> measurements

The longitudinal relaxation time  $T_1$  is the recovery time of the longitudinal component of the magnetization  $M_z$  to its equilibrium value  $M_0$ . Two common pulse sequences are used to measure  $T_1$ : the saturation recovery and the inversion recovery [43]. In the saturation recovery (Figure 7)  $M_z$  is initially destroyed by a series of aperiodic 90° pulses, whereas the inversion recovery sequence starts with a 180° pulse which rotates  $M_z$  from the positive to the negative *z*-axis. Immediately after the stimulus, the spins start to flip back at the rate of  $T_1$ . Then a Hahn echo sequence with a short echo time  $t_E$  is applied after the recovery time  $\tau_1$ , it is possible to

follow the longitudinal magnetization. The magnetization recovery curves are described by the following equations [43]:

Saturation recovery: 
$$M_z(t) = M_0(1 - e^{-\frac{\tau_1}{T_1}})$$
 [13]

Inversion recovery: 
$$M_z(t) = \frac{M_0(e^{\frac{t}{T_1}} - 2)}{e^{\frac{t}{T_1}}}$$
 [14]

For a correct determination, the maximum value of  $\tau_1$  has to be at least 5 times  $T_1$ .





# 2.4 Experimental Studies

NMR relaxometry has been incorporated in studying various topic ranging from agriculture and food science, to anthropology and oil industry. Obviously, NMR relaxometry has found its way as a novel method of testing in the field of civil and materials engineering. Experimental studies

using portable NMR tools have been focus on the following groups of materials: (i) cement-based materials, (ii) rocks, (ili) elastomers and (iv) hard polymers. In this review, the notable studies that applied NMR relaxometry as a means of investigation will be summarized and discussed. It should be noted that NMR relaxometry can be performed in various range of frequencies. Depending on the specification of the testing machine. In the following review, we covered the studies that could be verified or reproduced by the available testing machine.

#### 2.4.1 Cement-based materials

The basic binding element of concrete i.e. cement and cement-paste, which is its mixture with water has been an interesting topic of investigation for engineers and materials scientists. Relatively uniform structure of cement-paste, known chemistry of cement and convenient control of moisture in the materials are among the reasons to attract engineers and scientist to study the cement-paste from various angles. Boguszynska et al. measured the relaxation time and relaxation time distributions of hydrating Portland cement at various times in an inhomogeneous magnetic field and compared to the results obtained using a standard benchtop laboratory. These results compared favorably. They observed two peaks in their distributions and described that one peak is centered at 0.01 s and is attributed to water in the larger pores. A second much smaller peak is observed centered between 0.1 and 1.0 ms. This is attributed to the water in the fine pores of the hydrated calcium sulphate, analogous to the calcium silicate hydrate gel pores of Ordinary Portland Cement (OPC). Using the fast exchange relaxation theory [56] and an estimate of surface relaxivity of  $T_2$  <sup>s</sup>=10  $\mu$ s [57], the former corresponds to pore sizes of "10 nm and the latter to pore sizes of 0.3 Am [58]. Karakosta et al. monitored the dynamics of cement gel growth over time. They monitored the evolution of the pore structure during the

progressive hydration and setting of three white cement pastes with different hydration kinetics as illustrated in Figure 8. Using relaxation times and diffusion measurements it was possible to distinguish between gel and capillary pores, the growth dynamics of cement gel and the associated shrinkage of the capillary pore system. Moreover, they tested the sensitivity of the method on the ratio of capillary to gel pore populations by the addition of 25% limestone. The addition of limestone produced a significant increase of medium size capillary pores the so-called filler effects which otherwise was observable only invasively with mercury or nitrogen porosimetry. In parallel, they found out that the NMR spin echo decay (diffusion) experiments provided direct information about water mobility into the cement paste. By monitoring the decrease of the diffusion length *l<sub>D</sub>* as a function of hydration time, it was possible to have an estimate of diffusion tortuosity, and therefore the transition from an open pore fluid to a closed pore solid material [59].



**Figure 8. T**<sub>1</sub> **contour plots and T**<sub>1</sub> **distribution profiles vs hydration time for 3 specimens [59].** In another effort to study the hydration process and porosity, Tziotziou et al. applied NMR relaxation to lime-pozzolan mixtures and monitored the hydration and porosity evolution during setting and over 240 days. They also found two distinct peaks in relaxation times, corresponding to two groups of pores. The distributions of pore populations determined by MIP and nitrogen adsorption proved to be in a good agreement with those obtained by NMR relaxometry as shown in Figure 9 [60].



Figure 9. Comparison of NMR and MIP distribution profiles at selected hydration times for two specimens [60].

Van Landeghem et al. investigated the roles of hydration and evaporation of water during the drying of cement paste. This research is especially interesting because of its close look at capillary water in cement paste using the portable NMR relaxation techniques. Based on the published results, The  $T_2$  of the water in the capillary pores progressively decreased from a few ms to 400

 $\mu$ s. The T<sub>2</sub>=150  $\mu$ s of the gel water could be detected after 1 h and remained constant over time [61]. It is noteworthy to mention the research performed by McDonald et al. in characterizing the surface relaxation and chemical exchange in hydrating cement paste which is a twodimensional NMR relaxation NMR study. They reported the first NMR T<sub>1</sub>-T<sub>2</sub> and T<sub>2</sub>-T<sub>2</sub> measurement of hydrating pastes as shown in Figure 10. In said Figure and in each plot a series of discrete features lie close to the quarter diagonal: T<sub>1</sub>=4T<sub>2</sub> (lower solid line). There is also a single off-diagonal peak indicative of gel-capillary exchange in white cement 1. Their measurements provided evidence for surface dissolution model of 1H nuclear spin relaxation in cements. However, it should be noted that that experiment and similar experiments are performed using high-field NMR which is not the case for the research performed in this dissertation [62].



Figure 10. T<sub>1</sub>–T<sub>2</sub> two-dimensional relaxation correlation spectra of cement samples measured over 7days

In another effort, McDonald et al. performed a two-dimensional correlation relaxometry study of cement paste using a portable NMR magnet. Distinct pore size distributions features were revealed in their study. However, they used a homogeneous magnet for their measurements which is different from the magnet used in this research [63]. In a more recent study Gajewicz et al. discovered they evaluated the gel-pore drying shrinkage in cement paste using NMR relaxometry. They discovered that in "well" dried material, coarse (20 nm) pores are created at the expense of collapsing gel pores. When the sample is rewet, these effects are reversed over a period of days. The degree of the change was linked to the severity of the drying. In a first sorption cycle, part of the redistribution is reversible, part is not. In a second cycle the changes appear to be entirely reversible [64]. An explanation of their data is drawn schematically in Figure 11. The schematic is for a sample in which the gel porosity is completely emptied of water and then refilled. Top left drawing in Figure 11 shows some C-S-H sheets separated by interlayer spaces. Gel pores are seen between regions of locally aggregated sheets. Figure 11 makes clear that if the average gel pore size at the end is increased, then this increase is accompanied by locally thicker stacks of layers.



# Figure 11. Top left: A schematic of the water in the gel pores of an "as-prepared" paste. op right: The hydrate after sufficient drying to remove almost all the water from the gel pores [64].

In an effort to characterize the effect of carbonation in cement paste, P.F. de J et al. used portable NMR to obtain the CPMG  $T_2$  decay at different positions along 6 cm long cement paste samples. The aim was to detect the carbonation front based on changes in the pore structure caused by accelerated carbonation and to compare the results with the phenolphthalein test. NMR

measurements on vacuum saturated samples reveal significant changes in the porosity and the pore size distribution in the carbonated regions of the samples as illustrated in Figure 12.



Figure 12. T<sub>2</sub> values at various depths from the surface on the left and specimens treated with phenolphthalein on the right [65].

The observed changes included an increase of  $T_2$  rate and decrease in NMR signal intensity in the carbonated region. The position with the highest rate of  $T_2$  change was in agreement with the carbonation front indicated by the phenolphthalein test [65].

#### 2.4.2 Concrete Materials

Gallegos et al. are among the first researchers who applied NMR techniques to study the pore structure of concrete materials. Pore size distributions were determined for two series of porous solids by mercury porosimetry and an NMR method. A series of controlled-pore glasses with very narrow pore size distributions and a mean radius in the range 3.4 to 17.6 nm were studied. They found a strong correlation between pore size and relaxation times [66]. Wolter and Dobmann used NMR relaxometry to characterize the moisture-affected properties of concrete over time. By conducting a series of nondestructive NMR tests and destructive laboratory tests, they found a strong correlation between the spin-echo amplitude and moisture content of concrete (See Figure 13).



**Figure 13. Maximum of the FID-amplitude as a function of moisture content [67]** They concluded that the hydration state and so the concrete's processability could be continuously determined via NMR relaxation time measurements and the concrete quality by the determination of the solid-like FID-signal component. In addition, they suggested that the determination of capillary and gel pores in young concrete could help to estimate technological

parameters like 28-days strength, freeze-thaw resistance or water-tightness [67]. Valckenborg et al. estimated the pore size distribution of mortar specimens during the drying process by the development of the pore water distributions as a function of time, it could be concluded that the water in the capillary pores is extracted rapidly, while the gel pores remain filled. The suggested that pores relaxing at 600  $\mu$ s and less belong to gel pores and small capillary pores, while the pores relaxing between 600  $\mu$ s to 3 ms belong to larger capillary pores as illustrated in Figure 14 [68].



**Figure 14.** Pore water distribution of mortar determined from relaxation measurements [68] Sharma et al. also demonstrated the capabilities of portable NMR in characterizing the size distribution of building materials. They observed that the shapes and the positions of the relaxation time distributions are similar to those of the pore size distributions obtained by mercury intrusion porosimetry unless the samples exhibit very strong ferromagnetic contaminations. For short echo times the strong effect of internal gradient fields can be meliorated, so that the pore size distributions in weakly ferromagnetic bricks can be analyzed by NMR. Schönfelder et al. studied the pore formation and water diffusion in self-hardening cut-ff wall materials using a low-field portable NMR. Changes of the transverse relaxation time T<sub>2</sub> and NMR signal intensity in the hardening cut-off wall material were monitored by low-field CPMG NMR during the first 4 days after sample preparation. One h after sample preparation, when the mixture is still a low-viscous suspension, it is easy to distinguish between the mixes of different content of solids by the peak positions in the distribution of T<sub>2</sub> and the difference in signal intensity (area under the T<sub>2</sub> distribution). With increasing content of solids and, therefore, decreasing water content, the NMR signal intensity decreased, and the relaxation time distribution shifts towards shorter times. This behavior is due to the larger quantity of solid particles. They concluded that the water molecules interact with the surface of solids where – depending to the surface relaxivity – they lose their contribution to the total NMR signal with a certain probability and, thus, reduce the observed T<sub>2</sub> relaxation time [69]. In a different application of NMR in concrete, Orlowsky et al. implemented a portable NMR to measure some geometrical properties such as the thickness of different coating as well as functional properties such as ingress of water into the coating and ageing processes as shown in Figure 15 [36].



Figure 15. Application of the portable NMR on buildings. The device senses the composition of the substrate at the point where the magnetic field lines of the magnet and of the RF coil cross each other [70].

Blümich et al. applied a portable NMR towards depth profiling of historic walls and wall paintings. Different paint and mortar layers were identified, and further characterized using X-ray fluorescence spectroscopy. They established that by analyzing the moisture content in terms of proton density and mobility, portable NMR provides a method for distinguishing layer structure and properties. Such a difference can provide the means to distinguish restored and original portions of detached wall paintings when an otherwise consistent layer structure is observed [34, 71]. As one of the first efforts to employ the portable NMR to study the effect of common deterioration mechanisms on concrete, Milachowski et al. investigated the water transport processes during freeze-thaw deicing salt attack. They monitored the water content through the proton density at various depth during one cull cycle of freeze-thaw and repeated the same experiment multiple times for air-entrained and non-air-entrained concrete specimens. Moreover, they obtained the relaxation time distributions at various intervals of freeze-thaw cycles. Measurements during freeze-thaw cycles with 3% NaCl solution confirmed transport processes previously explained by the micro ice lens model. In addition, they observed that intermediate dry periods led to reduced moisture uptake of the near surface concrete on re-exposure as shown in Figure 16. This observation was in accordance with the measured scaling [37].



# Figure 16. a) Water content during freeze-thaw deicing salt exposure in the near surface b) Gravimetric determined solution uptake. c) Inverse Laplace transformation of the T<sub>2</sub> nAE d) IL transformation of the T<sub>2</sub> decay measured in the outer zone AE

As an effort to investigate the dehydration kinetics inside concrete during fire, Pel et al. relaxation time and moisture profiles of concrete specimens at elevated temperatures. They provided quantitative proof for the build-up of a moisture peak due to the vapor pressure build-up. In their study they reported the measurement of the moisture and temperature profiles with the measurement of the pressure at one position, which showed that the pressure build up was directly related to the moisture profiles [72]. Along the same lines, Stelzner et al. analyzed the moisture transport in heated dense high-strength concrete using NMR relaxometry. Moisture transport processes are based on evaporation and condensation mechanisms of liquid and gaseous water in the pores as well as the chemically bound water within the concrete. The low permeability of HSC and the formation of a saturated zone within building components (also known as a moisture clog) leads to high water-vapor pressures, which contributes to explosive spalling. NMR relaxometry accompanied by X-ray 3D computed tomography results were used to monitor the 3D changes of moisture content inside the specimen during thermal exposure. Therefore, the researchers can visualize areas with moisture accumulation as well as dehydrated areas inside the specimen [73].

# 2.5 Numerical and Analytical Studies

Various group of porous materials have been subjected to numerical modeling and analytical studies in the light of NMR relaxometry.

### 2.5.1 NMR models for permeability predication

The two widely applied permeability transforms, based on NMR measurements, are the Timur-Coates Equation [15] based on the work of Timur (1969) and the T<sub>2,LM</sub> Equation [16] developed by Kenyon et al. (1988):

Two permeability transforms can be used for NMR measurements; they use the Timur-Coates Equation based on the work of Timur (1969), and the T<sub>2,LM</sub> Equation developed by Kenyon et al. (1988):

$$k_{TM} = [(\frac{\phi}{10})^2 (\frac{FFV}{BFV})]^2$$
[15]

$$k_{T,LM} = a T^2_{2,LM} \phi^4$$
 [16]

In these equations, k is permeability in mD, FFV and BFV are the NMR-derived fractional volumes of bulk and bound water,  $T_{2,LM}$  is the logarithmic mean  $T_2$  value in ms, and 'a' is an empirically determined constant which depends on the relaxivity; it is determined based on different measurements such as previously measured values of permeability. Usually, for rocks with large pores (e.g. sandstones) a = 4 mD/(ms)<sup>2</sup> [74], whereas in rocks with smaller pores (e.g. carbonates), smaller factors have been used (e.g., a = 0.1) [75]. Both above equations are empirical, and permeability prediction by NMR always requires a local calibration to core data in each case. The Timur-Coates equation is frequently applied to oil reservoirs for interpretation of the NMR logging data. In contrast, the  $T_{2,LM}$  equation fails for hydrocarbon-bearing formations but works well in zones containing only water [76]. The rationalization for such correlation comes from the following: The Kozeny- Carman relationship proposes that permeability is inversely proportional to the square of the surface to volume ratio S/V of the pore space. This suggests that permeability is proportional to the square of a representative NMR relaxation time ( $T_{2,LM}$ )

$$T_{2,LM} = 10^{\left[\frac{\sum_{i=1}^{N} V_i \log(\frac{T_{2i}}{1ms})}{\sum_{i=1}^{N} V_i}\right]}$$
[17]

where, V<sub>i</sub> is the volume fraction of a pore *i* decaying with the relaxation time  $T_{2i}$ . Both models are not universally applicable considering realistic variations in structure, texture, and composition [77]. The cutoff method is also subject to the same concerns with changes in surface relaxivity and in pore throat/pore-body ratio as is permeability estimation from  $T_{2,LM}$  [78]. Both permeability models generate an appreciable amount of data scatter relative to the independently determined permeabilities for sandstone. However, the applicability of these methods on concrete is a matter of investigation.

#### 2.5.2 Permeability and size distribution

According to the Kozeny-Carman equation (Kozeny, 1927; Carman, 1956), permeability is related to porosity  $\Phi$ , tortuosity T and the effective hydraulic pore radius r<sub>eff</sub>:

$$k = \left(\frac{1}{8}\right)\left(\frac{\phi}{T}\right)r_{eff}^2$$
[18]

The term ( $\Phi/T$ ) can be replaced by the inverse formation factor F<sup>-1</sup>, and by  $\Phi^m/A$ , according to the first Archie equation (Archie, 1942) with the cementation or tortuosity factor m. Both m and A are the coefficients that are selected based on the texture of the porous media. The effective pore radius can be substituted by S<sub>por</sub>, the specific surface normalized by the pore volume. For cylindrical hydraulically connected pores r<sub>eff</sub> is related to S<sub>por</sub> by:

$$r_{eff} = \frac{2}{S_{por,hydr}}$$
[19]

In equation above, the effective pore radius is calculated as twice the ratio of the model capillary's volume and its surface. This equation assumes that the pores are bundles of smooth, cylindrical but tortuous capillaries of radius r<sub>eff</sub> (Figure 17) [79].



Figure 17. Simple model for porous media with smooth capillaries of radius  $r_{eff}$  [79]. In contrast, the simplest model for NMR relaxation which relates relaxation times  $T_1$  and  $T_2$  to

 $S_{\ensuremath{\text{por}}\ensuremath{\text{r}}}$  , was developed for isolated spherical pores yielding:

$$\frac{1}{T_{1,2}} = \rho_{1,2} \, S_{por,NMR} \tag{20}$$

where  $\rho_{1,2}$  is the surface relaxivity given in  $\mu m/s$  and

$$r_{eff} = \frac{3}{S_{por,NMR}}$$
[21]

Like Equation [19], Equation [21] follows for a model porous medium made up of smooth spherical pores (Figure 18).



Figure 18. Simple model for porous media with smooth spheres of radius rpor.
Based on a fractal model for porous rocks (Figure 19), several geometrical relations were established in which specific surface, pore radius, tortuosity, and porosity are connected through the fractal dimension D. This is the fundamental geometric parameter for the description of the pore-space structure. A standard value for sandstones is D = 2.36. The principal idea of the fractal concept is the dependence of the measure of geometrical parameters such as the area of a rough surface on the power of resolution of the measuring method. As a result, <sub>Spor,BET</sub> measured by nitrogen adsorption is larger than S<sub>por,hydr</sub> because the size of nitrogen atoms is smaller than the size of water molecules. According to Pape et al. (1987), this is described by

$$S_{por,hydr} = 0.1410 S_{por,BET} r_{eff}^{-0.36}$$
[22]

Then Equations [19] and [22] yield:

$$r_{eff} = \left(\frac{2}{0.141S_{por,BET}}\right)^{\frac{1}{0.64}}$$
[23]

From Equations [23] and [18] follows:

$$k_{S_{por,BET}} = 497 \left(\frac{\emptyset}{\tau}\right) S_{por,BET}^{-3.125}$$
[24]



Figure 19. Image showing a porous media (rock) according to the fractal pore space model composed of geometrical pores and hydraulic capillaries with effective radius r<sub>eff</sub> [79].

#### 2.5.3 Molecular dynamics modeling

A popular simulation method in materials at a molecular level is molecular dynamics modeling (MD). Researchers have used MD in the field of relaxation of protons in porous materials. Korb et al. in their computational simulations used classical MD algorithms to calculate the structure, dynamics, and energetics of water molecules on the surface of tobermorite, which has long been considered a model for the C-S-H structure based on X-ray diffraction and spectroscopic data. The tobermorite model used was the 9A° phase described by Merlino et al.[80] The interatomic potentials were those of the CLAYFF force field [81], which includes the SPC model for the water molecules. This model is known to reproduce the bulk crystal structure of tobermorite is illustrated in Figure 20. In this Figure Dark small balls and octahedra – Ca atoms in two different structural positions within the "tobermorite 9Å" structure; one clearly sees the Si tetrahedra and O atoms of tobermorite; "v" – O of water; gray cylinders – H atoms of water; large balls – Cl– ions; light intermediate-size balls – K+ ions. Only parts of the solution layers close to the interfaces are shown above and below the crystal.



Figure 20. MD simulation snapshot of the tobermorite, Ca<sub>5</sub>Si<sub>6</sub>O<sub>16</sub>(OH)<sub>2</sub>, interface with 0.25MKCl aqueous solution [82].

The self-diffusion coefficients obtained by NMR relaxation and those obtained by MD computations were compared. The authors suggested that the high level of agreements between the experimental and MD-computed surface diffusion coefficients was more than coincidental.

Faux and McDonald [83] proposed a model for molecular-scale dynamics of fluids confined to nano-pores to NMR relaxation rates. The model was fit to experimental NMR dispersions for water and oil in an oil shale assuming that each fluid is characterized by three-time constants and Levy statistics. Results yield meaningful and consistent intra-pore dynamical time constants, resonance (NMR). However, for the NMR methods to be useful, a model is required to link fluid molecular dynamics in pores to NMR relaxation rates. Korb's model [84], which is illustrated in Figure 21 re-produces the fundamental form of the T<sub>1</sub> dispersion curve at low frequency in most

systems and predicts the  $T_1/T_2$  ratio. The model supposes that the dominant relaxation mechanism involves repeated encounters of the diffusing surface layer molecules with static surface relaxation sites, most typically paramagnetic impurities.



Figure 21. At top, a model quasi-two-dimensional pore shows fluid (gray) confined by walls (black) [83].

In the above figure, Surface diffusion, desorption and bulk diffusion events are characterized by time constants  $\tau_l$ ,  $\tau_d$  and  $\tau_b$  respectively. Rare paramagnetic impurities are indicated by white crosses modelled by a layer of uniform density (white dashed line). The circle indicates diffusion mechanism consistent with  $\tau_l \approx \tau_d$ . At bottom, spin pair vectors used in the theory are shown for a mobile spin (black circle). A volume of fluid (gray  $\equiv$  surface or bulk fluid) has thickness *h* located distance *d* from the paramagnetic layer.

#### 2.6 Standard and Specifications

The following standards and specifications were used directly or indirectly in this research:

ASTM C1803 - Standard Guide for Abrasion Resistance of Mortar Surfaces Using a Rotary Platform Abraser.

ASTM C29 - Standard Test Method for Bulk Density ("Unit Weight") and Voids in Aggregate

ASTM C33 - Standard Specification for Concrete Aggregates

ASTM C70 - Standard Test Method for Surface Moisture in Fine Aggregate

ASTM C88 - Standard Test Method for Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate

ASTM C117 - Standard Test Method for Materials Finer than 75-μm (No. 200) Sieve in Mineral Aggregates by Washing

ASTM C127 - Standard Test Method for Relative Density (Specific Gravity) and Absorption of Coarse Aggregate

ASTM C128 - Standard Test Method for Relative Density (Specific Gravity) and Absorption of Fine Aggregate

ASTM C136 - Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates

ASTM C535 - Standard Test Method for Resistance to Degradation of Large-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine

ASTM C566 - Standard Test Method for Total Evaporable Moisture Content of Aggregate by Drying

ASTM C185 - Standard Test Method for Air Content of Hydraulic Cement Mortar

ASTM C702 - Standard Practice for Reducing Samples of Aggregate to Testing Size

ASTM C233 - Standard Test Method for Air-Entraining Admixtures for Concrete

ASTM C260 - Standard Specification for Air-Entraining Admixtures for Concrete

ASTM C1365 - Standard Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis

ASTM C642 - Standard Test Method for Density, Absorption, and Voids in Hardened Concrete

ASTM C1585 - Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes

ASTM C1792 - Standard Test Method for Measurement of Mass Loss versus Time for One-Dimensional Drying of Saturated Concretes

ASTM C227 - Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method)

ASTM C1017 - Standard Specification for Chemical Admixtures for Use in Producing Flowing Concrete

ASTM C1260 - Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)

ASTM C490 - Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste, Mortar, and Concrete

ASTM C1293 - Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction

ASTM 1567 - Standard Test Method for Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)

ASTM C511- Standard Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water Storage Tanks Used in the Testing of Hydraulic Cements and Concretes

ASTM C670 - Standard Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials

ASTM C802 - Standard Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods for Construction Materials

ASTM C330 - Standard Specification for Lightweight Aggregates for Structural Concrete

ASTM C215 - Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Resonant Frequencies of Concrete Specimens

ASTM C597 - Standard Test Method for Pulse Velocity Through Concrete

ASTM C856 - Standard Practice for Petrographic Examination of Hardened Concrete

ASTM C1723 - Standard Guide for Examination of Hardened Concrete Using Scanning Electron Microscopy

ASTM C666 - Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing

ASTM C39 - Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens

ASTM C78 - Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Third-Point Loading)

# 2.7 Knowledge Gap

Based on the introduction and the review above, there is a need to devise new nondestructive testing methods of concrete to maintain a functional and high-quality infrastructure while minimizing cost of operation and interpretation of these NDT methods. These demands call for a portable, accurate and NDT machine that can perform under various weather and climatic condition, obtain quick measurements and provide meaningful measurements to identify the cause and the extent of the damage in concrete. There is a lack of understanding of deterioration mechanisms of concrete through available NDT techniques. In this research unilateral (or one-sided) NMR relaxometery is proposed as a competitor to these methods. However, there is a lack of experimental work and data on concrete relaxation and diffusion parameters. Hence, further research is needed in following key areas:

- Different portable and semi-portable NMR devices have been produced over the past few decades. They offer different capabilities in terms of depth of penetration, the level of magnetic field homogeneity etc. depending on the shape and strength of magnets, open or closed magnets, the configuration of the RD coil and architecture of the spectrometer. One critical difference is the type of the object that can be tested. Some of the NMR machines are single-sided There is a need to find a portable NMR machine that fits the requirements of concrete testing.
- The models to be used in NMR relaxometry contain multiple constants and coefficients.
  Most of these models have been calibrated for mediums such as rock or cement-paste
  and not concrete specially mixed with various aggregates. Therefore, to yield accurate

and reliable results, these models must be calibrated with respect to concrete made of commonly used aggregates.

- Other than one or two studies, the effect of deterioration mechanisms of concrete on NMR relaxation signals have not been studied. In order to investigate this issue, an experimental study needs to be performed by directly exposing the concrete specimens to laboratory-controlled deterioration environments (i.e. alkali-silica reaction, freezethaw, carbonation, sulfate and chloride ion attack).
- Based on the above paragraph, there is a lack of information on the NMR data of concrete at various stages of deterioration. The experimental study mentioned above, will yield a database with NMR signatures of concrete at various stages of deterioration. The NMR signatures must be compared and evaluated with respect to the available NDT methods such as elastic modulus test or UPV.
- In previous numerical studies, the basis for measurements of porosity and permeability via NMR in porous media has been proposed. There is NMR data available for rocks too.
  However, there is a lack of data on cement and concrete obtained by NMR. Therefore, the future numerical models should test the available models for cement-based materials and verify the viability of these methods.
- There are virtually no data on concrete tested in the field via portable NMR. The effects of climate must be factored in the analysis by calibration and verification.
- The above stated knowledge gaps are to be overcome to enhance our understanding of various deterioration mechanisms on concrete in the laboratory and field and provide us with a new NDT technique that provides information on concrete at various depths

locations of concrete undergoing a deterioration mechanism. This dissertation is designed to undertake required studies for overcoming the above knowledge gaps.

## 3 MATERIALS AND SPECIMEN PREPARATION

#### 3.1 Concrete

Concrete materials within the ranges of strength and mix proportions commonly used in the concrete construction will be prepared using representative cementitious binder compositions, chemical admixtures and aggregate types. The binder compositions to be considered will include Type I Portland cement, Class F and Class C coal fly ash, ground granulated blast furnace slag, and silica fume. The chemical admixtures to be used in this task include water-reducer, high-range water-reducer, and air-entraining agent. The aggregate types evaluated in previous section will be used for preparation of concrete materials. Other variables to be considered include treatments applied to concrete (silane, siloxane, lithium compounds, etc.).

The chemical compositions of all raw materials, and the mineralogy of cementitious binders will be acquired. A data base will be developed on the NMR spectra of anhydrous cement [2, 85], ground granulated blast furnace slag, fly ash [85], and silica fume [86]. This data base, together with that developed for aggregates in previous task, will help analyze NMR signals of concrete by distinguishing between the signals corresponding to aggregates, anhydrous cementitious materials, and products of cement hydration and deterioration processes.

Concrete specimens will be subjected to curing conditions which represent those practiced in construction of the transportation infrastructure. Control specimens will be stored in unaged condition at room temperature and 50% relative humidity. Other specimens will be subjected to the following accelerated aging and damaging effects:

1. Alkali-silica reaction (ASR)

- 2. Sulfate attack
- 3. Chloride ion diffusion and corrosion of reinforcing steel
- 4. Freeze-thaw cycling
- 5. Carbonation
- 6. Application of increasing levels of compressive stress to induce microcracking

Concrete materials will be evaluated, as described in the next chapter, in different deterioration and damage conditions.

The experimental work involves consideration of a relatively large number of variables; an experimental design is devised to enable practically relevant consideration of these variables.

The experimental variables to be considered in the research include:

- Cementitious Binder Composition: Cement Type (I & II), and Pozzolan Type (Class F & C fly ash, Slag, Silica Fume)
- Coarse Aggregate Type: Limestone, Dolomite, Gravel, Sandstone, Granite, Basalt, Chert, Flint, Slag (natural sand will be used as fine aggregate)
- Chemical Admixtures: Water-Reducer, High-Range Water-Reducer, Air-Entraining Agent
- Concrete Mix Design: Normal-Strength, High-Strength
- Curing Condition: Moist Curing, Steam Curing
- Surface Treatment: None, Silane, Siloxane, Lithium Compounds
- Accelerated Aging: ASR, Sulfate, Chloride, Carbonation, Freeze-Thaw, Mechanical Loading

As noted earlier, judgment has been used to develop an experimental program which meets the time and cost constraints of this research. Two basic mix designs will be considered in this research: (i) normal-strength (air-entrained) concrete with Type I Portland cement; and (ii) high-strength concrete with Type I cement and Class F fly ash incorporating high-range water-reduce. The test methods noted in this table will be performed in subsequent work.

The mix designs presented in Table 1a allow for investigating the aggregate type effects on NMR data. Mix #1 is the basic mix which will be thoroughly characterized; two batches of this mix will be prepared and tested. Mixtures #2 through 9 will be subjected only to NMR and other analytical chemistry tests (and also to compression tests for a basic quality control). The specimens to be prepared for characterization of Mix #1 (Test Type A) are: 3 for NMR and other analytical chemistry tests, 3 for x-ray computed tomography and petrographic image analysis, 3 for compression, 3 for split tension, 3 for capillary sorption, 3 for length change, 3 for dynamic modulus, ultrasonic pulse velocity, and void content, specific gravity and absorption capacity. A total of 21 specimens will be required for performance of Type A tests. Characterization of Mixtures # 2 through 7 (Test Type B) will require 3 specimens for NMR and other analytical chemistry tests, and 3 for split tension tests. Type B tests require a total of 6 specimens. Mixtures #8 and 9 will be characterized using (Test Type C) 3 specimens for portable NMR, laboratory NMR and other analytical chemistry tests, 3 specimens for x-ray computed tomography, ultrasound pulse velocity and dynamic modulus tests, and 3 for split tension tests. Type C tests require a total of 9 specimens.

The mix designs presented in Table 1b emphasize investigation of the effects of cementitious binder composition on NMR and other analytical chemistry test data. The effects of mix designs,

chemical admixtures, surface treatments and curing conditions will be assessed using the mix designs introduced in Table 1c. These mixtures will be characterized using test types B or C introduced above. The test program summarized in Table 1d focuses on calibration of NMR test data in the presence of steel reinforcement at different depths. These specimens will be characterized (Test Type D) using portable NMR (9 specimens) and split tension tests (3 specimens). Type D tests require preparation of a total of 12 specimens.

# Table 1. Mix designs to be evaluated without accelerated aging, and the corresponding testmethods.

Mix #	Mix Design	Cementitious Binder	Coarse Aggregate Type	Chemical Admixtures	Cure/Surface Treat	Test Types <sup>(1)</sup>
1	Normal-Strength	Type I Cement	Limestone	Air-Entr. Agent	Moist/None	А
2	Normal-Strength	Type I Cement	Dolomite	Air-Entr. Agent	Moist/None	В
3	Normal-Strength	Type I Cement	Gravel	Air-Entr. Agent	Moist/None	В
4	Normal-Strength	Type I Cement	Sandstone	Air-Entr. Agent	Moist/None	В
5	Normal-Strength	Type I Cement	Granite	Air-Entr. Agent	Moist/None	В
6	Normal-Strength	Type I Cement	Basalt	Air-Entr. Agent	Moist/None	В
7	Normal-Strength	Type I Cement	Slag	Air-Entr. Agent	Moist/None	В
8	Normal-Strength	Type I Cement	Chert (Reactive)	Air-Entr. Agent	Moist/None	С
9	Normal-Strength	Type I Cement	Flint (Reactive)	Air-Entr. Agent	Moist/None	С

(a) Different aggregate types (total of 96 specimens)

(1) A: Portable NMR at Different Moisture Contents, Laboratory NMR, SEM/EDX, XRD, FTIR, X-Ray Computed Tomography, Petrographic Image Analysis, Compression, Split Tension, Capillary Sorption, Length Change, Dynamic Modulus, Ultrasonic Pulse Velocity, Void Content, Specific Gravity and Absorption Capacity

- B: Portable & Laboratory NMR, SEM/EDX, XRD, FTIR, Split Tension
- C. Portable & Laboratory NMR, SEM/EDX, XRD, FTIR, X-Ray Computed Tomography, Ultrasound Pulse Velocity, Dynamic Modulus, Split Tension

Mix #	Mix Design	Cementitious Binder	Coarse Aggregate Type	Chemical Admixtures	Cure/Surface Treat	Test Types <sup>(1)</sup>
1	Normal- Strength	Type I Cement	Limestone	Air-Entr. Agent	Moist/None	A (Table 1a)
10	Normal- Strength	Type II Cement	Limestone	Air-Entr. Agent	Moist/None	В
11	Normal- Strength	Type I Cem & Class F Fly Ash	Limestone	Air-Entr. Agent	Moist/None	С
12	Normal- Strength	Type I Cem & Class C Fly Ash	Limestone	Air-Entr. Agent	Moist/None	В
13	Normal- Strength	Type I Cem & Slag	Limestone	Air-Entr. Agent	Moist/None	В

#### (b) Different cementitious binder compositions (total of 27 specimens)

<sup>(1)</sup> B: Portable & Laboratory NMR, SEM/EDX, XRD, FTIR, Split Tension

C. Portable & Laboratory NMR, SEM/EDX, XRD, FTIR, X-Ray Computed Tomography, Ultrasound Pulse Velocity, Dynamic Modulus, Split Tension

#### Table1. (cont'd)

	(total of 66 specifiens)							
Mix #	Mix Design	Cementitious Binder	Coarse Aggregate Type	Chemical Admixtures	Surface Treatment	Test Types <sup>(1)</sup>		
1	Normal- Strength	Type I Cement	Limestone	Air-Entr. Agent	Moist/None	A (Table 1a)		
14	Normal- Strength	Type I Cement	Limestone	None	Moist/None	С		
15	Normal- Strength	Type I Cement	Limestone	Air Entr Agent & Water- Reducer	Moist/None	В		
16	High-Strength	Type I Cement & Class F Fly Ash	Limestone	AEA & HR Water-Reducer	Moist/None	С		
17	High-Strength	Type I Cem & Silica Fume	Limestone	AEA & HR Water-Reducer	Moist/None	В		
18	High-Strength	Type I Cem & Silica Fume	Limestone	AEA & HR Water-Reducer	Moist/None	В		
19	High-Strength	Type I Cem & Silica Fume	Limestone	AEA & HR Water-Reducer	Steam/None	С		
20	Normal- Strength	Type I Cement	Chert (Reactive)	Air-Entr. Agent	Moist/Silane	В		
21	Normal- Strength	Type I Cement	Chert (Reactive)	Air-Entr. Agent	Moist/Siloxane	С		
22	Normal- Strength	Type I Cement	Chert (Reactive)	Air-Entr. Agent	Moist/Lithium	В		

# (c) Different mix designs, chemical admixtures, curing conditions, and surface treatments (total of 66 specimens)

(1) B: Portable & Laboratory NMR, SEM/EDX, XRD, FTIR, Split Tension

C. Portable & Laboratory NMR, SEM/EDX, XRD, FTIR, X-Ray Computed Tomography, Ultrasound Pulse Velocity, Dynamic Modulus, Split Tension

# (d) Different reinforcement conditions (moist cure, no surface treatment) (total of 36 specimens)

Mix #	Mix Design	Cementitious Binder	Coarse Aggregate Type	Chemical Admixtures	Reinforcement	Test Types <sup>(1)</sup>
1	Normal- Strength	Type I Cement	Limestone	Air-Entr. Agent	None	A (Table 1a)
10	Normal- Strength	Type I Cement	Limestone	Air-Entr. Agent	Med. Cover	D
11	Normal- Strength	Type I Cement	Limestone	Air-Entr. Agent	Small Cover	D
12	Normal- Strength	Type I Cement	Limestone	Air-Entr. Agent	Large Cover	D

(1) D: Portable NMR, Split Tension

The mixtures introduced in Table 2 will be subjected to different accelerated aging conditions and mechanical damaging effects noted in the table. Two batches of Mix #1 will be prepared and subjected to accelerated aging/mechanical damage. Portable NMR, laboratory NMR and other analytical chemistry and nondestructive tests will be performed after different periods of accelerated aging or mechanical damage. Destructive tests will be performed at the conclusion of accelerated aging or mechanical damage. The test types noted in Table 2 are performed besides the measurements made (in 3 replicates) during accelerated aging. The combinations of material selections, mix proportions and aging/damaging effects represent those encountered more commonly in the transportation infrastructure.

Accel Age<sup>(1)</sup> Cementitious Coarse Chemical Cure/Surface Mix # Mix Design Binder Aggregate Type Admixtures Treat /Test Type<sup>(2)</sup> Normal-Strength Moist/None I/A 1 Type I Cement Limestone Air-Entr. Agent 8 Normal-Strength Type I Cement Chert (Reactive) Air-Entr. Agent Moist/None II/C 9 Normal-Strength Type I Cement Flint (Reactive) Air-Entr. Agent Moist/None II/C Type I Cem & I/C 11 Normal-Strength Limestone Air-Entr. Agent Moist/None Class F Fly Ash Type I Cement 14 Normal-Strength Limestone None Moist/None III/C Type I Cement & AEA & HR 16 **High-Strength** Limestone Moist/None IV/C Class F Fly Ash Water-Reducer Type I Cem & AEA & HR 19 IV/C **High-Strength** Limestone Steam/None Water-Reducer Silica Fume 21 Normal-Strength Chert (Reactive) Moist/Siloxane II/C Type I Cement Air-Entr. Agent

Table 2. Mix designs, accelerated aging conditions, and test methods (total of 303 specimens).

(1) I: ASR, Sulfate Attack, Chloride Diffusion/Corrosion, Freeze-Thaw, Carbonation, Mechanical Damage

II: ASR

III. Freeze-Thaw

IV. Chloride Diffusion/Corrosion, Carbonation, Mechanical Damage

(2) A: Portable NMR at Different Moisture Contents, Laboratory NMR, SEM/EDX, XRD, FTIR, X-Ray Computed Tomography, Petrographic Image Analysis, Compression, Split Tension, Capillary Sorption, Length Change, Dynamic Modulus, Ultrasonic Pulse Velocity, Void Content, Specific Gravity and Absorption Capacity

B: Portable & Laboratory NMR, SEM/EDX, XRD, FTIR, Split Tension

C. Portable & Laboratory NMR, SEM/EDX, XRD, FTIR, X-Ray Computed Tomography, Ultrasound Pulse Velocity, Dynamic Modulus, Split Tension

For mixing concrete, aggregates are thoroughly washed and dried overnight in the oven at 110°C

(230°F). Second, cement, aggregates and water are weighted to produce the mix design obtained

from Michigan Department of Transportation (MDOT). The mix design used for normal-strength

and high-strength concrete used in this research are included in Table 3.

Ingredients	Normal strength (lb/cyd)	High strength (containing ash)	High strength (containing silica fume)
Cement	564	568	731
Water	277	273	273
Coarse aggregates	1847	1787	1787
Fine aggregates	1243	1192	1192
Fly ash		245	
Silica fume/slag			81
Superplasticizer		8.1	8.1
Air entrainment agent	205 ml	205 ml	265 ml
Water to binder ratio	0.49	0.34	0.34

Table 5. With proportion for normal- and high-strength concrete	Table 3. Mix p	proportion for	r normal- and h	igh-strength	concrete
---	----------------	----------------	-----------------	--------------	----------

Most specimens are in the form of in 3in by 6in cylinders cast into a plastic mold (Figure 22a). However, for mixes in Table 1d, a different mold was used to account for rebar embedment as shown in Figure 22b. Also, several cubic and cuboid specimens are being prepared (Figure 22c).



Figure 22. Molds used for casting of specimens.

# 3.2 Aggregates

Aggregates are relatively inert granular materials such as sand, gravel, or crushed stone that, along with water and Portland cement, are essential ingredients in concrete.

In order to produce a long-lasting concrete mix, aggregates need to be clean, hard and free of absorbed chemicals or coatings of clay and other fine materials that could damage concrete itself or indirectly cause the deterioration of concrete. Aggregates, which account for 60 to 75 percent of the total volume of concrete (and 80 percent of the total weight of it), are divided into two distinct categories - fine and coarse. Fine aggregates generally consist of natural sand or crushed stone with most particles passing through a 3/8-inch sieve. Coarse aggregates are any particles greater than 0.19 inch, but generally range between 3/8 and 1.5 inch in diameter.

Natural gravel and sand are usually dug or dredged from a pit, river, lake, or seabed. Crushed aggregate is produced by crushing quarry rock, boulders, cobbles, or large-size gravel. Recycled concrete is a possible source of aggregate, and has been satisfactorily used in granular subbases, soil-cement, and occasionally in new concrete. Slag aggregates are obtained by crushing of smelter slag or by special treatment of the fire-liquid slag melt (molten slag aggregates).

In this study, a wide range of aggregates with various mineralogies and sources of formation are acquired and tested, and will be used for production of concrete specimens to be evaluated in this research. Representative samples of the following aggregates/rocks are evaluated in this study: (i) *sedimentary siliceous rocks*, including gravel, sand and sandstone as well as chert and flint (covering those susceptible to ASR); (ii) *sedimentary carbonate rocks*, including limestone and dolomite; (iii) *igneous rocks*, including (intrusive) granite and (shallow intrusive) basalt; and (iv) by-products aggregates (slag). The aggregates required for use in this research were obtained from the following quarries:

- 1. Fister Quarries Group, Inc. located in Batavia, IL (chert, flint, basalt, dolomite)
- 2. Builder's Redi-Mix located in Lansing, MI (natural sand, limestone, gravel)

- 3. Alamo Concrete located in Eagle Pass, TX (sandstone)
- 4. Kafka Granite located in Mosinee, WI (granite)

Aggregates strongly influence concrete's early-age and long-term properties, mixture proportions, economy, and more importantly the lifespan of the concrete infrastructure. Consequently, selection of aggregates is an important step in design and production of concrete. Therefore, a wide range of aggregates was selected in this research from various quarries. They were thoroughly washed and dried, and tested in order to assess their physical and chemical properties. Although some variation in aggregate properties is expected, characteristics that are considered here include:

- Particle shape and surface texture
- Grading (sieve analysis)
- Specific gravity and absorption capacity
- Water sorption rate
- Bulk density and voids in aggregates
- Los Angeles abrasion
- Ultrasonic pulse velocity

Along with the physical and other tests noted above, representative samples of aggregates were obtained, and ground to very fine particle size for chemical and mineralogical analyses, as follows:

- <sup>27</sup>Al and <sup>29</sup>Si NMR
- X-Ray Diffraction (XRD) spectroscopy

#### • X-Ray Fluorescence (XRF) spectroscopy

Furthermore, representative samples were obtained to test for Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). It should be noted that, after fabrication of the portable NMR device, other properties of aggregates will also be investigated.

In the next step, aggregates are subjected to the following tests: (a) alkali-silica reaction, and (b) soundness. Aggregates which show significant response to the aging conditions will be subjected to further analysis.

#### 3.2.1 Particle shape and surface texture

The shape and texture of aggregates affect the properties of fresh and hardened concrete. Concrete is more workable when rounded and smooth spherical aggregates are used instead of elongated or rough, angular aggregates with sharp edges. Most natural sands and gravels from riverbeds or seashores are smooth and rounded, and are usually strong, making them excellent aggregates for concrete production. Aggregates retrieved form crushed stone produces much more angular and elongated aggregates, which have a higher surface-to-volume ratio hence better bond characteristic, but require more cement paste to produce a workable mixture. The surface texture of aggregates can be either smooth or rough. A smooth surface can improve workability, yet a rougher surface generates a stronger bond between the paste and the aggregate, yielding concrete materials of higher strength. Figure 23 presents the aggregates used in this research, accompanied with a brief description of the shape, surface texture, angularity and other visual properties.

Aggregate type	Image	Description
Basalt		Basalt is a dark-colored, fine-grained, igneous rock composed mainly of plagioclase and pyroxene minerals. It most commonly forms as an extrusive rock, such as a lava flow, but can also form in small intrusive bodies, such as an igneous dike or a thin sill. It has a composition similar to gabbro. Basalt has sharp edges and relatively rough surface. Impurities and decolorized spots in dark orange and light brown can be seen with naked eyes.
Chert		Chert is a fine-grained, cryptocrystalline or microfibrous sedimentary rock that may contain small fossils. It varies greatly in color (from white to black), but most often manifests as gray, brown, grayish brown and light green to rusty red; its color is an expression of trace elements present in the rock, and both red and green are most often related to traces of iron (in its oxidized and reduced forms respectively). The obtained chert has a shiny black color and very smooth surface.
Dolomite		Dolomite is an anhydrous carbonate mineral composed of calcium magnesium carbonate. High content of carbonates makes dolomite very light in color (usually grey and with relatively large white spots). The surface is rough but small particles can be detached from the grain by applying normal force. Small shiny spots can be seen with medium spacing on the surface.
Flint		Where chert occurs on chalk or marl it is usually called flint. It looks like gravel, round with very smooth edges. Grains are colorful (usually orange to dark brown). The surface is neither rough nor very smooth.
Granite		Granite is a common type of felsic intrusive igneous rock which is granular and phaneritic in texture. Due to the crushing of the original rock, grains have very sharp edges and flat surfaces. It comes with a variety of colors from yellow to dark green, light orange to black. Granite is relatively heavy when compared with other aggregates, and has a rough surface.
Gravel		Gravel (bank gravel specifically) is composed of unconsolidated rock fragments that have a general particle size range and include size classes from granule- to boulder-sized fragments. Smaller grains are spherical. Larger particles have flat surfaces sometimes. The grains color ranges from white to black, yellow to brown. The surface is very smooth.

Figure 23. Visual appearance and description of aggregates

## Figure 23. (Cont'd)

Limestone	Limestone is a sedimentary rock composed largely of the minerals calcite and aragonite, which are different crystal forms of calcium carbonate. Like most other sedimentary rocks, most limestone is composed of grains. Aggregate particles due to the crushing process have sharp edges and flat surfaces. The color is consistent throughout the particles and usually grey.
Sandstone	Sandstone is a clastic sedimentary rock composed mainly of sand- sized minerals or rock grains. Particles are mostly spherical although elongated particles can be seen. The color of particles is very diverse with a tendency towards darker colors like dark grey and brown. Surface texture is variant among particles.
Natural sand	Natural sand is a naturally occurring granular material composed of finely divided rock and mineral particles. The color is usually brown and dark orange.

# 3.2.2 Grading (sieve analysis)

The sieve analysis, commonly known as the grading or gradation test, is an essential test for all projects involving aggregates. The sieve analysis determines the distribution of aggregate particles, by size, within a given sample in order to determine compliance with design and production requirements, and verification standards. The gradation data may be used to calculate relationships between various aggregate or aggregate blends, to check compliance with such blends, and to predict trends during production by plotting gradation curves graphically, to name just a few uses. Used in conjunction with other tests, the sieve analysis is a very good quality control and quality acceptance tool. Sieve analysis was performed according to AASHTO T27 for fine and coarse aggregates.

Samples were obtained and reduced to test size in accordance with AASHTO T 248. Next, samples were dried to a constant weight in an oven set at  $230 \pm 9^{\circ}$ F ( $110 \pm 5^{\circ}$ C), in an oven. They were then weighed to the nearest 0.1 gram, and placed on top of nested sieves. Finally, the stacked sieves were placed in a sieve shaker as shown in Figure 24. The gradation graphs are presented in Figure 25.

Maximum Aggregate size (MAS) and Nominal Maximum Aggregate Size (NMAS) for coarse aggregates, and fineness modulus of natural sand were measured along with sieve analysis which will be used later for designing the concrete mix.



Figure 24. Sieve shaker



(a)



(b)

Figure 25. Gradation of (a) coarse aggregates, and (b) fine aggregate.

#### 3.2.3 Specific gravity and absorption capacity

Specific gravity measurements are made on both fine and coarse aggregates. In the case of coarse aggregates, the specific gravity of a sample is obtained by determining the ratio of the weight of a given volume of aggregate to the weight of an equal volume of water. It is similar in nature to the fine aggregate specific gravity test. Specific gravity and absorption capacity measurements are performed according to ASTM C 127.

Four different types of specific gravity can be measured: (i) apparent specific gravity (volume measurement only includes the volume of the aggregate particle, excluding the volume of any water-permeable voids, and mass measurement only includes that of aggregate particles, G<sub>sa</sub>); (ii) bulk specific gravity G<sub>sb</sub> (volume measurement includes the overall volume of aggregate particles as well as the volume of water-permeable voids, and mass measurement includes the overall volume, bulk specific gravity is less than apparent specific gravity; (iii) bulk saturated surface dry (SSD) specific gravity (volume measurement includes the overall volume, bulk specific gravity is less than apparent specific gravity; (iii) bulk saturated surface dry (SSD) specific gravity (volume measurement includes the overall volume of aggregate particles as well as the volume of water-permeable voids, and mass measurement includes the aggregate particles as well as the volume of water-permeable voids, and mass measurement includes the aggregate particles as well as the volume of water-permeable voids, and mass measurement includes the aggregate particle as well as the volume of water-permeable voids); and (iv) effective specific gravity G<sub>se</sub> (volume measurement includes the volume of aggregate particles plus the void volume that gets filled with water during the test soak period minus the volume of voids that absorb asphalt); effective specific gravity lies between the apparent and the bulk specific gravity [87]. In this report, values for bulk specific gravity is calculated using Equation [25]:

Bulk Specific Gravity = 
$$G_{sb} = \frac{A}{B-C}$$
 [25]

where,

A: Mass of oven dry sample in air (g)

B: Mass of SSD samples in air (g)

C: Mass of SSD sample in water (g)

The absorption capacity of aggregates is calculated using Equation [26]:

$$\% Absorption = \frac{B-A}{A} \times 100$$
 [26]

The measured values for specific gravity and absorption capacity for all aggregates are summarized in Table 4.

Aggrogato tupo	Bulk specific	Absorption
Aggregate type	gravity	capacity (%)
Basalt	2.97	0.9
Chert	2.19	3.0
Dolomite	2.45	2.3
Flint	2.62	1.4
Granite	2.66	1.1
Gravel	2.60	4.4
Limestone	2.54	1.0
Sandstone	2.58	1.1
Natural sand	2.51	3.4

Table 4. The measured values of aggregate specific gravity and absorption capacity.

## 3.2.4 Bulk density and voids in aggregates

Bulk density of aggregates is the mass of aggregates required to fill the container of a unit volume after aggregates are batched based on volume. It depends on the packing of aggregate (i.e. loosely packed aggregates versus densely compacted), and can be measured in loose (noncompacted) or compacted condition. Loose bulk density can be determined by filling the container with dried aggregates until it overflows from the container, followed by leveling the top surface of container by rolling a rod on it. After that, the aggregate mass that is inside the container is weighed, and the measured value is divided by the volume of container. Compacted bulk density can be determined by filling the container in three layers, and tamping each layer using a 16mm diameter rounded nosed rod. The test setup is shown in Figure 26. The value of bulk density is calculated using Equation [27]. The bulk density measured here, and the specific gravity obtained before can be used to calculate the volume of voids in aggregates, as shown in Equation [27], which is the space between particles in an aggregate mass not occupied by the solid mineral matter. A summary presentation of the values measured for all aggregates is presented in Table 5.

$$M = \frac{(G-T)}{V}$$
[27]

where,

M = bulk density of aggregate, 
$$kg / m^3 [lb / ft^3]$$

G = mass of the aggregate plus the measure kg[lb]

T = mass of the measure kg[lb]

V = volume of the measure  $m^3[ft^3]$ 

$$\% Voids = \frac{100[(G_{sb} \times W) - M]}{G_{sb} \times W}$$
[28]

where,

G<sub>sb</sub> = bulk specific gravity (dry basis) as determined in accordance with test method C127

Aggregate type	Bulk density (kg/m³)	Absorption capacity (%)
Basalt	1506	49
Chert	1393	46
Dolomite	1538	37
Flint	1650	37
Granite	1554	42
Gravel	1746	33
Limestone	1522	40
Sandstone	1602	38

# Table 5. Measured values of bulk density (compacted) and voids in aggregates.



## Figure 26. Measure and rod for bulk density measurements.

# 3.2.5 Los Angeles abrasion

The Los Angeles (L.A.) abrasion test (Figure 27) is a common test method used to assess the aggregate toughness and abrasion characteristics. The aggregate abrasion attributes are important because the constituent aggregate in concrete must resist crushing, degradation and disintegration in order to produce a high-quality concrete material.

The standard L.A. abrasion test subjects a coarse aggregate sample (retained on the No. 12, 1.70 mm, sieve) to abrasion, impact, and grinding in a rotating steel drum containing a specified number of steel spheres depending on the gradation of aggregates. After being subjected to abrading effects in the rotating drum, the weight of aggregate that is retained on a No. 12 (1.70 mm) sieve is subtracted from the original weight to obtain a percentage of the total aggregate weight that has broken down and passed through the No. 12 (1.70 mm) sieve. For example, an L.A. abrasion loss value of 40 indicates that 40% of the original sample passed through the No. 12 (1.70 mm) sieve.



# Figure 27. The LA abrasion drum steel.

Coarse aggregates were subjected to the LA abrasion test according to ASTM C 131, and the

results are presented in Table 6.

Aggregate type	Loss due to the abrasion (%)
Basalt	17.6
Chert	46.0
Dolomite	55.0
Flint	20.6
Granite	21.2
Gravel	20.4
Limestone	26.9
Sandstone	24.0

# Table 6. LA abrasion test results.

A summary of the physical tests results on aggregates is presented in Table 7 for a quick comparison and evaluation of aggregates.

Aggregate Type	MAS – NMAS (inch)	Bulk density (kg/m³)	Specific gravity (Bulk)	Absorption capacity (%)	Void content (%)	LA abrasion (%)	Comment
Basalt	3/4" - 5/8"	1506	2.97	0.9	49.01	17.6	
Chert	5/8" - 1/2"	1393	2.19	3.0	36.12	46.0	
Dolomite	1 1/2" - 1"	1538	2.45	2.3	37.42	80.0	
Flint	3/4" - 5/8"	1650	2.62	1.4	36.87	20.6	
Granite	3/4" - 5/8"	1554	2.66	1.1	41.54	21.2	
Gravel	5/8" - 1/2"	1746	2.60	4.4	32.90	20.4	
Limestone	3/4" - 5/8"	1522	2.54	1.0	40.19	26.9	
Sandstone	1" - 3/4"	1602	2.58	1.1	37.88	24.0	
Natural sand	N.A.	N.A.	2.51	3.4	N.A.	N.A.	FM: 3.15

Table 7. Summary of the aggregate physical test results.

#### 3.2.6 Chemical composition of aggregates

To understand the chemical composition of aggregates, representative samples were gathered, washed and dried overnight in oven at 230±9°F (110±5°C). Samples were ground to finer than 150 µm particle size. X-ray Fluorescence (XRF) spectroscopy was used to determine the chemical composition of aggregates. XRF is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. Aggregates were analyzed by XRF for SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, MgO, MnO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> after HT-digestion in excess Li-tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>). Operating conditions of the XRF instrument were set at 50 kV and 50 mA. Bulk Loss on Ignition (LOI) was determined gravimetrically by weighing powdered sample material pre-dried at 105°C until constant weight before and after ignition at 1050°C. The weight loss includes both CO<sub>2</sub> and H<sub>2</sub>O [88]. A summary of the results is presented in Table 8. Some key findings based on these test results are as follows.

- The LOI for carbonate aggregates (dolomite and limestone) is higher compared to other aggregates due to the large quantity of CO<sub>2</sub> in the composition of these aggregates.
- Silicates and aggregates dominate the composition of flint and chert, which can induce alkali-silica reactions depending on the reactivity of the silicate phases.
- The abundance of ferromagnetic elements in basalt is notable. When testing this aggregate for NMR (either individually or as a constituent of concrete), this issue will be revisited.

	Chemical Composition											
Aggregate	SiO <sub>2</sub>	CaO	$AI_2O_3$	$Fe_2O_3$	MnO	MgO	$Na_2O$	K <sub>2</sub> O	TiO <sub>2</sub>	$P_2O_5$	Sum	LOI
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Basalt	48.50	9.00	14.65	14.99	0.18	6.26	2.49	0.70	1.95	0.19	98.91	0.86
Chert	71.14	0.89	12.85	1.10	<0.03	0.04	3.88	4.23	0.06	<0.01	94.19	5.52
Dolomite	1.65	55.56	0.13	0.30	<0.03	1.19	<0.01	0.03	0.02	0.09	58.97	41.09
Granite	39.92	17.17	5.50	4.86	0.07	9.63	0.84	1.19	0.22	0.04	79.44	20.32
Gravel	34.65	22.71	3.58	2.15	0.03	9.60	0.71	0.75	0.16	0.04	74.38	25.54
Flint	72.82	2.02	9.46	8.30	0.07	1.37	1.50	2.80	0.59	0.18	99.11	0.59
Limestone	2.18	53.54	0.47	0.31	<0.03	2.21	< 0.01	0.21	0.02	< 0.01	58.94	41.18
Sandstone	80.67	8.66	0.56	2.62	<0.03	0.14	< 0.01	0.13	0.07	0.03	92.88	6.90
Sand	62.99	11.94	3.56	2.08	0.03	4.38	0.62	0.89	0.14	0.03	86.66	13.26

Table 8. Chemical composition of aggregates.

#### 3.2.7 SEM – EDS of aggregates

A scanning electron microscope (SEM) is an instrument that produces images of a sample by using electrons instead of light. A beam of electrons is produced at the top of the microscope by an electron gun. The electrons interact with atoms in the sample, producing various signals that can be detected, and contain information about the sample's surface topography and composition. Detectors collect these signals (composed of X-rays, backscattered electrons, and secondary electrons), and convert them into a signal that is sent to a PC monitor. The SEM used in this research can achieve resolutions better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum (Environmental SEM), and at a wide range of cryogenic or elevated temperatures [89]. Figure 28 shows the JEOL 6610 LV scanning electron microscope which was used to scan the surface of aggregates.



Figure 28. The SEM- EDS system.

The SEM used in this research is also capable of performing Energy-dispersive X-ray spectroscopy (EDS), which is an analytical technique used for elemental analysis or chemical characterization of a sample. The interaction of the beam of electrons and the sample produces x-rays that can be detected with EDS detectors, and yields elemental analysis on a local geometric basis. This ability of EDS gives a unique and powerful means of scanning a particular spot of the sample, and extract is chemical composition and elemental distribution.

SEM is a powerful tool that allows us to observe the surface of aggregates at high magnifications (10 to 100 times higher than light microscope) with great resolution and depth of focus. SEM allows us to study the surface texture, pores and chemical composition of aggregates. The following procedure was carried out for preparing aggregate samples for examination using SEM:

- 1. For each aggregate type, two particles were selected, thoroughly cleaned and washed to remove loose particles, dried in oven at  $230 \pm 9^{\circ}$ F (110 ± 5°C) for 24 hours.
- 2. One side of each particle was sanded flat using grit sandpaper for mounting on metal stubs.
- 3. The other side of one particle was polished to a depth of nearly 2 mm, and cleaned with air compressor. The other particle remained unpolished at its natural state.
- The grains were mounted on metal stubs using fast-setting epoxy as shown in Figure 29.
  Samples were further dried in oven at 60°C for 24 hours.
- 5. Finally, the samples were stored in desiccators under vacuum until the day of experiment.



(a)

(b)

# Figure 29. SEM- EDS samples: (a) examples of polished and unpolished gravel; (b) different aggregate particles.

SEM/EDS invesigations were conducted using a JEOL 6610 LV SEM (Figure 28) equipped with the oxford image analysis software. The images were collected using a Backscattered Electron Shadow (BES) detector in low-vacuum (60 Pa) mode. The accelerating voltage was set at 20 kV,

and the spot size was varied from 35 to 55. Several images were taken from the particles with polished and unpolished surfaces. The SEM images for limestone are shown in Figures 30 to 39. Figure 30a shows the surface of limestone at 330X magnification. Large pores (~50  $\mu$ m) can be seen at the top right corner of the image, while smaller pores (sub-micrometers) are spread across the surface. Microcracks are also visible at the bottom right corner, that could occur either naturally or due the crushing process of larger rock pieces into aggregate particles. Figure 30b presents a higher-magnification (1000X) image of small pores and sub-micrometer grains found on the surface of the aggregate particle.

Figure 31a presents the polished surface of an aggregate particle at 350X magnification. The parallel lines indicate the residual traces of the polishing device. The image reveals the isolated pores underneath the surface, which can be seen at a higher magnification (4000X) in Figure 31b. These pores contribute to the overall porosity, density, specific gravity and engineering properties of aggregates (e.g., strength and Young's modulus). However, their presence cannot be easily verified using conventional tests. Some of these pores can absorb water through interconnected capillary pores, and some are completely isolated. Furthermore, some of these pores contain bound water, and some are free of water. Later, when testing these aggregates under portable NMR, the pores would influence the relaxation curves and other outputs.



(a)







#### Figure 31. Polished surface of limestone.

Figure 32a shows the natural surface of a basalt aggregate. Charging due the paramagnetic impurities is the major reason for the shiny part on the bottom left corner of the images. Nevertheless, this phenomenon does not obscure the pores which are about  $\sim 1 \,\mu$ m in size. The surface looks intact with almost no visible cracking. However, Figure 32b exposes some underlying microcracks and submicron-pores. It is worth mentioning that the cracks that follow each other (and usually occur in the direction of polishing) could be artifacts of the polishing

process, and the ones perpendicular to the polishing direction mostly pertain to the aggregate itself.



(b)

# Figure 32. BES images of basalt at different magnifications for a) natural surface, b) polished surface of aggregate particles

Figure 33a illustrates the surface of chert at 350X and 1200X magnifications. In both micrographs, very few microcracks are visible; they exhibit many residuals and small particles bound to the surface of the grain. Figure 33b exposes the layered structure of the grain (top right corner) and submicron pores. Moreover, many microcracks are revealed at 350X and 1200X magnifications on the polished surface of chert.


## Figure 33. BES images of chert at different magnifications for a) natural surface, b) polished surface of aggregate particles.

Figure 34a shows a large number of pores ranging from  $\sim 1 \ \mu m$  to  $\sim 10 \ \mu m$  in size. At 1400X magnification, even smaller pores can be detected. Figure 34b reveals more pores underneath the surface, but this time with a more uniform structure and consistency in size and location. Very limited number of microcracks could be observed while investigating both the natural and polished surface of the dolomite particles.



# Figure 34. BES images of dolomite at different magnifications for a) natural surface, b) polished surface of aggregate particles

Shiny white spots in Figure 357 indicate the existence of ferromagnetic impurities in the composition of flint aggregates. Small pores ( $\sim 1 \mu m$ ) are locally distributed all over the surface. However, the polished surface exposes more pores of nearly uniform size. Furthermore, microcracks start to appear at higher magnifications (1500X).



## Figure 35. BES images of flint at different magnifications for a) natural surface, b) polished surface of aggregate particles.

The natural surface of granite is shown if Figure 36a. In both magnifications (250X and 750X), very limited number of pores is visible. However, many grooves and indentations are observed, which provide a suitable place for water to dwell. These trench-like cutes also help the cement hydrates bind to the aggregate particles. Figure 36b exposes the micro-pores and crystal depositories underlying the surface.



# Figure 36. BES images of granite at different magnifications for a) natural surface, b) polished surface of aggregate particles.

A consistent pore structure of gravel is found in Figure 37. These pores are spread all over the

grain, and are smaller than ~1  $\mu$ m. The layer underneath also shows the same pattern as the

surface with pores of similar size and smaller.



# Figure 37. BES images of gravel at different magnifications for a) natural surface, b) polished surface of aggregate particles.

The structure of sandstone is very similar to that of gravel, both in natural and polished states.

However, sandstone contains larger pores and a less uniformed pore structure in underlying

layers when compared with gravel, as shown in Figures 38a and b.



Figure 38. BES images of sandstone at different magnifications for a) natural surface, b) polished surface of aggregate particles.

Figure 39a shows the smallest sand particles. The particles surfaces vary in nature, ranging from very porous (right and top right) to almost non-porous (middle). However, by zooming on the middle of the particle, submicron pores and cracks are revealed. The white, shiny spot in Figure 39b is an artifact of the magnetic impurity on the sand surface.





EDS analysis of aggregate surfaces was performed along with SEM observations. Spatial chemical composition analysis gives us the ability to analyze the anomalies, decolorized spots, suspicious or damaged locations, and local chemical compositions. The EDS spectra for the polished and natural surfaces of limestone aggregate particles are presented in Figure 40. In general, calcium is the dominant element with the highest x-ray count detected. Carbon and oxygen are the next most abundant elements constituting the bulk of minerals inside the particle. These findings corroborate the XRF results, and the common knowledge that limestone is a sedimentary rock composed largely of the minerals calcite and aragonite, which are different crystalline forms of calcium carbonate (CaCO<sub>3</sub>). The elemental spectra of aggregates are presented in Appendix A (Figures 40 to 49). This technique would be more useful later when studying the aged/damaged aggregates.



Figure 40. EDS spectra of a) natural surface b) polished surface of limestone.



Figure 41. EDS graph of basalt for a) natural surface and b) polished surface.



Figure 42. EDS graph of chert for a) natural surface and b) polished surface.



Figure 43. EDS graph of dolomite for a) natural surface and b) polished surface.



Figure 44. EDS graph of flint for a) natural surface and b) polished surface.



Figure 45. EDS graph of granite for a) natural surface and b) polished surface.



Figure 46. EDS graph of gravel for a) natural surface and b) polished surface.



Figure 47. EDS graph of limestone for a) natural surface and b) polished surface.



Figure 48. EDS graph of sandstone for a) natural surface and b) polished surface.





#### Figure 49. EDS graph of natural sand.

### 3.2.8 Ultrasonic pulse velocity

The inhomogeneous and variable nature of rocks (and thus aggregates) challenges direct investigation of aggregate properties. Once rock is crushed into aggregates and shipped for concrete production, access to solid rock specimens for performance of engineering (e.g., mechanical) tests would be difficult. One can use empirical relationships among various physical and mechanical properties of aggregates to estimate their properties by performing simple tests. Ultrasonic pulse velocity (UPV) is a nondestructive test that could be used for this purpose. This test method is commonly used for estimating concrete strength per ASTM C597 [90]. The method involves measurement of the time of travel of an ultrasonic pulse passing through a concrete specimen or component. Comparatively higher velocities are obtained for concrete materials of higher strength and density. UPV has also been used to estimate the engineering properties (strength, density and petrophysical qualities) of rocks [91-95].

The UPV instrument for measurement of the time of travel and the velocity of the ultrasound wave is shown in Figure 50. While UPV tests are commonly performed on solid specimens, aggregates are generally available in granular form for the purpose of testing. In order to make a

UPV test specimen from aggregates, a glass container (2 in diameter by 3 in height) with plasti cap was packed with aggregates, approaching the maximum packing density of aggregates (Figure 51). Replicated UPV tests were performed on samples of all aggregates, and the average values of travel time and speed of ultrasonic wave were derived (Table 9).

The UPV test results reported here for unaged aggregates will be compared against those of aged aggregates, and against the UPV test results to be produced for concrete materials made with these aggregates.



Figure 50. UPV instrument



Figure 51. UPV test sample

Туре	Travelling time (μs)	Velocity (m/s)
Basalt	54	2801
Chert	73	2086
Dolomite	53	2900
Flint	45	3366
Granite	59	2659
Gravel	72	2212
Limestone	57	2716
Sandstone	81	1856
Sand	69	2343

Table 9. Measured values of ultrasonic pulse travel time and velocity through packedaggregate particles.

#### 3.2.9 Rate of absorption

The water absorption capacity of fine and coarse aggregates was measured and reported earlier. In this reporting period, the rates at which aggregates approach their 24-h water absorption capacity was measured for all the aggregate types considered in this research. Information on the rate of absorption during the first few minutes, up to perhaps 1 h, is of considerable technical importance. For example, it is during this period that an aggregate removes water from fresh (unplaced) concrete, with a concurrent loss in slump [96]. Further, some researchers have reported that the early rate of water uptake is associated with the 24-hr absorption capacity of aggregates and, by inference, its freeze-thaw durability [97].

Representative samples of aggregates were selected, thoroughly washed, dried at 105°C for 24 hours, and finally cleaned with air compressor (to remove any possible debris blocking the surface pores).

The rate of water absorption was determined by hanging a sample of aggregates from one arm of an analytic balance, and surrounding it with deionized water. The apparent gain in mass was monitored and recorded over time. Due to absorption, water enters the pore system and replaces air, resulting in an apparent rise in the mass of the samples. This mass gain is equal to the amount of entering water because the departing air contributed a buoyant effect while the arriving water contributed none. Hence, the apparent rise in mass at any time is equal to its water absorption at that time [96].

The water uptake for each aggregate type was measured at different time intervals up to 24 hours. These values were normalized based on the maximum water uptake for each aggregate type (and expressed as percentage). The rates are compared in Figure 52. Sorption values during the first minute vary between 15 to 65%. For the first hour, sorption values range from 28 to 80%. Aggregates with higher absorption capacity tend to absorb more water at earlier times. Also, there could be a correlation between porosity, pore size distribution and sorption rate.

The particle size distribution and surface roughness of aggregates influence their surface-tovolume ratio which, together with surface porosity, play important roles in sorption characteristics of aggregates. One might suggest taking cores with similar size from different rocks may lead to a solid analysis. Tests on rock cores of similar size [96] indicate that water absorption varies greatly within different rocks, and sorption rate is not merely a function of the 24-hour absorption capacity. This investigation also found no correlation between the early sorption rate of an aggregate type and its potential freeze/thaw durability.

102



Figure 52. Percent of 24-hr absorption versus time for aggregates.

#### 3.2.10 X-Ray diffraction analysis of aggregates

X-Ray Diffractometry (XRD) is a powerful for identifying crystalline materials. XRD can be used as a stand-alone method, or in conjunction with other techniques in comprehensive chemical characterization and investigation of aggregates. Here we use XRD to identify the major crystalline constituents of aggregates. The presence or absence of certain crystalline structures will later help in analysis of the concrete deterioration phenomena under different exposure conditions.

XRD was performed using The Bruker Davinci Diffractometer shown in Figure 53. Samples of aggregates were washed and dried, and then ground to produce fine powder. Figures 54 through 61 present the XRD spectra of the aggregates considered in this research.



Figure 53. The Bruker Davinci Diffractometer.



## Figure 54. XRD spectrum of basalt.

(Peaks marked with Δ indicate the presence of augite with ideal chemical formulation of (Ca,Mg,Fe)<sub>2</sub>Si<sub>2</sub>O<sub>6</sub>. Augite possesses a monoclinic crystal system with the cell refinement output of a: 9.745(3)Å, b: 8.902(2)Å and c:
5.271(1)Å; alpha: 90°, beta: 106.10(2)°, gamma: 90° and Volume: 439.3(1)Å<sup>3</sup>. Olivine and feldspar are the other common crystals in basalt which were not found in the x-ray spectrum.)



#### Figure 55. XRD spectrum of chert.

(The x-ray spectrum of chert is completely different from other spectra. Some researchers believe that flint and chert are, speaking strictly, not minerals, but rocks. It is a textural variety of quartz that shares some properties with jasper. It contains considerable amounts of other silica modifications, mostly moganite [98] and perhaps opal. However, none of the expected crystalline structures were observed in the x-ray spectrum. Several different varieties of chert notably deviate from typically expected structures of this type of stone.)



Figure 56. XRD spectrum of dolomite.



#### Figure 57. XRD spectrum of limestone.

(The marked peaks in Figure 30 clearly show the existence of calcite in dolomite aggregates. It should be noted that dolomite could refer to the aggregate and the mineral. No trace of dolomite mineral was found in the x-ray spectrum. Calcite with ideal chemical formulation of CaCO<sub>3</sub> has a hexagonal crystal system with the cell refinement output of a: 4.9793(1)Å, b: 4.9793(1)Å, c: 17.0244(9)Å, alpha: 90°, beta: 90°, gamma: 120° and Volume: 365.55(2)Å<sup>3</sup>. Spectrum of limestone (Figure 31) is almost identical to dolomite because they are both sedimentary carbonate rocks, sharing calcite as their backbone of mineral structure.)



#### Figure 58. XRD spectrum of flint.

(Peaks pertaining to quartz are marked. Quartz also has a hexagonal crystal system with the cell refinement output of a: 4.9134(2)Å, b: 4.9134(2)Å and c: 5.4042(4)Å; alpha: 90°, beta: 90°, gamma: 120° and Volume: 112.991(5)Å<sup>3</sup>. Olivine and feldspar are the other common crystals in basalt which were not found in the x-ray spectrum. Peaks marked with o could belong to Potassium Aluminum hydride. However, there is not enough evidence to confirm or completely discard their existence. Raman or infrared spectrum could be used to investigate this matter if that is necessary.)





(Granite also contain quartz as the primary crystalline structure. Moreover, the peaks shown with o could belong to albite (which is a form of feldspar) with chemical formulation of NaAlSi<sub>3</sub>O<sub>8</sub> and triclinic pinacoidal crystal system with the cell refinement output of a: 8.16Å, b: 12.87Å, c: 7.11Å, alpha: 93.45°, beta: 116.4°, gamma: 90.28°.)



Figure 60. XRD spectrum of sandstone.



#### Figure 61. XRD spectrum of sand.

(The spectra in Figures 34 and 35 indicate the presence of quartz in both sandstone and sand. There are a few unresolved peaks in both Figures that most likely belong to feldspar although there is not enough evidence to support this claim.)

#### 3.2.11 Soundness of aggregates

The soundness test determines an aggregate's resistance to disintegration by weathering and, in particular, freeze-thaw cycles. Aggregates that are durable (resistant to weathering) are less likely to degrade in the field and cause premature damage and potentially, failure. The soundness test repeatedly submerges an aggregate sample in a sodium sulfate or magnesium sulfate solution. This process causes salt crystals to form in the aggregate's water permeable pores. The formation of these crystals creates internal forces that apply pressure on aggregate pores and tend to break the aggregate. After a specified number of submerging and drying repetitions, the aggregate is sieved to determine the percent loss of material.

Two standards are suggested for performing this test: ASTM C88 (used in this research) and AASHTO T104. The following steps were taken:

- Sulfate solution is prepared. When used, the sodium sulfate solution's specific gravity should be between 1.154 to 1.171. About 215 anhydrous sodium sulfate was used per 1 liter of water
- 2. **Coarse aggregate:** enough material is selected, washed and dried. Sieve numbers as indicated in Table 10 are stacked and the required retained material suggested by the standard are selected.

Sieve size	Minimum mass of specimen (gram)
2in (50mm)	3000
1.5in (37.5mm)	2000
1in (25mm)	1500
0.75in (19mm)	1000
0.5in (12.5mm)	750
0.375 (9.5mm)	500
No. 4 (4.75mm)	300

Table 10. Sample mass requirement for coarse aggregates.

3. **Fine aggregates:** enough material is selected, washed and dried. Sieve numbers as indicated in Table 11 are stacked and the required retained material suggested by the standard are selected.

Siovo sizo	Minimum mass of
Sleve size	specimen (gram)
No. 8	100
No. 16	100
No. 30	100
No. 50	100
No. 100	100

Table 11. Sample mass requirement for fine aggregates.

It should be noted that in Tables 10 and 11, if the sample contain less than 5-10% retained on

each sieve according to sieve analysis, that sieve size is neglected for testing.

Each sample is placed in a separate container.

- 4. Samples are immersed in sodium sulfate solution for 16 to 18 hours. The containers are covered to reduce evaporation and prevent contamination and temperature is maintained at 20°C for the immersion period
- 5. Samples are removed and drained for 15 minutes
- 6. Each sample is placed in a separate aluminum container and is dried in the oven at 100°C.
- 7. Every 4 hours the weight is measured until the change in mass less than 0.1 percent.
- 8. Samples are cool at 20°C.
- 9. Steps 4-9 are repeated 5 times.
- 10. After the fifth and final cycle, the samples are washed and dried to a constant weight.
- 11. Coarse aggregates are sieved using the guideline in Table 4 with agitation sufficient only to assure that all undersize material passes the designated sieve.
- 12. For fine aggregates the same sieve is used on which it was retained before the test.
- 13. The mass before and after cycles is recorded and compared.

Aggregate size	Sieve used
≥ 1.5in	1.25in
1.5in to 0.75in	5/8in
0.75in to 0.375	5/16in
0.375in to No. 4	No. 5

Table 12. Sieve used to determine loss after test.

Figure 62 compares the weight loss results in a bar graph. Moreover, the selected sieves and percent weight loss for all aggregate samples are summarized in Tables 13-21.



Figure 62. Summary of soundness test.

Among the coarse aggregates, granite, dolomite and flint show the best resistance to sodium sulfate with the weight loss of less than 2%. Gravel, chert and basalt seem to be very prone to situations similar to weathering where pore network plays an important role to keep the integrity of the aggregate grain together. Moreover, natural sand weight loss is quite significant. It should be noted that freeze-thaw cycles with appropriate aggregates will be performed on concrete specimens and the performance of aggregates and cement paste matrix in conjunction together will be revisited later. However, these test results provide useful insight towards a better understanding of the specific aggregates used in this research in harsh environments (e.g. freeze-thaw cycles).

It is worth mentioning, so far flint and granite exhibited strong performance in LA abrasion test (with ~21% weight loss) and in soundness test (less than 2%). Low accessible porosity of these aggregate enhances their resistance to various physical and chemical attacks involved in concrete. However, various types of flints cause ASR in concrete due to the existence of certain

111

silicate crystalline structure which reacts with cement alkali over time and causes excessive expansion and potentially failure.

Sieve Size	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 4.5 mm (No. 4)	0.4				
3/8" to No. 4	20.5				
1/2" to No. 3/8"	26.2	500	382.3	23.5	6.2
3/4" to 1/2"	52.9	750	675.4	9.9	5.3
1" to 3/4"	0				
Totals	100	1250	1057.7		11.4

## Table 13. Summary of soundness results for basalt

## Table 14. Summary of soundness results for chert.

Sieve Size	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 4.5 mm (No. 4)	2.5				
3/8" to No. 4	50.8	300	263.5	12.2	6.2
1/2" to No. 3/8"	35.8	500	409.6	18.1	6.5
3/4" to 1/2"	10.9	750	737.07	1.7	0.2
1" to 3/4"	0				
Totals	100	1550	1410.17		12.8

## Table 15. Summary of soundness results for dolomite.

Sieve Size	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 4.5 mm (No. 4)	7.7				
3/8" to No. 4	2.2				
1/2" to No. 3/8"	1.6				
3/4" to 1/2"	19				
1" to 3/4"	33.3	1000	994.8	0.52	0.2
1.5" to 1"	36.3	1500	1497	0.2	0.1
Totals	100	1000	994.8		0.3

## Table 16. Summary of soundness results for flint.

Sieve Size	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 4.5 mm (No. 4)	0.2				
3/8" to No. 4	4				
1/2" to No. 3/8"	29.6	500	493.3	1.3	0.4
3/4" to 1/2"	66.2	750	739.18	1.4	1.0
1" to 3/4"	0				
Totals	100	1250	1232.48		1.4

Sieve Size	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 4.5 mm (No. 4)	0.1				
3/8" to No. 4	4.4				
1/2" to No. 3/8"	30.1	500	484.8	3.0	0.9
3/4" to 1/2"	65.5	750	748	0.3	0.2
1" to 3/4"	0				
Totals	100	1250	1232.8		1.1

## Table 17. Summary of soundness results for granite.

## Table 18. Summary of soundness results for gravel.

Sieve Size	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 4.5 mm (No. 4)	16.9				
3/8" to No. 4	71.9	300	246.9	17.7	12.7
1/2" to No. 3/8"	8.2	500	474.5	5.1	0.4
3/4" to 1/2"	3				
1" to 3/4"	0				
Totals	100	800	721.4		13.1

## Table 19. Summary of soundness results for limestone.

Sieve Size	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 4.5 mm (No. 4)	6.1				
3/8" to No. 4	47	300	286.2	4.6	2.2
1/2" to No. 3/8"	26.5	500	432.6	13.5	3.6
3/4" to 1/2"	20.5	750	745.7	0.6	0.1
1" to 3/4"	0				
Totals	100	1550	1464.5		5.9

## Table 20. Summary of soundness results for sandstone

	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 4.5 mm (No. 4)	1				
3/8" to No. 4	26.3	300	275	8.3	2.2
1/2" to No. 3/8"	25.2	500	469.3	6.1	1.5
3/4" to 1/2"	39	750	736.3	1.8	0.7
1" to 3/4"	8.4				
Totals	100	1550	1480.6		4.5

Sieve Size	Grading of sample (%)	Weight of Test Fractions Before Test (g)	Weight of Test Fractions After Test (g)	Percentage Passing Designated Sieve	Weighted Percentage Loss
Minus 150 um (No. 100)	1.1				
No. 50 to No. 100	5.7	100	90.6	9.4	0.5
No 30 to No. 50	36.2	100	85.6	14.4	5.2
No. 16 to No. 30	28.1	100	80	20	5.6
No.8 to No.16	19.7	100	94.1	5.9	1.2
No. 4 to No. 8	9.2	100	92.4	7.6	0.7
3/8 in to No. 4	0				
Totals	100	500			13.2

Table 21. Summary of soundness results for sand

#### 3.2.12 X-ray µCT of aggregates

The x-ray computed tomography (X-ray CT) technique makes use of computer-processed combinations of many x-ray images taken from different angles to produce cross-sectional (tomographic) images (virtual 'slices') of specific areas of a scanned object, allowing the user to see inside the object without cutting it. X-ray CT has been widely used in medical imaging for computerized axial tomography scan (CAT scan). X-ray micro tomography, similar to x-ray computed tomography, uses x-rays to create cross-sections of a physical object that can be used to recreate a virtual model (3D model) without destroying the original object. The prefix micro-(symbol:  $\mu$ ) is used to indicate that the pixel sizes of the cross-sections are in the micrometer range.

Herein, x-ray micro-computed-tomography (X-ray µCT) is used to visually study the structure of aggregate grains from all angles in a non-destructive fashion. In this method, an x-ray beam transmitted through an aggregate particle along several different paths in different directions is detected, manipulated electronically, and stored in a computer. The intensity of the x-ray beam is measured before it enters the sample, and also after it passes through it. The transmitted X-ray beams have a modulated intensity dependent on the overall linear attenuation characteristics

of the intervening material. This modulated or the resulting CT image is a spatial distribution of the linear attenuation coefficients, where brighter regions correspond to higher values of the coefficient. Therefore, if phases with different linear attenuation coefficients are present in an aggregate specimen, they show up as having different brightness. The linear attenuation coefficients vary as a function of the composition and density of the material [99].

Figure 63 shows an aggregate particle (limestone) after it has been washed and dried. The x-ray machine scans the cross sections parallel to the x-y plane, and moves in depth of the particle (sample). The scanned data will be analyzed and rendered to yield 3D or layered images as shown in Figure 126. An animated image (.GIF) file is available which plays all the layers in sequence. Rendered image are in gray scale, presenting denser regions brighter, and showing empty pores and cracks in black. However, since the minimum scanning resolution was set at 46 µm, pores and other phases smaller than 46 µm cannot be observed and analyzed. The scanner has the capability to resolve regions as small as 27 µm. However, signal-to-noise ratio decreases, and time of scanning and data file volume dramatically increase for this scanning resolution.



Figure 63. Aggregate specimen used for X-ray µCT

Figure 64a shows a relatively large void inside the aggregate. The depth of the void (in z direction) is limited, and the effect of the void in Figure 64b disappears while other voids emerge. Furthermore, the darker gray spots in Figure 64b show impurities and phases with lower density compared to the major constituent of limestone. Figures 64c and 64d also show a mixture of voids and impurities spread across the grain cross-section. Figure 65 presents scans of the same sample with higher resolution.





Figure 64. Layered images of the aggregate X-ray scans at 46µm resolution





Figure 65. Layered images of the aggregate X-ray scans at  $27\mu m$  resolution

Figures 66 and 67 show the X-ray µCT scans of a basalt particle at two different scanning resolutions. In both figures, shiny white spots indicate a lump and dense phase which could be deposits of augite crystals as identified in XRD. Regardless of the scanning resolution, dark black spots (which, similar to Figure 65, represent voids or cracks) could not be found, indicating that the empty spaces (pores/cracks) in basalt are smaller than those in limestone. Although higher-resolution scans (Figure 67) reveal more crystalline deposits, due to the size of the pores and the reduction in SNR, pores cannot be easily identified.



(a)



(b)

Figure 66. X-ray µCT of basalt aggregates at 46µm resolution.



(a)



(b)

## Figure 67. X-ray $\mu$ CT of basalt aggregates at 27 $\mu$ m resolution.

Figure 68 shows the X-ray  $\mu$ CT images of a (natural) gravel particles. The layered structure of gravel is clear in both Figures 130a and b. Shinier regions represent materials of higher density while darker regions represent materials of lower density. Black spots are indicative of the empty spaces between layers.






(b)

# Figure 68. X-ray μCT of (natural) gravel particles at 27μm resolution.3.2.13 Visual inspection of damaged aggregates

The aggregates subjected to accelerated aging were evaluated using scanning electron microscope (SEM) in order to assess the manifestations of damage on the surface texture of aggregates. Figures 69-77 present the texture of different aggregates after repeated exposure to sodium sulfate solution and drying in the oven at 110°C, as observed via scanning electron microscopy.

Figures 69 and 70 show SEM images at different magnifications of the basalt and chert aggregate surfaces, respectively, after exposure. Cracks can be detected in both figures. In Figure 8a, a wide crack can be observed at the top right corner. In Figure 70, cracks are narrower but more prevalent. The weight losses of basalt and chert aggregates were among the highest when compared with the other aggregate types considered.



(a)

(b)

Figure 69. SEM micrographs of basalt aggregates.



Figure 70. SEM micrographs of chert aggregates.

In the case of dolomite (Figure 71), although some cracks are visible in Figure 71a, they seem to be unrelated to the soundness test. This crack pattern could also be observed in micrographs of

control (unaged) dolomite presented in Report 1. No significant cracking could also be detected in the micrographs of flint and granite (Figures 72 and 72, respectively). The weight losses for these 3 types of aggregates were among the lowest, pointing at their high weathering resistance.



(a)

(b)





Figure 72. SEM micrographs of flint aggregates.



(a) (b) Figure 73. SEM micrographs of granite aggregates.

At the first glance, it seems that the surface of (natural) gravel has not changed after exposure. However, a closer inspection of Figure 74b indicates that small narrow cracks appear across the gravel particle. Similar cracks with less frequency also appeared in limestone and sandstone shown Figures 75 and 76, respectively. These cracks are shorter and narrower than cracks in chert. Small cracks and deformation are also prevalent in the natural sand grains shown in Figure

77.



(a)

(b)

Figure 74. SEM micrographs of natural gravel aggregates.



(a)

(b)





(a)

(b)

Figure 76. SEM micrographs of sandstone aggregates.



Figure 77. SEM micrographs of natural sand.

## 3.3 Cementitious Binders

Different binder types are considered in this research to compositions which yield concrete materials of different properties (e.g. normal-strength and high-strength concrete). These binders are based on:

- 1. Cement Type I (from Lafarge)
- 2. Cement Type I/II (from Quikrete)
- 3. Fly ash Class C (from Headwaters Inc.)
- 4. Fly ash Class F (from Headwaters Inc.)
- 5. Silica fume (undensifed) (from Norchem)
- 6. Slag Newcem 100 (from Lafarge)

The chemical compositions of above cementitious materials, obtained suppliers, are presented in Table 22.

	Chemical Composition									
Binder	SiO <sub>2</sub>	CaO	$AI_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO₃	TiO <sub>2</sub>	LOI
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Cement Type I	20.2	62.0	4.7	3.1	3.8	0.68*		2.9		2.0
Cement Type I/II	19.5	62.2	5.1	3.2	2.6	0.3	1.2	3.4	0.3	2.5
Fly Ash Class C	41.5	19.7	20.6	5.7	4.3	1.9	0.7	0.9		0.7
Fly Ash Class F	43.7	12.5	23.2	9.9	2.7	0.9	1.8	1.7		1.2
Silica Fume	91.7					0.84*		0.6		3.6
Slag	37.3	37.4	10.0	0.4	12.2	0.2	0.3	1.9	0.5	0.5

 Table 22. Chemical composition of cementitious materials.

\*Represents equivalent Na<sub>2</sub>O (Na<sub>eq</sub>) instead of Na<sub>2</sub>O

## 3.3.1 X-Ray diffraction analysis of cementitious materials

XRD analyses were performed on all the cementitious materials considered in this research.

Figures 78 through 83 show the spectra for all these materials.

Figure 78 and 79 present the XRD spectra of ordinary Portland cements Type I and Type I/II, respectively. In general, cement clinker comprises four major phases: alite (C<sub>3</sub>S, 50-70 st.%), belite (C<sub>2</sub>S, 15-30% by mass), aluminate (C<sub>3</sub>A, 0-15% by mass) and ferrite (C<sub>4</sub>AF, 5-15%). It also contains minor phases: periclase (M), calcium oxide (C), and alkali sulfates ((K-Na<sub>2</sub>)SO<sub>4</sub>) [100]. In addition to clinker, cement contains gypsum and possibly other calcium sulfates. The cement powder diffraction patterns are complex, and the number of phases creates a composite pattern with many overlapping peaks. With most of the strong diffraction peaks overlapping, identification of various phases and the related measurements are often performed using the weaker peaks.



Figure 78. XRD spectrum of Type I cement.



Figure 79. XRD spectrum of Type I/II cement.

Figure 80 and 81 present the spectra Class C and Class F fly ash. Quartz is the predominant crystalline structure in both ashes, referred to as  $\Delta$ . A calcium aluminate crystalline structure was also identified in Class C fly ash.



Figure 80. XRD spectrum of Class C fly ash.



Figure 81. XRD spectrum of Class F fly ash.

The XRD spectra of silica fume and slag (Figures 82 and 83) do not present a significant, welldefined peak, which could indicate the lack of a significant crystalline structure in their composition.



Figure 82. XRD spectrum of silica fume.



Figure 83. XRD spectrum of slag.

## 4 INVESTIGATION OF CONCRETE USING NMR

#### 4.1 Understanding Relaxation Parameters

#### 4.1.1 Longitudinal relaxation time (T<sub>1</sub>)

Relaxation parameters can be investigated in nondestructive NMR tests using different pulse sequence programming included in the Prospa software. For most of the relaxation parameters, the most efficient pulse programs have been identified. Pulse programs suiting measurement of  $T_1$  and  $T_2$  were presented in previous Progress Reports. A previous recap is presented in the following.

<sup>1</sup>H-NMR is a spectroscopic technique which uses resonance interactions between electromagnetic waves and the hydrogen nuclei placed in an external magnetic field. NMR is based on nuclear spin, which is a quantum mechanics property of certain isotopes, including hydrogen (<sup>1</sup>H). This spin results in a magnetic dipole moment, which aligns with an applied external magnetic field, generally labelled as  $B_0$  (see Figure 84b). Additionally, the spin axis can be thought of as precessing, or revolving around the direction of  $B_0$ . The speed at which the axis rotates is the precessional frequency or Larmor resonant frequency. This frequency is directly proportional to the external field strength with a proportionality constant called gyromagnetic ratio ( $\gamma$ ),  $\omega_0 = \gamma$ .B<sub>0</sub>. The gyromagnetic ratio is fixed for each type of atomic nuclei. In an object volume with a large number of spins, part of the nuclear dipole moments are aligned in the direction of the external magnetic field and part are exactly the opposite. The former is a lower-energy state and the latter is in a higher state. The vector sum of all moments gives the net magnetization in the object volume. In thermodynamic equilibrium this magnetization is parallel

to the external magnetic field and therefore it is called longitudinal magnetization. The spins will be induced to resonate, absorb and afterwards emit energy by applying electromagnetic energy at Larmor frequency. This electromagnetic field will change the number of nuclei in the two energy states (see Figure 84c). The longitudinal magnetization is transferred into transverse magnetization. For magnetic fields between 10<sup>-2</sup> and 10<sup>1</sup> T, which is typical for most NMR experiments, the Larmor frequency is in the MHz range; as a result, the applied electromagnetic field is often called radiofrequency (rf) field.



Figure 84. Physical principles of Nuclear Magnetic Resonance. (1) Static magnetic field B<sub>0</sub>, (2) RF magnetic field B<sub>1</sub>, (3) NMR signal, (4) Spin-spin interactions, (5) spin-lattice interactions [101].

In pulsed NMR, the rf field is applied as a transient pulse, which is described by its amplitude magnetic field vector  $B_1$  and its duration  $t_p$ . Usually, a coil which is part of a resonant circuit transmits one or more such rf pulses to the object volume. After tuning off the pulse(s), the emitted energy is measured as an alternating voltage induced in the same (rf) coil. The amplitude of this NMR signal is proportional to number of resonant spins in the observed object volume. The absorbed excess energy dissipates due to interactions between spins and their atomic and molecular environment (spin-lattice interactions), and also due to the interactions of spins among each other (spin-spin interactions). These interactions are modulated in time by

molecular motions giving rise to two relaxation processes (see Figure 157d). A gradual recovery of the longitudinal magnetization is thus observed as well as a gradual loss of transverse magnetization. The former process is labelled as  $T_1$  relaxation, and the latter as  $T_2$  relaxation. In the simplest case, each process proceeds exponentially in time. It can thus be described by a single time-constant, i.e. by single relaxation times  $T_1$  and  $T_2$ .

For  $T_1$  measurement, the  $T_1$  saturation recovery pulse sequence is utilized. It consists of a series of 90° pulses which bring magnetization in the *xy* plane, and destroy it by totally dephasing it. This is a 2D experiment, and is used also for  $T_1$ - $T_2$  correlation experiments. During the recovery time,  $\tau_{re,r}$ , magnetization is restored on the *z* axis [32]. The signal is read out with a CPMG sequence. Therefore, the longer the recovery time the more signal amplitude we obtain, until magnetization is completely recovered, and the maximum signal intensity is recorded. A sketch of the pulse sequence is shown in Figure 85. For single-exponential relaxation the experimental signal is described as a function of the recovery time:



 $s(t) = A\{1 - \exp\{\frac{-\tau_{re}}{T_1}\}\}$ 

[29]

Figure 85. T<sub>1</sub> saturation recovery pulse sequence. In the first part of the sequence, net magnetization is destroyed. During the recovery time, magnetization is restored and read out with a CPMG sequence [32].

The spin-lattice relaxation time give us information on molecular mobility. Knowing the  $T_1$  value, we can determine the recycle delay, that is the time between two consecutive scans. Theoretically, this is  $5 \times T_1$  and corresponds to the time during which 99% of the magnetization recovers to the equilibrium state.

The Prospa software has all the built-in subroutines for operating the machine with various pulse sequence programs used in this investigation. Figure 86 shows the software GUI for T<sub>1</sub> saturation recovery. This subroutine has three tabs. 'Main' tab allows user to change the pulse sequence parameters. The correct parameters are obtained from past experience with cement paste and concrete. The 'Depths' tab (Figure 86b) allows the user to set the depth of investigation inside the sample. The 'File settings' tab (Figure 86c) gives multiple options to save and recover the acquired data.



Figure 86. The T<sub>1</sub> saturation recovery user interface.

## 4.1.2 Transverse relaxation time (T<sub>2</sub>)

The CPMG pulse sequence is used to measure the transverse relaxation time T<sub>2</sub>. A sketch of the sequence is presented in Figure 87. It consists of a 90° rf pulse followed by a train of 180° pulses. The 180° pulse is double in amplitude but has the same length as the 90° pulse. With the help of

the 180° pulses, magnetization, that starts to dephase due to  $B_0$  inhomogenities, gets refocused to form an echo. The envelope of the CPMG echo train is recorded. The echo amplitude decays with time. Its initial amplitude provides the proton density, which is proportional to the content of hydrogen atoms in the sample. The decay-time constant, T<sub>2</sub>, varies with the mobility of protons.





$$s(t) = \sum_{i} A_{i} \exp\{\frac{-t}{T_{2eff,i}}\}$$
 [30]

where,  $A_i$  is the relative spin density or mole fraction of components with relaxation times  $T_{2eff;i}$ in the sensitive volume if s(t) is normalized to one.

Figure 88 shows the software GUI for the CPMG pulse sequence. This subroutine has four tabs. The 'Main' tab (Figure 88) allows the user to change the pulse sequence parameters. Similar to  $T_1$  saturation recovery, suitable parameters are obtained from paste experience with cement paste and concrete. The 'Depths' tab (Figure 88) allows the user to set the depth of probing inside the sample. The 'Fitting' tab (Figure 88) provides the option to choose desired fitting techniques. The most used fitting techniques in NMR relaxometry are: exponential fit, bi-exponential fit, and inverse Laplace fit. The 'File settings' tab (Figure 161d) gives provides options to save and recover e acquired data.

CMPGFast AUTO	CMPGFast AUTO
MAIN       Depths       Fitting       File settings         ProbeHead       PM25-20mm par       upDate         Resolution (um)       100       Normalization       13.4         Repetition time (ms)       500       Number of scans       16         Number of echoes       128       Etup       Pref.       Close	Main       DEPTHS       Fitting       File settings         Measuring depths list       5000 4000 3000 2000       Max. depth (um) 6650         Edit       2000       Enable Lift Movement         Image: Construction of the setup       Fref.       Close
(a)	(b)
Main     Depths     FITING     File settings       Exponential fit     Relaxation range (ms)       Bi-exponential fit     Minimum     0.1       Inverse-Laplace fit     Maximum     10       No fit     Maximum     10	Main Depths Fitting FILE SETTINGS Working directory C:\data\metha-test Experiment name cpmgfastauto
Remove first points 1 Run Stop Load Setup Pref. Close	Experiment number 2 Auto increment Run Stop Load Setup Pref. Close
(c)	(d)

Figure 88. The T<sub>1</sub> saturation recovery user interface.

## 4.1.3 Self-diffusion coefficient (D)

The self-diffusion principles are described here using an isolated arbitrary pore in a porous material with volume V and surface S, shown in Figure 89. During an NMR experiment, the water molecule and therefore also the spin moment can move within the pore due to Brownian motion.

The velocity of this motion is characterized by the self-diffusion coefficient (D= $2.3 \times 10^{-9}$ m<sup>2</sup>/s for water at room temperature).

A stimulated echo sequence is used to measure the self-diffusion coefficient of the sample. The sketch of the pulse sequence is presented in Figure 164. This sequence enables measurement of diffusion, D, as a function of the evolution time,  $\Delta$ . It can be used to make measurements at longer evolution times when magnetization is stored in the *z* direction, and decays with T<sub>1</sub>.

In the first part, magnetization is stored in the *z* direction and spins are allowed to diffuse. The signal is read out by a CPMG sequence. The more time the spins are allowed to diffuse, the more the signal intensity will be attenuated.

The information obtained from the time-dependent diffusion coefficient is usually used in porous media to probe length scales. The measured signal is described by:

$$\ln\frac{I}{I_0} = -D\gamma^2 G^2 \delta^2 \left\{ \Delta + \frac{2}{3} \delta \right\}$$
[31]

where,  $\delta$  is the encoding time, and G is the magnetic field gradient.

In the Prospa software, the 'Main' tab (Figure 91a) allows the user to change the pulse sequence parameters. The correct parameters are obtained from past experience with cement paste and concrete so far. The 'Depths' tab (Figure 91b) allows the user to set the depth of investigation inside the sample. The 'File settings' tab (Figure 91c) gives multiple options to save and recover the acquired data.



Figure 89. A schematical representaiton of an isolated pore and a moving water molecule



Figure 90. Stimulated spin echo [102] sequence [32].



(a)

(b)

(c)

Figure 91. Stimulated spin echo.

#### 4.2 Studying Different Phases of Concrete

Concrete can be regarded as a three-phase material<sup>1</sup>: natural aggregates, cement-paste matrix and Interfacial Transition Zone (ITZ). These phases have significant effect on properties of concrete individually and in interaction with each other. Although they vary significantly in nature and functionality, they host a common resident: water.

Natural aggregates are porous materials which mean water can be absorbed into the body of the particles or retained on the surface of the particle as a film of moisture. Porosity values up to 2 percent are common for intrusive igneous rocks, up to 5 percent for dense sedimentary rocks, and 10 to 40 percent for very porous sandstones and limestone. However, many of the pores are isolated and trapped in the dense skeleton of aggregate grain and do not contribute to the moisture absorption/desorption. It is permeable pores (usually located on the first few millimeters of the surface of aggregate grain) that play an important role on the moisture absorption. The maximum possible moisture uptake of aggregate is referred to as "moisture capacity". Quality construction aggregate moisture capacity is usually less than 5% by weight of aggregate. Moreover, depending on the amount of absorbed water, aggregates can be found at various states of moisture absorption as shown in Figure 92.

<sup>&</sup>lt;sup>1</sup> Usually concrete phases are classified as: solid matrix (mortar and aggregates), a liquid phase (water) and a gas phase (vapor- air mixture). However, in this work the three-phase concrete, as mentioned in the text is used for better characterization using portable NMR.

State	Oven dry	Air dry	Saturated, surface dry	Damp or wet
Total moisture	None	Less than potential absorption	Equal to potential absorption	Greater than absorption

## Figure 92. Moisture conditions of aggregates [103].

The moisture absorption of aggregates depends on the overall porosity and pore size distribution. In a study by Kaneuji et al. [104] the pore size distribution of 13 different aggregates used for concrete construction was determined using Mercury Intrusion Porosimetry (MIP), as shown in Figure 93. Although MIP cannot distinguish between permeable and non-permeable pores, it could estimate the overall porosity of aggregates rather accurately. From MIP measurement of the tested aggregates, it can be seen that the pore size ranges from 10s of micrometers to 10s of nanometers. The total porosity falls between 0.005 and 0.125 (CC/G).



## Figure 93. Pore size distribution of test aggregates [104].

Unlike aggregate, cement paste has a uniform structure hence its properties are easier to predict. Zhou et al [105], obtained the pore size distribution of cement paste by measuring the throat pore volume using the Pressurization–Depressurization Cycling (PDC-MIP) method, as shown in Figure 94. The pore size ranges between 100µm to slightly less than 10nm for paste sample with w/c of 0.4 cured for 28 days. Furthermore, total measured porosity is 0.028ml/ml. However, the interaction between cement-paste matrix and aggregate and admixtures will significantly influence both total porosity and pore size distribution.



**Figure 94. Throat pore volume measured following the PDC-MIP testing sequence [105].** The interfacial transition zone (ITZ) (surrounding aggregates with up to 40μm thickness [106]), regarded as a weak link in concrete by many researchers, has a very different microstructure from the bulk paste. Some researchers claim that it may significantly compromise the mechanical properties and permeability of concrete, while others pointed out that no obvious negative effects of the ITZ were found. For conventional concrete, the ITZ stems from the so called "wall" effect: packing of cement grains against the relatively flat and large aggregate surface, which leads to a local increase in porosity. Another origin of the ITZ lies in the microbleeding effect where the ITZ accumulates free water around the aggregate surface, especially under large aggregates, and increases the local porosity [106]. According to its formation mechanism, the ITZ is believed to be affected by many factors, such as water/cement ratio, aggregate texture, and aggregates size distribution [107]. Ollivier et al. [108] studied ITZ in comparison with bulk paste. As shown in Figure 95, it seems that the pore size range of cement paste and ITZ are almost the same, while the total porosity is higher for ITZ.



Figure 95. Incremental porosity distribution of pure cement paste w/c= 0.4 and cement paste of mortar (3 months old). A new porous volume in excess for the pores bounded by 0.045 and 0.1  $\mu$ m may be observed [109].

As mentioned before, water plays a key role in all three phases. More importantly, water is generally involved in every form of deterioration and, with porous solids the ease of penetration of water into the solid usually determines its rate of deterioration [103]. Therefore, we pay special attention to water and its roll in ASR and other deterioration mechanisms in the remaining reports.

#### 4.2.1 NMR relaxometry of aggregates

Close to 75% of the normal-strength concrete volume is filled with aggregates. Therefore, performance of NMR spectroscopy and relaxometry on aggregates is a reasonable first step for building a data base that would help with interpretation of the NMR data produced on concrete. Portable NMR provides an open geometry and a good spatial resolution within the testing object. The portable NMR equipment developed in this research provides a sensitive volume (the specific volume inside the object that is being investigated by the NMR sensor at the time of testing) with a fixed size of 40mm×40mm×100µm. Therefore, when it comes to testing of aggregates, due to their relatively small particle size, testing is performed on relatively larger rocks which provide continuum and sizeable testing surfaces and volumes. The rock pieces shown in Figure 140 were

obtained from nearby quarries.<sup>1, 2, 3</sup> Finding the exact boulders that were crushed into the aggregates used in this research proved to be difficult due to the long way between aggregate quarrying and supply. The rock types considered, however, are of the same type as some of the aggregates considered in this research. Larger pieces of the following rock types (see Figure 96) were obtained for evaluation in this research: (i) gravel (ii) grindstone, (iii) limestone and (iv) sandstone.



(a) Gravel

(b) Grindstone (a type of sandstone)



(c) Limestone

(d) Sandstone

## Figure 96. Selected rocks for testing via portable NMR.

Rocks were tested in 2 different moisture conditions: (i) as-received (air dried); and (ii) saturated surface dry (SSD). The rocks were initially kept at room temperature (70°F) and 50% relative humidity for 14 days. This condition was named as-received, and the rock pieces were tested

using the portable NMR equipment (Figure 97). Subsequently, the rock pieces were brought to SSD condition by immersion in water for 24 hours, and then drying them with a towel in order to remove the extra moisture on their surfaces. The rocks in SSD conditions were then tested using the portable NMR equipment.



#### Figure 97. Testing a rock sample by the portable NMR equipment.

Values of the longitudinal relaxation time are 0.77 and 0.98 ms for cement paste and concrete, respectively. Green dots (and lines) are the gathered data, and red lines represent exponential fits to these data. Paste data are found to be smoother, and produce less variance of T<sub>1</sub> values when compared with concrete. This could be because many of the signals sent to the body of concrete face solid, dense and largely dry aggregate volume, translating into noise and ultimately reducing the signal-to-noise ratio.

Having the  $T_1$  values, the recycle time can be estimated, which enables measurement of the transverse relaxation time ( $T_2$ ) values. The CPMGFast program is used in preliminary investigations. The software settings and the transverse relaxation curves ( $T_2$ ) for paste and concrete specimens stored *in water* are shown in Figures 99 and 100 respectively. Values of the transverse relaxation time for saturated paste and concrete specimens were measured at 0.5 and

0.8 ms, respectively. Again, the data points for cement paste exhibit less variation around the fitted curve that those for concrete. This observation could be again attributed to the effect of aggregates on the signal-to-noise ratio (SNR). Therefore, more data points (i.e. scans) are required for concrete in order to produce reliable results.



Figure 98. T<sub>1</sub> longitudinal relaxation curves for (a) cement paste, and (b) concrete.





(b)

## Figure 99. CPMGFast program settings for (a) paste and (b) concrete specimens stored in water.







(b)

Figure 100. T<sub>2</sub> relaxation curves for (a) paste and (b) concrete specimens stored in water. Similar steps were taken to perform NMR on the air-dried specimens. The same setting was used for obtaining  $T_1$  and  $T_2$  curves.



Figure 101. The T<sub>1</sub> longitudinal relaxation curves for (a) paste and (b) concrete specimens stored in water.



Figure 102. T<sub>2</sub> relaxation curves for (a) paste and (b) concrete specimens stored in water.

In testing of rock specimens with the portable NMR system, air-dried rock did not produce significant signal intensity. This observation indicates that, unlike cementitious paste, common concrete aggregates do not retain physically adsorbed water in finer pores. This is partly due to strong resistance of aggregates to water sorption, which is due to the discontinuous nature of pore system in undamaged aggregates. Aggregates could thus absorb moisture mainly into surface pores; the (isolated) pores of aggregates are also relatively large in size. These conditions lead to more thorough loss of moisture from aggregates (when compared with cementitious paste) upon drying. Given the prevalence of aggregates in concrete volume, this is an important observation in analysis of the concrete NMR data. After immersion in water, rock specimens in saturated surface dry (SSD) concrete produce NMR signals, which are shown in Figures 103 and 104 together with the calculated values of  $T_1$  and  $T_2$ . The  $T_1$  values for different rocks vary from 1.5ms to 40ms, and T<sub>2</sub> values from 1ms to 40ms. The large ranges covered by these values point at important differences in the pore systems and microstructures of the rocks considered here. The test data indicate that limestone has the highest porosity and the largest pores ( $T_2$  = 40ms), while sandstone has the lowest porosity and the smallest pores ( $T_2 = 2.1$ ms).  $T_1$  and  $T_2$  relaxation curves for gravel seem to be obscured by either the high magnetic impurity or the small pores of this specimen. These results for gravel cannot be interpreted unless a better SNR is achieved. Comparatively, Limestone and sandstone produce well-defined  $T_1$  and  $T_2$  relaxation curves. This could be due to a well-distributed pore network and the lack of magnetic impurity in these rock specimens.

Due to the various options provided by the Prospa software, the portable NMR settings will be varied later to obtain the best curves within the shortest time possible.







(b)Grindstone



## (c)Sandstone



(d)Limestone

Figure 103. T<sub>1</sub> relaxation curves for saturated rocks.



(a)Gravel



(b)Grindstone



(c)Sandstone



(d)Limestone

Figure 104. T<sub>2</sub> relaxation curves for saturated rocks.

#### 4.3 Role of Water in Concrete Deterioration

Water in its various forms, such as seawater, groundwater, river water, lake water, snow, ice, and vapor, is undoubtedly the most abundant fluid in nature. Water molecules are very small and, therefore, are able to penetrate into extremely fine pores or cavities. As a solvent, water is noted for its ability to dissolve more substances than any other known liquid. This property accounts for the presence of many ions and gases in some waters which, in turn, become instrumental in causing chemical decomposition of solid materials. Also, water has the highest heat of vaporization among the common liquids; therefore, at ordinary temperatures it has a tendency to exist in the liquid state in concrete, rather than vaporizing and leaving the material dry. Furthermore, with porous concrete, internal moisture movements and structural transformations of water are known to cause disruptive volume changes of many types. For example, influx of water into the hydrophilic ASR gel can lead to high internal stresses and microcracking. Therefore, investigating the water content, water transport processes and its distribution an exchange between the gel and capillary pores becomes a priori.

While the dissolution of silica as the first stage of the ASR is well understood and accepted by many researches, there is an ongoing debate how the swelling of the gel exactly relates to the macroscopically observable expansion and deterioration of ASR affected concrete, see e.g. Reference [110]. The ASR model proposed by Bazant and Steffens [111] is based on the idea, that the imbibition of water generates a pressure in the gel, which pushes the gel to permeate the pores in the cement paste located very near the surface of the aggregate particles.

149

A macroscopic expansion is initiated only when the volume of the gel exceeds the accessible pore volume resulting in a pressurization of the interfacial transition zone. Dron and Brivot [112] even go that far to assume a through-solution mechanism, where the dissolved silica may diffuse away from the aggregate particles and the subsequent expansive reactions may then take place anywhere in the connected pore space of the cement paste. On the other hand Idorn [111] states, that the expansive pressure develops directly at the reaction sites inside the reacting aggregate particles and not in pores or cracks of the cement paste. Idorn argues, that gel, which possibly penetrates into cracks and pores absorbs calcium ions from the pore liquid, what makes the gel rigid and non-swelling [113].

Bazant's theory could be expanded in the way that when water pressurize the gel, small pores (gel pores) are flooded with ASR gel while the capillary pores facilitate the transport of water into the ASR gel and gel pores back and forth. Many of the capillary pores will eventually shut off by gel. This effect will be occurring at a faster rate closer to the aggregate surface. NMR can track and distinguish the hydrogen nuclei at different confinement conditions. Therefore, investigation of different pores, transport processes and variation of water in content and formation via NMR will be useful to identify and monitor ASR.

#### 4.4 Water Content Measurements

The essence of nuclear magnetic resonance NMR is that the nuclei of many elements selectively absorb electromagnetic energy when present in a steady magnetic field. In the case of watercontent measurement, one uses the direct proportionality in the parameters of the NMR signal and the number of hydrogen nuclei (protons) in the water in the material. In pulse methods the

150

parameters are the spin-echo signal amplitude and/or the initial amplitude obtained by extrapolating the envelope of the signal amplitude in spin echo to the start of precession [114]. In order to measure the water quantity of paste-matrix, 12 cement paste cubes (50mm × 50mm) with water to cement ratio of 0.5 were fabricated and stored in water for 28 days. Cured samples were placed on portable NMR (as shown in Figure 105a). CPMG pulse sequence was used to perform relaxometry on paste cube and water sample. Pulse sequence parameters (as listed in Table 23) for relaxometry measurements were optimized before testing cubes.



(a)



(b)

#### Figure 105. Test setup for water content measurements.

Table 23. CPMG	pulse sequence	parameters.
----------------	----------------	-------------

Parameter	Cement paste	Water
Pulse sequence	CPMG	CPMG
Number of echoes	32	32
Pulse length (µs)	5.5	5.5
Echo time (µs)	54	54
Number of scans	256	256
Repetition time (s)	0.2	10

Relaxometry was performed at 2.5mm and 5mm from the surface of the cube. At each depth,

the measured sensitive volume is a very thin rectangular prism (40mm × 40mm × 0.65mm). Using

CPMG, the signal intensities were obtained at each depth as shown in Figure 106. Exponential fitting was used to fit the data points.

Next, the signal intensity of bulk water was measured with similar CPMG pulse sequence used for paste cube. To measure the signal intensity, tap water was poured in a thin glass container. The water container was placed on the portable NMR (Figure 107b) and the signal intensity was obtained as shown in Figure 107.



Figure 106. Signal intensity of paste cube at (a) 2.5mm and (b) 5mm from the surface.



(b)

**Figure 107. Signal intensity of bulk water at (a) 2.5mm and (b) 5mm from the surface.** Normalization of the maximum signal intensity of the sample with the maximum signal intensity of the water sample provides information on the total water content within the screened volume [115].

By extrapolating the echo integral curves to zero time (Figures 106 and 107) using the first 4 point (Figure 108), the maximum signal intensity for cement paste and pure water was obtained (summarized in Table 24). Extrapolating will account for the chemically bound water which due to the very short relaxation time, that is less that the dead time of the sensor are automatically neglected by the portable NMR. The maximum signal intensity of pure water (3<sup>rd</sup> column) corresponds to 100% water while the maximum signal intensity of paste (2<sup>nd</sup> column) is only a fraction of water signal intensity and can be proportionally estimated as the water content if normalized with paste density. However, further verification and calibration will be conducted by performing Thermogravimetry Analysis (TGA) on cement paste.



## Figure 108. Four-point back-tracked extrapolation of signal amplitude for (a) water and (b) cement paste

Table 24. Maximum signal intensity and water content.						
Depth	Maximum intensity	Maximum	Water			
	of cement paste	intensity of water	content <sup>1</sup>			
2.5mm	5.5815	16.033	18.32			
5mm	5.5058	16.108	17.99			

#### Table 24. Maximum signal intensity and water content.

<sup>1</sup>The water content of paste is normalized with density of paste. Coming TGA results will enable us with more accurate estimation.

## 4.5 Water Distribution in Cement Paste

To provide information about the distribution of water inside the specimen data processing was carried out on the relaxation decay results using bi-exponential fit and inverse Laplace transformation. Both techniques enable us to distinguish between gel pore water and capillary pore water, Figure 109.



Figure 109. (a) T<sub>2</sub> decay of a saturated paste sample. (b) Bi-exponential fit. (c) Inverse Laplace.
While pure liquid water at room temperature shows values for T<sub>2</sub> in the range of seconds the relaxation time is severely reduced if a water molecule is chemically combined or adsorbed by a surface. As a consequence, T<sub>2</sub> of chemically bound <sup>1</sup>H nuclei becomes so short that it cannot be observed within low-field NMR. However, hydrogen of water in concrete capillary and gel pores covers a range of T<sub>2</sub> values from approximately 10ms for capillary pores up to about 0.1ms for gel pores.

The inverse Laplace transformations of decay of Hydrogen nuclei in cement paste at 2.5mm and 5mm depths are shown in Figure 110. The transformation measures the distribution of relaxation times measured in the sensitive volume. The range of the relaxation times are measured to be between 1ms and 100ms for the paste cubes, covering most of the pores found in cement paste matrix. Sharp peaks in the figures indicate the prevalence of the pore sizes corresponding to that relaxation times. In Figure 110a, two distinguished peaks are visible with corresponding relaxation times of 1.68ms and 17.66ms, respectively. Higher amplitude of the peak at 1.68ms compared to 17.66ms, indicates that there are larger number of pore sizes with 1.68ms relaxation time compared to the pores with 17.66ms relaxation times. Moreover, the area under the first curve (shorter relaxation times), when normalized with respect to the total area, estimates of the gel pores percentage while the area under the second curve (longer relaxation times) estimates the capillary pores percentage. The total area and area under peaks are computed using a MATLAB routine as presented in Table 25.



Figure 110. Inverse Laplace transformation of cement paste at (a) 2.5mm and (b) 5mm depth.

Table 25. Alea measurements.							
Denth		Area under 1st peak (a.u.)	Area under 2nd neak (a.u.)	Total			
(mm)	Peaks (ms)	(normalized w.r.t. total	(normalized wirt total area)	area			
		area)		(a.u.)			
2.5mm	1.68, 17.66	0.3883 (64.4%)	0.2142 (35.6%)	0.6025			
5mm	2, 45.39	0.4192 (65.3%)	0.2225 (34.7%)	0.6417			

Table 25. Area measurements

The results shown in Figure 110 and Table 25 suggest that gel pores account for two-third and capillary pores account for about one-third of the pores in the cement paste. However, the number of gel pores slightly increases and the number of capillary prose slightly decreases as we probe deeper. Moreover, the pores become larger as we go in depth. This fact can be verified by the increase in the total area under curves as well as the range of relaxation times. At 2.5mm from the surface, pores cover a range between approximately 1 and 20ms while at 5mm the range extends, between 1 and 100ms.

## 5 PORTABLE NMR SYSTEM COMPONENTS AND OPERATION

The portable NMR system consists of three major components: (i) a precision lift (Figure 111a); (ii) a profiling sensor (Figure 111b); and (iii) a spectrometer (Figure 111c). The sensor is installed on the precision lift, and then connected to the spectrometer using a cable (Figure 112). The spectrometer connects to a laptop computer through the USB port (Figure 113).



(a) (b) (c)





Figure 112. The sensor and lift assembly.



Figure 113. The spectrometer and laptop assembly.

The portable NMR works with a software (Prospa) designed for the spectrometer, which can

control the measurement settings and the operation details.





### 5.1 NMR Probe

The NMR probe is the unit in charge of producing the magnetic field required to initiate the resonance of certain nuclei by magnetizing and spin them in the same direction (either clockwise or counter clockwise) inside the sample geometry using permanent magnets. It also pulse-tips the magnetized nuclei and receives the data from the excited nuclei using the RF coil embedded inside the probe. The data can be collected from various depth of the object by the help of a

precision lift which moves the sensitive volume precisely within the depth of the object. Figure 115 shows the schematic of the probe and lift.



Figure 115. (a) Magnets and coil configuration (b) probe and lift [116].

#### 5.1.1 Magnets

The magnets (indicated by **a** in Figure 115) are neodymium-iron-boron (NeFeB) blocks of 40, 50, and 45mm along *x*, *y* and *z*, the gaps (indicated by **c** and **d**) are  $G_b$  = 19mm and  $G_s$  = 4mm respectively, and the iron yoke (indicated by **b**) is 20mm thick.

The magnetic field was measured using a Lakeshore Hall probe, and its spatial dependence along the two lateral directions is shown at three different depths. While the behavior of the field along z is quadratic at the surface and become flat for larger depths, the field along x becomes flat at a depth of 15mm away from the magnet, a distance that depends on the  $G_S$  chosen. The magnetic field at 15mm from the surface and in the center of the device has a value of about 0.25T along z, and has a strong uniform gradient of 8T/m along the depth direction. At this depth, the device defines a plane of constant field intensity parallel to the surface with a field variation smaller than 0.1mT in a region of 20mm along x and 10mm along z. The lateral selection of a sensitive region with these dimensions will be achieved by choosing a RF coil with suitable dimensions.

5.1.2 RF coil

The radio-frequency coil in Figure 115a and tuning circuit to be used in combination with this magnet must satisfy a number of requirements. First, the dimension of the coil is determined by the lateral dimensions of the sensitive region where the magnet system defines a flat slice. For the present prototype, this region is smaller than 40x40 mm<sup>2</sup> in the *x-z* plane. Second, the coil must have a low inductance to reduce the detuning generated during the scanning procedure, which involves the movement of the sensor with respect to the object and can change the load of the coil. Third, the maximum depth desired determines the distance at which the coil must be positioned away from the magnet surface.

#### 5.1.3 Spectrometer

The goal here is to have a battery powered system that can be easily transported and used by a single user. It is also desirable to produce a more compact unit specifically for the NMR probe. Therefore the flexible modular system is enclosed in a standard readily available enclosure and allows us to change RF front ends to accommodate different probes [117].

#### 5.2 Device Specifications

A summary of the device specifications is presented below and in Table 26.

Operating frequency: 12.76 MHz

Lateral size of sensitive volume: 40mm × 40mm

Gradient strength: 290 kHz/mm

Spacer (mm)	Pulse length (μs)	Rf- att <sup>1</sup> (dB)	TE <sub>min</sub> ² (μs)	Signal <sup>3</sup>	Signal 100 μm	Echo shift (µs)	Phase (∘)
20	5.5	-7/0	54	14.5	3.3	0.6	185
15	9	-7/0	62	6	2.1	0.6	185
10	15	-7/0	75	2.5	1.5	0.6	185
5	25	-7/0	95	1.11	1.0	0.6	185
0	35	-7/0	125	0.60	0.6	0.6	185

Table 26. Settings and performance parameters for different measurement depths

1. Attenuation used in a 750W amplifier

2. The minimum echo time that can be applied, when using the acquisition equal to the pulse length

3. Signal of water acquired with a CPMG setting TE =  $200\mu$ s, Acq = 64  $\mu$ s, and Nechoes = 8

#### 5.3 Signal-to-Noise Ratio and Ways to Improve

Increasing SNR for portable NMR systems with inhomogeneous and relatively weak magnetic fields is an important consideration in mobilizing the full potential of the technique. The sensitivity of portable NMR systems can be significantly enhanced by using multi-echo detection methods based on the application of CMPG-like pulse trains. By adding the echoes of a train, the measuring times can be reduced by up to two orders of magnitude when compared with single-echo methods (e.g., Hahn echo) [118, 119]. Optimization of the hardware is another consideration which is complicated due to the lack of theoretical formulations for quantifying the signal-to-noise ratio (SNR) in inhomogeneous fields. Hoult's formulation of SNR [120] cannot be applied in a straightforward way to single-sided sensors. These sensors are used to study samples much larger than the sensor itself, and only a small portion of the sample can be reached in a single experiment. This fact leads to the definition of the sensitive volume, which depends on the

magnet, rf-coil geometry, and the pulse sequence applied. The optimization of a magnet requires a delicate balance between field and gradient strength. A stronger field yields a higher sensitivity, but if this is achieved at the expense of a more pronounced gradient, a smaller sensitive volume would be excited, manipulating the SNR [38].

#### 5.4 Software Preparation and Execution

Once the device is calibrated, testing of various specimens can be conducted. First of all, the software settings should be selected carefully. Depending on the type of NMR characteristic (e.g.  $T_1$  or  $T_2$ ) that is being investigated, the software parameters and options should be set to correct values. These parameters include: the repetition time, pulse length, echo time, number of echoes, etc. These parameters are the variables of relaxation equations.

#### 5.4.1 Pulse sequences

The portable NMR device nondestructively investigates into the depth of materials by sending magnetic pulses generated by strong magnets mounted on the device. These pulses excite the hydrogen nuclei so that they start spinning in the same direction. Once the pulse sequence is stopped, the nuclei start to lose their coherence and re-emit their energy as signals which are detected by the sensor in the device. Pulses can be sequenced in a fashion that is time-efficient, and yields high signal-to-noise ratio (SNR). Selection of a suitable pulse sequences is thus vital to successful use of the portable NMR device.

The simplest form pulse is called Free Induction Decay (FID). FID is the observable NMR signal generated by the non-equilibrium nuclear spin magnetization precessing about the magnetic field. As shown in the Figure 116, a 90° single pulse is followed by a short spectrometer dead

time (light grey), after which the signal may be observed. The signal from a solid, decays more rapidly than that from a liquid. It is partially obscured by the spectrometer dead time (dotted line, shaded region).



#### Figure 116. The FID signal [1].

Due to the inhomogeneity of the static field generated by the open geometry of the portable NMR, no FID is available ( $T_2^*$ ~ RF, pulse length ~ 5µs). Therefore, the spin echoes must be used. The basic sequence used with the single-sided NMR sensors is the CPMG sequence. It consists of a 90° pulse followed by a train of 180° ones, which generates a train of spin echoes in order to refocus the B0 inhomogeneities. The envelope of the decay can be used to obtain the spin density as well the transverse relaxation time. Furthermore, sensitivity can be increased dramatically by co-adding the echoes of the train, which results in reasonably short measurement times. While the spin density can be simply related to the initial amplitude of the decay, the effective transverse relaxation time,  $T_{2eff}$ , can be extracted from the signal decay.

When programming a CPMG sequence to work with the portable NMR system, it is essential to make suitable selections of the timing of pulses, free evolution periods, and acquisition windows.

A mistake of only a few microseconds could be determinant. Figure 117 shows the CPMG pulse sequence.



Figure 117. The CPMP pulse sequence.

In the CPMG pulse sequence shown in Figure 117, all rf pulses are set to have the same length *pl*. In the case of 90-180-echo, the RF output of the first must be attenuated by 6dB extra. By using the time intervals as shown in the figure, one should obtain the echo at the middle of the acquisition window. In many cases, however, the presence of filters shifts the echo by few microseconds. This can be corrected by simply shifting the acquisition window by adding an extra delay to the first period, and subtracting it from the period after the echo. For example:  $180^{\circ}$  - ( $\tau$  -*pl/2-acq/2+ acq\_shift*) - *acq* - ( $\tau$  -*pl/2-acq/2 - acq\_shift*) -  $180^{\circ}$ ; in this way, the total free evolution period is still 2  $\tau$  -*pl*.

**Pulse length (pl)**: The CPMG sequence consists of two types of pulses. The initial 90° pulse turns the initial longitudinal magnetization into detectable transverse magnetization, while the following train of 180° pulses refocuses the effect of B0 inhomogeneities generating spin echoes. When using the portable NMR, 90° and 180° pulses are set to have the same length; therefore, the rf output for the 180° must be 6 dB higher. The optimum pulse length is determined by

measuring the signal intensity as a function of the pulse length. The 90° condition is fulfilled when the maximum signal intensity is detected.

**Echo time (2** $\tau$ ): The echo time (2 $\tau$ ) is the delay between two echoes. It is determined by the delay between the different pulses. The delay between the 90° and the 180° pulses has to be  $\tau$ -pl, and the delay between two 180° pulses has to be 2 $\tau$ -pl. The echo signals are acquired in the center between two consecutives 180° pulses. In order to achieve the maximum sensitivity, the echo time should be as short as possible. However, the minimum echo time is limited by the dead time of the probe and the length of the acquisition window.

Acquisition time (*acq*): The echoes are acquired in the center between two consecutive scans. For the purpose of acquisition, it is very important to set a fast dwell time (i.e. dwell time =  $1\mu$ s, broad bandwidth = 1MHz). The dwell time is the delay between consecutive acquired points during one echo. To maximize the detection sensitivity, the acquisition time should be set in a way that the echo is acquired from half-to-half intensity. However, the length of the acquisition window also determines the spatial resolution. It should be noted that, in many cases, the presence of filters shifts the echo some microseconds. To correct for this, one can simply shift the acquisition window by adding an extra delay to the first period, and subtracting it from the period after the echo.

**No of scans:** In order to achieve an adequate signal-to-noise ratio (SNR), the CPMG sequence is repeated several times, and the signal of these scans is averaged. Consecutive scans have to be separated by a time called the recycle delay. During this time, z-magnetization is recovered, which is required for performing the next scan. To achieve a maximum recovery of

magnetization, the recycle delay should be of the order of 5T<sub>1</sub> (longitudinal relaxation time). However, maximum sensitivity/time is reached with a recycle delay of about 1.5T<sub>1</sub>.

#### 5.4.1.1 A general sequence

A general approach to be adopted uses a multiecho detection scheme in combination with diverse encoding sequences. This allows for improving the detection sensitivity by co-adding the echoes generated during the train. Depending on the specimen type, the experimental time reduction can be up to two orders of magnitude. Figure 64 shows the structure of a general sequence (*encoding + detection*). As an example, a Hahn echo sequence can be used as the encoding period. This sequence enables measurement of the diffusion coefficient of liquids. A stimulated echo can be used as the encoding period to measure the restricted diffusion phenomena in porous media.

In Figure 118, the encoding sequence generates an echo, and at its maximum begins the CPMG detection train. The detection echo time  $(2\tau_{det})$  is always set as short as possible (limited by the dead time) in order to maximize the number of echoes that can be acquired, while the echo time during the encoding period  $(2\tau_{enc})$  can be set either to introduce attenuation (used as a filter or to introduce contrast), or can be varied to sample the decay (amplitude *vs*  $\tau_{enc}$ ).





For the purpose of T<sub>1</sub> measurement, due to the impossibility of defining "perfect" inversion pulses, the choice of saturation recovery is more convenient than the inversion recovery. The sequence requires a saturation period, a recovery period  $\Delta$ , plus a CPMG train for detecting the M<sub>2</sub> magnetization at the end of the recovery period (Figure 119). Since FID cannot be used, an echo must be generated. As saturation period, we are using five "90°" pulses with the following delays between them: 10, 25, 40, and 75 µs. The repetition delay between consecutive accumulations (d1) does not need to be of the order 5T<sub>1</sub>; in principle, it could be zero.



Figure 119. Saturation recovering + Hahn Echo sequence (encoding period) followed by CPMG detection train (detection period).

By varying  $\Delta$ , recovering of the M<sub>2</sub> magnetization is sampled. The addition of all echoes generated during the train is proportional to M<sub>2</sub>. For example, if the sample has a T<sub>2</sub> of 50ms, and the echo time is 0.050ms, one can acquire 1000 echoes per shot, equivalent to 1000/2 = 500 experiments with a single Hahn echo detection.

Paste and concrete specimens (which were stored in two different environments: air and water) were tested using the portable NMR system. The paste and concrete specimens were place on

top of the portable NMR as shown in Figure 120. The T1SatAuto program is performed on paste and concrete to measure  $T_1$ .





(a)

(b)

# Figure 120. Testing of cubic paste (left) and cylindrical concrete (right) specimens with the portable NMR system.

After inputting the pulse program values, running of the program prompts the NMR sensor to send and receive signals which are transferred to the spectrometer. The data is processed by the spectrometer, and sent to the Prospa software. The GUI of the software shows the data acquisition process as they the data is recorded; the results are presented on the screen at the conclusion of the acquisition process. Examples of longitudinal relaxation curves (T<sub>1</sub>), produced for cement paste and concrete specimens stored *in water*, are shown in Figure 121. Values of the longitudinal relaxation time are 0.77 and 0.98 ms for cement paste and concrete, respectively. Green dots (and lines) are the actually gathered data, and red lines represent exponential fits to these data. Paste data are found to be smoother, and produce less variance of T<sub>1</sub> values when

compared with concrete. This could be because many of the signals sent to the body of concrete face solid, dense and largely dry aggregate volume, translating into noise and ultimately reducing the signal-to-noise ratio.

Having the T<sub>1</sub> values, the recycle time can be estimated, which enables measurement of the transverse relaxation time (T<sub>2</sub>) values. The CPMGFast program is used in preliminary investigations. T<sub>1</sub> and T<sub>2</sub> for paste and concrete specimens stored *in water* are shown in Figures 121 and 122, respectively. Values of the transverse relaxation time for saturated paste and concrete specimens were measured at 0.5 and 0.8 ms, respectively. Again, the data points for cement paste exhibit less variation around the fitted curve that those for concrete. This observation could be again attributed to the effect of aggregates on the signal-to-noise ratio (SNR). Therefore, more data points (i.e. scans) are required for concrete in order to produce reliable results.



Figure 121. T<sub>1</sub> longitudinal relaxation curves for (a) cement paste, and (b) concrete.



Figure 122. T<sub>2</sub> relaxation curves for (a) paste and (b) concrete specimens stored in water.

Similar steps were taken to perform NMR on the air dried specimens. The same setting was used for obtaining  $T_1$  and  $T_2$  curves.



Figure 123. The T<sub>1</sub> longitudinal relaxation curves for (a) paste and (b) concrete specimens stored in water.



Figure 124. T<sub>2</sub> relaxation curves for (a) paste and (b) concrete specimens stored in water. In testing of rock specimens with the portable NMR system, air-dried rock did not produce significant signal intensity. This observation indicates that, unlike cementitious paste, common concrete aggregates do not retain physically adsorbed water in finer pores. This is partly due to strong resistance of aggregates to water sorption, which is due to the discontinuous nature of pore system in undamaged aggregates. Aggregates could thus absorb moisture mainly into surface pores; the (isolated) pores of aggregates are also relatively large in size. These conditions lead to more thorough loss of moisture from aggregates in concrete volume, this is an important observation in analysis of the concrete NMR data. After immersion in water, rock specimens in saturated surface dry (SSD) concrete produce NMR signals, which are shown in Figures 125 and 126 together with the calculated values of T<sub>1</sub> and T<sub>2</sub>. The T<sub>1</sub> values for different rocks vary from 1.5ms to 40ms, and T<sub>2</sub> values from 1ms to 40ms. The large ranges covered by these values point at important differences in the pore systems and microstructures of the rocks considered here.

The test data indicate that limestone has the highest porosity and the largest pores ( $T_2 = 40ms$ ), while sandstone has the lowest porosity and the smallest pores ( $T_2 = 2.1ms$ ).  $T_1$  and  $T_2$  relaxation curves for gravel seem to be obscured by either the high magnetic impurity or the small pores of this specimen. These results for gravel cannot be interpreted unless a better SNR is achieved. Comparatively, Limestone and sandstone produce well-defined  $T_1$  and  $T_2$  relaxation curves. This could be due to a well-distributed pore network and the lack of magnetic impurity in these rock specimens.

Due to the various options provided by the Prospa software, the portable NMR settings will be varied later to obtain the best curves within the shortest time possible.



Figure 125. T<sub>1</sub> relaxation curves for saturated rocks.



(d) Limestone

Figure 126. T<sub>2</sub> relaxation curves for saturated rocks.

#### 5.4.2 Software Integration

The system has been designed to cater for a wide range of users. Modular is the general-purpose NMR development platform that is intended for those who are both knowledgeable and

unfamiliar about NMR. The software, therefore, needs to be able to support a range of users without compromising flexibility and performance. The types of users can be divided into a series of levels as follows:

- Non-NMR user, can operate using just one button.
- Standard NMR user, can access a set of provided control panels and pulse sequences.
- NMR developer, can design control panels, macros and high-level pulse programs.
- NMR expert, can develop pulse programs with "C" or Assembler for the DSP and new functions using the Prospa DLL interface.

Each of these different types of users are easily accommodated by simply building layers of software on top of each other and then restricting the user's access to the various layers. In the case of the user interface this can be implemented using the Prospa macro capabilities and in the case of the DSP/USB system this can be implemented by providing various pulse program development tools. Restricting users is important as the more privileges a user has the more damage they can do. Therefore the aim is to always try and keep users at the highest possible level [117].

The software integration consists of interfacing two parts. The Prospa software and the DSP pulse programs. The data transfer between the two parts can be found somewhere else [38, 117] where a virtual link between Prospa and the DSP/USB system was formed using a DLL that contained "MyAPI". However, a protocol is still required to define the method of passing parameters from Prospa to the DSP/USB system. The idea here is that Prospa sends a preassembled pulse program, together with some parameters, to the DSP/USB system and then requests that it execute it. Experiments such as a  $T_2$  experiment would be implemented by getting

the DSP/USB system to execute a spin echo pulse program multiple times but with different parameters. These parameters would be sent in between each individual execution. The way that was chosen to implement this is to develop a Prospa macro and a DSP pulse program for each type of NMR experiment. This is now demonstrated using the example of a spin echo experiment.

# 6 NONDESTRUCTIVE NMR EVALUATION OF THE DAMAGING EFFECTS OF ALKALI-SILICA REACTION ON CONCRETE

6.1 General

This chapter documents the application of nondestructive NMR techniques towards detection and characterization of progressive Alkali-Silica Reaction (ASR) in standard concrete specimens made with reactive aggregates exposed to accelerated ASR aging. Relaxation times and selfdiffusion coefficient were measured using the nondestructive NMR test system for specimens (prior to and) after different aging periods to study the formation of ASR gel and microcracks in cement-paste matrix. The formation of ASR gel and the subsequent imbibing of water into the gel alter the water distribution and binding condition in concrete. An increased concentration of water in ASR gel where it can exist in a distinct binding (mobility) condition is expected. The swelling of ASR gel is accompanied by formation of microcracks where water could reside in bulk form, and can create new structural gradients with respect to depth. The nondestructive NMR test data were interpreted in light of these effects of ASR aging on concrete structure, and distinct trends in NMR test data that point at the presence and extend of ASR were identified. Corroborative nondestructive tests were also conducted in order to verify the trends identified in NMR tests. These nondestructive tests involved measurement of ultrasound pulse velocity (UPV), dynamic elastic modulus, petrographic analysis, dye treatment and weight and volume changes.

#### 6.2 Introduction

There is a long-standing interest in identifying the occurrence of ASR in concrete and monitoring the extent of deterioration caused by it in a nondestructive fashion. Existing nondestructive inspection techniques provide information on the health condition of concrete, but generally cannot identify the causes of concrete deterioration [121]. The common practice employs nondestructive testing (or simply visual inspection) to make a general assessment of the health condition of concrete structures. In case problems are suspected, then destructive tests (e.g., petrographic examination of cores) are performed to gain more insight into the primary cause and the extent of deterioration. Given the prevalence of ASR in aging concrete-based infrastructure, there is a need for an expedient nondestructive method of identifying and quantifying the ASR damage [122, 123]. This investigation evaluates the merits of <sup>1</sup>H NMR relaxometry/diffusometry as an effective tool for addressing this need.

Among the nondestructive test techniques applied to the concrete infrastructure experiencing ASR, measurement of ultrasonic pulse velocity is probably most common [122-126]. Other than UPV, resonant frequency [121, 123, 127] and nonlinear acoustic methods [128, 129] have also been used, largely with laboratory specimens, to assess the ASR deterioration of concrete specimens. Stauffer et al. [130] compared UPV, resonant frequency and nonlinear acoustic methods of assessing the ASR damage in concrete specimens. UPV and resonance frequency tests were generally less sensitive to damage up to moderate to advanced stages of deterioration [121]. Rivard et al. [123] found that electrical resistivity is not effective in detecting the ASR damage because a number of parameters influence this concrete property. The <sup>1</sup>H NMR

relaxometry principles, which were used in this investigation for detection of ASR damage, are briefly introduced in the following.

NMR is a physical resonance phenomenon of magnetic atomic nuclei that precess in a magnetic field [38]. In conventional NMR, massive, superconducting magnets with field strengths of up to 22 T are used to analyze matter with high sensitivity. Since the object of interest needs to be located inside the test instrument, these magnets are not suitable for nondestructive analysis of large objects. Also, such magnets cannot be transported easily, as they are heavy and must be cooled with liquid nitrogen and liquid helium. This is why mobile permanent magnets were introduced to materials testing markets where the object of interest is positioned in the stray field outside the magnet. Portable NMR systems detect and analyze <sup>1</sup>H nuclei in the test object (thus the name <sup>1</sup>H NMR).

Two relaxation times for hydrogen nuclei within water molecules are generally measured in these <sup>1</sup>H NMR experiments: T<sub>1</sub>, the spin-lattice relaxation time, and T<sub>2</sub>, the spin-spin relaxation time. The T<sub>1</sub> is associated with dissipation processes from the spin system through all the other degrees of freedom (lattice). The T<sub>2</sub> controls the dephasing within the spin system. These times differ widely for chemically bound hydrogen, hydrogen adsorbed onto surfaces, hydrogen in water confined to small pores and large pores [62].

A typical measurement with portable NMR applies a string of rf impulses. The first impulse invokes an impulse response, which decays rapidly owing to the inhomogeneity of the stray field of the NMR magnet. Echoes of the original impulse response are recalled many times with the subsequent rf impulses. This way of measuring is referred to as the CPMG method (the name refers to its discoverers Carr, Purcell, Meiboom, and Gill) [53, 131]. The envelope of the CPMG

echo train, which decays with time, is recorded [132]. Its initial amplitude provides the proton density, which is proportional to the content of water and organic material in the test object. The relaxation times of hydrogen nuclei within water molecules are determined by the detailed dynamics and chemical and physical environment of the water. In consequence, the measurement of <sup>1</sup>H nuclear spin relaxation times provides information on pore-water interactions and water dynamics in concrete pore system.

Over the years, portable tools for <sup>1</sup>H NMR relaxometry have been developed and used for nondestructive investigation of heterogeneous and porous materials. NMR has provided valuable information related to time-dependent evolution of water in different states within concrete [63], changes in the pore size of hydrating cement [62], quantitative monitoring of water transport processes [115], the interconnection between solid content and pore size [69], and the pore size distributions and hydration kinetics in cement-based materials [49, 59, 60, 62, 63, 66, 69, 133]. This investigation focused on the application 1H NMR relaxometry/diffusometry to monitoring the progress of ASR in concrete.

Moisture is a key factor affecting ASR; it is the transport medium of ions, and also plays an important role in the expansion stage. The overall expansion and cracking of concrete under ASR attack is presumably caused by the sorption of water into the alkali–silica gel, which in turn causes swelling and internal damage as illustrated in Figure 127. Attraction of water by ASR gel, and the associated water transport phenomena could change the environment within (e.g. gel pores, interfacial transition zone and capillaries) which water molecules occur, and thus produce distinct <sup>1</sup>H NMR signals for identification of the ASR damage in concrete. The literature covering the theories of portable low-field <sup>1</sup>H NMR relaxometry can be found elsewhere [38].



Figure 127. Microstructure and mineralogy at aggregate-paste interfaces in concrete undergoing ASR [134].

In the work reported herein we investigated the effects of the presence of ASR gel and the extent of its formation in concrete specimens incorporating reactive aggregates exposed to accelerated aging. A two-step method is proposed to examine the reactivity of aggregates. After examination of aggregates, normal-strength concrete specimens were fabricated using these aggregates, with sodium hydroxide introduced in the mixing water. The resulting specimens were aged under accelerated conditions, and tested at different depths at different time periods using a portable NMR. Corroborative test methods were also performed in order to verify the portable NMR nondestructive test results. These corroborative tests included UPV, resonant frequency, optic microscopy of dye-treated specimens, and scanning electron microscopy.

#### 6.3 Materials and Methods

#### <u>Materials</u>

Cylindrical concrete specimens with 75 mm (≈3 inch) diameter and 150 mm (≈6 inch) height were fabricated using chert and flint (reactive) coarse aggregates (obtained from Fister Quarries, Illinois), limestone (non-reactive) coarse aggregate (obtained from Highgrade Materials, Michigan), siliceous (reactive) fine aggregate referred to as TX sand (provided by Texas DOT), and non-reactive fine aggregate referred to as MI sand (obtained from Builders Redi-Mix, Michigan). Type I Portland cement supplied by Lafarge was used as binder. A water-to-cement ratio of 0.49 was used to prepare all concrete mixtures with coarse aggregate content of 1096 kg/m<sup>3</sup> (1847) lb/yd<sup>3</sup>) and fine aggregate content of 737 kg/m<sup>3</sup> (1243 lb/yd<sup>3</sup>). This mix design is commonly used as normal-strength concrete in Michigan Department of Transportation construction projects. Table 27 presents the mix designs considered in this investigation as well as the method of accelerated aging (internal versus external, as described later in this section). Chemical compositions of the aggregates and cement used in this investigation, obtained by XRF spectroscopy, are presented in Table 28. Chert, flint and TX sand are observed to have relatively high silica contents. Although less than other siliceous aggregates, MI sand also has a relatively high silica content. The reactivity of all aggregates was tested via a two-step method described in the following.

Mix No.	Coarse aggregate	Fine aggregate	Water/Cement	Total Aggregate/Cement	Coarse Agg./Fine Agg.	Alkali Source
M1	Chert	TX sand	0.49	5.70	1.49	Internal
M2	Flint	MI sand	0.49	5.70	1.49	External
M3	Limestone	MI sand	0.49	5.70	1.49	External

Table 27. Concrete mix designs.

Table 28. Chemical compositions of aggregates and cement (weight percent).

Materials	Chemical Composition (%)											
	SiO <sub>2</sub>	CaO	$AI_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	$P_2O_5$	Sum	LOI
Chert	71.14	0.89	12.85	1.1	<0.03	0.04	3.88	4.23	0.06	< 0.01	94.19	5.52
Flint	72.82	2.02	9.46	8.3	0.07	1.37	1.5	2.8	0.59	0.18	99.11	0.59
Limestone	2.18	53.54	0.47	0.31	<0.03	2.21	< 0.01	0.21	0.02	< 0.01	58.94	41.18
MI sand	62.99	11.94	3.56	2.08	0.03	4.38	0.62	0.89	0.14	0.03	86.66	13.26
TX sand	70.86	8.24	7.16	3.03	0.04	0.31	1.6	2.32	0.4	0.07	94.03	5.76
Cement	20.2	62	4.7	3.1		3.8	0.68					2

#### Test Method for Assessment of the Aggregate ASR Susceptibility

A two-step test method was used to detect and verify the ASR susceptibility of aggregates. In the first step, a preliminary assessment of ASR susceptibility was made using the method suggested by Chatterji [135]. In this test, 60g of coarse aggregate (crushed to pass No. 4 sieve), TX sand and MI sand were collected. CaO powder (obtained from Sigma-Aldrich) and a saturated solution of KCI (at room temperature) were prepared. 120ml of the KCI solution together with 3.5g of CaO powder were placed in a glass tube and mixed thoroughly. The tube was then sealed and placed in an oven maintained at 70°C. At the same time, aggregates were placed in an oven at 70°C. Next morning, sand was added to the KCI-Ca[49]<sub>2</sub> solution and mixed thoroughly. The tube was sealed again, and returned to the oven. For the first 8 hours, the contents of the tubes were shaken at 2-hour intervals. After 24 hours, the tubes were stored in a water bath at 20°C for at least 3 hours; during this cooling period, the content of each tube was shaken at 2-hour intervals. The liquid phase of each tube was then filtered under suction through a 0.45mm membrane filter.

The OH<sup>-</sup> ion concentration of each of the filtrates was determined by titration against a 0.025N HCI solution using phenolphthalein as indicator.

In the second step, aggregates were used for preparation of mortar bars. Coarse aggregates were ground to less than 4.75mm [124 sieve] particle size (and not passing #200 sieve). Four mortar bars were prepared for each aggregate type according to ASTM C1260. The mortar bars were removed from molds after 24 hours, and placed in water at room temperature. The temperature of water was then raised to 80°C (176°F) in an oven, and the mortar bars were stored in this condition for 24 hours. After the bars were removed from water, their initial length was measured. They were subsequently submerged in a 1M NaOH solution at 80°C (176°F), where they were stored for 36 days. Length change measurements were made periodically during this storage period using a Humboldt length comparator.

The accelerated aging methods used with concrete specimens were either internal or external. For the purpose of internal accelerated aging, anhydrous sodium hydroxide (pellet) was added to the mixing water of concrete containing chert to boost the sodium equivalent (Na<sub>2</sub>O<sub>e</sub>) of concrete to 1.53%. In external aging (which was used with all other mixtures), tap water was used as mixing water, and the resulting specimens were submerged in 1M NaOH solution. The specimens were demolded after 24 hours, and cured in lime-saturated water for 28 days. Subsequently, for the purpose of internal accelerated ASR aging, concrete specimens were placed in a steam chamber at 100% RH and 80°C (176°F). In external accelerate aging, the specimens were submerged in 80°C (176°F) 1M NaOH solution. Test specimens were taken out and tested after 7, 18 and 30 days of accelerated ASR aging.

#### NMR Relaxomety & Diffusometry

NMR relaxometry tests were performed on concrete specimens prior to and after accelerated ASR aging. Relaxation times and self-diffusion coefficients were obtained non-destructively at various depths.

#### UPV, Dynamic Modulus and Weight Change

The ultrasonic pulse velocity (UPV) and dynamic modulus of elasticity were also measured for concrete specimens parallel with NMR testing. In addition, weight and volume changes of specimens were recorded over time.

#### Visual Observation

Cross sections of concrete specimens were treated by applying uranyl acetate and observed under UV light (ASTM C 856 and AASHTO T 299).

#### 6.4 Results and Discussion

#### 6.4.1 ASR susceptibility of aggregates

The titration test results are presented in Table 29. The first row in Table 29 shows the amount of HCI required for the reference solution containing no aggregate. The difference in Ca[49]<sub>2</sub> contents of the test mixture and a control mixture with a non-reactive aggregate corresponds to the amount of K<sup>+</sup> that has entered the hydrated lime–alkali–silica complex. The titrated solution of limestone (a carbonate rock) contains higher amounts of OH<sup>-</sup>, indicating lower tendency of this aggregate to react with the alkaline solution. Chert, flint, TX sand and MI sand, with high silicate contents, react with alkaline solution and leave lower amounts of OH<sup>-</sup> in the titrated solution. It should be noted that there are some silicate phases in limestone which react with  $OH^-$ . Therefore, the  $\Delta$  [ $OH^-$ ] is not equal to zero. The MI sand considered here has not been reported as alkali-reactive. Therefore, additional tests were performed to more thoroughly assess the reactivity potential of MI sand (among others).

Aggregate type	Titrated HCl (ml)	[OH⁻] (mg/l)	∆ [OH <sup>-</sup> ]
None	6.50	110.50	0
Limestone	4.12	70.10	40.40
Flint	0.53	9.01	101.49
Chert	0.86	14.62	95.88
MI sand	0.69	11.73	98.77
TX sand	0.98	16.66	93.84

Table 29. Summary of the titration data for aggregates.

In the next step, mortar bars were fabricated with crushed coarse aggregate and (as-received) fine aggregate. These specimens were subjected to alkali-silica expansion tests per ASTM C1260. This test method provides a means of detecting the potential of an aggregate to undergo deleterious alkali-silica reaction. It is based on the NBRI Accelerated Test Method [136]. This test is especially useful for aggregates that react slowly or produce expansion late in the reaction process. It does not evaluate combinations of aggregates with different cementitious materials; the test conditions also do not represent those encountered by concrete subjected to weathering effects. Aggregates were washed and dried, and then ball-milled in order to reduce large grains into smaller pieces as suggested by ASTM. Aggregates, cement and water were mixed in a mortar mixer at aggregate: cement: water weight ratios of 2.25: 1: 0.45. After the ingredients were mixed well, they were cast into molds. The molds were filled in two approximately equal layers, with each layer compacted using a tamper until a well-consolidated specimen was obtained. After demolding at 24 hours of age, the initial length was recorded using a Humboldt length comparator (which was also used for subsequent length measurements). Length change

measurements were performed per ASTM C490. The specimens were immersed in tap water. The container was then sealed and placed in an oven at 80°C (176°F). The expansion test results presented in Figure 128 indicate that chert is the most expansive of the aggregates considered in this investigation. Flint and TX sand exhibited an initially high rate of expansion, which dropped significantly after about 8 days.



Figure 128. Measured values of expansion versus time.

#### 6.4.2 XRD results

XRD was used to identify the major crystalline constituents of aggregates. The presence or absence of certain crystalline structures will help with evaluating potential susceptibility of aggregates to deleterious reactions in harsh alkaline solutions. Samples of aggregates were washed and dried, and then ground to produce fine powder. XRD was performed using a Bruker Davinci Diffractometer. The marked peaks in XRD spectrum of limestone (Figure 129) point at the existence of calcite as the backbone of mineral structure. No trace of dolomite was found in the XRD spectrum. In the case of flint, peaks pertaining to quartz are marked in Figure 130. Olivine and feldspar are the other common crystals in flint, which could not be identified in the x-ray spectrum generated for the specific flint aggregate considered in this investigation. Peaks marked with o could belong to Potassium Aluminum hydride; there is, however, inadequate evidence for confirming or totally rejecting its existence. The x-ray spectrum of chert, shown in Figure 131, is completely different from the other spectra. Chert is a textural variety of quartz that shares some properties with jasper. It contains considerable amounts of other silica species, mostly moganite [98] and perhaps opal. None of the expected crystalline structures, however, were observed in the x-ray spectrum. Several different varieties of chert deviate from the typically expected structures of this rock. Both MI and TX sands contain quartz as their primary mineral, as shown in Figures 132 and 133. The quartz crystals in TX sand seems to be more expansive based on micro bar testing, although titration data point out at roughly even degrees of reaction with hydroxyl ions for TX and MI sands.



Figure 129. XRD spectrum of limestone.











Figure 132. XRD spectrum of MI sand.



Figure 133. XRD spectrum of TX sand.

#### 6.4.3 NMR test results

Three Cylindrical concrete specimens with different aggregate types exposed to accelerated aging were examined with the portable NMR at room temperature (22-25°C).

 $T_1$  values were measured and Two-sample t-test was performed on all  $T_1$  values obtained (irrespective of depth) prior to and after exposure to the early stages of accelerated ASR. The  $T_1$  values for unaged specimens were considered as group 1 (Var (1)), and for exposed specimens as group 2 (Var(2)). T-test yielded a p-value of 0.960, accepting the null hypothesis at the 5% significance level. Hence, the change in  $T_1$  (longitudinal relaxation) produced at early stages of accelerated ASR exposure is not statistically significant. Furthermore, the t-test indicated that the  $T_1$  value of 7.8s (shown by asterisk in Figure 134a) is an outlier.

Normal probability plots were produced for the measured values of  $T_1$  in order to assess whether the test data have a normal distribution. For this purpose, cumulative distributions of the test data were drawn versus the theoretical cumulative distribution function of a normal distribution. In these plots (Figures 134b and 134c for unaged specimens and those exposed to early stages of
accelerated ASR, respectively. The horizontal axis corresponds to experimental results, and the vertical axis to the normal order statistic medians calculated using the uniform order statistic medians and the inverse cumulative distribution function (icdf) of the normal distribution. If the sample data has a normal distribution, then the plot appears linear. Distributions other than normal introduce curvature in the plot. The method superimposes a fit line onto the plot using a robust linear fit of the sample order statistics for the data in second and third quartile of the sample data. Then it extrapolates linearly to the minimum and maximum values in the sample to help visually assess the data in the tails. Figures 134b and 134c indicate that the measured values of  $T_1$  (at different depths) prior to and after exposure to early stages of ASR, respectively, follow normal distributions. Figure 134c further implies that the measured  $T_1$  value of 7.8 ms deviates from normal distribution, and is probably an outlier.



(c) Normal probably plot for specimens subjected to early stages of accelerated ASR aging

# Figure 134. Statistical evaluation of the measured values of $T_1$ .

Figure 135 displays the T<sub>2</sub> spin-echo decays (on the left) and the T<sub>2</sub> distributions obtained from Inverse-Laplace Transformation (on the right). For each mix design, these plots were obtained in control condition and after 7, 18 and 36 days of accelerated aging. The NMR signals were collected at 5mm depth from the surface of concrete specimens. The slice tested in concrete (nondestructively) is 40 mm by 40 mm in planar dimensions, and 0.65mm thick (also referred to as sensitive volume). Source of alkali for mix M1 was internal, while that for M2 and M3 was external. Two (fast and slow) decay components are present at the initial and later stages of relaxation. Correspondingly, the T<sub>2</sub> distribution shows the presence of more than one peak. The fast decay component is represented by the main bell-shaped peak with T<sub>2</sub> values ranging from 0.1 ms to 1ms, corresponding to gel pores and small capillaries. A couple of slower decay components appear in the T<sub>2</sub> range of 1 to 30 ms; the lower amplitudes at longer T<sub>2</sub> values correspond to larger capillaries, microcracks and voids.

Figures 135b, d and f show the T<sub>2</sub> distribution of concrete specimens. Concrete containing reactive aggregates (Figures 135b and d) exhibit a slight shift of the first peak (from left) after 7 days of accelerated aging. The shift moves to the right (larger T<sub>2</sub> values) as aging continues. This could result from the formation of ASR gel. At 36 days, the first and second peaks disappear for concrete containing chert (M1 in Figure 135b), and a new peak appears somewhere in between them. The amplitude of this peak decreases at later stages of accelerated ASR deterioration. ASR gel imbibes water from surrounding pores and cracks through capillaries [137], yielding amorphous hydrous silica. The trapped water in the amorphous gel is at lower energy states; therefore, the newly formed peaks shift towards left of the capillary pore peaks (second peak) [111]. Furthermore, as ASR gel swells, a network of microcracks forms with various lengths and

193

widths, which explain the widening and bell-shaped distribution of  $T_2$  values. Concrete containing flint (M2) seems to react slower, although the peaks tend to follow the same trends. Given a long enough aging time, a monomial distribution is expected for mix M2.



(a)



Figure 135. T<sub>2</sub> decays (left) and the T<sub>2</sub> distributions obtained from inverse Laplace transformation (right) of Mixes M1 (a,b), M2 (c,d) and M3 (e, f).



(c)



(d)



Using the peak fitting subroutine in MATLAB, peaks of the T<sub>2</sub> distribution curves prior and after exposure to ASR were obtained. The subroutine uses an unconstrained non-linear optimization algorithm to decompose a complex, overlapping-peak signal into its component parts. The results for sample M25A1 at 5mm depth are presented in Figures 136a and 136b for control and aged

specimens, respectively. The blue dots represent the test data obtained using the portable NMR. The red line is the fitted curve to the data. The green curves are the curves fitted to the peaks. For specimen M25A1 in control condition, 3 peaks are found at  $T_2 = 10^{-1.097}$  (0.08ms),  $10^{0.2607}$  (0.55ms) and  $10^{2.751}$  (563ms). Since the T values (on x axis) are in logarithmic scale, the actual T values are obtained by taking the values to the power of 10. After exposure to ASR, 2 distinct peaks are found at  $10^{-1.004}$  (0.1ms) and  $10^{-.0545}$  (0.88ms). These results suggest that although the first peak does not vary (0.08ms and 0.1ms), the second peak moves from 0.55ms to 0.88ms. This shift could be due to the contribution of newly formed ASR gel pores as well as the microcracks formed as a consequence of the ASR gel expansion.



Figure 136. The T<sub>2</sub> distribution peak fitting for the specimen M25A1 (a) in unaged conditions, and (b) after early stages of exposure to accelerated ASR condition.



(b)

The initial amplitude of the relaxation curves, which corresponds to total moisture content, increases for M1 and M2 (containing reactive chert and flint), but decreases slightly for M3 (containing limestone). Expansion and cracking in concrete materials experiencing ASR deterioration could be caused by the osmotic pressure resulting from the imbibing of pore solution by the ASR gel [138]. The interaction of the pore solution with the already formed gel leads to a significant macroscopic expansion of the material [22]. There would be a negligible reduction of expansion by the classical capillary shrinkage due to the transfer of capillary water to the ASR gel. One could argue that some shrinkage cracking could also occurs [20]. The apparent specific volume of silica in solution has been calculated at 0.384 mL/g SiO2 [21], that is nearly the same as the specific volume of  $\alpha$ -quartz at 0.377 (2.65 density) or chalcedony. Hence, the volume change associated with dissolution is negligible. XRD analyses of the aggregates used in this

experimental work confirmed the presence of quartz in sand and flint; no crystalline mineral was found in chert. Amorphous silica, however, could exist in various forms in chert. The significant expansion of microbars containing chert could be explained based on this observation. With progress of alkali-silica reactions, the resulting microcracks accommodate more water, and thus raise the initial decay amplitude.

The volume of water dwelling in concrete pores can be estimated using the initial amplitude of the relaxation decay curve [68, 139]. Figure 137 presents the percent change of the initial amplitude of decay curve (relative to control condition) over time, for mixes used in this study. The moisture content of Mix 1 (M1 – with internal source of alkali) increases steadily over time, pointing at a positive flow of water into the sensitive volume. This can be explained by the formation of ASR gel, and transport of water into this gel. Continuous flow of water to ASR gel causes swelling and cracking of concrete, which can then accommodate even more water with progress of ASR deterioration [140, 141]. The initial amplitude of Mix M2 decreases during the first 18 days of accelerated aging, and picks up after that. This could be due to the deposition of sodium salts within the pores and the associated consumption of water. After 36 days, the relative change is positive, indicating accumulation of water in the resulting cracks. The reduction of amplitude for Mix M3 (made with limestone) could also be due to the deposition of sodium salt in pores. Formation of microcracks is not expected in this mix due the inert nature of aggregates, which explains why moisture content does not increase with time.



Figure 137. Moisture content of concrete specimens as a function of the accelerated aging duration.

As mentioned earlier, the relaxation decay curve has a fast and also a slow relaxing component. Fitting a bi-exponential curve will yield two relaxation times, short T<sub>2</sub> and long T<sub>2</sub>, corresponding to slow and fast decay components, respectively. Figures 138 shows the short T<sub>2</sub> components of concrete specimens representing three different mix proportions subjected to accelerated ASR aging. Short T<sub>2</sub> is observed to generally increase with progress of ASR aging for concrete mixtures M1 and M2, while it is almost constant for M3. Mixes M1 and M2 were made with reactive aggregates; mix M1 was made with chert which seems to be more reactive. In addition, the source of alkali is internal in the case of mix M1, indicating that aggregates are readily surrounded by a highly alkaline pore solution that promotes ASR as soon as the specimens are fabricated. Mix M2, on the other hand, was subjected to external alkali attack where the alkaline solution needs to diffuse inward to reach aggregates with reactive silica phases. The concrete mix M3 was prepared with apparently non-reactive limestone, which explains why its short T<sub>2</sub> remained nearly constant under accelerated ASR aging.



# Figure 138. Effects of accelerated ASR aging on the short component of T<sub>2</sub> for three different concrete mixtures.

6.4.4 Corroborative tests

#### UPV and dynamic modulus of elasticity

The results of nondestructive UPV and dynamic modulus measurements are presented in Figures 139 and 140, respectively. The general trends point at a minor drop in UPV and a consistent drop in dynamic modulus with progress of aging for concrete mixes M1 and M2, which are expected due to the deterioration of these concrete mixtures that were made with reactive aggregates. Microcrack formation and growth around and within the reactive aggregates cause concrete degradation, which reflect upon the UPV and dynamic modulus measurements. The trends in nondestructive UPV measurements, however, are weak and statistically insignificant. Dynamic modulus measurements, which cannot be performed nondestructively in field, support the T<sub>2</sub> measurements made nondestructively using the NMR instrument. In both these experiments,

mixes M1 and M2 with reactive aggregates produce notable changes with progress of accelerated aging. Mix M3 with non-reactive aggregates, however does not experience any significant changes in dynamic modulus and T<sub>2</sub> values under exposure conditions that accelerate ASR aging. Both the top (exposed) surface was sprayed soon after placement and finishing of UHPC. Both these tests suggest that the pace of ASR attack picks up towards the end of the accelerated aging period considered in this investigation.



Figure 139. Ultrasound pulse velocity (UPV) of specimens prior to and after aging.



# Figure 140. Dynamic elastic modulus of specimens prior to and after aging. Uranyl treatment and visual observation

A freshly exposed concrete surface is sprayed with a solution of uranyl acetate, rinsed with water, and then viewed under ultraviolet light. Reacted particles and gel appear as bright yellow or green areas as shown in Figure 141 for concrete made of chert and flint.

As it appears, colored areas are more widespread in concrete containing chert. Reacted areas in concrete made of flint are lest wide spread. Moreover, yellow-greenish color tends to be more intense in mix M1 compared to M2. This could be due to the internal source of alkali and use of more reactive aggregate in mix M1.



Figure 141. Uranyl-acetate treated cross section of concrete (a) mix M1 (made of chert) and (b) mix M2 (made of flint).

## 6.5 Conclusions

<sup>1</sup>H portable NMR was used to study the alkali-silica reaction in concrete. 3 types of aggregates, namely chert, flint and limestone were incorporated into mix designs. Concrete specimens were subjected to accelerated aging conditions with external and internal sources of alkali at elevated temperatures. The specimens were tested nondestructively using <sup>1</sup>H portable NMR over time. Relaxation curves of unaged and aged concrete at various time intervals were compared to study the moisture content of concrete to allow to study the effect of ASR in moisture uptake and water transport in and out of concrete. Concrete containing reactive chert and flint experience increasing moisture uptake as accelerated aging continues while concrete containing non-reactive limestone seems to relatively unaffected in this regard. Relaxation times and their distributions were also determined to investigate the effect of ASR gel formation and consequent cracking on concrete pore system. Concrete made of chert seems to have a distinguished relaxation time distribution. Compared to chert, concrete made of limestone seems to be

unchanged over time and the relaxation time distribution does not vary significantly. The modulus of elasticity decreases for concrete containing chert and flint while it remains relatively constant for concrete made of limestone. The uranyl acetate treatment of concrete cross-sections indicated the presence of ASR products, especially around coarse aggregates.

# 7 NONDESTRUCTIVE EVALUATION OF FREEZE-THAW DAMAGE USING PORTABLE NMR

#### 7.1 General

The work presented herein covered application of a portable <sup>1</sup>H Nuclear Magnetic Resonance device for nondestructive evaluation of concrete subjected to freeze-thaw cycles. Concrete materials prepared with different aggregates and cementitious materials, with or without air entraining agent, were exposed to accelerated freeze-thaw aging. They were subjected to <sup>1</sup>H NMR at testing at different stages of accelerated aging. The NMR relaxation decay curves, the relaxation time distributions and other relaxation parameters were used to evaluate the effects of freeze-thaw cycles on concrete microstructure and the associated water transport properties. The NMR test data confirmed that air-entrained concrete made with aggregates of low porosity experienced minimal damage after exposure to 450 cycles of freezing and thawing in water. Use of fly ash as partial replacement for Portland cement did not compromise the freeze-thaw durability of concrete. The NMR test data also confirmed that non-air-entrained concrete as well as concrete made with porous aggregates were susceptible to freeze-thaw damage. The effects of concrete deterioration under freeze-thaw attack on water transport processes were investigated nondestructively using the NMR device. Comparisons were made between the capabilities offered by NMR versus other nondestructive test methods for monitoring concrete deterioration under freeze-thaw attack. A distinguishing feature of NMR relaxometry was found to be its ability to monitor damage at a particular depth, and to quantify the extent of concrete deterioration. The freeze-thaw damage to concrete microstructure was also evaluated via scanning electron microscopy in order to verify the trends established nondestructively via NMR relaxometry.

#### 7.2 Introduction

#### Freeze-thaw effects on concrete

The damage caused by repeated freezing and thawing of water can lead to deterioration of concrete in cold climates. Degradation of concrete exposed to freeze-thaw cycles can be categorized into surface scaling and internal crack growth [142]. Surface scaling, which is the loss of cement paste or mortar from the surface, could lead to loosening of coarse aggregates in extreme cases. Use of deicing chemicals exacerbates surface scaling. Various experimental results have shown that the mass loss ratio due to scaling does not exceed 5% even after prolonged freeze-thaw cycles [143]. Internal cracking under freeze-thaw cycles in the presence of moisture results in disintegration and eventual total deterioration of concrete. Internal cracking of concrete exposed to freeze-thaw cycles is caused by the accumulation of microcracks due to stress buildup in concrete. The buildup of stress results primarily from partial freezing of the concrete pore solution [103, 144], which prompts a tendency towards forceful redistribution of water within the concrete pore structure [115]. Entrainment of concrete with fine, closely spaced air voids reduces the extent of stress buildup under frost action by providing closely spaced escape boundaries for the pressured water to enter air voids that remain partly empty (of water) even in saturated concrete, thus relieving pressure and reducing the extent of freezethaw damage

Forceful water transport phenomena induced by the freezing of bulk water in larger capillary pores is believed to be the primary cause of expansion in concrete under freeze-thaw attack [145]. The theory proposed by Litvan [146] indicates that the rigidly held (physically bound) water in C-S-H interlayers and in finer (0.5-5 nm) capillary pores cannot rearrange to form ice at the normal freezing point of water because the mobility of water existing in an ordered state is rather limited. Therefore, when a saturated cement paste is subjected to normal freezing temperatures, water in larger cavities turns into ice (i.e., assumes a low-energy state) while the physically bound water continues to exist as liquid water in a supercooled (high-energy) state. The thermodynamic disequilibrium between water in different states forces migration of water from the high-energystate locations towards larger capillary pores and cavities where water has assumed a lowerenergy state via freezing. The continuous supply of water from gel and finer capillary pores increases the volume of ice in larger capillary pores steadily until there is no room to accommodate more ice. Any subsequent tendency for the supercooled water to flow toward the ice-bearing regions would produce internal pressure, expansion and cracking of the system. It should be noted that the moisture transport associated with frost action may not necessarily lead to visible concrete deterioration (e.g., formation of visible surface cracks). Deterioration is triggered when the rate of moisture transport is less than that demanded by the situation, and accumulates under repeated cycles of freezing and thawing.

The goal of the work reported herein was to monitor water transport phenomena and their impact on the concrete microstructure and health condition. In that respect, evaluation of the state and the distribution of water molecules within the paste is crucial. Nuclear Magnetic Resonance (NMR) is a nondestructive method that can provide this information. It is now well

208

established that <sup>1</sup>H NMR measurements of proton relaxation times enable nondestructive monitoring of the dynamic transport processes of water in concrete [71]. This technique also enables evaluation of concrete porosity and pore size distribution [60, 68]; it can be used to gain information on the mobility states of water in capillaries and gel pores [67].

NMR could be helpful in studying the water transport phenomena under freeze-thaw effects, and the associated impact on the pore network of concrete. In this work, concrete specimens with different raw materials and mix designs were prepared and exposed to freeze-thaw cycles in the presence of water. NMR relaxation data were obtained nondestructively at different depths after different periods of exposure to freeze-thaw cycles. Other nondestructive test methods involving ultrasound pulse velocity (UPV) and dynamic modulus measurements were also used to monitored concrete deterioration under freeze-thaw attack. The cross-sections of concrete specimens exposed to cycles of freezing and thawing were evaluated via scanning electron microscopy in order to gain further insight into the extent of concrete deterioration.

### 7.3 Experimental Program

Four groups of concrete specimens were prepared. The coarse aggregate type, presence of airentraining agent, and composition of the cementitious binder were varied in these four mixtures (Table 30). Nine 3in × 6in (7.5mm × 15mm) cylindrical concrete specimens were fabricated and cured per ASTM C192 with each mix design.

Mix #	Cementitious Binder	Coarse Aggregate Type	Air Entrained
M1	Type I Cement	Limestone	Yes
M11	Type I Cement & Class F Fly Ash	Limestone	Yes
M14	Type I Cement	Limestone	No
M23	Type I Cement	Lightweight - Slag	Yes

Tab	le	30.	Concr	ete	mix	designs
-----	----	-----	-------	-----	-----	---------

The specimens were subjected to 28 days of moist curing via immersion in lime-saturated water. They were then subjected to repeated cycles of freezing and thawing in water per ASTM C666. For this purpose, the specimens were submerged in water where temperature varied between 4.4 and -17.8°C (40 and 0°F) in equally timed cycles. The cylindrical specimens were subjected to NMR and other nondestructive tests after exposure to 65, 230 and 450 cycles of freezing and thawing.

Nondestructive NMR relaxometry experiments were performed on concrete specimens in order to capture the effects of freeze-thaw cycles on the concrete microstructure. The transverse relaxation times (T<sub>2</sub>) was measured at different depths after exposure to freeze-thaw cycles. The ultrasound pulse velocity and the dynamic modulus of concrete specimens were also measured nondestructively in order to provide partial verification for the NMR test data. The weight and volume changes of concrete specimens were also measured at different stages of freeze-thaw attack in order to gain further insight into the effects of freeze-thaw cycles on concrete specimens. At later stages of deterioration, sections were cut into the deteriorated specimens for visual evaluation as well as optic and scanning electron microscopy.

#### 7.4 Results and Discussion

#### 7.4.1 Visual observations

Examples of test specimens after exposure to 450 cycles of freezing and thawing in water are shown in Figure 142. Specimens made with Mixes M1 and M11 exhibited light scaling; those made with Mixes M14 and M23, on the other hand, experienced severe scaling. The scaled regions of the specimen surfaces were avoided when NMR tests were performed.

210





Figure 142. Test specimens after exposure to 450 cycles of freezing and thawing: (a) Mix M1; (b) Mix M11; (c) Mix M14; and (d) Mix M23.

7.4.2 NMR relaxometry

The relaxation decay curves for the concrete mixtures considered in this investigation were obtained using the CPMG pulse sequence with 256 echoes and 1024 scans. The resulting relaxation decay curves for all mix designs at different depths are presented in Figure 221. Mixes M1 and M11 were prepared using air-entraining agent and low-porosity aggregates to endure freeze-thaw cycles. The relative reduction of decay curves versus depth prior to aging (Figures 143a and 143c) is expected in these mix designs. The moisture content of concrete generally decreases with increasing depth, and the moisture left at smaller depths is less mobile. The decay curves have a lower initial amplitude at lower depths. Similar trends with depth are observed in the decay curves of Mixes M1 and M11 after 450 cycles (Figures 143b and 143d). The addition of air entraining agent and the use of low-porosity aggregates seems to have kept the moisture gradient almost unchanged throughout the depth. In contrast, mixes M14 and M23, that were prepared to be susceptible to freeze-thaw attack (without air-entraining agent and with low-porosity aggregates, respectively), exhibit different trends in relaxation decay curves. As noted in Figures 143e and 143g, the initial amplitude and the rate of decay are similar to other mixtures prior to accelerated aging. The moisture gradient in unaged condition seems to remain unaffected throughout the depth by the measures taken to accelerate their degradation under freeze-thaw attack. After exposure to freeze-thaw cycles, however, different relaxation patterns are noted. This could be due the nature and the depth gradient of the damage caused by freeze-thaw cycles, and corresponding effects on moisture gradient and the mobility of water at different depths.

The relative change in the initial amplitude with depth for different concrete mixtures is shown in Figure 144. The initial amplitudes are larger for Mixes M1 and M11 in aged versus unaged specimens

Figure 144 shows the relative change in the initial amplitude of concrete with respect to depth. The amplitude gradient after accelerated aging in Mixes M1 and M11 is smaller than and similar to, respectively, to that before aging. In Mixes M14 and M23 which are susceptible to freezethaw attack, however, the amplitude gradient with depth increases after aging.

212



Figure 143. Relaxation decay curves of different concrete materials prior to and after accelerated freeze-thaw aging.



Figure 144. Relative change of amplitude with depth for: (a) Mix M1; (b) Mix M11; (c) Mix M14; and (d) Mix M23.

#### T<sub>1</sub> measurements

Determination of  $T_1$  is less prone to artifacts caused by water molecule diffusion in field inhomogeneities, and may thus be considered suitable for investigating the freeze-thaw damage in concrete [59]. The values of  $T_1$  measured at different depths for three specimens subjected to various numbers of freeze-thaw cycles are presented in Figure 145. The general trends suggest a gradual increase in  $T_1$  with the progress of freeze-thaw degradation. In order to check this hypothesis, t-tests were performed on the  $T_1$  values measured after different freeze-thaw cycles.  $T_1$  values prior to exposure to freeze-thaw cycles (*Var(1)*) and after 230 cycles (*Var(2)*) were used subjected to statistical analysis. The T-test yielded a p-value of 0.272, which is not excessively large to reject the null hypothesis of rise in in  $T_1$  under freeze-thaw cycles. However, the p-value of 0.272 obtained at this level of freeze-thaw damage is still relatively large, and the test will be repeated after application of further freeze-thaw cycles. The graph generated in t-test (Figure 146) points at a notable rise in the median value of  $T_1$  (compare the red and blue box plots). The normal distribution of  $T_1$  values before and after damage, and the relative shift of the bell-curve to higher  $T_1$  values after exposure to freeze-thaw cycles are also noteworthy.



(b)

Figure 145. T<sub>1</sub> values measured for concrete specimens (a) M23FT1, (b) M23FT2, (c) M23FT3.



Table 31. Summary of  $T_{1}\ measurements.$ 

Variable	Mean Difference	95.00% Confidence Interval Lower Limit Upper Lim		t	df	<mark>p-Value</mark>
VAR(1) VAR(2)	-1.556	-4.451 1.340		-1.139	16.000	<mark>0.272</mark>
	15 10 5 -		T T T T T T T T T T T T T T T T T T T	• VAR(	1)	

Figure 146. Two-sample t-test graph for measured values of  $T_1$  prior to and after deterioration under freeze-thaw cycles.

4

8

Count

0 L 12

8

4

Count

0

o ×

0 12 VAR(2)

The NMR relaxation time distributions are presented in Figure 147. Two general trends are observed in all relaxation time distributions regardless of the mix proportions. Two distinct peaks are commonly observed for unaged specimens. One peak occurs around 1ms (pertaining to gel pores and small capillaries), and the other is larger than 1ms (corresponding to large capillaries, voids and microcracks). After exposure to freeze-thaw cycles, the second peak starts to diminish. This phenomenon can be explained by the water transport processes associated with freezing and thawing. During thawing, the gel pores are expected to take up water from capillaries and external surfaces due to the gradient generated in water redistribution during freezing. Additionally, a general shift in T<sub>2</sub> towards smaller values is observed. This trend corresponds to saturation of small pores which in turn reduces the mobility water confined in these pores. This shift is more pronounced for Mixes M14 and M23.



Figure 147. Relaxation time distributions.

The short and long relaxation times were obtained using a bi-exponential fit to the decay curve. The relative change of each relaxation time with respect to depth are presented in Figure 148. For Mixtures M1 and M11 which are freeze-thaw resistant, the relative changes in short and long T<sub>2</sub> times with respect to depth are similar prior to and after aging. For Mixes M14 and M23 that are susceptible to freeze-thaw damage, however, the short and long T<sub>2</sub> gradients with respect to depth become steeper after aging. This trend seems to be the marker for identifying the freezethaw deterioration of concrete via nondestructive NMR testing. It can be attributed to the rise in the rate of moisture movement towards the surface due to the freeze-thaw deterioration of concrete.



Figure 148. The relative change in the short and long components of T<sub>2</sub> for different concrete mixtures.

One-way Analysis of Variance (ANOVA) was performed to estimate the effects of the three levels of freeze-thaw damage considered so far (i.e., control, 65 and 230 freeze-thaw cycles) on the short component of T<sub>2</sub>. The resulting p-value for ANOVA was 0.2 (Table 43). Although the desired value is 0.05, a p-value of 0.2 is relatively small and indicates a rather meaningful trend in the freeze-thaw effects on the short component of T<sub>2</sub>. The calculated least squares means of T<sub>2</sub> values, shown in Figure 149, suggests a decreasing trend of the short component of T<sub>2</sub> with the progress of freeze-thaw damage. This drop in T<sub>2</sub> could be because the drive for moisture transport towards sites of ice formation subjects the water in gel pores to pressure, thus lowering their entropy and the short component of T<sub>2</sub> which corresponds to gel pores.

Table 32. Outcomes of the analysis of variance of the short component of T2 measured after different numbers of freeze-thaw cycles



Damage Level



The measured values of the large component of T<sub>2</sub> for all specimens and depths were also subjected to analysis of variance in order to assess the effects of the number of freeze-thaw cycles. Table 33 summarizes the outcomes of this analysis of variance. The resulting p-value of 0.403 indicates that freeze-thaw cycles do not significantly alter the large component of T<sub>2</sub>. Figure 150 shows a mean trend towards increasing values of the long T<sub>2</sub> component with progress of freeze-thaw damage. The relatively large variations of the measurements made at each level of freeze-thaw damage, however, undermine the statistical significance of this trend. This effect of freeze-thaw cycles will be further assessed at more advanced levels of freeze-thaw damage.

Table 33. Outcomes of the analysis of variance performed at different levels of freeze-thaw damage on the long component of T<sub>2</sub>.



Figure 150. Effects of freeze-thaw damage on the long component of T<sub>2</sub>.

#### 7.4.3 Ultrasound Pulse Velocity (UPV) and Dynamic Elastic Modulus

The velocity of ultrasonic pulse and the dynamic modulus of elasticity of concrete were also measured in unaged condition and after 65, 230 and 450 freeze-thaw cycles. At least 3 specimens were tested, and the results were averaged. Figures 151a and 151b show the changes in UPV and elastic modulus, respectively, of different concrete mixtures with progress of freeze-thaw damage. For Mixes M1 and M11, which were designed to resist freeze-thaw damage, the drops in UPV and dynamic elastic modulus were minor and statistically insignificant. These trends were more pronounced for Mixes M14 and M23 which were susceptible to freeze-thaw attack.



■ Control ■ 65 cycles ■ 230 cycles ■ 450 cycles

(b) Dynamic elastic modulus

Figure 151. Effects of freeze-thaw cycles on UPV and dynamic elastic modulus.

#### 7.4.4 Scanning Electron Microscopy

Cross sections of concrete specimens subjected to 450 cycles of freezing and thawing were examined using a scanning electron microscope. The interfacial transition zones, aggregates and cement-paste were observed. The SEM micrographs are presented in Figure 152. SEM images of Mix M1 showed minimal cracking. Figure 152a shows some of the microcracks found in specimens made with Mix M1. These cracks are less than a few micrometers wide and 1mm long. Minimal cracking was also observed in mix M11. The crack lengths and widths were of the same size as in M1. In contrast, wide and long cracks were found in the non-air-entrained mix M14. The cracks found in this case were at least 10 micrometer wide and a few millimeter long. Some cracks were found to surround aggregates or run throughout the paste. Similar observations were made, but to a lesser extent, for mix M23 that was air-entrained but made with porous aggregate. The lack of air entrainment seemed to make a greater impact on the width and length of cracks formed under freeze-thaw attack when compared with the use of aggregates of high porosity.



(a) Mix M1



(b) Mix M11



(c) Mix M14



(d) Mix M23



### 7.5 Nondestructive NMR Testing at the Michigan Department of Transportation

Michigan Department of Transportation (MDOT) receives aggregates from quarries to perform tests for evaluating their quality versus the MDOT, AASHTO and ASTM specifications. MDOT has been supportive of this research, and has provided us with access to their facilities for testing purposes. In the latest testing at MDOT, three freeze-thaw beams (Figure 153) were evaluated using a portable NMR. These prismatic (16" by 4" by 4") beams were made with different aggregates received by MDOT. The beams have been subjected to freeze-thaw cycles over a onemonth period.





(b)



(c)

Figure 153. The beams subjected to freeze-thaw cycles by the Michigan DOT.
The beams were saturated in water for 24 hours prior to NMR testing. The NMR experiments (Figure 154) measured the relaxation decay curves, the relaxation time distribution, and the self-diffusion coefficient. These measurements were made at 2, 4 and 6mm of depth.



# Figure 154. NMR testing of freeze-thaw beams at the MDOT facility.

Figure 155 presents the relaxation decay curves of beams at depths of 2, 4 and 6mm. The initial amplitudes for beams '41-148' and '82-019' decreased with increasing depth. The initial and secondary rates of relaxation seem to be unaffected by depth. The initial amplitudes for beam '58-011' were rather similar at different depths. Additionally, the secondary rate of relaxation decreased with increasing depth. Based on the trends established previously, we can assume that beam '58-011' experienced more deterioration under freeze-thaw cycles when compared with the other two beams.



Figure 155. Relaxation decay curves of the beams subjected to freeze-thaw cycles.

The relaxation time distributions were obtained via inverse Laplace transformation of the decay

curved in order to produce further insight into the presence and extent of damage. The resulting

relaxation time distributions are presented in Figure 156. Figures, 156a and 156c show minimal shift in T<sub>2</sub> and amplitude with respect to depth. The shift in the second peak for beam '58-011' (Figure 156b) seems, based on the trends established previously, to be affected the most by freeze-thaw both in amplitude and shift. The amplitude of the first peak in Figure 156b has decreased significantly at 6mm depth. To confirm these observation, the short and long T<sub>2</sub> components were obtained using the relaxation decay curves.



Figure 156. Relaxation time distributions of the freeze-thaw beams.



The short and long components of T<sub>2</sub> were obtained at different depths (Figure 157). The short value of T<sub>2</sub> seems to remain constant (i.e., unaffected by freeze-thaw cycles) in all three beams. The long component of T<sub>2</sub>, however, increased significantly with increasing depth for beam 58-011 (Figure 157b). The increase in long T<sub>2</sub> with depth, based on the trends established earlier, provides an indication of freeze-thaw damage (microcracking, etc.) that increases the accumulation of water in capillaries and microcracks. For better understanding of widening of microcracks and capillaries, the self-diffusion coefficient of water was also measured at different depths.





Figure 157. Relative changes in the short and long components of  $T_2$  with depth. The absolute value of the self-diffusion coefficient (D) is significantly larger for the beam '58-011'

(Figure 158b) when compared with beams '41-148' (Figure 158a) and '82-019' (Figure 158c). In

the case of beam '82-019' (Figure 158c), D is relatively large (about 0.2  $m^2/s$ ) at 4mm depth, which could point at local damage at this depth.



Figure 158. Self-diffusion coefficient for beams subjected to freeze-thaw cycles.

The measured values of dilation for the beams exposed to freeze-thaw cycles, and the short and long values of T<sub>2</sub> measured via NMR relaxometry are plotted in Figure 159. Beam '58-011' dilated the most (about 0.15 inch) compared the other two beams. The average value of the large T<sub>2</sub> value was also the highest for this beam, pointing at the greater freeze-thaw deterioration experienced by this beam. This finding is also confirmed by the relaxation decay curves and the T<sub>2</sub> distributions obtained nondestructively via NMR relaxometry.



(b) Short and long components of T<sub>2</sub>



### 7.6 Conclusions

The use of a portable NMR relaxometer towards nondestructive identification and quantification of the freeze-thaw deterioration of concrete was demonstrated. NMR relaxometry was found to provide insight into the damaging effects of freeze-thaw cycles, and the consequent changes in the moisture transport attributes of concrete. Moreover, the depth profiling capability of portable NMR proved to be a valuable feature for identifying the freeze-thaw deterioration of concrete. For concrete mixes prone to freeze-thaw damage, relaxation decay curves suggested that the moisture gradient with respect to depth remained unaffected by exposure to freezethaw cycles. The measured value of the initial amplitude at the concrete surface, however, was larger after exposure to freeze-thaw aging and decreases into depth. This could be due the surface microcracks formed under freeze-thaw cycles, and the moisture gradient formed as a consequence. The relaxation time distributions pointed at an increasing shift towards smaller relaxation times which correspond to the saturation of small pores where water resides largely in a confined and less mobile state. This shift was more pronounced for concrete mixtures that were more susceptible to freeze-thaw attack. Both short and long T<sub>2</sub> values remained constant with respect to depth for mixes that were resistant to freeze-thaw attack, while they changed with respect to depth for mixes that were susceptible to freeze-thaw attack. The relative change in the short and long components of the relaxation time with respect to depth also pointed at the value of this gradient as an indicator of the freeze-thaw deterioration of concrete.

Although UPV and dynamic modulus of elasticity showed a drop in integrity of concrete under freeze-thaw attack, the corresponding trends were not as strong as those in NMR signals. They also did not produce the multitude of signals that reflected on various damage phenomena and

234

consequences under freeze-thaw attack. Scanning electron microscopic observations confirmed that the extent of damage was greater in concrete materials that were designed to be more susceptible to freeze-thaw attack.

Moreover, nondestructive NMR relaxometry/diffusometry tests were performed on prismatic concrete beams prepared with different aggregates, and subjected to freeze-thaw cycles by the Michigan DOT. Relaxation decay curves indicated that for two of the three beams the initial decay amplitude decreased with respect to depth. The initial and secondary rate of relaxation were unaffected by depth. For the third beam, however, the initial amplitudes were almost constant at different depths. Additionally, the secondary rate of relaxation decreased with respect to depth. Based on the trends established previously, the NMR test data indicate that the third beam experienced more freeze-thaw damage than the other two beams. The short value of the transverse relaxation time (T<sub>2</sub>), measured nondestructively via NMR relaxometry, was constant with respect to depth in all three beams. The long value of  $T_2$ , however, increased significantly throughout the depth for the third beam. The increase in long T<sub>2</sub> is, based on the trends established earlier, an indicator of microcracking and pore widening under freeze-thaw cycles, which leads to further accumulation of water in capillaries and microcracks. In parallel, the absolute values of self-diffusion coefficient are the largest for the third beam. The values of dilation resulting from exposure to freeze-thaw cycles, measured by the Michigan DOT, correlated well with the nondestructive NMR test data. The third beam, which experienced more freeze-thaw damage per NMR test results, also experiences the greatest dilation under exposure to freeze-thaw cycles.

# 8 NONDESTRUCTIVE NMR EVALUATION OF THE DAMAGING EFFECTS OF CARBONATION ON CONCRETE

### 8.1 Abstract

Concrete exposed to air of moderate relative humidity experiences carbonation which have adverse effects on the dimensional and chemical stability of the hydrated cement paste, and its ability to protect reinforcing steel against corrosion. Various factors, such as diffusivity and use of pozzolans, influence the rate and extent of carbonation of the hydrated cement paste in concrete. The NMR nondestructive test method could provide easy and rapid information on the evolution of concrete microstructure as it undergoes carbonation reactions. In this chapter, NMR relaxometry and diffusometry measurements were performed on concrete materials exposed to accelerated carbonation effects. Corroborative (UPV and dynamic modulus) nondestructive tests were also performed in order to substantiate the NMR test results. Scanning electron microscope images of control and aged specimens were also obtained in order to assess effects of carbonation on the microstructure of concrete, and to produce information that could support the nondestructive NMR measurements.

## 8.2 Carbonation of Concrete

The hydrated cement paste is prone to carbonation reactions in air at moderate levels of relative humidity. The carbon dioxide in air dissolves in pore solution; the resultant carbonate anions react with the calcium cations in the pore solution, and precipitate calcium carbonate with very low solubility [147]. Carbonation attack initially takes place on calcium hydroxide which has some solubility; it can eventually extend to calcium silicate hydrate when the integrity of the hydrated cement paste would be compromised. There are shrinkage movements associated with carbonation. The alkalinity of pore solution would also be lowered as a result of carbonation, which compromises the ability of the hydrated cement paste to protect the embedded steel against corrosion.

Carbon dioxide currently constitutes 0.04% of the Earth's atmosphere [148]. Gaseous CO<sub>2</sub> cannot react directly with cement hydrates. The CO<sub>2</sub> gas must first dissolve in water and form carbonate anions which react with the Ca ions of the pore solution. The type of carbonate ions formed in water depends on the pH of the pore solution. When CO<sub>2</sub> comes into contact with water at neutral pH, it forms bicarbonate. The pH of pore solution in concrete, however, is high; as a result, bicarbonate dissociates and forms carbonate ions [149]. Hence, after some period of carbonation, bicarbonates can form near the surface where pH has dropped as a result of carbonation. Inside concrete, where carbonation has not progressed, carbonate ions would be more prevalent in the concrete pore solution. The calcium carbonate formed as a result of carbonation reactions in concrete generally comprises calcite and vaterite [150, 151].

The carbonation process in concrete can be described by the following chemical equations [149]:

1. 
$$CO_2(g) + H_2O = HCO_3^{-}$$
 (bicarbonate ion) + H<sup>+</sup>

2.  $HCO_3^- = CO_3^{2^-}$  (carbonate ion) +  $H^+$ 

The carbonate ion will react with the Ca ions in the pore solution:

3.  $Ca^{2+}+CO_3^{2-}=CaCO_3$ 

This will yield a lower concentration of Ca<sup>2+</sup> which in turn causes dissolution of primarily calcium hydroxide (CH) (solubility of carbonate crystals is much lower than that of CH):

4. 
$$Ca(OH)_2 = Ca^{2+} + 2OH^{-}$$
 (solubility 9.95 x 10<sup>-4</sup>)

5. 
$$Ca^{2+} + CO_3^{2-} = CaCO_3$$
 (solubility 0.99 x 10<sup>-8</sup>)

Carbonation of concrete can be deleterious because: (i) it induces near-surface shrinkage which can produce restrained shrinkage microcracking/cracking; (ii) it lowers the pH of the concrete pore solution [152] which compromises the protective role of concrete against corrosion of reinforcing steel [153-155], and also it compromises the chemical stability of cement hydrates. At the same time, carbonation can yield some positive effects associated with the densification of concrete and blocking of its capillary pores.

Carbonation starts from the surface of concrete, and penetrates deeper over time at a rate that is proportional to the square root of time. For a moderate relative humidity, the depth of carbonation reaches about 1 mm after about one year for concrete that has a dense microstructure and a low diffusivity (i.e., a low water/cement ratio). The depth of carbonation after one year in moderate humidity can reach 5 mm for concrete of high diffusivity (i.e., high water/cement ratio).

# 8.3 Materials and Methods

Four concrete mixtures with different strength levels, cementitious binder compositions and chemical admixtures (Table 34) were used in carbonation experiments

Mix #	Mix Design	Cementitious Binder	Coarse Aggregate Type	Chemical Admixtures	Cure/Surfa ce Treat
1	Normal- Strength	Type I Cement	Limestone	Air-Entr. Agent	Moist/Non e
11	Normal- Strength	Type I Cem & Class F Fly Ash	Limestone	Air-Entr. Agent	Moist/Non e
16	High-Strength	Type I Cement & Class F Fly Ash	Limestone	AEA & HR Water- Reducer	Moist/Non e
19	High-Strength	Type I Cem & Silica Fume	Limestone	AEA & HR Water- Reducer	Steam/Non e

Table 34. The concrete mix proportions used in the carbonation experiments.

A TS Auto Flow carbonation chamber (Figure 160) was used to accelerate carbonation of concrete specimens. Figure 161 shows the schematics of the accelerated carbonation test setup. The relative humidity of the system was maintained using a dehumidifier. A timer is used to control the system operations. The timer switches the system on for 15 min, and off for 15 min. This maintains a relative humidity at 65±5%. Temperature of the system was maintained at 20±2°C. A pressure regulator mounted on the CO<sub>2</sub> supply tube was used to control the pressure inside the accelerated carbonation chamber. The  $CO_2$  concentration of the chamber was fixed at 1%. Concrete specimens were placed in the chamber, and were exposed to 1% CO<sub>2</sub> environment. This is a relatively low concentration when compared with the alternative accelerated carbonation test methods used in the literature. After 1 month, the concrete specimens were removed from the chamber for testing. The extent of carbonation, however, was found to be minor. As a result, the accelerated test method proposed by Atis [156] was implemented. In this method, a standard cylinder containing 5% CO<sub>2</sub> and 20% O<sub>2</sub> Nitrogen supplies gas to the test chamber. The following steps were taken to implement this procedure [156]:

1. Start with the apparatus full of air at ambient condition;

- 2. Pressurize with the CO<sub>2</sub>-containing gas blend by running pump to reach 2.5% CO<sub>2</sub> at 1 bar above ambient, then release the pressure through vent to reach the ambient level;
- 3. Repeat Step 2 to reach 3.75% CO2 at ambient condition;
- 4. Repeat Step 2 to reach 4.375% CO2 at ambient condition;
- 5. Pressurize to reach approximately 4.70% CO<sub>2</sub> at 1 bar above ambient.
- 6. Pressurize to reach approximately 20% CO<sub>2</sub> at 1 bar above ambient.



Figure 160. Carbonation test chamber.

The accelerated carbonation test was initiated for concrete specimens of 14, 28 days and 3 months of age. The specimens removed from the curing chamber were placed directly in the

accelerated carbonation chamber. Surfaces of the moist-cured concrete specimens were dried prior to placing them in the carbonation chamber. Air-dried specimens were also placed in the carbonation chamber together with the specimens that were transferred to the carbonation chamber immediately after moist curing. Exposure of the concrete specimens to accelerated carbonation was continued for two weeks. Subsequently, the specimens were removed from the carbonation chamber, and the depth of carbonation was measured by treating the surface of a freshly broken concrete cube specimen with a pH indicator that was a 1% solution of phenolphthalein in water. In this test, the non-carbonated part of the specimen, where concrete was still highly alkaline, a purple-red coloration is obtained; no coloration occurs in the carbonated part of the specimen where alkalinity has dropped [156]. <sup>1</sup>H NMR relaxometry and diffusometry as well as the corroborative nondestructive tests were performed on specimens after different exposure intervals.



Figure 161. Schematics of the accelerated carbonation test set-up [156].

# 8.4 Results and Discussions

# 8.4.1 NMR relaxometry

Nondestructive NMR relaxometry and diffusometry tests were performed on concrete specimens made with the mix proportions introduced in Table 34 prior to and after accelerated carbonation. The T<sub>2</sub> relaxation (decay) curves were obtained using the CPMG pulse sequence (Figure 162). The initial (maximum) relaxation amplitude was observed to decrease with increasing depth. This trend was more pronounced for Mixes M1 and M11 (in Table 34) when compared with Mixes M16 and M19.



Figure 162. Relaxation decay curves of concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19.

In order to compare the trends in the drop in maximum (initial) amplitude with depth for different mixtures, the initial (maximum) amplitude (normalized with respect to the surface amplitude) was plotted versus depth, as shown in Figure 163. These trends confirm that the maximum decay amplitude decreases in all concrete mixtures with respect to depth. This could be attributed to the drop in concrete porosity with depth, which reduces the moisture content of concrete and thus the amplitude of the NMR signal. In addition, the porosity and moisture content of concrete depends upon the dep the water-to-cement ratio, max aggregate size and other parameters of the concrete mix design. Additionally, external factors such as physiochemical phenomena associated with deterioration mechanisms could impact the porosity of concrete and thus its moisture content in saturated condition. The blue curves (prior to accelerated carbonation) in Figure 163 clearly point at the drop in maximum amplitude in call cases. The rates of drop are observed vary between different mix designs. For normal-strength concrete mixtures (M1 and M11), the maximum amplitude dropped by about 50%; this drop was only 15-20% for high-strength concrete mixtures (M16 and M19). After accelerated carbonation (red curves in Figure 163), the relative amplitudes experienced a greater drop with depth those for control mixtures (not exposed to accelerated carbonation – blue curves). This could be at least partly attributed to the microcracking of the concrete surface due to the internal restraint of the surface carbonation shrinkage movements. Except for Mix M1, the drop in maximum amplitude with depth occurs at a significantly reduced rate beyond 3 mm of depth. This could suggest that the surface microcracks caused by carbonation shrinkage are about 3 mm in depth.



Figure 163. Relative change of amplitude versus depth for concrete mixtures (a) M1, (b) M11, (c) M16, and (d) M19.

The relaxation distribution curves obtained for all concrete mixtures are presented in Figure 164. The T<sub>2</sub> distributions of all specimens embody 2 distinct peaks: (i) between 0.1-1ms, corresponding to gel pores; and (ii) between 1 to 10ms, corresponding to capillary pores. The T<sub>2</sub> values exceeding 10ms are generally associated with the water present in larger voids and cracks. After 60 days of accelerated carbonation, when compared with the control (unaged) concrete, the second (longer) peaks for all mixtures experienced drops in area and amplitude. An explanation for this observation is presented below. The carbonate may precipitate on the surface of the CH or in the pore solution depending on the concentration of carbonate and calcium ions [157]. The most soluble phase among cement hydrates is CH; it will thus be the first to dissolve and form calcium carbonate. If carbonate anions move faster than Ca cations, calcium carbonate precipitates on the surface of CH crystals, forming a shell around the CH that would hinder or slow down further carbonation reactions. If Ca<sup>2+</sup> moves faster than carbonate anions, then CH would dissolve, and calcium carbonate would precipitate as minute crystals within the capillary pore system. In this case, which is typical for Portland cement pastes [149], the resultant carbonates would partially fill the capillary pore system, resulting in overall densification of hydrates and reduction on their capillary porosity. This seems to be case in the carbonation tests conducted here where the longer peak associated with the capillary pore system is observed to decrease in amplitude and area.

Normal-strength concrete mixes M1 and M11 (Figure 164a-d) show more pronounced variations with depth when compared with high-strength concrete mixes M16 and M19 (Figures 164e-h). This phenomenon can be explained by the higher uniformity of the pore structure in high-strength concrete when compared with normal-strength concrete. Lower water-to-cement ratios and use of high-range water reducers produce a more homogenous pore network and less variability in porosity. The homogeneity of the pore structure in high-strength concrete, however, seems to be compromised near surface (first 2-3mm) after accelerated carbonation (Figures 164f-h).

Moreover, with slow diffusion of carbonate anions, the near-surface C-S-H could consume all the inward-diffusing carbonate ions before they can penetrate further to react with CH deeper inside concrete. This phenomenon produces a rather distinct carbonation front. Occasionally, a double

246

carbonation front can be observed where carbonation of CH forms an inner front, and carbonation of C-S-H forms an outer front. This seems to be common at lower humidity conditions where the rate of carbonation can be high (because water is less available in capillary pores to reduce the diffusion rate of carbon dioxide into the concrete depth) [149]. One can thus presume that calcium carbonate would precipitate close the C-S-H and affect the gel porosity. This phenomenon could explain the differences observed in Figure 5 in the first (shorter) peak between the control (unaged) concrete and the concrete subjected to 60 days of accelerated carbonation.



Figure 164. The relaxation time distributions for concrete mixtures (a) M1, (b) M11, (c) M16, and (d) M19.

Carbonation promotes the dissolution of CH and, in advanced stages (achieved here in accelerated carbonation) disintegration of C-S-H which disturbs the gel pores. Moreover, the reaction of calcium cations with carbonate anions leads to precipitation of calcium carbonate in capillary and possibly gel pores. This would produce less porous structures. Figure 165 compares the effects of accelerated carbonation and depth on the T<sub>2</sub> values at the short peak which corresponds to gel pores (and smaller capillary pores). Once again, the high-strength concrete mixtures M16 and M19 (Figures 165c and 165d, respectively) are observed to produce more homogenous gel (nano) pore systems with respect to depth. In normal-strength concrete mixtures M1 and M11 (Figures 165a and 165b, respectively), on the other hand, the short T<sub>2</sub> values dropped by 40% at 4-6 mm depth (versus the corresponding surface values). Accelerated carbonation (aging) reduced the shorter peak at 4-6 mm depths. This was true for high-strength concrete materials (10-20% drop) and especially for normal-strength concrete materials (about 50% drop). One can attribute this trend to the densification effects of carbonation at 4-6 mm depth which produce finer pore systems.



Figure 165. Relative changes of short T2 with accelerated carbonation and with age for concrete mixes (a) M1, (b)M11, (c) M16, and (d) M19.

As shown in Figure 166 and 167, the decreasing trend was found to be significant (with a p value of 0.032 in ANOVA). Furthermore, large T<sub>2</sub>s seem to be decreasing slightly; ANOVA, however, returned a p-value of 0.6 which indicates a non-significant change in large T<sub>2</sub>s. This is not surprising as carbonation reactions start in very small pores, and largely influence the nano- and micro-pore systems of concrete.





 $T_1$  measurements were also made for all concrete mixtures prior to and after accelerated carbonation. The results are presented in Figure 168. When considering the general trends for all mixtures, the variation of  $T_1$  with respect to depth was smaller for concrete materials exposed to accelerated carbonation when compared with the control (non-exposed) concrete materials.



Figure 168. Relative change on T1 (a) M1, (b)M11, (c) M16 and (d)M19.

 $T_1$  values of all specimens were collected over time at different depths. The measured values of  $T_1$  with respect to depth are plotted in Figure 168. These results indicate that at 10mm depth  $T_1$  changes more dramatically compared to 5 and 15mm depths. This finding suggests that precipitation of calcium carbonates is occurring at a faster rate at 10mm depth from the surface. Two-sample paired t-test was also performed on  $T_1$  values before and after accelerated carbonation. T-test yielded a p-value of 0.038, suggesting a significant increase in  $T_1$  due to the carbonation effects on pores. The shifts in normal distribution and box plots in Figure 169 confirm this trend.



Figure 169. Normal distribution and box plot of T1 values.

Variable	Mean Difference	95.00% Confidence Interval		+	dt	
Variable		Lower Limit	Upper Limit	ι	ai	p-value
VAR(1): Control	VAR(1): Control		0.11	2 262	15.065	0.029
VAR(2): After 14 days	-1.750	-3.401	-0.11	-2.202	12.905	0.038

The coefficient of self-diffusion (D) was also measured, and the results are presented in Figure 170. Carbonated normal-strength concrete materials (M1 and M11 in Figures 170a and 170b) exhibited a significant (about 80%) drop in the D values at longer depths, compared to only 20% for carbonated high-strength concrete materials (M16 and M19 in Figures 170c and 170d). The denser structure and better barrier qualities of high-strength concrete materials make them less prone to carbonation and the corresponding effects and the pore network and the concrete microstructure.



Figure 170. Relative change of self-diffusion coefficient (D) with respect to depth prior to and after accelerated carbonation for concrete mixtures (a) M1, (b)M11, (c) M16, and (d) M19.

8.4.2 UPV and dynamic modulus

Carbonation, especially in extreme conditions (such as in the accelerated conditions considered here) slightly increases the strength of concrete. This is because CaCO<sub>3</sub> occupies a greater volume than Ca(OH)<sub>2</sub>, which reduces the porosity of carbonated (surface) layers in concrete [149]. As shown in Figure 171a, there is a minor (and statistically insignificant but consistent) trend towards increasing ultrasound pulse velocity (UPV) with carbonation. The same is true for the dynamic modulus test results presented in Figure 171b. These results are in agreement with the

outcomes of previous studies which have shown an increase of elastic modulus due to carbonation [158, 159].



# Figure 171. (a)Ultrasound pulse velocity (UPV) and (b) dynamic elastic modulus test results for different concrete materials exposed to various periods of accelerated carbonation.

8.4.3 Scanning electron microscopy

Scanning electron microscope (SEM) images of concrete cross-sections were obtained for concrete mixtures M1 and M19 prior to and after accelerated carbonation. When compared with the normal-strength concrete mix M1 (Figures 172c, d), the high-strength concrete mix M19 (Figures 172a, b) exhibited a denser microstructure both prior to and after accelerated carbonation. Accelerated carbonation of the high-strength concrete produced minor microstructural changes (Figures 172a, b). More geometrically defined could be identified after carbonation, which is probably due to the formation of crystalline carbonate structures. More microstructural changes resulted from accelerated carbonation of the normal-strength concrete (Figures 172c, d).



(c)

(d)



# 8.5 Conclusions

Portable NMR was used to monitor the progress of accelerated carbonation in different normaland high-strength concrete materials. Concrete specimens were test via NMR prior to and after exposure to CO<sub>2</sub> gas; the relaxation and diffusion parameters of concrete were measured. Under carbonation effects, carbonates precipitates as minute crystals in the capillary pore system, causing a partial filling of pores and thus densifying the hydrated cement paste. The shift in the initial amplitude of the relaxation decay curve (which represents hydrogen density) and the relaxation time distributions (that reflects upon the pore size distribution) were compatible with this established trend in carbonation effects on the concrete microstructure. Accelerated carbonation lowered the long peak in T<sub>2</sub> distribution which is associated with the larger capillary pores that tend to be partially filled with the products of carbonation reactions.

Moreover, the reaction of calcium cations released to the pore solution by cement hydrates with carbonate cations leads to precipitation of calcium carbonate in the vicinity of gel pores and in capillary pores. The short T<sub>2</sub> component of the transverse relaxation time distribution reflected this effect of carbonation on gel and finer capillary pores.

The distinctions between the variations of pore systems for normal- versus high-strength concrete as well as their different levels of susceptibility to carbonation produced distinct trends in the NMR test data generated at different depths for normal- versus high-strength concrete.

The effects of carbonation on the corroborative nondestructive tests used in this investigation (ultrasound pulse velocity and dynamic elastic modulus) were minor (statistically insignificant) but consistent with the densification of cement hydrates under accelerate carbonation. Scanning electron microscopic observation of the non-carbonated and carbonated concrete materials could reveal the greater extent of carbonation effects on the hydrated cement paste microstructure in normal-strength concrete when compared with high-strength concrete.

257

# 9 SULFATE ATTACK IN CONCRETE STRUCTURES

#### 9.1 Abstract

Concrete specimens were prepared and exposed to an accelerated aging environment to simulate sulfate attack on concrete structures. NMR measurements were made prior to and after exposure to accelerated aging conditions. Relaxation decay curves, relaxation time distributions, and short and long components of the relaxation time were obtained by processing the NMR test data in order to devise methodologies for nondestructive identification and evaluation of sulfate attack on concrete via NMR relaxometry. Short and long components of the transverse relaxation time (T<sub>2</sub>) as well as the T<sub>2</sub> distribution curve provide valuable information on the formation of anomalies (such as gypsum and ettringite), water transport phenomena and exchange between gel and capillary pores, and wet porosity of concrete. The NMR decay amplitude and the information collected nondestructively on T<sub>2</sub> distribution were studied with respect to gradient in depth in order to analyze the extent of sulfate attack on concrete. Corroborative nondestructive (UPV and dynamic modulus of elasticity) measurements were also performed in order produce supporting data for the findings of nondestructive NMR tests.

### 9.2 Sulfate Attack in Concrete Structures

Concrete structures are vulnerable to attack by sulfate solutions. Although the coastal and underground concrete infrastructure are most vulnerable [160], the transportation infrastructure (foundations) have also been damaged by the sulfate that may be present in groundwater [161, 162].

258

Deterioration of concrete due to salt crystallization within pores has been investigated extensively [163]. According to Scherer [164], concrete can be vulnerable to damage when salt crystals grow from a supersaturated solution in its pores. This process has been described as a physical attack on concrete; sulfate attack would also involve chemical interactions between sulfate ions and the concrete hydration products [165]. The consequences of physical sulfate attack on concrete are different from those associated with chemical sulfate attack; physical sulfate attack leads to surface degradation phenomena similar to those caused by cycles of freezing and thawing. Chemical sulfate attack usually results in expansion and cracking due to the formation of ettringite and gypsum [166, 167].

Field experience with concrete exposed to sulfates suggests that concrete mainly suffers from surface scaling caused by physical sulfate attack. Such damage is generally limited to the aboveground portion of concrete, while the portion embedded in sulfate-rich soil, which is directly exposed to chemical sulfate attack, is mostly found in intact condition [168]. The physical damage process involves capillary rise and evaporation of the groundwater containing sulfates at aboveground concrete surfaces, resulting in crystal growth in concrete pores and subsequent damage [169-171]. Furthermore, Liu et al [172] performed a micro-analysis on concrete specimens after 8 months of exposure, concluding that in the upper part of concrete above the Na<sub>2</sub>SO<sub>4</sub> solution, damage initiated in the interfacial transition zone (ITZ) between paste and aggregate due to the formation of ettringite and gypsum. Salt crystallization cannot occur on the paste surface in the ITZ, but it was found on the aggregate surface after damage initiation due to chemical sulfate attack. On the other hand, salt crystallization could occur in carbonated concrete. Additionally, observation made by Irssar [173] clearly showed that deterioration was influenced strongly by the water/cement ratio and the C<sub>3</sub>A content of cement. Surface damage tends to be controlled in the case of concrete with relatively low effective w/c ratio made with low-C<sub>3</sub>A-content cement. Thaumasite was formed at the final stage of deterioration in the different sulfate environments. Nevertheless, current standards that evaluate the performance of concrete under sulfate attack, such as ASTM C1012 (Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution) and CSA A3004-C8 (Test Method for Determination of Sulfate Resistance of Mortar Bars Exposed to Sulfate Solution) only deal with the chemical aspect of sulfate attack.

### 9.3 Materials and Methods

ASTM standards include two accelerated test methods for evaluating the performance of hydraulic cement-based binders in sulfate-rich environments: (i) ASTM C452 Standard Test Method for Potential Expansion of Portland Cement Mortars Exposed to Sulfate; and (ii) ASTM C1012 Test Method for Length Changes of Hydraulic Cement Mortars Exposed to a Sulfate Solution. Both these ASTM test methods have been subject of much criticism. Cohen and Mather identified improvements in sulfate testing as a top priority, stating that "the current need for reliably predicting long-term durability performance and service life that are based on short-term accelerated tests is more than ever justified" [174]. Many researchers, including Mehta and Gjorv (1974), Mehta (1975), Brown (1981), Cohen and Mather (1991), Idorn, et al. (1992), Mehta (1992), and Tumidajski and Turc (1995), have expressed concern that existing accelerated test methods do not adequately predict field performance [174-179]. Many of the criticisms relate to the specimen size, specimen curing, form of sulfate exposure, duration of test, and assessment of resistance to sulfate attack via expansion measurements.

An example reflecting the inadequacy of the accepted test methods is described by Mehta et al. [180]. Alite cements ( $C_3S$ ) tested per ASTM C452 exhibited minimal expansion because the cements contained no C<sub>3</sub>A, and therefore would not produce ettringite upon exposure to sulfate ions. However, after six years of curing, spalling occurred, and it was discovered that C-S-H had converted to aragonite (CaCO<sub>3</sub>) and gypsum. The observed spalling was attributed to the crystallization of gypsum caused by sulfate attack. It is important to note that the deteriorations most often reported in the field are not caused by ettringite formation; they are due to the decomposition of CH and C-S-H by sulfate ions to form gypsum, and conversion of these hydration products into aragonite (presumably due to carbonation). Neither of the existing ASTM test methods predicts this form of damage. Because both ASTM C452 and C1012 methods use mortar bar expansion as a measure of sulfate resistance, only the ettringite form of sulfate attack is considered. The accelerated test method described by Mehta and Gjorv uses strength loss as a measure of susceptibility to sulfate attack. Cracking caused by ettringite or gypsum formation and ettringite expansion as well as loss of C-S-H will adversely affect compressive strength. Thus, both forms of sulfate attack are considered when strength loss is used as the measure of damage experienced during sulfate exposure.

# 9.4 Experimental Program

A schematic of the test apparatus used for exposure of concrete specimens to sulfate solution is shown in Figure 173. Under the control of three pumps, sulfate solution circulates among two

261

22.7-liter capacity polypropylene tanks. One of the tanks contains approximately 14L of sulfate solution, and acts as a reservoir. Sulfate solution is pumped from the reservoir through chemical-resistant polyethylene tubing. The pH of solution before it flows into the tank containing the specimens is monitored. If the pH measures below 7.2, aliquots of 0.1N H<sub>2</sub>SO<sub>4</sub> are added into the reservoir tank. In the second 22.7-liter polypropylene tank, the specimens are arranged on a mesh, which allows the solution to flow around them, increasing the potential for reaction between the cementitious binder and sulfates. The sample tank contains approximately 19L of sulfate solution. This test procedure maintains a constant pH because leaching of CH from the paste can alter the pH of the sulfate solution [181]. In addition, Brown demonstrated that controlling the pH through addition of sulfuric acid ensures that the sulfate ion concentration of the solution remains constant over time [182]. The conditions provided in this accelerated test method are more representative of field conditions because, unlike other accelerated test methods, the sulfate concentration and the pH of solution remain constant, which is more representative of field conditions.




Three different concrete mixtures were aged and evaluated for sulfate resistance. These mixtures are presented in Table 36; they cover different cementitious binder compositions, coarse aggregate types, and surface treatments.

Mix #	Mix Design	Cementitious Binder	Coarse Aggregate Type	Chemical Admixtures	Cure/Surface Treat
1	Normal-Strength	Type I Cement	Limestone	Air-Entr. Agent	Moist/None
11	Normal-Strength	Type I Cem & Class F Fly Ash	Limestone	Air-Entr. Agent	Moist/None

Table 36. Concrete mix designs considered in sulfate attack tests.

As described earlier, concrete specimens were immersed in a circulating 4 percent Na<sub>2</sub>SO<sub>4</sub> solution maintained at a pH of 7.2. The sulfate solution with pH of 7.2 simulates sulfate attack under the slightly acidic conditions typically present in field. Given that specimen dimensions as well as concrete permeability affect ingress of sulfate ions into a concrete specimen, the specimen dimensions were selected to maximize the surface-to-volume ratio, thus increasing the potential for reaction with the sulfate solution. With a high surface-to-volume ratio, the test time required to determine the susceptibility of cementitious binders to sulfate attack is reduced to between four and nine weeks. The lower the surface-to-volume ratio, the less likely it is for the sulfate ions to permeate throughout the specimen and react to cause strength reduction [22].

<sup>1</sup>H NMR relaxometry and diffusometry were performed on aged and unaged specimens for identification and evaluation of sulfate deterioration mechanisms. Ultrasound pulse velocity (UPV) and dynamic modulus measurements were also made in order to corroborate the NMR test data.

## 9.5 Results and Discussion

NMR relaxometry was performed on concrete specimens prior to and after accelerated aging. The T<sub>2</sub> decay curve was obtained using the CPMG pulse sequence. A bi-exponential line was fitted to the decay curve. The two dominant water-containing pores in concrete (gel and capillary pores) appear as short and long T<sub>2</sub> peaks, respectively. Furthermore, by performing inverse Laplace transform on the decay curve, the distribution of various T<sub>2</sub> values is obtained. Each T<sub>2</sub> value corresponds to a certain pore size with its unique geometry and relaxation properties. Due to the continuous nature of the pore network in concrete, T<sub>2</sub> distribution is also continuous. Short and long T<sub>2</sub>, as well as the T<sub>2</sub> distribution curve can provide valuable information on the transfer of water between pores and voids in concrete, the wet porosity of concrete, the water exchange between gel and capillary pore systems, and formation of anomalies (such as gypsum and ettringite).

Figures 174 shows the T<sub>2</sub> distribution of concrete specimens prior to and after 60 days of exposure to sulfate solution at various depths from the surface. The T<sub>2</sub> distributions of control specimens revealed two distinct peak: (i) within the 0.1-1ms range corresponding to gel pores; and (ii) within the 1-10ms range corresponding to capillary pores. T<sub>2</sub> values larger than 10ms correspond to water in larger voids and cracks. For all specimens at all depths, the intensity of the peak associated with gel pores decreased with progress of sulfate attack. The chemical reactions associated with sulfate attack could be a factor. Depending on the cation type associated with the sulfate solution (i.e., Na<sup>+</sup>, K<sup>+</sup>, or Mg<sup>2+</sup>), both calcium hydroxide and C-S-H present among cement hydrates may be attached by the sulfate solution. The chemical attack on calcium hydroxide can be expressed as follows.

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + 2NaOH$$

Conversion of the gel pore water into gypsum chemically binds the free water into gypsum molecules, and reduces their mobility.

Moreover, the intensity of peaks associated with capillaries also decreased with progress of sulfate attack. This could be attributed to the formation of ettringite in capillaries and around aggregates. Calcium hydroxide and alumina-bearing phases of hydrated Portland cement are more vulnerable to attack by sulfate ions. On hydration, Portland cements with more than 5 percent C<sub>3</sub>A content will contain most of the alumina in the form of monosulfate hydrate, C<sub>3</sub>A·CS-··H<sub>18</sub>. If the C<sub>3</sub>A content of the cement is more than 8 percent, the hydration products will also contain C<sub>3</sub>A·CH·H<sub>18</sub>. Due to the presence of calcium hydroxide in hydrated Portland cement paste, when a cement paste comes in contact with sulfate ions, both the alumina-containing hydrates are converted to the high-sulfate form (ettringite, C<sub>3</sub>A·3CS-··H<sub>32</sub>) as shown by the following equations:

 $C_{3}A.CH.H_{18} + 2CH + 3S + 11H \rightarrow C_{3}A.3CS.H$ 

 $C_{3}A.CS.H18 + 2CH + 2S + 12H \rightarrow C_{3}A.3CS.H$ 

The transformation of free water in capillaries to the bound water in ettringite could be a key factor in reduction of the intensity of peaks in cement paste.



**Figure 174. Relaxation time distributions of concrete mixtures M1 (a,b) and M11 (c,d)** The relaxation decay curves of concrete materials prior to and after sulfate attack are presented in Figure 175. The initial amplitudes of these curves are presented in Figure 176 where the initial amplitude is normalized with respect to the corresponding value at the concrete surface. For both mixes in control and aged concrete, the initial amplitude decreased with increasing depth as expected. The drop rates, however, was different in control versus aged specimens. While the specifics of the trends seem to differ in concrete mixtures M1 and M11, both Figure 176a and 176b indicate that the trend in sulfate attack with depth reached a plateau at about 4-5 mm depth.



Figure 175. Relaxation decay curves of concrete mixtures M1 (a,b) and M11 (c,d)



Figure 176. Initial amplitude versus depth for concrete mixtures M1 (a) and M11 (b).

The short and long values of T<sub>2</sub> obtained from bi-exponential fit to decay curves indicated a decreasing trend for both short and long T<sub>2</sub> components with depth (as shown in Figure 177 and 178). The stage of sulfate attack reached at the conclusion of accelerated tests is expected to cause salt crystallization which alters the pore system. There is also a chance that attack extends to C-S-H, producing gypsum and altering the gel pore structure. One-way analysis of variance (ANOVA) was performed on the measured values of T<sub>2</sub> in order to identify statistically significant trends in the NMR test data. Probably due to the relatively short period of exposure in this accelerated aging test, the effect of sulfate attack on the short values of T<sub>2</sub> was not statistically significant (0.4 significance level). This observation points at the possibility that the extent of sulfate attack in the accelerated aging condition considered here did not extend to the C-S-H (and gel pore) structure. Conversely, large T<sub>2</sub>s seem to be increasing under sulfate attack, with significance level of 0.04. The rise in the large T<sub>2</sub> value could thus be a statistically significant marker of sulfate attack. It could have resulted from filling of smaller capillary pores via salt crystallization which raises the remnant pore size and thus the T<sub>2</sub> value.



Figure 177. Measured values of short T2 versus depth for concrete mixtures M1 (a) and M11 (b).



Figure 178. Measured values of long T2 versus depth for concrete mixtures M1 (a) and M11 (b).

## 9.6 UPV and dynamic modulus of elasticity

The measured values of ultrasound pulse velocity (UPV) before and after exposure to sulfate solution are presented in Figure 179a. In the early stages of deterioration, UPV seems to be unaffected by sulfate solution. Work of other researchers also show that UPV does not detect the damage in concrete specimens until advanced stages of sulfate attack are reached when the signs of sulfate attack are visible [183].

The measured values of elastic modulus for concrete specimens are presented in Figure 179b. Elastic modulus increased by about 5% for all specimens at the conclusion of the accelerated approach to sulfate attack considered here. According to Roziere et al [184] elastic modulus is not a sensitive indicator of damage at early stages of sulfate attack even if significant expansion and damage can be observed. Lee et al. [185] and Sahmaran et al. [186] have found positive effects of sulfate attack on mechanical properties before they finally decrease with further progress of sulfate attack. This could be attributed to the pore-filling effects of salt crystallization before expansive phenomena cause cracking of concrete under sulfate attack.



Figure 179. UPV (a) and dynamic modulus (b) data for concrete mixtures M1 and M11, measured at different stages of sulfate attack.

## 9.7 Conclusions

Concrete specimens subjected to accelerated sulfate attack were examined nondestructively via NMR relaxometry. The transverse relaxation time distributions obtained by processing the NMR test data were used to assess the size distributions and the prevalence of gel and capillary pores in hydrated cement paste. For all specimens at all depths, the intensity of the peak associated with gel pores decreased. Reactions involving calcium silicate hydrates could contribute to this trend. Depending on the cation type associated with the sulfate in solution (i.e., Na<sup>+</sup>, K<sup>+</sup>, or Mg<sup>2+</sup>), both calcium hydroxide and C-S-H present in the hydrated Portland cement paste could be attached by the sulfate solution. In addition, for both concrete mixtures evaluated in unaged and aged states, the initial amplitude decreased with increasing depth as a result of salt crystallization within the pore structure. The rates, however, varied between unaged and aged concrete materials. The trends seemed to differ in concrete mixtures M1 and M11. Sulfate attack was found to produce a statistically significant rise in transverse relaxation times corresponding to capillary pores, but not those corresponding to gel pores. This trend suggest that the accelerated

aging conditions considered here did not reach advanced stages of sulfate attack where the C-S-H structure is altered. Salt crystallization, however, produced statistically significant effects on the capillary pore structure. The weak trends in the ultrasound pulse velocity (UPV) and dynamic modulus test results confirmed that the sulfate attack levels reached here raised the UPV and dynamic modulus of concrete, suggesting that the sulfate attack was still limited to the state of filling pores via salt crystallization, and did not advance to produce expansive and phenomena and notable chemical reactions.

## 10 NONDESTRUCTIVE NMR EVALUATION OF THE CHLORIDE ION DIFFUSION AND BINDING IN CONCRETE

## 10.1 Abstract

Research on chloride diffusion into concrete has largely focused on the corrosion of reinforcing and prestressing steel in concrete. Chloride diffusion into concrete is accompanied with its chemical binding with some cement hydrates. This phenomenon alters the physio-chemical environment of water held in hydrated cement paste. Nondestructive NMR tests were conducted in order to identify the trends in NMR signals which reflect upon these physio-chemical changes brought about by chloride diffusion into concrete.

Concrete specimens with different types of aggregate, binder and surface treatment were prepared and moist-cured. The specimens were exposed to sodium chloride solution. NMR relaxometry and diffusometry as well as corroborative tests were performed on the specimens at different time intervals.

Distribution of the transverse NMR relaxation time, T<sub>2</sub>, can track the environment and mobility of water, which can be affected by the formation of Friedel's salt that is the product of chloride chemical binding with some cement hydrates. Short and long T<sub>2</sub> values reflect the variations in the binding condition of water resulting from changes in the physio-chemical environment of the hydrated cement paste. Furthermore, the longitudinal relaxation time, T<sub>1</sub>, seems to capture the role of cations in formation of Friedel's salt.

Other nondestructive measurements, ultrasound pulse velocity and dynamic modulus, seem to exhibit some sensitivity to the evolution of the physio-chemical environment of concrete associated with chloride diffusion and binding. Chloride diffusion was not accompanied with any notable volume change, although minor trends towards weight gain were detected.

## 10.2 Chloride Ion Diffusion and Binding

Concrete in various applications can be exposed to sources of chloride ions. These sources range from deicer salt and seawater to some soils in arid/semi-arid regions and some accelerators. Chloride diffusion into concrete can accelerate corrosion of steel, and also can bring about some chemical changes of cement hydrates. Accumulation of chlorides and other salts resulting from capillary sorption of salt solutions followed by evaporation of water can also produce salt crystals with potentially deleterious (expansive) effects in concrete [187]. The mechanism of chlorideinduced corrosion of steel embedded in concrete, the ingress of chlorides into concrete, and the threshold chloride content for corrosion of steel have been discussed thoroughly in the literature [188-191]. The effects of chloride solutions on cement hydrates is also of practical interest [192, 193]. The results obtained by previous investigators were summarized by Biczok [194]; exposure of cement hydrates to chloride containing solutions generally leads to the formation of calcium chloroaluminate [195]. The present study is an attempt to elucidate some of the physical and chemical processes involved in chloride diffusion and binding using NMR relaxometry and diffusometry.

It has been suggested that the presence of sodium or potassium chloride solutions as well as magnesium or calcium chloride solutions, at relatively low concentrations that do not induce

formation of expansive chloro-hydroxide hydrates, can cause a loss of solid calcium hydroxide from the hardened cement paste. This will increase the porosity and reduce the strength of concrete. This phenomenon has been used to explain the relatively high diffusion rate of chloride ions when compared with metal ions. Since the electric charge of concrete must be kept constant, it has been suggested that diffusion of chloride anions into concrete is accompanied with departure of hydroxyl ions from cement hydrates to compensate for the entry of excess chlorides. This phenomenon is suggested to be more pronounced for magnesium chloride than for potassium or even sodium chloride.

Smolczyk [196] performed tests involving storage of cube mortar specimens in saturated solutions of sodium chloride. No visible signs of mortar deterioration were noted after two years, but the compressive strength of Portland cement mortar was reduced to about 60% of the strength obtained with the specimens stored in water. Mortar with blast furnace slag cement incorporating 75% slag did not experience as much strength loss in similar tests. X-ray diffraction analyses of mortar specimens pointed at the formation of sodium chloride crystals in specimens immersed in saturated sodium chloride solutions. The crystalline phase 3CaO.(Al,Fe)<sub>2</sub>O<sub>3</sub>.(CaCl<sub>2</sub>.10H<sub>2</sub>O, referred to as Friedel's salt, was also detected. The amount of Friedel's salt was greater after storage in saturated sodium chloride solution than in calcium chloride solution. The formation mechanism of Friedel's salt [197], its role in chloride binding [198], and its effect on AFm phases [199] have been investigated.

Midgley and Illston [200] investigated the diffusion of chloride ions into hardened Portland cement pastes with different water/cement ratios. They used solutions of sodium chloride at different concentrations, and measured chloride ion penetration. A rise in water/cement ratio

accelerated the penetration of chloride ions. Other investigations involving X-ray diffraction analysis have confirmed formation of Friedel's salt (calcium chloro-aluminate 3CaO.Al<sub>2</sub>O<sub>3</sub>.CaCl<sub>2</sub>.12H<sub>2</sub>O) with diffusion of chloride anions into hydrated cement paste [201]. A considerable amount of chloride may not be locked up in the crystalline phase. Instead, it may be present as free chloride ions in fine capillaries, or may bind into the calcium silicate hydrate lattice.

## 10.3 Materials and Methods

Two different test methods were used in this investigation. The AASHTO T259 test (commonly referred to as the salt ponding test) is a long-term experiment for measuring the penetration of chlorides into concrete. This test requires three concrete specimens that are at least 75 mm (3 in) thick, and have a surface area of 300 mm<sup>2</sup> (~ 0.47 in<sup>2</sup>). These specimens are moist cured for 14 days, and then stored in a drying room at 50 percent relative humidity for 28 days. The sides of specimens are sealed but the bottom and top faces are not. After the conditioning period, a 3% NaCl solution is ponded on the top surface for 90 days, while the bottom face is left exposed to the drying environment (Figure 180). There is difficulty, however, in determining what the results mean. This is partly due to the complicated testing conditions, discussed in the following, and partly due to the crudeness of the evaluation. McGrath et al [202] re-evaluated this test method, and concluded that it can be improved by using a depth of penetration approach rather than an integral chloride content, and by limiting the transport process to diffusion only [202].



#### Figure 180. AASHTO T259 test setup [203].

The bulk diffusion test (NordTest NTBuild 443) has been developed to overcome some deficiencies of the salt ponding test for measurement of chloride ion diffusion. Though not the first of similar tests, the NordTest is the first formally standardized version of the bulk diffusion test. It is distinguished from the salt ponding test by the sample's initial moisture condition. Instead of being dried for 28 days as with the salt ponding test, the test specimen is saturated with limewater. This prevents any initial sorption effects when the chloride solution is introduced. Also, instead of coating just the sides of the sample and leaving one face exposed to air, the only face left uncovered is the one exposed to a 2.8 M NaCl solution (Figure 181). It is left this way for a minimum of 35 days before evaluation [204]. To evaluate the sample, the chloride profile of concrete is determined by mounting the sample in either a mill or lathe with a diamond tipped bit. The sample is kept level so that the axis of advance of the bit is perpendicular to its surface. A pass is made at each depth to grind the concrete sample into dust, which is then collected. This is repeated at different depths, with depth increments on the order of 0.5 mm.



Figure 181. Nordtest setup [203].

## 10.4 Experimental Program

Both test methods described in previous section were evaluated, and finally NordTest (Figure 259) was selected as the primary test procedure. Four different concrete mixtures were aged and evaluated for chloride ion diffusion (Table 37). These mixtures cover different cementitious binder compositions, admixture types, curing conditions, and concrete strengths.

Table 37. Mix designs and curing conditions considered in the chloride diffusion tests.

Mix #	Mix Design	Cementitious Binder	Coarse Aggregate Type	Chemical Admixtures	Cure/Surface Treat
1	Normal-Strength	Type I Cement	Limestone	Air-Entr. Agent	Moist/None
11	Normal-Strength	Type I Cem & Class F Fly Ash	Limestone	Air-Entr. Agent	Moist/None
16	High-Strength	Type I Cement & Class F Fly Ash	Limestone	AEA & HR Water-Reducer	Moist/None
19	High-Strength	Type I Cem & Silica Fume	Limestone	AEA & HR Water-Reducer	Steam/None

<sup>1</sup>H NMR relaxometry and diffusometry tests were performed on specimens subjected to chloride ion diffusion and also on control concrete specimens. The results were used to identify the effects of chloride ion diffusion on the nondestructive NMR test results. UPV and dynamic modulus tests were also performed to support NMR measurements.

## 10.5 Results and Discussions

The relaxation decay curves for different concrete materials are presented in Figure 182. Figure 183 displays the change in initial amplitude with depth. For all concrete mixtures in control and aged condition, the initial amplitude decreased with increasing depth, which reflects upon the moisture and porosity gradients with respect to depth. The rate and trend of this change, however, vary for different concrete materials and state of chloride diffusion.

The rates of decrease in initial amplitudes is slower in high-strength concrete materials M16 and M19 (with lower diffusion coefficient) when compared with other (normal-strength) concrete materials. The effect of chloride on mix M19 seems to be negligible whereas in the case of mix M11 the initial amplitude drops by 50%.



Figure 182. Relaxation decay curves for concrete mixtures M1 (a, b), M11 (c, d), M16 (e, f), M19 (g, h).



Figure 183. Relative change of amplitude with depth for concrete mixtures (a)M1, (b)M11, (c)M16 and (d)M19.

Figures 184 shows the  $T_2$  distributions for different materials prior to and after 90 days of exposure to sodium chloride solution. The  $T_2$  distributions of all specimens exhibits 2 distinct peaks: (i) within 0.1 to 1ms, corresponding to gel pores; and (ii) within 1 to 10ms, corresponding to capillary pores.  $T_2$ s larger than 10ms are associated with water in larger voids and cracks. The intensity of the short peak reduces slightly with increasing depth in almost all cases while the intensity and location of the second peak varies significantly for different concrete materials and chloride diffusion states. The effects of chloride ion diffusion and Friedels's salt formation on the  $T_2$  distributions are discussed in the following.



**Figure 184. Relaxation time distribution of (a) M1, (b) M11, (c) M16 and (d)M19.** In the presence of NaCl, binding of chloride ions to form Friedel's salt can occur via either an adsorption mechanism or an anion-exchange mechanism. In the adsorption mechanism, Friedel's

salt forms due to the adsorption of the bulk  $Cl^-$  ions present in the pore solution into the interlayers of principal layers,  $[Ca_2Al(OH^-)_6.2H_2O]^+$ , of the AFm (Aluminate Ferrite mono) structure, to balance the charge. In the anion-exchange mechanism, a fraction of the free-chloride ions bind with the AFm hydrates (C<sub>4</sub>AH<sub>13</sub> and its derivatives) to form Friedel's salt via anion-exchange with the OH<sup>-</sup> ions present in the interlayers of the principal layer,  $[Ca_2Al[205]_6.nH2O]^+$  [206].

Because of Friedel's salt formation by the adsorption mechanism, an amount of Na<sup>+</sup> ions equivalent to the adsorbed chloride ions (in moles) are removed from the pore solution to maintain the ionic charge neutrality. The Na<sup>+</sup> ions thus removed from the pore solution bind with the calcium silicate hydrate (C-S-H) gel lattice to balance the charge arising due to the replacement of Si<sup>4+</sup> ions by Al<sup>3+</sup> and Fe<sup>3+</sup> ions. In contrast, the Friedel's salt formation by the anion-exchange mechanism involves release of OH<sup>-</sup> ions from the AFm hydrates into the pore solution, thereby increasing the pH of the pore solution [206].

An investigation conducted by Kalinchev et al [207] on Friedel's salt showed that the mobility of water molecules increases with formation of Friedel's salt when compared with the case involving chloride ions, whether chloride ions are adsorbed on the interlayers or the inner and outer spheres of available surfaces.

The short and long T<sub>2</sub> components derived via bi-exponential fitting to the decay curve indicate a decreasing trend for the short T<sub>2</sub> component, supporting the trends noted by Kalinchev. Oneway ANOVA was performed on the measured T<sub>2</sub> values to test the statistical significance of this trend. Probably due to the relatively short period of exposure to salt solution, the decreasing

trend was statistically significant at 0.09 p-value (but not at the commonly desired 0.05 level of significance).



Figure 185. Relative change of short T<sub>2</sub> for concrete mixtures (a) M1, (b)M11, (c) M16 and (d)M19 at different states of exposure to chloride solution.

The entry of saturated salt solution into capillaries and microcracks could raise the long component of T<sub>2</sub>. Conte et al [208] investigated the effects of ions on the water structure using low-field <sup>1</sup>H NMR, and concluded that sodium chloride acts as *kosmotropes*. Ions (either cations or anions) that are able to break the H-bond network among water molecular structure in the first hydration shell, thus favoring formation of an ordered ice-like structure, are regarded as makers or kosmotropes [209]. Upon charge density reduction, a decrease of the electrostatic

force between ions and surrounding water occurs. This leads to stronger water–water H bonds in the first hydration shell. As a consequence, less ice-like structured water is retrieved. In addition, H bonds between water molecules in the first and in the outermost hydration shells are weaker than in the case of high-charge-density ions. Again, as the distance from the ions increases, water molecules regain their normal behavior, thus behaving as bulk water. Therefore, due to the weaker bonds of locally restructured water, larger values of long T<sub>2</sub> are expected.

The long  $T_2$  components are shown in Figure 186. Although the significance level calculated in statistical analysis of variance is 0.12 (compared to the desired significance level of 0.05), nevertheless there is a notable increase in the median value of long  $T_2$ .



Figure 186. Relative change of the measured values of long T<sub>2</sub> for concrete mixtures (a) M1, (b)M11, (c) M16 and (d)M19 prior to and after exposure to chloride solution.

The values of self-diffusion coefficient, D, measured for concrete materials ranged from 0.55 to 0.65 10<sup>-9</sup> m<sup>2</sup>/s. After 60 days of exposure to chloride ion solution, D decreased consistently for all concrete materials.

The measured values of longitudinal relaxation time  $T_1$  are presented in Figure 187. Two-sample paired t-tests were performed on all  $T_1$  values prior to and after 60 days of exposure to chloride solution. The computed significance level was 0.34, indicating a statistically insignificant change in  $T_1$  values after exposure to chloride ion solution.



Figure 187. Relative change of T<sub>1</sub> for concrete mixtures (a) M1, (b)M11, (c) M16 and (d)M19 prior to and after exposure to chloride solution.

## 10.5.1 UPV and Elastic Modulus Measurements

The measured values of ultrasound pulse velocity (UPV) prior to and after exposure to sodium chloride solution are presented in Figure 188a. The measured values of UPV are rather insensitive to chloride ion diffusion. The slight rise of UPV could be due to the deposition of salt crystals in water saturated voids. Kawadkar et al [210] also showed that there is a no significant changes UPV for concrete specimens exposed to 2.3 mol sodium chloride solution. The effects of chloride ion diffusion on the measured values of dynamic modulus presented in Figure 188b were statistically insignificant although a minor trend towards reduction of dynamic modulus with chloride diffusion was noted.



Figure 188. (a)UPV and (b) elastic modulus of carbonation mixes.

The measured values of weight and volume of concrete specimens pointed at the insensitivity of these concrete attributes to chloride ion diffusion.

## 10.5.2 Scanning Electron Microscopy

SEM images of concrete prior to and after exposure to chloride ion solution are displayed in Figures 189a and 189b, respectively. Figure 189b shows bright spots on aggregates and hydration products which are probably the compounds formed and deposited during the chloride diffusion process into concrete. These bright spots are not visible in concrete prior to exposure to chloride solution.



Figure 189. SEM images of the concrete mix M1 (a) prior to and (b) after exposure to chloride solution.

## 10.6 Conclusions

The effects of chloride ion diffusion into concrete on the nondestructive NMR test data were evaluated. The results demonstrated the capabilities of a portable NMR relaxometer in detecting chloride ion diffusion into concrete.

The measured values of transverse relaxation time, T<sub>2</sub>, showed that the mobility of water molecules decreased with diffusion of chloride ions, with chloride ions adsorbed onto the interlayer or the inner and outer surfaces of hydrates. Bi-exponential fitting to the T<sub>2</sub> decay curves indicated a decreasing trend for the short T<sub>2</sub> values corresponding to the gel pores in cement hydrates. The T<sub>2</sub> distribution test results suggested that the intensity of the peak corresponding

to gel pores decreased in almost all cases with chloride ion diffusion, while the intensity and location of the peaks corresponding to capillary pores varied significantly for different concrete materials prior to and after exposure to chloride solutions. In contrast, the values of longitudinal relaxation time, T<sub>1</sub>, seemed to be insensitive to the diffusion of chloride ions.

The values of self-diffusion coefficient, D, measured for concrete materials ranged from 0.55 to  $0.65 \ 10^{-9} \ m^2/s$ . After 60 days of exposure to chloride ion solution, D decreased consistently for all concrete materials.

The measured values of ultrasonic pulse velocity and dynamic modulus of elasticity did not exhibit statistically significant sensitivities to the diffusion of chloride ions. The UPV values increased slightly, probably due to the deposition of salt crystals in voids. Conversely, the measured values of dynamic elastic modulus decreased slightly. The measured values of weight and volume of concrete specimens pointed at the insensitivity of these concrete attributes to chloride ion diffusion.

## 11 NUMERICAL AND ANALYTICAL STUDIES

## 11.1 Indirect Measurements of Concrete Porosity

Single-sided NMR has been used to measure the porosity and permeability of rocks by the oil and gas industry. The work reported herein evaluated the capability of NMR as a nondestructive tool for measurement of concrete porosity and barrier qualities. It should be noted that the pore system of concrete is distinguished by the presence of a continuous capillary pore structure with capillary sorption capability.

Distribution of the transverse relaxation time, T<sub>2</sub>, measured by NMR can be calibrated to reflect the porosity of concrete, which is an important parameter associated with the quality and the evolution of various damage mechanisms. The T<sub>2</sub> distribution measured via NMR relaxometry also reflects upon the pore size distribution of cement hydrates. This distribution together with the known attributes of the concrete capillary pore structure reflect upon the barrier qualities of concrete which can be partly assessed via the moisture sorptivity test (ASTM C1585).

#### 11.1.1 Porosity measurements

Porosity is defined as the ratio of the void volume (the space in cement paste matrix and aggregates) in concrete to its bulk volume (the overall volume of voids plus grains):

$$\emptyset = \frac{V_p}{V_b} = \frac{V_p}{V_p + V_s}$$

where,  $\emptyset$  is porosity, V<sub>p</sub> is void space or pore volume, V<sub>b</sub> is bulk volume, and V<sub>s</sub> is the solid volume. The total porosity observed via NMR relaxometry in concrete can be divided into three major components: free-fluid porosity (or bulk water) with long T<sub>2</sub> values (> 30 ms), capillary-bound water with  $T_2$  values between 3 ms and 33 ms, and finally the fast decaying gel pore water with  $T_2$  values below 3 ms (Allen et al., 2000). It should be noted that the  $T_2$  cutoff values for different components of the pore system are variable, and depend upon the concrete water-to-cement ratio, type of aggregate, and the influence of magnetic field gradients.

In water-saturated concrete, the number of spins in the fluid within the sensitive volume of the sensor is proportional to the sample porosity. The initial amplitude of the NMR signal,  $Amp_{ini}$  is the integral of the T<sub>2</sub> distribution, P(T<sub>2</sub>), where the distribution function P represents probability densities:

$$Amp_{ini} = \int P \, d \, \log \left(\frac{T_2}{1ms}\right)$$

It is directly related to the number of the spins in the sensitive volume probed by NMR. Hence, porosity can be determined using the initial amplitude measured on water-saturated pores that is normalized to the amplitude measured on pure water which is equivalent to 100 % porosity. For improved accuracy, the full CPMG decay curve is reconstructed from the T<sub>2</sub> distribution, and extrapolated to zero echo time. The measured value of porosity is a function of the shortest T<sub>2</sub>, the decay constant due to spin-spin relaxation that can be detected by the NMR and this, in turn, depends on the echo spacing. Modern NMR instruments that can detect a T<sub>2</sub> as short as approximately 0.3 ms are thought to include most of the (C-S-H) gel pore water in their measurement, yielding a porosity that compares reasonably well to values from helium porosimetry (Allen et al, 2000). Older NMR instruments which can only detect T<sub>2</sub> values above approximately 3 ms are thought to measure an effective porosity [211]. T<sub>2</sub> measurements on concrete specimens by the portable NMR instrument used in this study are performed at echo

times of 0.1 ms and less. Hence, they yield a total porosity including the gel pore water, which is comparable to values obtained via helium core porosimetry. The NMR measurements were normalized in this investigation with respect to the measurements made on distilled water in glass tubes, which correspond to 100 % porosity.

#### 11.1.1.1 Measurement of Barrier Qualities

Low-field NMR can provide essential information on the size distribution of water-saturated pore bodies in rock, because in the fast-diffusion limit the relaxation times are proportional to pore size [48, 78]. Hence, NMR results can be used to predict the permeability coefficient k. Permeability is the transport coefficient for flow through a porous medium in units of mD (1 mD = Millidarcy; darcy = 1 D =  $9.87 \times 10^{-13}$  m<sup>2</sup>). However, measurements of T<sub>2</sub> are potentially affected not only by the properties of interest such as the pore size but also by the inhomogeneity of the static magnetic field and the internal magnetic field gradients [212], causing further reduction in relaxation times. Internal magnetic field gradients arise from magnetic susceptibility contrasts between the aggregate mineral surfaces and the pore fluid [213]. The magnetic susceptibility value of water is negative (-9.26 × 10-6 SI at 20°C) like for diamagnetic minerals such as rock salt, calcite, gypsum, quartz and graphite. In contrast, most minerals and rocks have positive values of magnetic susceptibility [51].

#### 11.1.2 Experimental investigations

#### Porosity Measurements

Concrete samples subjected to accelerated aging via freeze-thaw cycling or carbonation were used in this investigation. Several transverse relaxation measurements were made with the

portable NMR instrument on representative specimens of various mix designs. Amp<sub>ini</sub> was measured and calibrated with pure water. Additionally, concrete specimens with 75mm (3inch) diameter and 50mm (2inch) height were used for direct measurement of moisture absorption and sorptivity (Figure 190). Sorption tests were continued for 7 days while measurements were taken at certain time intervals specified by ASTM C1585.



Figure 190. Sorptivity and sorption measurement test setup.

Figure 191 shows the correlation between the porosity values measured using the portable NMR versus the values of porosity measured directly using the moisture sorption test method. A linear regression yields a correlation coefficient R<sup>2</sup> of 0.83. Clearly there is a difference in the actual porosity values obtained using the two test methods. This is partly because thorough capturing of the gel pore water is difficult for NMR relaxometry due to their very fast decays which vanish during the echo spacing. Further reduction in relaxation times occurs due to the presence of internal field gradients which increase with decreasing pore radii. The shortest echo spacing is limited by transient processes in the transmitter-receiver system, and the pulse length. The gel pore water signals were studied using the shortest possible echo time of 0.05 ms. Hence, some of the water held tightly in gel pores could not be resolved as their decays occurred too early for detection. It should be noted that measurement of porosity via the moisture sorption test

accounts for capillary porosity and the larger fraction of the gel pore system. This measurement, however, does not involve the NMR error caused by the presence of magnetic field gradients. The difference between the fractions of the gel porosity captured by the two test methods is unknown.



## Figure 191. Correlation of the concrete porosities determined with the portable NMR instrument (ΦNMR) versus the method involving moisture sorption measurement.

While NMR measurements were performed on a sensitive volume captured nondestructively from the concrete interior, the reference porosities determined via moisture sorption measurements were obtained for the entire sample volume. Hence, these comparisons are influenced by the inherent inhomogeneity of concrete that is sampled by the NMR sensitive volume.

Despite the static magnetic field gradient, the portable NMR can be used for estimating the porosity of saturated concrete. However, for samples with porosities below 5%, the currently achievable signal-to-noise ratio of the portable NMR does not allow for precise data processing via inverse Laplace transformation. Fortunately, total concrete porosity generally exceeds 5%. The near-surface porosity of unaged concrete ranged from 7.5 % to 11.5%. The measured values

of sorptivity obtained using the ASTM C1585 test method for the same specimens fell within a narrow range of 12.5% to 15%. Once concrete was aged, the near-surface porosity varied depending upon the mechanism of deterioration. As shown in Figure 192, the near-surface porosity increased after freeze-thaw cycling, but decreased after carbonation. Considering that porosity is influenced (raised) by the presence of microcracks, the rise in porosity after freezethaw cycling is consistent with the mechanisms of freeze-thaw duration. The slight reduction of near-surface porosity upon carbonation is also consistent with the mechanism of carbonation which tends to fill pores via deposition of carbonates.



# Figure 192. Porosity measurements via NMR relaxometry for concrete materials prior to and after exposure to accelerated freeze-thaw cycling and carbonation.

#### Permeability Measurements

Two permeability transforms can be used for NMR measurements; they use the Timur-Coates Equation based on the work of Timur (1969), and the T<sub>2,LM</sub> Equation developed by Kenyon et al. (1988):

$$k_{TM} = \left[\left(\frac{\emptyset}{10}\right)^2 \left(\frac{FFV}{BFV}\right)\right]^2$$
$$k_{T,LM} = aT^2_{2,LM} \emptyset^4$$

In these equations, k is permeability in mD, FFV and BFV are the NMR-derived fractional volumes of bulk and bound water,  $T_{2,LM}$  is the logarithmic mean  $T_2$  value in ms, and 'a' is an empirically determined constant which depends on the relaxivity; it is determined based on different measurements such as previously measured values of permeability. Usually, for rocks with large pores (e.g. sandstones) a = 4 mD/(ms)<sup>2</sup> [74], whereas in rocks with smaller pores (e.g. carbonates), smaller factors have been used (e.g., a = 0.1) [75]. Both above equations are empirical, and permeability prediction by NMR always requires a local calibration to core data in each case. The Timur-Coates equation is frequently applied to oil reservoirs for interpretation of the NMR logging data. In contrast, the  $T_{2,LM}$  equation fails for hydrocarbon-bearing formations but works well in zones containing only water [76]. The rationalization for such correlation comes from the following: The Kozeny- Carman relationship proposes that permeability is inversely proportional to the square of the surface to volume ratio S/V of the pore space. This suggests that permeability is proportional to the square of a representative NMR relaxation time ( $T_{2,LM}$ )

$$T_{2,LM} = 10^{\left[\frac{\sum_{i=1}^{N} V_i \log(\frac{I_{2i}}{1ms})}{\sum_{i=1}^{N} V_i}\right]}$$

where,  $V_i$  is the volume fraction of a pore *i* decaying with the relaxation time  $T_{2i}$ .

Both models are not universally applicable considering realistic variations in structure, texture, and composition [77]. The cutoff method is also subject to the same concerns with changes in surface relaxivity and in pore throat/pore-body ratio as is permeability estimation from  $T_{2,LM}$  [78]. Both permeability models generate an appreciable amount of data scatter relative to the independently determined permeabilities. In this work, the  $T_{2,LM}$  equation was used for NMR measurements made on different concrete materials exposed to carbonation or freeze-thaw cycling. T<sub>2</sub> distributions were measured at 5 different positions along three concrete specimens for each mix design.

The magnetic susceptibility of all specimens was measured (Figure 179a); the resulting mean values are presented in Figures 193b and 193c.



(a) Measurement of magnetic susceptibility



(b) Mean values for carbonated concrete materials



(c) Mean values for concrete materials subjected to freeze-thaw cycling

Figure 193. Magnetic susceptibility values of concrete materials.

A good correlation between the measured value of permeability coefficient (k) and sorption rate was found with  $R^2 = 0.81$  (Figure 180).



Figure 194. Correlation of the permeability coefficients measured with the NMR instrument and sorptivity measurements per ASTM C1585.

The estimated values of concrete permeability before and after exposure to accelerated aging are presented in Figure 195. NMR estimations indicate that concrete permeability increased after freeze-thaw cycling, and decreased after carbonation. These trends are consistent with the potential for the formation of microcracks in concrete under freeze-thaw cycles, and the filling



of pores via carbonation.

Figure 195. Estimated permeability values based on NMR measurements for concrete materials prior to and after accelerated aging via freeze-thaw cycling or carbonation.

#### 11.2 NMR Data Interpretation Software

Interpretation of the NMR data could be rather complicated for a highway engineer. Moreover, A relatively large number of scans might be needed (depending on the type of structure and the extent of damage) to make a reliable judgement on the health condition of the structure. Handling of these data could be pretty time consuming. Therefore, a software module is required to streamline the management and interpretation of data. A standalone software is under development (using the MATLAB<sup>®</sup> GUI) to further facilitate and accelerate the NMR data handling and interpretation task.

GUIs (also known as graphical user interfaces or UIs) provide point-and-click control of software applications, eliminating the need to learn a language or to type commands in order to run the application.

MATLAB apps are self-contained MATLAB programs with GUI front ends that automate a task or calculation. The GUI typically contains controls such as menus, toolbars, buttons, and sliders. Many MATLAB products, such as Curve Fitting Toolbox<sup>™</sup>, Signal Processing Toolbox<sup>™</sup>, and Control System Toolbox<sup>™</sup> include apps with custom user interfaces. You can also create your own custom apps, including their corresponding UIs, for others to use.

App Designer is an environment for building MATLAB apps. It integrates the two primary tasks of app building—laying out the visual components and programming app behavior—and allows you to quickly move between visual design in the canvas and code development in an integrated version of the MATLAB Editor.
The layout of the NMR Relaxation Analysis (NRA) is shown in Figure 196. This program contains 5 essential sub-modules: (i) structural inputs; (ii) climate/weather inputs; (iii) surface appearance; (iv) relaxation data; and (v) damage analysis and condition rating. In the following, the function of each sub-module is explained.

📣 nmr_software	- 0
- Structural Input-	- Input Relaxation Data 1
Please enter any available information listed below:	
Type of Structure: Bridge column Bridge column Bridge dirder	Input T2 Dist.
W/C:	
Aggregate type: Aggregate type	Amp (a.u.) .5 .
Air entrainment: Yes No	
Surface orientation: Vertical Horizental	0 T2 (ms) 0.2
Climate/Weather Condition-	Input Relaxation Data 2
Average 7-day temperature (F):	Input T2 Dist.
Annual min and max temperature (r):	1
Average 7-day realitive numidity (%): %	
Mean annual precipitation (78). % Mean annual potential evapotranspiration (mm/month): mm/month	Amp (a.u.)) 5 -
Average 7-day precipitation (in):	
- Surface Appearance	
	0 T2 (ms) 0.2
	Input T2
	Short T2 @ location 1 ms Long T2 @ location 1 ms Short T2 @ location 2 ms Long T2 @ location 2 ms
· · · · · · · · · · · · · · · · · · ·	Damage Analysis and Condition Rating
HAR HAR HAR AND HAR AN	Parimary Damage Mechanisms:
	Statstical Confidence: %
	Extent of Damage: %
	Secondary Damage Mechanisms:
	Statstical Confidence: %

Figure 196. NMR Relaxation Software layout.

It should be noted that this version is in beta stage, and will be refined based on the suggestions of the technical working group and the experience gained in applications of the module. Once the program is completed, the package will be available in the form of an executable file that can be installed and used in any computer operated on the Windows platform. Note that this software package will be standalone; MATLAB will not be required to install and run its modules.

## 11.2.1 Structural Inputs

In this sub-module (Figure 197), the type of targeted structure (bridge deck, column, girder, pavement, parking lot, sidewalk, swear pipe, reactor etc.) is input to the software. Moreover, some of the most important material characteristics are also input in order to enhance the accuracy of predictions; these material characteristics include: (i) water-to-cement ratio, (ii) aggregate type, (iii) air entrainment; and (iv) surface orientation of the structure or the structural element.

- Structural Input	
Please enter any available	e information listed below:
Type of Structure:	Bridge deck Bridge column Bridge girder V
W/C:	
Aggregate type:	Limestone  Granite Gravel  V
Air entrainment:	Yes No
Surface orientation:	Vertical Horizental

Figure 197. NMR Relaxation software – Structural Input.

#### 11.2.2 Climate/Weather Inputs

In this sub-module (Figure 198), the most important climatic or weather data that influence the concrete internal moisture content are input. This data includes: (i) average 7-day temperature; (ii) annual minimum and maximum temperatures; (iii) average 7-day relative humidity; (iv) mean annual precipitation; (v) mean annual potential evapotranspiration; and (vi) average 7-day precipitation.

<ul> <li>Climate/Weather Condition</li> </ul>		
Average 7-day temperature (F):	F	
Annual min and max temperature (F):	F	F
Average 7-day realtive humidty (%):	%	
Mean annual precipitation (%):	%	
Mean annual potential evapotranspiration	mm/month	
Average 7-day precipitation (in):	in	

## Figure 198. NMR Relaxation software – Climate/Weather input.

# 11.2.3 Surface Appearance

Some of the deterioration mechanisms have unique impacts on the surface texture and color of concrete. Some of them have regular crack patterns. In most cases, surface appearance could be related to two or more deterioration mechanisms. In this sub-module (Figure 199), several pictures are included. Selection is not necessary for the user, but it would benefit the accuracy of predictions and reduce the chance of erroneous interpretation of the NMR test data.



Figure 199. NMR Relaxation software – Surface appearance input. 11.2.4 Relaxation Results

The relaxation (.dat) files explained in previously can be input to the software all at once. These files contain the relaxation information obtained from various locations of the structure. These spots are selected using the Latin Hypecube Sampling principle as explained in previous reports. The software will take in these files, and will display the distributions. An option is provided in the software (Figure 200) to input the short and long T<sub>2</sub> values (that can be obtained from the Prospa software). Providing the T<sub>2</sub> values will increase the speed of calculations.



Figure 200. NMR Relaxation software – Relaxation input.

## 11.2.5 Damage Analysis and Condition Rating

Finally, by comparing the obtained results from field against the laboratory data base, and applying the necessary calibration coefficients, the type and extent of damage are inferred (Figure 201). The comparison of field results with our laboratory and field data is possible for drawing meaningful correlations between the trends. Artificial Neural Network is another strong tool that might help us later to establish trends correlating the laboratory and test data.



Figure 201. NMR Relaxation software – Analysis output.

# 11.3 Conclusion

In this chapter, the issue of NMR measurements in the presence of steel reinforcement was addressed. Steel reinforcement with 4 and 6 inches of clear cover had negligible effects on the NMR signal. With 1.5-2 inches of clear cover, changes in T<sub>2</sub> peak were noted depending on the depth of nondestructive investigation. At 2mm depth from surface, the T<sub>2</sub> value shifted toward higher levels (from 0.8ms for 0 reinforcing bars to 0.9 for 4 bars). The amplitude decreased from 0.15 for 0 reinforcing bars to 0.01 for 4 reinforcing bars. At 4mm depth, on the other hand, the T<sub>2</sub> peaks for different reinforcement condition occurred all at the same location (0.8ms) while the amplitudes increased slightly as the number of steel bars increases. At 6mm depth, the effect of reinforcement seemed to vanish completely. Similar trends were observed, to a lesser extent, with 4 and 6 inches of clear cover. To overcome the interference of reinforcing bars, especially when it is very close to the surface, measurements should be taken at different depths, and

amplitudes should be compared. The NMR signal with the greatest amplitude should be considered in analysis of the results.

MR data analysis and interpretation software is under preparation. The prototype will be completed soon based on the experience gained in laboratory and field applications of the system. The completed package will be available as an executable file that can be installed and used in any computer using the Windows platform. This software package is developed within MATLAB, but will be made available as a standalone package that does not require MATLAB for installation and operation of its modules. This software takes as input the type of the structure that is under investigation (bridge deck, column, girder, pavement, parking lot, sidewalk, sewer pipe, reactor, etc.). Some important materials characteristics (e.g., water-to-cement ratio, aggregate type, air entrainment, and surface orientation and appearance) can also be input to the software. The weather condition during the past 7 days is a required input. These optional and required inputs would improve the accuracy of the predictions made based on nondestructive NMR analysis of the infrastructure.

The NMR (relaxation) data files (the .dat files) can be input to the analysis software all at once. These files are the relaxation information obtained from various depths and locations of the structure. The locations would be selected based on Latin Hypercube Sampling principles. The software will use the input files to produce data on the distribution of deterioration conditions within the structure. The collected diffusion coefficients are also input to the software for various locations. The software uses the system calibration based on the laboratory and field data base generated in this research to infer information on the type and extent of concrete deterioration.

305

#### 12 FIELD OPERATION OF PORTABLE NMR

#### 12.1 General

Use of the portable NMR in field requires careful considerations to provide accurate measurements and meaningful interpretations. One issue that can potentially create difficulties with respect to portable NMR testing is the presence of metallic objects in the test structures. The metallic object embedded in concrete, including steel reinforcing bars, could potentially interfere with the magnetic field of NMR. Prismatic concrete bars and steel reinforcement were used to generate different possible scenarios. The effects of concrete cover, number of reinforcement and depth of investigation on the NMR signals were investigated. The sample size required for precise estimation of the average value is derived. Additionally, host rocks (used for aggregate making) were tested at a Michigan DOT facility. These rocks were received by MDOT from various quarries to check their quality for used in concrete pavement and bridge construction. Three types of rocks (sedimentary limestone, sedimentary dolostone, sedimentary hematite and jasper) were tested using the portable NMR. Finally, freeze-thaw beams made of various aggregates (obtained from different quarries), prepared by MDOT, and cores taken from US-23 in Michigan were tested using the portable NMR.

#### 12.2 Operating of Portable NMR

By analyzing the relaxometry and diffusometry data generated by processing of NMR signals, the following key parameters have been calculated and correlated with the type and extent of concrete deterioration: (i) longitudinal relaxation time  $(T_1)$ ; (ii) transverse relaxation time  $(T_2)$  distribution; and (iii) diffusivity (D). Figure 182 shows the main components of the portable NMR,

including the NMR probe (embodying the magnet and the RF coil), precision mechanical lift, and spectrometer.



Figure 202. (a) Portable NMR components, (b) spectrometer and

Different field locations where concrete is experiencing known and unknown deterioration mechanisms are subject of field experiments using the portable NMR (Figure 183). The sequence of events, marked by numbers in Figure 203, for field operation of the portable NMR is as follows: (1) the software sends the pulse program and other user-input information (e.g. depth of investigation) to the spectrometer; (2) the spectrometer sends the signal to the probe; (3) the probe implements the process of sending electromagnetic (EM) signals to the sensitive volume; (4) the signals returned from the sensitive volume are collected by the probe; (5) the collected

signals are transmitted to the spectrometer; and (6) the software receives and processes the data from the spectrometer.

Further details on used pulse sequences and their programming are presented in the following.



Figure 203. Portable NMR testing and processing sequence.

# 12.3 NMR Field Testing

Thorough field investigations were performed in various states (Michigan, Pennsylvania, and Indiana) to identify and test various structures suffering from unknown deterioration mechanisms using portable NMR system.

In this chapter, the NMR relaxation parameters of those structures are recorded and analyzed. The trends obtained in the field are compared with our previous knowledge of concrete deterioration mechanisms gathered through our previous laboratory and field testing. Corroborative tests are also performed on pieces of concrete obtained from field to verify and calibrate the NMR test predictions

#### 12.3.1 Testing at Michigan DOT

Michigan Department of Transportation (MDOT) commonly takes samples of concrete from pavements and bridges, and also samples of rocks from quarries for evaluation in its test laboratories. The NMR system is used at the MDOT test laboratories for nondestructive evaluation of some available samples of rocks and concrete.

Three types of rock samples (boulders) were subjected to nondestructive NMR testing: rock A (sedimentary limestone), rock B (sedimentary dolostone), and rock C (sedimentary hematite and jasper). They were all obtained from quarries to be tested and approved by MDOT for use (after crushing) as concrete aggregates. The boulders were immersed in water for 48 hours, and taken out at the day of NMR testing. Figure 204 shows the Rock A, and the setup used for its nondestructive NMR testing at the MDOT aggregated testing laboratory. Measurements were made on the distribution of the transverse relaxation time (T<sub>2</sub>) and the self-diffusion coefficient.



(a)



(b)

Figure 204. (a) Rock A and (b) nondestructive NMR testing.

Figure 205 shows the relaxation curves at different depths of Rock A. Prevalence of magnetic species in the tested boulders, creates strong and local internal magnetic gradients, which decreases the signal-to-noise ratio (SNR). The limited access time at the Michigan DOT laboratory did not allow for the use of a large number of scans to overcome the noise caused by the presence of any magnetic species within rocks. Such species produce local magnetic field gradients (i.e., added inhomogeneity of the magnetic field distribution) which can reduce the signal-to-noise ratio (SNR) of the NMR instrument. SNR can be improved by increasing the number of scans, which was not possible given the limited access time to the MDOT laboratory. Nonetheless, Figure 285 suggests that all three decaying curves follow a bi-exponential trend. The decay occurs due to the dephasing of the water molecules in different groups of pores in rocks. It should be noted that not all the pores are filled with water; only accessible pores would be saturated. This ('apparent') porosity contributes to various types of concrete deterioration. These are types of pore in which water resides and evaporates rather quickly. These pore types are considered in adjusting the water-to-cement ratio used in concrete production. They could be categorized into two groups: small pores (ranging from nanometer to sub-micrometer) and large pores (larger than 1 micrometer).





The total moisture content of rocks at various depths could be estimated using the initial amplitude of decay curves of Figure 205 for different depths of measurement. The relative change in amplitudes at various depths with respect to that at the surface is shown in Figure 206. For this type of rock (which is dense and heavy), the moisture content is at its highest on the surface; it decreases with the depth at which NMR measurements are taken.



Figure 206. Relative change in NMR amplitude with respect to surface, reflecting the change in moisture content for Rock A.

The relaxation time distributions of Rock A at various depths is illustrated in Figure 207. As expected from literature, two groups of pores are recovered from inverse Laplace transformation at each depth. The first peak (from left) occurs between 0.8 to 5 ms, and the second one between 10 to 80 ms. The amplitude of the second peak is twice as large the first peak, suggesting that larger pores constitute the majority of the pore structure. As the testing moves in depth, the amplitudes of the first and the second peaks decrease significantly. Since the boulder represents the volume of rock, this drop in amplitudes can be attributed to the limited depth of diffusion of water. It can also be observed that at greater depths, small relaxation times are measured for small and large groups of pores. This could be an artifact of moisture diffusion patterns into rock.



**Figure 207. Relaxation time distribution of Rock A at various depths.** The self-diffusion coefficient of Rock A is shown in Figure 208. Fastest diffusion occurs at surface,

and the diffusion from 4 to 6mm depth seems to be relatively unchanged. This finding correlate with that related to  $T_2$  distribution, and points at particular moisture diffusion patterns into rocks of relatively low porosity that are used in concrete construction.



Figure 208. The self-diffusion coefficient of Rock A at various depths.

Rock B was also tested for relaxation and diffusion parameters as shown in Figure 209.



(a)

(b)

# Figure 209. (a) Rock B and (b) NMR testing.

The relaxation decay curves for Rock B are presented in Figure 210. The decay curves follow similar bi-exponential trend as noted for Rock A. The difference here is that the initial amplitudes occur around 0.9 for all depths, which are thus largely overlapped.



Figure 210. Relaxation decay curves at different depths of Rock B.

The initial amplitudes were compared; their relative change with respect to depth are presented in Figure 211. The moisture content seems to slightly increase with respect to depth in this case. The tested rock appears highly porous, which could allow for thorough diffusion of water within the depths evaluated here.



Figure 211. Relative change in NMR amplitude with respect to surface, reflecting the change in moisture content for Rock B.

The relaxation time distributions for Rock B are similar to those for Rock A. However, the first and second peaks are higher at 4 and 6 mm depths versus those near surface. Rock B was stored in air (after 48 hours of immersion in water) as Rock A was tested first. This could have caused some moisture loss from surface, which explains the drop in amplitude (and area under the peak) observed in Figure 212. The porosity of Rock B seems to have led to thorough diffusion of moisture within the depths considered here.



Figure 212. Relaxation decay of rock B.

The self-diffusion coefficient test results for Rock B are presented in Figure 213. A slight decrease

with respect to depth is also observed for this type of rock.



# Figure 213. The self-diffusion coefficient of Rock B at different depths.

Rock C (Figure 214) had a high concentration of magnetic constituents. As a result, no signal could be recovered from NMR measurements. The magnetic concentration in this rock was so high that it was pulled towards and held on the surface of the portable NMR instrument (under the effect of the NMR magnetic field).



Figure 214. Rock C.

In addition to testing of rocks at the Michigan DOT laboratories, concrete beams prepared with different aggregates were also subjected to nondestructive NMR testing (Figure 215). These beams have been prepared for freeze-thaw testing. They incorporated aggregates with 1-inch maximum particle size collected from different quarries in Michigan (which have been used after washing and sieving). The beams are prisms with 4inx4inx12 dimensions; they are subjected to freeze-thaw cycles, and their dilation is measured throughout the test.



# Figure 215. NMR testing of a freeze-thaw prismatic specimen at Michigan DOT.

Additionally, concrete cores taken from US-23 were tested using the portable NMR instrument

(Figure 216). These cores have been obtained at different locations (Table 38).



Figure 216. NMR testing of cores taken from US-23.

Table 38. List of concrete cores	obtained from differe	ent locations of US-23	by MDOT.
----------------------------------	-----------------------	------------------------	----------

Core	STA	REL	Date	Lane
16	611+32	29	05/01/2017	NB
24	594+47	32	05/01/2017	SB
27	573+77	30	05/01/2017	SB
36	409+23	14	05/25/2017	Ramp D

# 12.3.2 Various structures

The images of this concrete structure are shown in Figure 217. Regions of the structure where no visible signs of deterioration were noted (Figure 217a) were tested as control. This was followed by testing of deteriorated areas where pattern cracking was observed (Figure 217b).



Figure 217. Pictures of structure I in (a) undamaged and (b) damaged condition.

Figure 218 shows the short value of transverse relaxation time ( $T_2$ ) derived through analysis of the test data. These results indicated that the value of short  $T_2$  was about 100% higher in the cracked region when compared with the intact region of the structure. In addition, the initial amplitude of the relaxation decay curve increased by about 15% moving from the intact to the cracked region of the structure. These trends in the short  $T_2$  value and the initial amplitude of the decay curve match the trends established for alkali-silica reactions.



Figure 218. Change of short T<sub>2</sub> in intact and cracked locations.

SEM images of the concrete pieces obtained from Structure I are presented in Figure 219. Figure 219a shows the presence of some microcracks in the interfacial transition zone (ITZ). Figure 219b shows some microcracks propagating through the cement paste. Similar microcracking trends were found in laboratory specimens subjected to accelerated alkali-silica reactions.





(a)

(b)

Figure 219. SEM images of concrete structure I.

Figure 220 shows the visually noted deterioration conditions of the second structure selected for

testing. Regions of this structure with less and more visually notable damage are shown in Figures

220a and 220b, respectively.



(a)

(b)

## Figure 220. Pictures of structure II in (a) damaged and (b) damaged condition.

The trends in the NMR data found for Structure II are summarized in Figure 221. Figure 221a displays the relative change in the short and long values of T<sub>2</sub> with respect to the depth of concrete. Short T<sub>2</sub> remains almost constant while long T<sub>2</sub> decreases at larger depths. Long T<sub>2</sub> dropped by as much as 20% with increasing depth. The initial decay amplitudes for both less and more deteriorated sections of the structure also decrease; the drop in the decay amplitude in the more deteriorated region, however, is notably greater. These trends are similar to those observed for concrete specimens tested in laboratory after exposure to accelerated freeze-thaw testing.



(b)

# Figure 221. The trends observed in the NMR data generated for the T<sub>2</sub> values (a) and the percent change in decay amplitude with respect to depth.

SEM images of concrete obtained in the field are shown in Figure 222. Several microcracks are observed across specimens, mostly within the cement paste. Although it seems the concrete has been air-entrained, microcracks are prevalent in this piece of concrete obtained from field. The pictures taken in field (Figure 220) hint at serious damage to the concrete surface which could have been caused by phenomena similar to deicer salt scaling associated with exposure to freezethaw cycles and deicer salt.





(a)

(b)

# Figure 222. SEM images of concrete structure II.

Concrete specimens obtained from Structures III and IV were powdered and subjected to XRD analysis. Figures 223a and 223b display the XRD patterns of concrete specimens obtained from Structures III and IV, respectively. While the peak pertaining to quartz (at  $2\theta = 26-27^{\circ}$ ) intensity is relatively large for structure IV (Figure 223b), it is relatively small for structure I (Figure 303a). This could be due to the consumption of quartz by the alkali-silica reaction and production of amorphous ASR gel.





#### Figure 223. XRD patterns of (a) structure III and (b) structure IV.

Finally, the NMR data interpretation software package developed in the project was used to assess the deterioration conditions of the structures introduced above. The software is still in beta condition, and the experience accumulated here is used to verify and further improve the package.

Figure 224 shows the software interface after analyzing the NMR data generated for Structure III and Structure 2 (Figure 224b). For Structure I, the software predicts ASR as the primary cause of deterioration, and carbonation as a secondary cause. For Structure IV, the software identifies freeze-thaw cycling as both the primary and secondary causes of deterioration.



(a)

Figure 224. The NMR software analysis of Structure III (a), and Structure IV (b).



#### Figure 224. (cont'd)

(b)

Pictures taken from the intact and deteriorated regions of Structures III and IV evaluated for this chapter are presented in Figures 225 and 226, respectively. Visual observation of the deteriorated region of Structure III pointed at discoloration and alteration of texture at the surface (Figure 225b). Deterioration of Structure IV occurred mostly at edges where concrete was severely disintegrated (Figure 226b).



(a)







(a)



Figure 226. Pictures of the intact (a) and deteriorated (b) regions of Structure IV.

The trends in some NMR data generated for Structures I and II are presented in Figures 227 and 228, respectively. These figures show the changes in measured values of the transverse relaxation time (T<sub>2</sub>) and decay amplitude with increasing depth.

In the case of Structure III (Figure 227), the changes in T<sub>2</sub> value and decay amplitude with respect to depth are relatively small (less than about 10%); the seemingly damaged and undamaged regions of the structure exhibit similar trends (<5% difference). These trends, considering the data base generated through laboratory tests, suggest that concrete in Structure III has not experienced any notable deterioration. The surface phenomena observed may have thus been caused by minor efflorescence, with no significant deleterious effects.

In the case of Structure IV (Figure 308), the obviously deteriorated regions of the structure exhibit close to 20% drop in T<sub>2</sub> and 40% drop in decay amplitude with depth. The data interpretation schemes developed based on laboratory test data point at severed freeze-thaw deterioration of this structure. The seemingly undaged region of the structure exhibited 10% drop in T<sub>2</sub> and 20% drop in decay amplitude with depth. These trends are, based on the data base generated in laboratory, indicative of moderate freeze-thaw damage.



Figure 227. The trends in the transverse relaxation time (T<sub>2</sub>) and amplitude change with depth for the undamaged and damaged regions of Structure III.



Figure 228. The trends in the transverse relaxation time (T<sub>2</sub>) and decay amplitude change with depth for the undamaged and damaged regions of Structure IV.

#### 12.3.3 Corroborative SEM and XRD Investigations

Small pieces of concrete were extracted from the structures, and were subjected to SEM and XRD investigations in laboratory. The SEM images of Structures III and IV are presented in Figures 229 and 230, respectively. Structure III (Figure 229) exhibited minor microcracking, which is consistent with the NMR assessment of health condition. This concrete seems to have been reinforced with fine polymer fibers. Structure III (Figure 230), on the other hand, exhibited extensive formation of networked microcracks. This observation together with the lack of entrained air voids at adequately small spacing support the finding of the nondestructive NMR experiment, which points at extensive freeze-thaw deterioration of this structure.



Figure 229. Typical SEM image of Structure III.



Figure 230. Typical SEM image of Structure IV.

The XRD patterns of concrete specimens obtained from structures I and II are presented in Figure 231a and b respectively. The XRD patterns do not reveal any signs of chemical deterioration, which is consistent with the NMR findings that one structure does not exhibit any signs of deterioration, and the other has experienced physical damage caused by freeze-thaw deterioration. The XRD pattern for Structure II points at possible use of an opal feldspar as aggregate in concrete.



(b) Structure IV

Figure 231. XRD patterns of Structures III and IV.

# 12.4 Measurements in the Presence of Reinforcing Bars

Portable NMR conducts nondestructive relaxometry tests at various depths of a concrete system. The presence of metallic objects embedded in concrete, such as reinforcing bars, could potentially interfere with the magnetic field of NMR.

No. 4 reinforcing bars were purchased from Harris Rebar in Lansing, MI. Three prismatic concrete beams (2in by 2in by 10in) were fabricated. A water-to-cement ratio of 0.49 and a total aggregate-to-cement ratio of 5 were used for preparation of concrete specimens. Crushed limestone and sand were used as coarse and fine aggregates, respectively.

All three prisms were stacked on top of each other to represent 6 in cover over reinforcement, and placed on a portable NMR as shown in Figure 232. One or more No. 4 rebars were placed at the center of the stack. The NMR relaxation signal was measured for the sensitive volume highlighted as a green bar in Figure 232a. The measurement was repeated at 2mm, 4mm and 6mm depths from the concrete (bottom) surface. T<sub>2</sub> distributions at each depth with 1, 2 and 4 rebars placed on top were obtained (Figure 233).


(a)







(c)

# Figure 232. Prismatic specimens with different number of rebars (6 in clear cover over reinforcement).

The results presented in Figure 233 indicated that, at 2mm depth, the  $T_2$  shift for concrete without any rebar placed on top (0 RF) is about 0.8ms. This shift remains unchanged as the

number of steel rebars increases. The amplitude slightly drops after addition of rebars. At 4mm and 6mm depths also, the T<sub>2</sub> shift looks unaffected by the addition of reinforcing bars. The amplitude of the main peak remains unchanged with the addition of rebars. The second peak occurring at 10-20ms has an insignificant amplitude (less than 0.03), which could be an artifact of the smoothing parameters used in inverse Laplace transformation.



Figure 233. The effect of steel reinforcement with 6 in clear cover on NMR signal of concrete at (a) 2mm, (b) 4mm, and (c) 6mm from surface.

Next, one prism was removed to simulate the effect of steel reinforcement with 4in cover. Figure

234 shows the prisms, rebars and the sensitive volume for NMR measurements.



(a)



(b)



(c)

# Figure 234. Prismatic beams and number of rebars in NMR testing with 4 in clear cover over reinforcing bars.

The NMR measurements at different depths with different number of rebars were performed

similarly. The results are presented in Figure 235. With 4 inch clear cover over reinforcement, the

 $T_2$  shift remained unchanged at all depths. At 2 and 6mm depths, the amplitude changed slightly with the addition of rebars.



Figure 235. The effect of rebars with 4 in clear cover on the NMR signal of concrete at (a) 2mm, (b) 4mm and (c) 6mm from surface.

Finally, the NMR measurements were with only 1 prismatic beam as shown in Figure 236. The exact thickness of the bottom beam was 1.7 in (simulating 1.7 in clear cover over reinforcing bars).











(c)

# Figure 236. Prismatic beams simulating 1.7 in clear cover over reinforcement, and the number of rebars used in NMR testing.

The results of the NMR measurements for this setup that simulates 1.7 in clear cover over reinforcing bars are presented in Figure 237. The NMR sensitive volume in this test setup is positioned above (but not in between) the reinforcing bars. The effects of reinforcing bars on the

shift in T<sub>2</sub> peak varies depending on the depth of investigation. At 2mm depth from surface, the T<sub>2</sub> shift toward higher values (from 0.8ms for 0 reinforcement to 0.9 for 4 reinforcements. The amplitude decreases from 0.15 for 0 reinforcement to 0.01 for 4 reinforcing bars. At 4mm depth, on the other hand, the T<sub>2</sub> peaks all occur at the same location (0.8ms) while the amplitudes increase slightly as the number of reinforcing bars increases. At 6mm depth, the effect of reinforcement seems to vanish completely. Similar trends were also observed, to a lesser extent, when 4 and 6 inches of cover were used. This finding can be explained by the variation of magnetic field in space. Magnetic forces act at a distance, which is why magnetic field is defined to represent magnetic forces. A pictorial representation of the magnetic field lines is very useful in visualizing the strength and direction of the magnetic field. Magnetic field lines are like the contour lines (constant altitude) on a topographic map in that they represent continuous features, and a different mapping scale would show more or fewer lines. For example, iron filings placed in a magnetic field line up to form lines that correspond to "field lines" as shown in Figure 238.



Figure 237. The effect of reinforcing bars with 1.7 in clear cover on the NMR signal of concrete at (a) 2mm, (b) 4mm and (c) 6mm from surface.

To overcome the interference of reinforcing bars, especially when they are very close to the surface, NMR measurements much be taken at different depths, and the resulting amplitudes should be compared. The results presented above indicate that the NMR signal with the highest amplitude should be considered for further analysis.



Figure 238. Visual representation of magnetic field lines around a bar magnet. 12.5 Field testing: Mapping and Sampling Methods

NMR testing of large concrete infrastructure should be performed efficiently such that the measurements cover the entire infrastructure (or a targeted region of it) without spending excess time and effort.

ASTM E122 covers simple methods for calculating the number of units to be included in a random approach to sampling in order to estimate, with a specified precision, a measure of quality for all units that constitute the infrastructure. This practice yields the sample size required to estimate the average value of some property at a specified precision. The practice treats the common situation where the sampling units can be considered to exhibit a single (overall) source of variability. Based on a normal distribution for the property of interest, the equation for the size, n, of the sample is as follows:

$$n = (\beta \sigma_0 / E)^2$$

where, E = maximum acceptable difference between the true average and the sample average; and  $\sigma_0 =$  The estimate of lot or process standard deviation of X, the result of measuring all the units of a finite lot or process, and the factor  $\beta$  depends upon the acceptable probability of the sampling error exceeding E:

Acceptable Probability	β
0.3%	3
1%	2.56
4.5%	2
5%	1.96
10%	1.64

A simple estimate for  $\sigma_0$  may be computed by using the average range ( $\overline{R}$ ) taken from the several

previous data sets that have the same group size.

$$\sigma_0 = \bar{R}/d_2$$

The factor  $d_2$  from Table 39 converts the average range into an unbiased estimate of  $\sigma_0$ .

Sample Size (n <sub>j</sub> )	d <sub>2</sub>
2	1.13
4	2.06
5	2.33
8	2.85
10	3.08

### Table 39 Values of the Correction Factor.

Where,  $n_i$  is the sample size in the dataset.

Besides the sample size, decisions should also be made on the locations of the infrastructure that need to be tested for representing the entire infrastructure system. Various methods are available to address this need. Latin Hypercube Sampling (LHS) is a powerful method that can be used to specify random locations along the length (and width) of a bridge deck or a pavement that represent the entire infrastructure. LHS is a statistical method for generating samples of plausible collections of parameter values from a multidimensional distribution. The method is used commonly to reduce the number of runs necessary for a Monte Carlo simulation to achieve a reasonably accurate random distribution as shown graphically in Figure 239. In this Figure, x<sub>1</sub> and x<sub>2</sub> are two parameters (here the length and width of the testing object) which form a two-dimensional problem domain. To cover the entire domain shown in Figure 239a, Monte Carlo and LHS are used separately. For this example, Monte Carlo needs 100 samples (Figure 239b) while the LHS requires 25 samples (Figure 239c) to cover the same problem domain. LHS provides significantly improved efficiency while still maintaining similar accuracy. LHS can be conveniently incorporated into an existing Monte Carlo model.



## Figure 239. Comparison between Monte Carlo and LHS simulations: (a) Entire domain; (b) Monte Carlo; and (c) LHS

Figure 240 shows two parameters (x<sub>1</sub> and x<sub>2</sub>) with minimum values of zero and maximum values of a and b, respectively. For example, if 3 samples are required, each parameter range is divided into 3 equal intervals forming a square grid containing sample positions if (and only if) there is only one sample in each row and each column (which is referred as Latin Square as shown in Figure 240). This approach reduces the number of locations that need to be tested for adequate covering of the entire system.



Figure 240. Example of sampling in LHS method.

Figure 241 shows an example of the LHS test locations on a bridge deck that is 0.1 mile long and 42 ft wide with the required number of samples (n) decided to be 10. It should be noted that the LHS rules can be satisfied by testing different (alternative) combinations of locations.





#### Figure 241. Example of a randomly generated test spots using the LHS rules.

## 12.6 Conclusions

The portable NMR system was used to nondestructively identify the cause of damage in four concrete structures. Signs of surface deterioration were noticeable in some regions of these structures. Nondestructive NMR tests were performed at different depths for the regions of structures with no (or minor) and major indications of surface deterioration. The NMR data generated for both locations of each structure were analyzed. The trends in the processed NMR data were compared with those established in the project for different mechanisms of deterioration. It was concluded that the first structure was experiencing deterioration due to alkali-silica reaction, and the second structure was experiencing freeze-thaw deterioration.

Concrete pieces were obtained from field, and subjected to XRD and SEM investigations in laboratory. In the case of Structure I, SEM images revealed microcracks around and inside aggregates propagating through the cement paste, which is consistent with the microcrack patterns we had observed for concrete experiencing ASR under accelerated aging conditions in laboratory. For Structure II, microcracks were found to be different in width and length, and

346

followed propagation patterns similar to those we had noted in concrete subjected to accelerated freeze-thaw aging in laboratory. The XRD pattern of Structure I pointed at the consumption of quartz mineral, perhaps to form amorphous silica gel under alkali-silica reactions. The findings of these corroborative tests supported the conclusions derived based on the nondestructive NMR test data generated in field.

Additional nondestructive field tests were performed using the portable NMR system. The NMR relaxation parameters were measured, and subjected to data analysis and interpretation steps using the software developed in the project. The results pointed at no major deterioration of the first structure tested here, and extensive freeze-thaw deterioration of the second structure. Corroborative SEM and XRD investigations were performed in laboratory on pieces of concrete extracted from these structures. The results of these tests were supportive of the NMR findings. XRD patterns pointed at the physical nature of deteriorations, and SEM observations produced damage patterns in the second structure which were consisted with freeze-thaw deterioration. The SEM images of concrete from the first structure confirmed the NMR finding that no major deterioration occurred in this structure.

## **13 CONCLUSION AND RECOMMENDATIONS**

### 13.1 General

In this research, an experimental-numerical approach was adopted to investigate the damage caused by various deterioration mechanisms in concrete using a portable NMR machine. The relaxation properties of water molecules in the microstructure of the damaged and control concrete was obtained. The relaxation time values and time series in these specimens were obtained and analyzed with respect the type of damage, extent of deterioration and curing and treatment conditions. Certain trends were associated with various type of deterioration mechanisms. Subsequently, corroborative tests such as UPV, dynamic modulus of elasticity test and microscopy were performed as corroborative measures. Additionally, through a series of numerical analysis, porosity and permeability properties of concrete were estimated and compared to experimental results. A software package (powered by MATLAB) was deployed to streamline the data analysis associated with NMR measurements, by comparing the new data with the previously established trends. Finally, NMR relaxometry were performed in field or on specimens obtained from field to assess the viability of the portable NMR relaxometry as an insitu nondestructive testing method. In this chapter, the key findings from this study are summarized, the research impact and its practical implications are outlined, and recommendations are lastly provided for future study.

### 13.2 Key Findings

- Concrete containing reactive aggregates experienced increasing moisture uptake as accelerated aging continues while concrete containing non-reactive limestone seemed

relatively unaffected in this regard. Relaxation times and their distributions were also determined to investigate the effect of ASR gel formation and consequent cracking on concrete pore system. Concrete made of chert seemed to have a distinguished relaxation time distribution. Compared to chert, concrete made of limestone remained unchanged over time and the relaxation time distribution does not vary significantly. The modulus of elasticity decreases for concrete containing chert and flint while it remains relatively constant for concrete made of limestone. The uranyl acetate treatment of concrete crosssections indicated the presence of ASR products, especially around coarse aggregates.

For concrete mixes prone to freeze-thaw damage, relaxation decay curves suggested that the moisture gradient with respect to depth remained unaffected by exposure to freezethaw cycles. The measured value of the initial amplitude at the concrete surface, however, was larger after exposure to freeze-thaw aging and decreases into depth. This could be due the surface microcracks formed under freeze-thaw cycles, and the moisture gradient formed as a consequence. The relaxation time distributions pointed at an increasing shift towards smaller relaxation times which correspond to the saturation of small pores where water resides largely in a confined and less mobile state. This shift was more pronounced for concrete mixtures that were more susceptible to freeze-thaw attack. Both short and long T<sub>2</sub> values remained constant with respect to depth for mixes that were resistant to freeze-thaw attack, while they changed with respect to depth for mixes that were susceptible to freeze-thaw attack. The relative change in the short and long components of the relaxation time with respect to depth also pointed at the value of this gradient as an indicator of the freeze-thaw deterioration of concrete. Although

UPV and dynamic modulus of elasticity suggested the decreased integrity of concrete under freeze-thaw attack, the corresponding trends were not as strong as those in NMR signals. Moreover, nondestructive NMR relaxometry/diffusometry tests were performed on prismatic concrete beams prepared with different aggregates, and subjected to freezethaw cycles by the Michigan DOT. Relaxation decay curves indicated that for two of the three beams the initial decay amplitude decreased with respect to depth. The initial and secondary rate of relaxation were unaffected by depth. For the third beam, however, the initial amplitudes were almost constant at different depths. Additionally, the secondary rate of relaxation decreased with respect to depth. Based on the trends established previously, the NMR test data indicate that the third beam experienced more freeze-thaw damage than the other two beams. The short value of the transverse relaxation time  $(T_2)$ , measured nondestructively via NMR relaxometry, was constant with respect to depth in all three beams. The long value of  $T_2$ , however, increased significantly throughout the depth for the third beam. The increase in long  $T_2$  is, based on the trends established earlier, an indicator of microcracking and pore widening under freeze-thaw cycles, which leads to further accumulation of water in capillaries and microcracks. In parallel, the absolute values of self-diffusion coefficient are the largest for the third beam. The values of dilation resulting from exposure to freeze-thaw cycles, measured by the Michigan DOT, correlated well with the nondestructive NMR test data. The third beam, which experienced more freeze-thaw damage per NMR test results, also experiences the greatest dilation under exposure to freeze-thaw cycles.

Under carbonation effects, carbonates precipitated as minute crystals in the capillary pore system, causing a partial filling of pores and thus densifying the hydrated cement paste. The shift in the initial amplitude of the relaxation decay curve (which represents hydrogen density) and the relaxation time distributions (that reflects upon the pore size distribution) were compatible with this established trend in carbonation effects on the concrete microstructure. Accelerated carbonation lowered the long peak in T<sub>2</sub> distribution which is associated with the larger capillary pores that tend to be partially filled with the products of carbonation reactions. Moreover, the reaction of calcium cations released to the pore solution by cement hydrates with carbonate cations leads to precipitation of calcium carbonate in the vicinity of gel pores and in capillary pores. The short  $T_2$  component of the transverse relaxation time distribution reflected this effect of carbonation on gel and finer capillary pores. The distinctions between the variations of pore systems for normal-versus high-strength concrete as well as their different levels of susceptibility to carbonation produced distinct trends in the NMR test data generated at different depths for normal-versus high-strength concrete. The effects of carbonation on the corroborative nondestructive tests used in this investigation (ultrasound pulse velocity and dynamic elastic modulus) were minor (statistically insignificant) but consistent with the densification of cement hydrates under accelerate carbonation. Scanning electron microscopic observation of the non-carbonated and carbonated concrete materials could reveal the greater extent of carbonation effects on the hydrated cement paste microstructure in normal-strength concrete when compared with highstrength concrete.

Concrete specimens subjected to accelerated sulfate attack were examined nondestructively via NMR relaxometry. The transverse relaxation time distributions obtained by processing the NMR test data were used to assess the size distributions and the prevalence of gel and capillary pores in hydrated cement paste. For all specimens at all depths, the intensity of the peak associated with gel pores decreased. Reactions involving calcium silicate hydrates could contribute to this trend. Depending on the cation type associated with the sulfate in solution (i.e., Na+, K+, or Mg2+), both calcium hydroxide and C-S-H present in the hydrated Portland cement paste could be attached by the sulfate solution. In addition, for both concrete mixtures evaluated in unaged and aged states, the initial amplitude decreased with increasing depth as a result of salt crystallization within the pore structure. The rates, however, varied between unaged and aged concrete materials. The trends seemed to differ in concrete mixtures M1 and M11. Sulfate attack was found to produce a statistically significant rise in transverse relaxation times corresponding to capillary pores, but not those corresponding to gel pores. This trend suggest that the accelerated aging conditions considered here did not reach advanced stages of sulfate attack where the C-S-H structure is altered. Salt crystallization, however, produced statistically significant effects on the capillary pore structure. The weak trends in the ultrasound pulse velocity (UPV) and dynamic modulus test results confirmed that the sulfate attack levels reached here raised the UPV and dynamic modulus of concrete, suggesting that the sulfate attack was still limited to the state of filling pores via salt crystallization, and did not advance to produce expansive and phenomena and notable chemical reactions.

- The measured values of transverse relaxation time,  $T_2$ , for concrete exposed to chloride ion showed that the mobility of water molecules decreased with diffusion of chloride ions, with chloride ions adsorbed onto the interlayer or the inner and outer surfaces of hydrates. Bi-exponential fitting to the T<sub>2</sub> decay curves indicated a decreasing trend for the short T<sub>2</sub> values corresponding to the gel pores in cement hydrates. The T2 distribution test results suggested that the intensity of the peak corresponding to gel pores decreased in almost all cases with chloride ion diffusion, while the intensity and location of the peaks corresponding to capillary pores varied significantly for different concrete materials prior to and after exposure to chloride solutions. In contrast, the values of longitudinal relaxation time, T<sub>1</sub>, seemed to be insensitive to the diffusion of chloride ions. The values of self-diffusion coefficient, D, measured for concrete materials ranged from 0.55 to 0.65 10-9 m2/s. After 60 days of exposure to chloride ion solution, D decreased consistently for all concrete materials. The measured values of ultrasonic pulse velocity and dynamic modulus of elasticity did not exhibit statistically significant sensitivities to the diffusion of chloride ions. The UPV values increased slightly, probably due to the deposition of salt crystals in voids. Conversely, the measured values of dynamic elastic modulus decreased slightly. The measured values of weight and volume of concrete specimens pointed at the insensitivity of these concrete attributes to chloride ion diffusion.
- The presence of rebar could alter the NMR results, therefore special attention must be considered. To overcome the interference of reinforcing bars, especially when they are very close to the surface, NMR measurements much be taken at different depths, and the

resulting amplitudes should be compared. The results presented above indicate that the NMR signal with the highest amplitude should be considered for further analysis.

- The numerical studies presented here, yielded plausible prediction of porosity and permeability. Selecting the appropriate coefficients is, however of great importance.
   More work is required to obtain these coefficients for concrete made of various class of aggregates.
- Portable NMR relaxometry was performed on existing concrete structures with unknown cause of damage. The obtained trained were compared to previously established trends via the home-made software package. The corroborative laboratory tests supported the findings obtained and interpreted by the NMR machine and the software respectively.

## 13.3 Research Impact and Practical Implications

The current NDT techniques are unable to rationally assess the health condition of concrete undergoing deterioration mechanisms such as cracking due to the alkali-silica reaction, repetitive freezing and thawing, carbonation among others. ASTM standards and specifications are outdated and require update based on the recent findings. However, the results presented in this study demonstrate the capabilities of portable NMR machine as a novel technique that can be implemented to identify the cause of damage in various concrete structures. Moreover, due to the relatively small size of the machine and portability of it, the location of the damage can be pin-pointed. Using the step-motor embedded in the machine, the profile of concrete structure up to a few inches in also obtainable. The proposed methodology and established trends can effectively be utilized in determination of damage when the causes of damage are unknown. In fact, portable NMR can provide a new perspective on microstate of concrete and alteration to it caused by various deterioration mechanisms.

The proposed research aimed to produce two main results. First, the proposed experimentalnumerical approach initiated the application of portable NMR in evaluating concrete undergoing various deterioration mechanisms. Second, since proposed study aimed to identify the impact of various deterioration mechanisms on NMR signals, the outcomes of research was useful to rectify the drawbacks associated with current destructive or nondestructive methods of concrete analysis.

## 13.4 Recommendations for Future Research

This study is the first research dedicated to understanding the effects of various deterioration mechanisms of concrete on the NMR relaxation signals obtained from damaged and undamaged concrete and subsequently implementing the portable NMR technique as a novel nondestructive testing method of concrete infrastructure. However, there are many questions yet to be answered to comprehensively understand the complex nature of concrete, and the broad range of phenomena associated with each deterioration mechanism of concrete. Some of the potential research topics are recommended in below:

Increase the penetration depth of magnets, to obtain a larger profile of concrete.
 Subsequently, investigate the effects of deterioration mechanisms at a higher depth and compare to their effect on the surface and near the surface.

355

- Perform NMR relaxometry near the location of steel rebar corrosion, where the concrete is being cracked. Resolve the issue of interaction between NMR magnetic field and rebars near the surface of rebar.
- Carry out NMR relaxometry testing on concrete specimens undergoing coupled deterioration mechanisms such as ASR and repetitive freezing and thawing. Subsequently perform NMR tests on concrete obtained from field that are prone to both deterioration mechanisms to check the validity of the results.
- Carry out NMR relaxometry testing on concrete specimens subjected to a combined effect of mechanical loading and other deterioration mechanisms such as ASR, repetitive freezing and thawing among others.
- Complete the database of NMR relaxation parameters started in this research. Perform
   NMR relaxometry on concrete made of different mix proportion with different cement
   supplementary materials, various admixtures at different water-to-cement ratios.
- Perform molecular dynamics simulations for relaxation phenomena in deteriorating concrete (such as in the case of alkali-silica reaction)
- Validate the permeability and porosity models of concrete presented in this study and apply them to concrete of other mix proportions. Utilize those findings towards a better understanding of processes associated with the physical and chemical deterioration mechanisms of concrete.

REFERENCES

## REFERENCES

- 1. Skibsted, J. and C. Hall, *Characterization of cement minerals, cements and their reaction products at the atomic and nano scale.* Cement and Concrete Research, 2008. **38**(2): p. 205-225.
- 2. Porteneuve, C., et al., *Nuclear magnetic resonance characterization of high-and ultrahigh-performance concrete: Application to the study of water leaching.* Cement and concrete research, 2001. **31**(12): p. 1887-1893.
- 3. Bloch, F., *Nuclear induction*. Physical review, 1946. **70**(7-8): p. 460.
- 4. Tomsett, H., *The practical use of ultrasonic pulse velocity measurements in the assessment of concrete quality.* Magazine of Concrete Research, 1980. **32**(110): p. 7-16.
- 5. Carino, N.J. *The impact-echo method: an overview*. in *Proceedings of the 2001 Structures Congress & Exposition*. 2001.
- 6. Maierhofer, C., *Nondestructive evaluation of concrete infrastructure with ground penetrating radar.* Journal of Materials in Civil Engineering, 2003. **15**(3): p. 287-297.
- Clark, M., D. McCann, and M. Forde, Application of infrared thermography to the nondestructive testing of concrete and masonry bridges. Ndt & E International, 2003. 36(4): p. 265-275.
- 8. No, T.C.S., *Guidebook on non-destructive testing of concrete structures.* 2002.
- 9. Barreira, E. and V.P. de Freitas, *Evaluation of building materials using infrared thermography*. Construction and Building Materials, 2007. **21**(1): p. 218-224.
- Suzuki, T., et al., Use of acoustic emission and X-ray computed tomography for damage evaluation of freeze-thawed concrete. Construction and Building Materials, 2010. 24(12): p. 2347-2352.
- 11. *Recommendations for testing concrete by hardness methods.* Matériaux et Construction, 1977. **10**(5): p. 313-316.
- 12. Malhotra, V.M., *Evaluation of the pull-out test to determine strength of in-situ concrete.* Matériaux et Construction, 1975. **8**(1): p. 19-31.
- 13. Nazarian, S., et al., Use of spectral analysis of surface waves method for determination of moduli and thicknesses of pavement systems. 1983.

- 14. Colombo, I.S., I. Main, and M. Forde, *Assessing damage of reinforced concrete beam using "b-value" analysis of acoustic emission signals.* Journal of materials in civil engineering, 2003. **15**(3): p. 280-286.
- 15. Polder, R.B. and W.H. Peelen, *Characterisation of chloride transport and reinforcement corrosion in concrete under cyclic wetting and drying by electrical resistivity.* Cement and Concrete Composites, 2002. **24**(5): p. 427-435.
- 16. Gonzalez, J., et al., *Errors in the electrochemical evaluation of very small corrosion rates I. polarization resistance method applied to corrosion of steel in concrete.* Corrosion Science, 1985. **25**(10): p. 917-930.
- 17. Zhang, T. and O.E. Gjørv, *An electrochemical method for accelerated testing of chloride diffusivity in concrete.* Cement and Concrete Research, 1994. **24**(8): p. 1534-1548.
- 18. Alldred, J., J. Chua, and D. Chamberlain, *Determination of reinforcing bar diameter and cover by analysing traverse profiles from a cover meter.* Deutsche Gesellschaft fur Zerstorungsfreie Prufung E. V.(Germany), 1995: p. 721-728.
- 19. Belkebir, T., et al. *Microwave tomography system for reinforced concrete structures*. in *Microwave Conference, 1994. 24th European*. 1994. IEEE.
- 20. Bolomey, J.C. and C. Pichot, *Microwave tomography: from theory to practical imaging systems*. International Journal of Imaging Systems and Technology, 1990. **2**(2): p. 144-156.
- 21. Ulrich, K., et al., *Absorption and diffusion measurements of water in acrylic paint films by single-sided NMR.* Progress in Organic Coatings, 2011. **71**(3): p. 283-289.
- 22. Kehlet, C., A. Catalano, and J. Dittmer, *Degradation of natural rubber in works of art studied by unilateral NMR and high field NMR spectroscopy.* Polymer Degradation and Stability, (0).
- 23. Kwamen, R., B. Blümich, and A. Adams, *Estimation of Self-Diffusion Coefficients of Small Penetrants in Semicrystalline Polymers Using Single-Sided NMR.* Macromolecular rapid communications, 2012. **33**(10): p. 943-947.
- 24. Guthausen, A., et al., *Measurement of fat content of food with single-sided NMR*. Journal of the American Oil Chemists Society, 2004. **81**(8): p. 727-731.
- 25. Blümich, B., et al., *Mobile NMR for analysis of polyethylene pipes*. Acta Physica Polonica A, 2005. **108**(1): p. 13-23.
- 26. Senni, L., et al., A portable NMR sensor for moisture monitoring of wooden works of art, particularly of paintings on wood. Wood Science and Technology, 2009. **43**(1-2): p. 167-180.

- 27. Danieli, E. and B. Blümich, *Single-sided magnetic resonance profiling in biological and materials science.* Journal of Magnetic Resonance, 2013. **229**(0): p. 142-154.
- 28. Adams, A. and B. Blümich. *Single-Sided NMR of Semicrystalline Polymers*. in *Macromolecular Symposia*. 2013. Wiley Online Library.
- 29. Kleinberg, R.L. and J.A. Jackson, *An introduction to the history of NMR well logging.* Concepts in Magnetic Resonance, 2001. **13**(6): p. 340-342.
- 30. Yaramanci, U., Surface Nuclear Magnetic Resonance (SNMR). A new method for exploration of ground water and aquifer properties. 2000.
- 31. Dlugosch, R., et al., Assessment of the potential of a new generation of surface nuclear magnetic resonance instruments. Near Surface Geophysics, 2011. **9**(2): p. 89-102.
- 32. Haber, A., *Analysis of porous media and objects of cultural heritage by mobile NMR*. 2012: Universitätsbibliothek.
- 33. Poli, T., et al., *A portable NMR device for the evaluation of water presence in building materials.* Journal of Cultural Heritage, 2007. **8**(2): p. 134-140.
- Orlowsky, J., Measuring the layer thicknesses of concrete coatings by mobile NMR–A study on the influence of steel reinforcements. Construction and Building Materials, 2012. 27(1): p. 341-349.
- 35. Orlowsky, J., *Mobile NMR–A Powerful Tool to Measure Coating Thicknesses in Concrete Buildings*, in *Nondestructive Testing of Materials and Structures*. 2013, Springer. p. 125-130.
- 36. Orlowsky, J., et al. *Application of the NMR-technique to concrete coatings*. in *Proceedings of the 2nd International Conference on Concrete Repair, Rehabilitation and Retrofitting*. 2008.
- 37. Milachowski, C., D. Lowke, and C. Gehlen, *Detection of transport processes during freezethaw deicing salt attack using single-sided NMR.* 2nd International conference on Microstructural-related Durability of Cementitious Composites, 2013.
- 38. Casanova, F., J. Perlo, and B. Blümich, *Single-Sided NMR*, in *Single-Sided NMR*, F. Casanova, J. Perlo, and B. Blümich, Editors. 2011, Springer Berlin Heidelberg. p. 1-10.
- 39. Timur, A., Pulsed nuclear magnetic resonance studies of porosity movable fluid and permeability of sandstones. Journal of Petroleum Technology, 1969. **21**(06): p. 775-786.
- 40. Howard, J.J. and W.E. Kenyon, *Determination of pore size distribution in sedimentary rocks by proton nuclear magnetic resonance.* Marine and petroleum geology, 1992. **9**(2): p. 139-145.

- 41. Kenyon, W., *Petrophysical principles of applications of NMR logging.* Log Analyst, 1997. **38**: p. 21-43.
- 42. Toumelin, E., et al., *Reconciling NMR measurements and numerical simulations: assessment of temperature and diffusive coupling effects on two-phase carbonate samples.* PETROPHYSICS-HOUSTON-, 2003. **44**(2): p. 91-107.
- 43. Dunn, K.-J., D.J. Bergman, and G.A. LaTorraca, *Nuclear magnetic resonance: petrophysical and logging applications*. 2002: Elsevier.
- 44. Coates, G.R., L. Xiao, and M.G. Prammer, *NMR logging: principles and applications*. 1999: Gulf Professional Publishing.
- 45. Arnold, J., *Mobile NMR for rock porosity and permeability*. 2007.
- 46. Sun, B. and K.-J. Dunn. *Core analysis with two dimensional NMR*. in *2002 International Symposium of the society of Core Analysts*. 2002. Monterey, SCA.
- 47. Cohen, M.H. and K.S. Mendelson, *Nuclear magnetic relaxation and the internal geometry of sedimentary rocks.* Journal of Applied Physics, 1982. **53**(2): p. 1127-1135.
- 48. Kleinberg, R., W. Kenyon, and P. Mitra, *Mechanism of NMR relaxation of fluids in rock.* Journal of Magnetic Resonance, Series A, 1994. **108**(2): p. 206-214.
- 49. Stingaciu, L., et al., *Determination of pore size distribution and hydraulic properties using nuclear magnetic resonance relaxometry: A comparative study of laboratory methods.* Water Resources Research, 2010. **46**(11).
- 50. Brownstein, K.R. and C. Tarr, *Importance of classical diffusion in NMR studies of water in biological cells.* Physical Review A, 1979. **19**(6): p. 2446.
- 51. Kleinberg, R.L. and M.A. Horsfield, *Transverse relaxation processes in porous sedimentary rock.* Journal of Magnetic Resonance (1969), 1990. **88**(1): p. 9-19.
- 52. Echoes, E.S., 1 EL Hahn. Spin echoes. Phys. Rev., 80 (4): 580, 1950. 2 LG Rowan, EL Hahn, and WB Mims. Electron-spin-echo envelope modulation. Phys. Rev, 1950. **80**(4): p. 580.
- 53. Carr, H.Y. and E.M. Purcell, *Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments.* Physical Review, 1954. **94**(3): p. 630-638.
- 54. Anferova, S., et al., A mobile NMR device for measurements of porosity and pore size distributions of drilled core samples. Concepts in Magnetic Resonance Part B: Magnetic Resonance Engineering, 2004. **23**(1): p. 26-32.
- 55. Borgia, G., R. Brown, and P. Fantazzini, *Uniform-penalty inversion of multiexponential decay data*. Journal of Magnetic Resonance, 1998. **132**(1): p. 65-77.

- 56. Zimmerman, J. and W.E. Brittin, *Nuclear magnetic resonance studies in multiple phase systems: lifetime of a water molecule in an adsorbing phase on silica gel.* The Journal of Physical Chemistry, 1957. **61**(10): p. 1328-1333.
- 57. Bohris, A., et al., *A broad line NMR and MRI study of water and water transport in Portland cement pastes*. Magnetic Resonance Imaging, 1998. **16**(5): p. 455-461.
- 58. Boguszynska, J., et al., *Magnetic resonance studies of cement based materials in inhomogeneous magnetic fields.* Cement and Concrete Research, 2005. **35**(10): p. 2033-2040.
- 59. Karakosta, E., et al., *In situ monitoring of cement gel growth dynamics. Use of a miniaturized permanent Halbach magnet for precise 1H NMR studies.* Industrial & Engineering Chemistry Research, 2009. **49**(2): p. 613-622.
- 60. Tziotziou, M., et al., *Application of sup> 1</sup> H NMR to hydration and porosity studies of lime–pozzolan mixtures.* Microporous and Mesoporous Materials, 2011. **139**(1): p. 16-24.
- 61. Van Landeghem, M., et al., *The roles of hydration and evaporation during the drying of a cement paste by localized NMR*. Cement and Concrete Research, 2013. **48**: p. 86-96.
- 62. McDonald, P., et al., Surface relaxation and chemical exchange in hydrating cement pastes: a two-dimensional NMR relaxation study. Physical Review E, 2005. **72**(1): p. 011409.
- 63. McDonald, P.J., et al., *Two-dimensional correlation relaxometry studies of cement pastes performed using a new one-sided NMR magnet.* Cement and concrete research, 2007.
   37(3): p. 303-309.
- 64. Gajewicz, A., et al., *A 1H NMR relaxometry investigation of gel-pore drying shrinkage in cement pastes.* Cement and Concrete Research, 2016. **86**: p. 12-19.
- 65. Cano-Barrita, P.d.J., B. Balcom, and F. Castellanos, *Carbonation front in cement paste detected by T 2 NMR measurements using a low field unilateral magnet.* Materials and Structures, 2017. **50**(2): p. 150.
- 66. Gallegos, D.P., et al., A NMR technique for the analysis of pore structure: application to materials with well-defined pore structure. Journal of colloid and interface science, 1987.
  119(1): p. 127-140.
- 67. Wolter, B. and G. Dobmann. *Nuclear magnetic resonance as a tool for the characterisation of concrete in different stages of its development*. in *Proc. Int. Symp. on Non-Destructive Testing in Civil Engineering (NDT-CE)*. 1995.

- 68. Valckenborg, R., et al., *Pore water distribution in mortar during drying as determined by NMR*. Materials and Structures, 2001. **34**(10): p. 599-604.
- 69. Schönfelder, W., et al., *NMR studies of pore formation and water diffusion in self-hardening cut-off wall materials.* Cement and concrete research, 2007. **37**(6): p. 902-908.
- 70. Orlowsky, J., Measuring the layer thicknesses of concrete coatings by mobile NMR A study on the influence of steel reinforcements. Construction and Building Materials, 2012.
   27(1): p. 341-349.
- 71. Blumich, B., et al. *Noninvasive depth profiling of walls by portable nuclear magnetic resonance*. in *Raman Spectroscopy (pp. 2629-2760) / Mass Spectrometry (pp. 2761-2916)*. 2010. Tiergartenstrasse 17, Heidelberg, D-69121, Germany: Springer Verlag.
- 72. Pel, L., et al. *Combined NMR moisture, temperature and pressure measurements during heating*. in *MATEC Web of Conferences*. 2013. EDP Sciences.
- 73. Stelzner, L., Analysis of moisture transport in unilateral-heated dense high-strength concrete. 2017.
- 74. Liakopoulou-Morris, F., et al., *Microseismic properties of a homogeneous sandstone during fault nucleation and frictional sliding.* Geophysical Journal International, 1994. **119**(1): p. 219-230.
- 75. Kenyon, W.E. and J.A. Kolleeny, *NMR surface relaxivity of calcite with adsorbed Mn2+.* Journal of colloid and interface science, 1995. **170**(2): p. 502-514.
- 76. Coates, J.D., et al., *Geothrix fermentans gen. nov., sp. nov., a novel Fe (III)-reducing bacterium from a hydrocarbon-contaminated aquifer.* International journal of systematic and evolutionary microbiology, 1999. **49**(4): p. 1615-1622.
- 77. Mirotchnik, K., et al., *Determination of oil and water compositions of oil/water emulsions using low field NMR relaxometry*. 2004, Google Patents.
- 78. Kenyon, W., *Petrophysical principles of applications of NMR logging.* The Log Analyst, 1997. **38**(02).
- 79. Pape, H., et al., *Permeability prediction for low porosity rocks by mobile NMR*. Pure and Applied Geophysics, 2009. **166**(5-7): p. 1125-1163.
- 80. Merlino, S., E. Bonaccorsi, and T. Armbruster, *Tobermorites: Their real structure and order-disorder (OD) character.* American Mineralogist, 1999. **84**(10): p. 1613-1621.
- 81. Cygan, R.T., J.-J. Liang, and A.G. Kalinichev, *Molecular models of hydroxide, oxyhydroxide, and clay phases and the development of a general force field.* The Journal of Physical Chemistry B, 2004. **108**(4): p. 1255-1266.

- 82. Korb, J.-P., et al., *Comparison of proton field-cycling relaxometry and molecular dynamics simulations for proton–water surface dynamics in cement-based materials.* Cement and Concrete Research, 2007. **37**(3): p. 348-350.
- 83. Faux, D.A. and P.J. McDonald, *Explicit calculation of nuclear-magnetic-resonance relaxation rates in small pores to elucidate molecular-scale fluid dynamics*. Physical Review E, 2017. **95**(3): p. 033117.
- 84. Faux, D., et al., *Model for the interpretation of nuclear magnetic resonance relaxometry of hydrated porous silicate materials.* Physical Review E, 2015. **91**(3): p. 032311.
- Brunet, F., et al., Characterization by solid-state NMR and selective dissolution techniques of anhydrous and hydrated CEM V cement pastes. Cement and Concrete Research, 2010.
   40(2): p. 208-219.
- 86. Sun, G.-k. and J.F. Young, *Quantitative determination of residual silica fume in DSP cement pastes by 29-SI NMR.* Cement and concrete research, 1993. **23**(2): p. 480-483.
- 87. *Coarse Aggregate Specific Gravity*. 2011; Available from: <u>http://www.pavementinteractive.org/article/coarse-aggregate-specific-gravity/</u>.
- Broekmans, M.A.T.M., Petrography as an essential complementary method in forensic assessment of concrete deterioration: Two case studies. Materials Characterization, 2009.
   60(7): p. 644-654.
- 89. *Scanning electron microscope*. Available from: <u>http://en.wikipedia.org/wiki/Scanning electron microscope</u>.
- 90. Kewalramani, M.A. and R. Gupta, *Concrete compressive strength prediction using ultrasonic pulse velocity through artificial neural networks*. Automation in Construction, 2006. **15**(3): p. 374-379.
- 91. Johnston, D.H. and M.N. Toksöz, *Ultrasonic P and S wave attenuation in dry and saturated rocks under pressure.* Journal of Geophysical Research: Solid Earth (1978–2012), 1980. **85**(B2): p. 925-936.
- 92. Birch, F., *The velocity of compressional waves in rocks to 10 kilobars: 1.* Journal of Geophysical Research, 1960. **65**(4): p. 1083-1102.
- 93. Winkler, K. and T. Plona, *Technique for measuring ultrasonic velocity and attenuation spectra in rocks under pressure.* Journal of Geophysical Research: Solid Earth (1978–2012), 1982. **87**(B13): p. 10776-10780.
- 94. Chary, K., et al. Evaluation of engineering properties of rock using ultrasonic pulse velocity and uniaxial compressive strength. in Proceedings of the national seminar on non-destructive evaluation, NDE. 2006. Citeseer.

- 95. Vasconcelos, G., et al., *Prediction of the mechanical properties of granites by ultrasonic pulse velocity and Schmidt hammer hardness.* 2007.
- 96. Winslow, D.N., *The rate of absorption of aggregates*. Cement, concrete and aggregates, 1987. **9**(2).
- 97. Dolar-Mantuani, L., *Handbook of concrete aggregates: A petrographic and technological evaluation.* NOYES DATA CORP., MILL RD. AT GRAND AVE., PARK RIDGE, NJ 07656, USA, 1983, 345, 1983.
- 98. Heaney, P.J. and J.E. Post, *The widespread distribution of a novel silica polymorph in microcrystalline quartz varieties.* Science, 1992. **255**(5043): p. 441-443.
- 99. Inefuku, H.W. *Iowa State University: Digital Repository@ Iowa State University*. in *Digital Repository Conference Papers, Posters and Presentations*. 2014.
- Stutzman, P.E., Guide for X-ray powder diffraction analysis of Portland cement and clinker.
   1996: US Department of Commerce, Technology Administration, National Institute of Standards and Technology, Office of Applied Economics, Building and Fire Research Laboratory.
- 101. Dobmann, G., et al. The Potential of Nuclear Magnetic Resonance (NMR) to Non-Destructively Characterize Early-Age Concrete by an One-Sided Access (OSA) Techniqu. in National Seminar of ISNT. 2002. Chennai, India.
- 102. Patural, L., et al., A pulsed field gradient and NMR imaging investigations of the water retention mechanism by cellulose ethers in mortars. Cement and Concrete Research, 2010. **40**(9): p. 1378-1385.
- 103. Mehta, P.K., *Concrete. Structure, properties and materials.* 1986.
- 104. Kaneuji, M., D. Winslow, and W. Dolch, *The relationship between an aggregate's pore size distribution and its freeze thaw durability in concrete.* Cement and concrete Research, 1980. **10**(3): p. 433-441.
- 105. Zhou, J., G. Ye, and K. Van Breugel, *Characterization of pore structure in cement-based materials using pressurization—depressurization cycling mercury intrusion porosimetry (PDC-MIP).* Cement and Concrete Research, 2010. **40**(7): p. 1120-1128.
- 106. Scrivener, K.L., A.K. Crumbie, and P. Laugesen, *The interfacial transition zone (ITZ)* between cement paste and aggregate in concrete. Interface Science, 2004. **12**(4): p. 411-421.
- 107. Xie, Y., et al., *Experimental study of the interfacial transition zone (ITZ) of model rock-filled concrete (RFC).* Cement and Concrete Composites, 2015. **55**: p. 223-231.

- 108. Ollivier, J., J. Maso, and B. Bourdette, *Interfacial transition zone in concrete*. Advanced Cement Based Materials, 1995. **2**(1): p. 30-38.
- 109. Bourdette, B., E. Ringot, and J. Ollivier, *Modelling of the transition zone porosity.* Cement and concrete research, 1995. **25**(4): p. 741-751.
- 110. Lemarchand, E., L. Dormieux, and F. Ulm, *Elements of micromechanics of ASR-induced swelling in concrete structures*. Concrete science and engineering, 2002. **4**(13): p. 12-22.
- 111. Bažant, Z.P. and A. Steffens, *Mathematical model for kinetics of alkali–silica reaction in concrete.* Cement and Concrete Research, 2000. **30**(3): p. 419-428.
- 112. Dron, R. and F. Brivot, *Thermodynamic and kinetic approach to the alkali-silica reaction*. *Part 2: Experiment.* Cement and Concrete Research, 1993. **23**(1): p. 93-103.
- 113. Bangert, F., D. Kuhl, and G. Meschke, *Chemo-hygro-mechanical modelling and numerical simulation of concrete deterioration caused by alkali-silica reaction.* International Journal for Numerical and Analytical Methods in Geomechanics, 2004. **28**(7-8): p. 689-714.
- 114. Danilyuk, I. and B. Rytsar, *Errors in measuring water content of materials containing hydrogen with NMR content meters.* Measurement Techniques, 1981. **24**(10): p. 875-878.
- 115. Milachowski, C., D. Lowke, and C. Gehlen. *Detection of Transport Processes During Freeze-Thaw Deicing Salt Attach Using Single-Sided NMR*. in *Second International Conference on Microstructural-Related Durability of Cementitious Composites*. 2012. Amsterdam, The Netherlands.
- 116. Blümich, B., F. Casanova, and J. Perlo, *Single-sided NMR sensor with microscopic depth resolution*. 2008, Google Patents.
- 117. Dykstra, R., *The development of a spectrometer for portable NMR systems*. 2006.
- 118. Hürlimann, M. and D. Griffin, *Spin dynamics of Carr–Purcell–Meiboom–Gill-like sequences in grossly inhomogeneous B 0 and B 1 fields and application to NMR well logging.* Journal of Magnetic Resonance, 2000. **143**(1): p. 120-135.
- 119. Perlo, J., F. Casanova, and B. Blümich, *3D imaging with a single-sided sensor: an open tomograph.* Journal of Magnetic Resonance, 2004. **166**(2): p. 228-235.
- 120. Hoult, D.I. and R.E. Richards, *The signal-to-noise ratio of the nuclear magnetic resonance experiment.* Journal of Magnetic Resonance (1969), 1976. **24**(1): p. 71-85.
- 121. Sargolzahi, M., et al., *Effectiveness of nondestructive testing for the evaluation of alkalisilica reaction in concrete.* Construction and Building Materials, 2010. **24**(8): p. 1398-1403.

- 122. Ahmed, T., et al., *The effect of alkali reactivity on the mechanical properties of concrete.* Construction and Building Materials, 2003. **17**(2): p. 123-144.
- Rivard, P. and F. Saint-Pierre, Assessing alkali-silica reaction damage to concrete with nondestructive methods: From the lab to the field. Construction and Building Materials, 2009.
   23(2): p. 902-909.
- 124. Rivard, P., et al., *Monitoring of an hydraulic structure affected by ASR: A case study.* Cement and concrete research, 2010. **40**(4): p. 676-680.
- 125. Swamy, R. and M. Al-Asali, *Engineering properties of concrete affected by alkali-silica reaction*. ACI Materials Journal, 1988. **85**(5): p. 367-374.
- 126. Saint-Pierre, F., P. Rivard, and G. Ballivy, *Measurement of alkali–silica reaction progression by ultrasonic waves attenuation.* Cement and Concrete Research, 2007. **37**(6): p. 948-956.
- 127. Chen, J., et al., *Rapid evaluation of alkali–silica reactivity of aggregates using a nonlinear resonance spectroscopy technique.* Cement and Concrete Research, 2010. **40**(6): p. 914-923.
- 128. Leśnicki, K.J., et al., *Characterization of ASR damage in concrete using nonlinear impact resonance acoustic spectroscopy technique.* NDT & E International, 2011. **44**(8): p. 721-727.
- Moradi-Marani, F., et al., Nonlinear acoustic technique of time shift for evaluation of alkali-silica reaction damage in concrete structures. ACI Materials Journal, 2014. 111(5): p. 581-592.
- Stauffer, J.D., C.B. Woodward, and K.R. White, Nonlinear ultrasonic testing with resonant and pulse velocity parameters for early damage in concrete. ACI materials journal, 2005. 102(2): p. 118-121.
- 131. Purcell, E.M., H. Torrey, and R.V. Pound, *Resonance absorption by nuclear magnetic moments in a solid.* Physical review, 1946. **69**(1-2): p. 37.
- 132. Blinc, R., et al., *NMR Relaxation Study of Adsorbed Water in Cement and C3S Pastes.* Journal of the American Ceramic Society, 1978. **61**(1-2): p. 35-37.
- Friedemann, K., F. Stallmach, and J. Kärger, NMR diffusion and relaxation studies during cement hydration—A non-destructive approach for clarification of the mechanism of internal post curing of cementitious materials. Cement and Concrete Research, 2006.
   36(5): p. 817-826.
- 134. Swamy, R.N., *The alkali-silica reaction in concrete*. 2002: CRC Press.

- 135. Chatterji, S., *Chemistry of alkali–silica reaction and testing of aggregates.* Cement and Concrete Composites, 2005. **27**(7–8): p. 788-795.
- 136. Oberholster, R. and G. Davies, *An accelerated method for testing the potential alkali reactivity of siliceous aggregates.* Cement and Concrete Research, 1986. **16**(2): p. 181-189.
- 137. Hagelia, P., CHEMISTRY OF ASR-GELS AND PORE FLUIDS IN ULTRA-ACCELERATED MORTAR BARS: EVIDENCE FOR SI-CONTROL ON GEL EXPANSION PROPERTIES.
- 138. Chatterji, S. and M. Kawamura, *Electrical double layer, ion transport and reactions in hardened cement paste.* Cement and Concrete Research, 1992. **22**(5): p. 774-782.
- 139. Sørland, G.H., et al., *Absolute pore size distributions from NMR*. Diffusion Fundamentals, 2007. **5**: p. 4.1-4.15.
- 140. Copuroglu, O., *Effect of Silica Dissolution on the Mechanical Characteristics of Alkali-Reactive Aggregates.* Journal of Advanced Concrete Technology, 2010. **8**(1): p. 5-14.
- 141. Gillott, J.E., *Review of expansive alkali-aggregate reactions in concrete.* Journal of Materials in Civil Engineering, 1995. **7**(4): p. 278-282.
- 142. Cho, T., *Prediction of cyclic freeze*—thaw damage in concrete structures based on response surface method. Construction and Building Materials, 2007. **21**(12): p. 2031-2040.
- 143. Setzer, M.J. and A. Liebrecht. *Modeling and testing the freeze-thaw attack by micro-icelens model and cdf/cif-test.* in *Hokk Workshop.* 2004.
- 144. Powers, T.C., *The physical structure and engineering properties of concrete*. 1900.
- 145. Meier, U. and A. Harnik, *Das gefrieren von wasser in zementstein bei verhinderter verdunstung*. Cement and Concrete Research, 1978. **8**(5): p. 545-551.
- 146. Setzer, M., *Action of frost and deicing chemicals: basic phenomena and testing.* Freeze—thaw durability of concrete, 1976: p. 3-21.
- 147. Bary, B. and A. Sellier, *Coupled moisture—carbon dioxide—calcium transfer model for carbonation of concrete.* Cement and concrete research, 2004. **34**(10): p. 1859-1872.
- 148. Dlugokencky, E. *ESRL Global Monitoring Division*. 2015; Available from: http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html.
- 149. Lagerblad, B., *Carbon dioxide uptake during concrete life cycle–state of the art.* Swedish Cement and Concrete Research Institute CBI, Stockholm, 2005.

- 150. Šauman, Z., *Carbonization of porous concrete and its main binding components*. Cement and Concrete Research, 1971. **1**(6): p. 645-662.
- 151. Puertas, F., M. Palacios, and T. Vázquez, *Carbonation process of alkali-activated slag mortars.* Journal of Materials Science, 2006. **41**(10): p. 3071-3082.
- 152. Pu, Q., et al., *Evolution of pH and chemical composition of pore solution in carbonated concrete.* Construction and Building Materials, 2012. **28**(1): p. 519-524.
- 153. Roy, S.K., K.B. Poh, and D.o. Northwood, *Durability of concrete—accelerated carbonation and weathering studies*. Building and Environment, 1999. **34**(5): p. 597-606.
- 154. Sufian Badar, M., et al., *Corrosion of steel bars induced by accelerated carbonation in low and high calcium fly ash geopolymer concretes.* Construction and Building Materials, 2014. **61**(0): p. 79-89.
- 155. Claisse, P.A., *The properties and performance of high strength silica fume concrete*. 1988, University of Leeds.
- 156. Atiş, C.D., Accelerated carbonation and testing of concrete made with fly ash. Construction and Building Materials, 2003. **17**(3): p. 147-152.
- 157. Andrade, C., J. Sarría, and C. Alonso, *Relative humidity in the interior of concrete exposed to natural and artificial weathering.* Cement and concrete research, 1999. **29**(8): p. 1249-1259.
- 158. Lagerblad, B., Mechanism and mode of carbonation of cementitious materials, in proceedings of the International Conference on Sustainability in the Cement and Concrete Industry, ed. by Jacobsen S. Jahren P, Kjellsen KO, Lillehammer, Norway, 2007.
- 159. Meland, I. *Carbonation effects in hardened fly ash cements*. in *MRS Proceedings*. 1985. Cambridge Univ Press.
- 160. Rozière, E., R. El-Hachem, and A. Loukili, *Construction Degradation by External Sulfate Attacks*. Structure Design and Degradation Mechanisms in Coastal Environments: p. 197-245.
- 161. Sims, I. and S.A. Huntley, *The thaumasite form of sulfate attack-breaking the rules*. Cement and concrete composites, 2004. **26**(7): p. 837-844.
- 162. Hill, J., et al., *An experimental study of combined acid and sulfate attack of concrete.* Cement and concrete composites, 2003. **25**(8): p. 997-1003.
- 163. Goudie, A. and H.A. Viles, *Salt weathering hazard*. 1997: Wiley.

- 164. Scherer, G.W., *Stress from crystallization of salt.* Cement and concrete research, 2004. **34**(9): p. 1613-1624.
- 165. Haynes, H., R. O'Neill, and P.K. Mehta, *Concrete Deterioration From Phusical Attack By Salts.* Concrete International, 1996. **18**(1): p. 63-68.
- 166. Mehta, P.K., *Sulfate attack on concrete separating myths from reality.* Concrete International, 2000. **22**(8): p. 57-61.
- 167. Nehdi, M., A. Suleiman, and A. Soliman, *Investigation of concrete exposed to dual sulfate attack.* Cement and Concrete Research, 2014. **64**: p. 42-53.
- 168. Irassar, E., A. Di Maio, and O. Batic, *Sulfate attack on concrete with mineral admixtures.* Cement and Concrete Research, 1996. **26**(1): p. 113-123.
- 169. Amirpasha Peyvandi, P.S. and J. Shervin, *Structural Design Methodologies for Concrete Pipes with Steel and Synthetic Fiber Reinforcement.* Structural Journal. **111**(1).
- 170. Stark, D., *Durability of concrete in sulfate-rich soils*. 1989: Portland Cement Association.
- 171. Yoshida, N., et al., *Salt weathering in residential concrete foundations exposed to sulfatebearing ground.* Journal of Advanced Concrete Technology, 2010. **8**(2): p. 121-134.
- 172. Liu, Z., et al., *Micro-analysis of the role of interfacial transition zone in "salt weathering" on concrete.* Construction and Building Materials, 2010. **24**(11): p. 2052-2059.
- 173. Irassar, E., *Sulfate attack on cementitious materials containing limestone filler—A review.* Cement and Concrete Research, 2009. **39**(3): p. 241-254.
- 174. Cohen, M.D. and B. Mather, *Sulfate attack on concrete: research needs.* ACI Materials Journal, 1991. **88**(1).
- 175. Mehta, P. and O. Gjorv, *New Test For Sulfate Resistance Of Cements.* ASTM Journal of Testing and Evaluation, 1974. **2**(6).
- 176. Mehta, P.K. *Evaluation of sulfate-resisting cements by a new test method*. in *ACI Journal Proceedings*. 1975. ACI.
- 177. Idom, G., V. Johansen, and N. Thaulow, *Assessment of causes of cracking in concrete*. Materials Science in Concrete III, Amer. Ceramic Sot., New York, 1992.
- 178. Mehta, P., Sulfate attack on concrete--a critical review. Mater. Sci. Concr., IIIpp., 1992.
   105.
- 179. Tumidajski, P.J. and I. Turc, *A rapid test for sulfate ingress into concrete.* Cement and concrete research, 1995. **25**(5): p. 924-928.
- 180. Mehta, P.K., D. Pirtz, and M. Polivka, *Properties of alite cements*. Cement and concrete research, 1979. **9**(4): p. 439-450.
- 181. Accelerated Test for Measuring Sulfate Resistance of Hydraulic Cements for Caltrans LLPRS Program.
- 182. Brown, P.W., An evaluation of the sulfate resistance of cements in a controlled environment. Cement and Concrete Research, 1981. **11**(5): p. 719-727.
- 183. ultShannag, M. and H.A. Shaia, *Sulfate resistance of high-performance concrete*. Cement and Concrete Composites, 2003. **25**(3): p. 363-369.
- 184. Rozière, E., et al., *Durability of concrete exposed to leaching and external sulphate attacks*. Cement and Concrete Research, 2009. **39**(12): p. 1188-1198.
- 185. Lee, S., H. Moon, and R. Swamy, *Sulfate attack and role of silica fume in resisting strength loss.* Cement and Concrete Composites, 2005. **27**(1): p. 65-76.
- Sahmaran, M., et al., Effects of mix composition and water-cement ratio on the sulfate resistance of blended cements. Cement and Concrete composites, 2007. 29(3): p. 159-167.
- 187. Peterson, O., Chemical attack of strong chloride solutions on concrete. Does experience confirm that different chloride salts may influence concrete in different ways? Report TVBM, 1984.
- 188. Neville, A., *Chloride attack of reinforced concrete: an overview.* Materials and Structures, 1995. **28**(2): p. 63-70.
- 189. Samson, E., et al., *Modelling ion diffusion mechanisms in porous media*. International journal for numerical methods in engineering, 1999. **46**(12): p. 2043-2060.
- 190. Buenfeld, N. and J. Newman, *Examination of three methods for studying ion diffusion in cement pastes, mortars and concrete.* Materials and Structures, 1987. **20**(1): p. 3-10.
- 191. Takewaka, K., T. Yamaguchi, and S. Maeda, *Simulation model for deterioration of concrete structures due to chloride attack.* Journal of Advanced concrete technology, 2003. **1**(2): p. 139-146.
- 192. Zhan, H., F. Wittmann, and T. Zhao, *Chloride barrier for concrete in saline environment established by water repellent treatment.* International Journal for restoration of Buildings and Monuments, 2003. **9**(5): p. 535-550.
- 193. Polder, R.B., *Electrochemical chloride removal from concrete prisms containing chloride penetrated from sea water.* Construction and Building Materials, 1996. **10**(1): p. 83-88.

- 194. Biczok, I. and Z. Szilvássy, *Concrete corrosion and concrete protection*. 1964.
- 195. Heller, L. and M. Ben-Yair, *Effect of sulphate solutions on normal and sulphate-resisting portland cement.* Journal of Applied Chemistry, 1964. **14**(1): p. 20-30.
- 196. Rehsi, S. and A. Majumdar, *Quantitative determination of uncombined MgO in portland cement clinker by X-ray diffractometry.* Journal of Applied Chemistry, 1968. **18**(10): p. 297-300.
- 197. Suryavanshi, A.K., J.D. Scantlebury, and S.B. Lyon, *Mechanism of Friedel's salt formation in cements rich in tri-calcium aluminate.* Cement and Concrete Research, 1996. **26**(5): p. 717-727.
- 198. Birnin-Yauri, U.A. and F.P. Glasser, *Friedel's salt, Ca2Al(OH)6(Cl,OH)·2H2O: its solid solutions and their role in chloride binding.* Cement and Concrete Research, 1998. **28**(12): p. 1713-1723.
- Glasser, F.P., A. Kindness, and S.A. Stronach, Stability and solubility relationships in AFm phases: Part I. Chloride, sulfate and hydroxide. Cement and Concrete Research, 1999.
  29(6): p. 861-866.
- 200. Midgley, H. and J. Illston, *The penetration of chlorides into hardened cement pastes*. Cement and Concrete Research, 1984. **14**(4): p. 546-558.
- 201. Kalousek, G. and E.J. Benton, *Mechanism of seawater attack on cement pastes*. Am Concrete Inst Journal & Proceedings, 1970.
- 202. McGrath, P.F. and R.D. Hooton, *Re-evaluation of the AASHTO T259 90-day salt ponding test.* Cement and Concrete Research, 1999. **29**(8): p. 1239-1248.
- 203. Stanish, K., R. Hooton, and M. Thomas, *Testing the chloride penetration resistance of concrete: a literature review.* FHWA contract DTFH61, 1997: p. 19-22.
- 204. Build, N.T., *443.* Concrete, Hardened: Accelerated Chloride Penetration," NORDTEST, Espoo, Finland, 1995.
- 205. Spohr, E., et al., *Water in porous glasses. A computer simulation study.* Journal of Molecular Liquids, 1999. **80**(2): p. 165-178.
- 206. Suryavanshi, A., J. Scantlebury, and S. Lyon, *Mechanism of Friedel's salt formation in cements rich in tri-calcium aluminate.* Cement and concrete research, 1996. **26**(5): p. 717-727.
- 207. Kalinichev, A.G., R.J. Kirkpatrick, and R.T. Cygan, *Molecular modeling of the structure and dynamics of the interlayer and surface species of mixed-metal layered hydroxides: chloride*

*and water in hydrocalumite (Friedel's salt).* American Mineralogist, 2000. **85**(7-8): p. 1046-1052.

- 208. Conte, P., *Effects of ions on water structure: a low-field 1H T1 NMR relaxometry approach.* Magnetic Resonance in Chemistry, 2015. **53**(9): p. 711-718.
- 209. Kanno, H., et al., *Structure-making ions become structure breakers in glassy aqueous electrolyte solutions*. Chemical Physics Letters, 2006. **427**(1–3): p. 82-86.
- 210. Kawadkar, K.G. and S. Krishnamoorthy, *Behaviour of cement concrete under common salt solution both under hydrostatic and atmospheric pressures.* Cement and Concrete Research, 1981. **11**(1): p. 103-113.
- 211. Hook, J.R., *An introduction to porosity*. Petrophysics, 2003. **44**(03).
- 212. Kleinberg, R., et al. *Nuclear magnetic resonance of rocks: T1 vs. T2*. in *SPE annual technical conference and exhibition*. 1993. Society of Petroleum Engineers.
- 213. Lonnes, S., A. Guzman-Garcia, and R. Holland. *NMR petrophysical predictions on cores*. in *SPWLA 44th Annual Logging Symposium*. 2003. Society of Petrophysicists and Well-Log Analysts.