

**REVISITING THE CHLORIDE DIFFUSION COEFFICIENT
MEASUREMENT FOR CEMENT PASTE AND MORTAR AND
A PROPOSED NEW METHODOLOGY**

VANDANA C PADMANABHAN



**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JANUARY 2024**

**REVISITING THE CHLORIDE DIFFUSION COEFFICIENT
MEASUREMENT FOR CEMENT PASTE AND MORTAR AND
A PROPOSED NEW METHODOLOGY**

by

VANDANA C PADMANABHAN

Department of Civil Engineering

Submitted
in fulfillment of the requirements of degree of
Doctor of Philosophy

to the



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
JANUARY 2024**

CERTIFICATE

This is to certify that the thesis titled “**REVISITING THE CHLORIDE DIFFUSION COEFFICIENT MEASUREMENT FOR CEMENT PASTE AND MORTAR AND A PROPOSED NEW METHODOLOGY**” being submitted by **Ms. Vandana C Padmanabhan** to the Indian Institute of Technology Delhi, India, for the award of the degree of **Doctor of Philosophy** in Civil Engineering, is a record of original bona fide research work carried out by her under my guidance and supervision. To the best of my knowledge, the thesis has reached the requisite standard, fulfilling the requirements for the degree of Doctor of Philosophy. The material contained in this thesis, in part or in full, has not been submitted to any other university or institute for the award of any degree or diploma.

Prof. Bishwajit Bhattacharjee

Emeritus Professor

Department of Civil Engineering

Indian Institute of Technology Delhi

Hauz Khas, New Delhi - 110016

Acknowledgements

I would like to thank Prof. Bhattacharjee, guide and a mentor to me over the last eight years of my doctoral research journey. He is kind, motivating and encouraging while giving me the space and freedom to conduct research and I am honoured to have worked with such a great teacher and researcher.

My son, Aarav deserves a special thank you. He has been a constant source of energy, affection and a burst of positivity I needed to see this through. I would like to express my gratitude to Appa and Amma, who would drop whatever they were doing to step in and take over whenever I needed them to. Appa (backed by Amma) was a pillar of support, and instrumental in the completion of all my experimental work just in time before the nationwide lockdown in 2020 happened. Narayanan, my partner has been a constant cheerleader for all the things I do and Ashwin, who helped me out with Anova. It has taken a village to reach here and I am grateful. In the little time on campus, I made some friendships which I am sure I will be taking with me for life: Suresh, Nabeel, Sreejith, Arun and Aswathy gave me memories of fun conversations over tea and lunches and sharing the good, bad and ugly of the PhD journey. Thank you! I am thankful to the lab staff specially Tarun and the group of enthusiastic interns who helped me with the numerous trials of experimental work over two years. I have to mention Albert and Ann who motivated me at the right time to overcome a slump and finish writing.

I would like to thank the team at Community Design Agency, for being supportive and understanding of the demands of pursuing a part time PhD. The team, especially Sandhya and Delight have been very encouraging and absolute cheerleaders, doing whatever they could to ensure that I get the time and the space for research.

I would like to thank all the teachers from whom I have learnt so many different things over these years. I owe my English language abilities to (Late) Sarada mami, who inculcated a love for writing and reading from a very young age. I would also like to thank Prof. Gettu, who has been my mentor at all stages.

Last but never the least I would like to thank God for his blessings and grace without which none of this would be possible!

Vandana

Thesis title:

**REVISITING THE CHLORIDE DIFFUSION COEFFICIENT
MEASUREMENT FOR CEMENT PASTE AND MORTAR AND A
PROPOSED NEW METHODOLOGY**

Name of student:

Vandana C Padmanabhan

Entry number:

2015CEZ8361

Name of supervisor:

Prof. B Bhattacharjee

ABSTRACT

Chloride is the most commonly present contaminant which results in corrosion of rebars. Chloride can enter concrete from sea water, ground water or as an aerosol in the coastal areas. The attack is aggressive and results in wide spread damage. The mechanism of chloride diffusion in concrete has been studied by various researchers since many years and recent research is focused on accelerated testing methods which may not provide an accurate representation of the chloride diffusion process. The impact of chloride concentration on the experimentally determined effective diffusion coefficient has also not been studied in sufficient detail. The commonly adopted models used for calculation of effective chloride diffusion does not consider chloride concentration as a parameter that impacts the diffusion coefficient value. There is a need to study the process thoroughly and gain a better understanding of the fundamentals of chloride transport. This research focuses on developing a new methodology for the calculation of effective chloride diffusion coefficient in cement paste and mortar specimens. While the traditional models calculate effective chloride diffusion coefficient by incorporating many parameters, the calculation itself becomes tedious and the parameters to be estimated are difficult. In this research, a new model has been developed by considering the parameters which have the most impact on diffusion coefficient while also being quantifiable with much ease. This ensures that the model is not intimidating and has improved applicability. A methodology has also been developed to obtain the required parameters in the least possible duration.

The methodology developed reduces the time required for the test significantly without compromising on the accuracy of results. The major contributors to chloride diffusion coefficient: water to cement ratio, type of cation, duration of curing and exposure have been considered in the development of this methodology. The results show that the chloride diffusion coefficient in cement based porous media is a function of the chloride concentration at a given depth and also depends on material parameters such as curing duration and water to cement ratio.

सार

क्लोराइड सबसे आम तौर पर मौजूद संदूषक है जिसके परिणामस्वरूप सरिया का क्षरण होता है। क्लोराइड समुद्र के पानी, भूजल या तटीय क्षेत्रों में एरोसोल के रूप में कंक्रीट में प्रवेश करता है। कंक्रीट में क्लोराइड प्रसार के तंत्र का अध्ययन विभिन्न शोधकर्ताओं द्वारा कई वर्षों से किया जा रहा है और हालिया शोध त्वरित परीक्षण तेज़ विधियों पर केंद्रित है जो क्लोराइड प्रसार प्रक्रिया का सटीक प्रतिनिधित्व प्रदान नहीं कर सकते हैं। प्रयोगात्मक रूप से निर्धारित प्रभावी प्रसार गुणांक पर क्लोराइड एकाग्रता के प्रभाव का भी पर्याप्त विस्तार से अध्ययन नहीं किया गया है। प्रभावी क्लोराइड प्रसार की गणना के लिए उपयोग किए जाने वाले आमतौर पर अपनाए गए मॉडल क्लोराइड एकाग्रता को एक प्राचल के रूप में नहीं मानते हैं जो प्रसार गुणांक मान को प्रभावित करता है। प्रक्रिया का गहन अध्ययन करने और क्लोराइड परिवहन के बुनियादी सिद्धांतों की बेहतर समझ हासिल करने की आवश्यकता है। यह शोध सीमेंट पेस्ट और मोर्टार नमूनों में प्रभावी क्लोराइड प्रसार गुणांक की गणना के लिए एक नई पद्धति विकसित करने पर केंद्रित है। जबकि परंपरागत मॉडल कई मापदंडों को शामिल करके प्रभावी क्लोराइड प्रसार गुणांक की गणना करते हैं, गणना स्वयं कठिन हो जाती है और अनुमानित मापदंडों का अनुमान लगाना कठिन होता है। उन मापदंडों पर विचार करके एक मॉडल विकसित किया गया है जो प्रसार गुणांक पर सबसे अधिक प्रभाव डालते हैं और बहुत आसानी से मात्रात्मक भी होते हैं। यह सुनिश्चित करता है कि मॉडल प्रयोज्यता में सुधार हुआ है। न्यूनतम संभव अवधि में आवश्यक पैरामीटर प्राप्त करने के लिए एक पद्धति भी विकसित की गई है।

विकसित की गई पद्धति परिणामों की सटीकता से समझौता किए बिना परीक्षण के लिए आवश्यक समय को काफी कम कर देती है। क्लोराइड प्रसार गुणांक में प्रमुख योगदानकर्ता: इस पद्धति के विकास में पानी से सीमेंट अनुपात, केटायन का प्रकार, इलाज की अवधि और एक्सपोज़र पर विचार किया गया है। नतीजे बताते हैं कि सीमेंट आधारित छिद्रपूर्ण मीडिया में क्लोराइड प्रसार गुणांक एक निश्चित गहराई पर क्लोराइड एकाग्रता पर निर्भर है और यह सामग्री के मापदंडों जैसे कि इलाज की अवधि और पानी से सीमेंट अनुपात पर भी निर्भर करता है।

Contents

A Certificate	i
B Acknowledgements	ii
C Abstract	iii
1 Introduction	1
1.1 Thesis structure	3
2 Literature Review	4
2.1 General	4
2.2 Corrosion of steel in concrete	4
2.2.1. General corrosion	4
2.2.2. Pitting corrosion	5
2.3 Chlorides induced corrosion in reinforcement steel	6
2.4 Transport mechanisms in concrete with reference to chloride ingress	6
2.4.1. Permeation	7
2.4.2. Absorption and hydraulic diffusivity	8
2.4.3. Diffusion	8
2.4.4. Migration	8
2.5 Chloride ingress in concrete	9
2.6 Mechanism of chloride transport in unsaturated concrete	9
2.7 Mechanism of chloride transport in water-saturated concrete	13
2.8 Basic equations of molecular diffusion	16
2.9 Continuity equation for diffusion	18
2.9.1 Diffusion and ionic mobility	21
2.10 Material parameters affecting chloride ingress in concrete	22
2.10.1 Formation factor	23
2.10.2 Porosity and pore size distribution	24
2.10.3 Tortuosity and other material parameters	25
2.11.4. Exposure temperature	26
2.11.5. Supplementary cementitious materials and chlorides binding	26

2.11.6.	Curing conditions	27
2.11	Chloride ingress in the service life context	28
2.12.1.	Theory of failure probability and service life	30
2.12	Methodologies adopted for measurement of chloride diffusion coefficient	32
2.13	Research Gap	33
2.14	Objectives	34
3	Comparison of methodologies adopted for the calculation of chloride diffusion coefficient	36
3.1	General	36
3.2	Test methods for measurement of chloride diffusion coefficient	36
3.3	Bulk Diffusion Test	37
3.4	NORD Test: NT Build 443	37
3.5	AFREM Method	38
3.6	Alkali leaching method	39
3.7	ASTM Standard Test Method for Water-Soluble Chloride in Mortar and Concrete	40
3.8	Volhard's method RILEM TC 178	40
3.9	Gran's method	40
3.10	Maultzsch's procedure	41
3.11	The Rapid Migration Test (CTH Test)	41
3.12	Accelerated chloride migration test NT Build 492	43
3.13	Advantages and drawbacks of test methods to measure chlorides in concrete	44
3.14	Drawbacks of the methods currently adopted	46
3.15	Drawbacks of the models presently adopted	47
3.16	Comparison of migration and immersion test	48
4	Proposed new methodology for estimation of Chloride diffusion coefficient and Experimental Program	54
4.1	General	54
4.2	Experimental methodology developed	54
4.2.1	Basis for design of experimental methodology	54
4.3	Design and Dimensions of experimental set-up	56

4.4	Sample conditioning and exposure duration	58
4.5	Calculation of chloride diffusion coefficient	58
4.6	Calculation of chloride diffusion coefficient as a function of concentration	59
4.7	Experimental procedure	62
4.7.1	Testing for free chlorides	66
4.7.2	Testing for total chlorides	66
4.8	Advantages of using this method	66
4.9	Experimental Parameters Investigated	67
4.10	Materials required for the experiment	67
4.10.1	Casting and curing:	67
4.10.2	Chloride exposure	67
4.10.3	Chlorides testing by titration	68
4.11	Experimental Design	68
4.11.1	Water to cement ratio	68
4.11.2	Curing duration	68
4.11.3	Exposure duration	68
4.11.4	Type of cation	68
4.11.5	Concentration of chloride ion in solution	69
4.12	Materials used in casting and curing	70
4.12.1	Ordinary Portland Cement 43 grade	70
4.12.2	Sand	72
4.12.3	Superplasticizer	72
4.13	Materials used in Chloride exposure	73
4.13.1	Chlorides salts	73
4.13.2	Damp Proof Epoxy Coating	73
4.13.3	Silicone water repellent	74
4.14	Materials used for testing	74
4.15	Quantum of experimental work performed	74
5	Results and Discussions	77
5.1	General	77

5.2	NORD Test (NT Build 443) for calculation of chloride diffusion coefficient	77
5.3	Procedure adopted by the new methodology proposed for calculating effective chloride diffusion coefficient in cement paste and cement mortar samples	80
5.4	Results of cement paste	82
5.5	Influence of type of cation of chloride diffusion coefficient for cement paste samples	85
5.6	Results of cement mortar	86
5.7	Influence of type of cation of chloride diffusion coefficient for cement mortar samples	90
6	Conclusions and recommendations for further studies	91
6.1	General	91
6.2	Conclusions and Salient contributions from this study	91
6.3	Recommendations for future study	92
7	References	93

List of tables and figures

Figure 2-1 Mechanism of chlorides induced corrosion.....	5
Figure 2-2 Diffusion in a binary solution.....	17
Figure 2-3 An elemental fluid volume	18
Figure 2-4 Stages of deterioration.....	29
Figure 2-5 Illustration of increase of failure probability with time	31
Figure 3-1 Salt ponding test set up	37
Figure 3-2 Graph of results obtained from AFREM Method.....	39
Figure 3-6 Comparison of immersion and migration test	50
Figure 4-1 Experimental set up developed in this research.....	56
Figure 4-2 Samples placed for exposure and samples being crushed for testing	64
Figure 4-3 Samples sieved through 90 micron sieve and samples bagged and placed in temperature and humidity controlled environment until testing.....	65
Figure 4-4 Details of experimental design	70
Figure 4-5 Particle size distribution of sand.....	73
Figure 5-1 Chlorides profile obtained from NORD Test	79
Figure 5-2 Diffusion coefficient calculation using error function solution as recommended by NORD Test	80
Figure 5-3 $\ln w$ versus Φ^2 showing poor linear correlation	81
Figure 5-6,5-7,5-8 Variation in diffusion coefficient at the surface and at 50 mm depth from the surface.....	87
 Table 4-1 Concentration of cation considered.....	 69
Table 4-2 Results of XRF conducted on cement	71
Table 4-3 Samples tested in the experimental scheme (example for Sodium chloride)	75
Table 5-1 Test criteria for NORD Test	77
Table 5-2 Results of ANOVA performed on cement paste samples	84
Table 5-3 ANOVA analysis performed on chloride diffusion values of cement mortar samples	89