MICROSTRUCTURE, MASS TRANSPORT, AND CORROSION OF STEEL IN CARBONATED SYSTEMS WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS

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By

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Submitted

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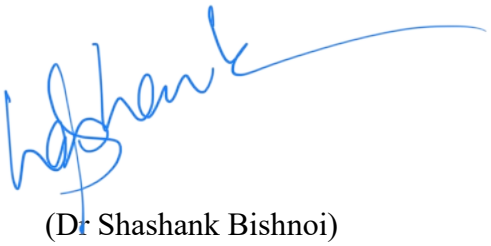
CERTIFICATE

This is to certify that the thesis entitled "**MICROSTRUCTURE, MASS TRANSPORT, AND CORROSION OF STEEL IN CARBONATED SYSTEMS WITH SUPPLEMENTARY CEMENTITIOUS MATERIALS**," being submitted by **Mr. Lupesh** to the Indian Institute of Technology Delhi, for the award of '**Doctor of Philosophy**' in Department of Civil Engineering is a record of the bonafide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for submission of this thesis, which, to the best of our knowledge, has reached the requisite standard.

The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any other degree or diploma.



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ABSTRACT

With the increasing use of supplementary cementitious materials (SCMs) to reduce the clinker factor and move toward near-zero emissions in construction, the potential risk of reinforcement corrosion due to carbonation poses a major roadblock to the acceptance of low-clinker cements. The physicochemical process of carbonation involves the reaction of carbon dioxide with the alkaline constituents of the cementitious matrix, leading to the formation of calcium carbonate. The dissolution, neutralization, and precipitation processes happening within the pore network, results in notable changes in mineralogy, pore solution composition, and pore structure characteristics. In a near-neutral pH environment (8~9), the natural passive film on reinforcing steel maintained by the high alkalinity of the cementitious matrix deteriorates. Consequently, when the carbonation front reaches the reinforcement depth, a significant level of corrosion may initiate, potentially impacting the long-term durability of reinforced concrete structures.

The objective of this study was to investigate the mass transport properties and corrosion kinetics in carbonated mortars with various binder compositions. The research investigated mortars cast at water-to-binder ratio (w/b) – 0.4, 0.5, and 0.6 cast with a control binder ordinary Portland cement (PC), along with binary binders consisting of PC-Fly ash and PC-Slag, and ternary binders incorporating PC-Calcined Clay-Limestone and PC-Slag-Fly ash. The study focused on understanding the microstructural evolution, mass transport characteristics, and corrosion kinetics under carbonation exposure.

Mass transport properties were evaluated through sorption, oxygen permeability, and chloride migration experiments, which were then correlated with pore structure characteristics determined using Mercury Intrusion Porosimetry (MIP), nitrogen adsorption, water-accessible porosity, and degree of water saturation. The phase assemblage and microstructural evolution upon carbonation were analyzed using X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), nitrogen adsorption, Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). Finally, the corrosion kinetics in different binder compositions under varying external relative humidity were studied using Linear Polarization Resistance (LPR), resistivity, half-cell potential, pore solution characteristics, and moisture content.

Upon carbonation, significant changes in transport properties and pore structure characteristics were observed. Blended binder compositions exhibited an increase in mass transport rates, whereas PC showed a decrease. The primary reason for the increased transport rate in blended compositions after carbonation was the higher pore connectivity factor, larger critical pore

diameter, and increased threshold pore diameter. Furthermore, carbonation-induced changes led to a cement-agnostic correlation between mass transport properties and pore structure characteristics, with a strong correlation observed between water-accessible porosity and various transport properties. The analysis of phase assemblage and microstructural evolution in cement paste at different degrees of carbonation revealed that C-S-H decalcification leads to the formation of de-calcified C-S-H/silica gel, resulting in an open and larger-pore structure. Consequently, a higher degree of carbonation in blended cements results in a greater extent of C-S-H decalcification, leading to increased pore connectivity, reduced tortuosity, and enhanced transport properties.

Across different binder compositions, corrosion rate was found to depend mainly on the available moisture content and pore connectivity, dictating the percentage area actively corroding and movement of ferrous ions away from the corroding surface. Additionally, the slope and intercept of the corrosion rate–resistivity linear relationship were found to depend on the interplay of pore structure characteristics, pore solution composition, and capillary condensation. Specifically, binders with higher $[Cl^-]/[OH^-]/[SO_4^{2-}]/[OH^-]$, lower resistivity, greater porosity, and higher pore connectivity exhibited lower intercepts and slopes. The laboratory study and the investigation of a 50-year-old RC structure demonstrated that carbonation or loss of passivity does not necessarily result in significant reinforcement corrosion. Notably, when external relative humidity falls below 75%, the corrosion rate remains practically negligible. Based on Evans' diagram and corrosion kinetics parameters, a corrosion rate prediction model was developed using corrosion potential and resistivity measurements. This model was validated through results from inspection of a real RC structure, confirming its applicability in assessing corrosion risk under carbonated conditions.

सार

निर्माण क्षेत्र में क्लिंकर कारक को घटाकर शून्य उत्सर्जन की दिशा में बढ़ने हेतु सहायक सीमेंटयुक्त पदार्थों का उपयोग तेजी से बढ़ रहा है। हालांकि, इसके कारण कार्बोनीकरण से उत्पन्न इस्पात सुदृढीकरण (reinforcement) के क्षरण की संभावना, कम-क्लिंकर सीमेंट को अपनाने में एक महत्वपूर्ण बाधा बनकर उभरती है। कार्बोनीकरण एक भौतिक-रासायनिक प्रक्रिया है जिसमें सीमेंटित मैट्रिक्स की क्षारीय घटकों के साथ कार्बन डाइऑक्साइड की अभिक्रिया होकर कैल्शियम कार्बोनेट का निर्माण होता है। यह प्रक्रिया छिद्र संरचना में घुलनशीलता, उदासीनता, और अवक्षेपण जैसी घटनाओं के माध्यम से खनिज संरचना, छिद्र विलयन संरचना, तथा छिद्र संरचना विशेषताओं में महत्वपूर्ण परिवर्तन लाती है। जब pH मान ~8-9 के निकट पहुँचता है, तो सीमेंट मैट्रिक्स द्वारा बनी प्राकृतिक निष्क्रिय परत बिगड़ जाती है। फलस्वरूप, जब कार्बोनीकरण अग्रभाग सुदृढीकरण की गहराई तक पहुँचता है, तब इस्पात क्षरण प्रारंभ हो सकता है, जो दीर्घकालिक स्थायित्व को प्रभावित करता है।

इस शोध का उद्देश्य विभिन्न बाइंडर संरचनाओं वाली कार्बोनेटेड मोर्टार में द्रव्यमान परिवहन गुणों एवं क्षरण गतिकी का अध्ययन करना था। जल-बाइंडर अनुपात (w/b) 0.4, 0.5 एवं 0.6 पर डाले गए मोर्टार का उपयोग किया गया, जिनमें सामान्य पोर्टलैंड सीमेंट (OPC) को नियंत्रण बाइंडर के रूप में तथा द्विआधारी (PC-Fly ash, PC-Slag) एवं त्रिआधारी (PC-Calcined Clay-Limestone, PC-Slag-Fly ash) बाइंडर संरचनाओं को सम्मिलित किया गया। अध्ययन में सूक्ष्मसंरचना विकास, द्रव्यमान परिवहन विशेषताएँ तथा कार्बोनीकरण के तहत क्षरण गतिकी पर ध्यान केंद्रित किया गया।

द्रव्यमान परिवहन विशेषताओं का मूल्यांकन सोर्प्शन, ऑक्सीजन पारगम्यता, एवं क्लोराइड प्रवास प्रयोगों द्वारा किया गया, जिसे मर्करी इंट्रूजन पोरोसिमीट्री (MIP), नाइट्रोजन अवशोषण, जल-सुलभ रंध्रता, एवं जल संतृप्ति स्तर से प्राप्त छिद्र संरचना गुणों के साथ सहसंबद्ध किया गया। कार्बोनीकरण के प्रभाव से खनिज संरचना एवं सूक्ष्म संरचना में परिवर्तन का विश्लेषण XRD, TGA, FTIR, SEM एवं नाइट्रोजन अवशोषण द्वारा किया गया। साथ ही, विभिन्न सापेक्ष आर्द्रता स्थितियों में विभिन्न बाइंडरों की क्षरण गतिकी को LPR, रेसिस्टिविटी, हाफ-सेल पोटेंशियल, छिद्र विलयन संरचना एवं नमी सामग्री द्वारा समझा गया।

कार्बोनीकरण के पश्चात परिवहन गुणों और छिद्र संरचना में उल्लेखनीय परिवर्तन देखे गए। मिश्रित बाइंडरों में परिवहन दर में वृद्धि हुई, जबकि OPC में इसमें कमी आई। इसका मुख्य कारण मिश्रित बाइंडरों में उच्च रंध्र जुड़ाव, बड़ा क्रांतिक रंध्र व्यास, तथा बढ़ा हुआ थ्रेशोल्ड रंध्र व्यास पाया गया। इसके अतिरिक्त, कार्बोनीकरण ने सीमेंट-स्वतंत्र सहसंबंध उत्पन्न किया, जहाँ जल-सुलभ रंध्रता और विभिन्न

परिवहन गुणों के मध्य मजबूत सहसंबंध देखा गया। सीमेंट पेस्ट में विभिन्न कार्बोनीकरण स्तरों पर सूक्ष्मसंरचना विकास के विश्लेषण से ज्ञात हुआ कि C-S-H के डी-कैल्सीफिकेशन के कारण डीकैल्सीफाइड C-S-H/सिलिका जेल का निर्माण होता है, जिससे अधिक खुली एवं बड़ी रंध्र संरचना बनती है। विशेषतः मिश्रित सीमेंट में अधिक कार्बोनीकरण डिग्री के कारण C-S-H का उच्च डी-कैल्सीफिकेशन, अधिक रंध्र जुड़ाव, कम पेचीदगी (tortuosity), एवं उच्च परिवहन दर होती है।

क्षरण दर मुख्यतः उपलब्ध नमी सामग्री एवं रंध्र जुड़ाव पर निर्भर पाई गई, जो क्षरणशील सतह से लौह आयनों की गति एवं सक्रिय क्षरण क्षेत्र को नियंत्रित करता है। क्षरण दर–रेसिस्टिविटी रेखीय संबंध का ढलान एवं इंटरसेप्ट रंध्र संरचना, छिद्र विलयन संरचना, एवं कैपिलरी संघनन की अंतःक्रिया पर आधारित पाया गया। उच्च $[Cl^-]/[OH^-]$ और $[SO_4^{2-}]/[OH^-]$, कम रेसिस्टिविटी, अधिक रंध्रता, एवं उच्च रंध्र जुड़ाव वाले बाइंडरों में यह ढलान एवं इंटरसेप्ट कम पाया गया। प्रयोगशाला परीक्षण एवं 50-वर्षीय आर.सी. संरचना के अध्ययन से यह सिद्ध हुआ कि कार्बोनीकरण या निष्क्रियता की हानि अपने आप में महत्वपूर्ण क्षरण को उत्पन्न नहीं करती। विशेषतः जब बाह्य सापेक्ष आर्द्रता 75% से कम हो, तो क्षरण दर नगण्य बनी रहती है। अंततः, Evans आरेख एवं क्षरण गतिकी मानदंडों के आधार पर एक क्षरण पूर्वानुमान मॉडल विकसित किया गया, जो पोटेंशियल एवं रेसिस्टिविटी मापन पर आधारित है। वास्तविक संरचना से प्राप्त परीक्षण परिणामों द्वारा इस मॉडल की पुष्टि की गई, जिससे कार्बोनीकृत परिस्थितियों में क्षरण जोखिम मूल्यांकन हेतु इसकी उपयोगिता सिद्ध हुई।

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Glossary

A	Alumina Oxide (Al_2O_3)
AFm	Al_2O_3 – Fe_2O_3 – Mono
AFt	Al_2O_3 – Fe_2O_3 – Tri
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BSE	Backscattered Electron
CH_2$	Gypsum
C_2S	Dicalcium Silicate ($2CaO.SiO_2$)
C_3S	Tricalcium Silicate ($3CaO.SiO_2$)
C_3A	Tricaclium Sluminate ($3CaO.Al_2O_3$)
C_4AF	Tetracalcium Ferrite ($4CaO.Al_2O_3.Fe_2O_3$)
C	Calcium Oxide (CaO)
CC	Composite Cement
CH	Portlandite
C-S-H	Calcium Silicate Hydrate gel
C/S	Calcium to Silica ratio in C-S-H
DTG	Differential Thermogravimetry
EDS	Energy Dispersive Spectroscopy
F	Iron oxide (Fe_2O_3)
FTIR	Fourier Transform Infrared Spectroscopy
H	H_2O
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
ITZ	Interfacial Transition Zone
LC^2	Limestone Calcined Clay
LC^3	Limestone Calcined Clay Cement

LPR	Linear Polarization Resistance
LOI	Loss on Ignition
MIP	Mercury Intrusion Porosimetry
NC	Non Carbonated
PC	Ordinary Portland Cement
PF	Portland Pozzolana Cement – Fly Ash
PS	Portland Pozzolana Cement – Slag
PSD	Particle Size Distribution
RC	Reinforced Concrete
RH	Relative Humidity
S	Silicon Dioxide (SiO_2)
SCM	Supplementary Cementitious Material
SEM	Scanning Electron Microscopy
TGA	Thermo-gravimetric Analysis
w/b	water-to-binder ratio
XRD	X-ray Diffraction
XRF	X-Ray Fluorescence