# CARBONATION OF CONCRETE CONTAINING SUPPLEMENTARY CEMENTITIOUS MATERIALS

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

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DEPARTMENT OF CIVIL ENGINEERING

Submitted

in fulfillment of the requirements of the degree of DOCTOR OF PHILOSOPHY

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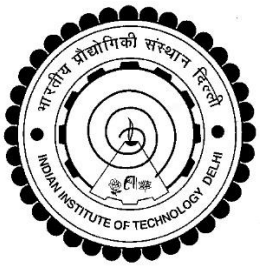


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## CERTIFICATE

This is to certify that the thesis entitled "**CARBONATION OF CONCRETE CONTAINING SUPPLEMENTARY CEMENTITIOUS MATERIALS**", being submitted by **Mr. Vineet Pawan Shah**, 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 our 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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Vineet Shah

## ABSTRACT

Corrosion of steel reinforcement in concrete is the leading cause of deterioration of concrete structures. Chloride ingress and carbonation are the two major processes that lead to the corrosion of reinforcement. Carbonation is the reaction of the calcium bearing phases of cement with carbon dioxide present in the environment. The majority of cement available worldwide contains supplementary cementitious materials (SCMs) to improve their engineering, economic and environmental performance. The total amount of calcium hydroxide present in cement containing SCMs after hydration is lower than Ordinary Portland Cement (OPC) due to the dilution effect and pozzolanic reaction of SCMs, which reduces the capacity of the concrete to bind $CO_2$, making it more susceptible to carbonation.

The objective of this study was to investigate the effect of carbonation on cements containing SCMs under different environmental exposure conditions. Binary binders comprising of OPC/Fly Ash and OPC/Slag and ternary binders comprising of OPC/Calcined Clay/Limestone and OPC/Slag/Fly Ash and control blend of only OPC were investigated for carbonation performance. X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were used to characterize the hydrated and carbonated products. Mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) were used to characterize the changes occurring in the microstructure. Thermodynamic modeling was also used to evaluate the potential long term changes in solid volume on carbonation. Changes in transport properties of concrete on carbonation and influence of physical and chemical parameters on rate of carbonation in concrete was also investigated.

XRD results show carbonation of calcium hydroxide and other hydrated phases takes place simultaneously and precipitation of all the three polymorphs of calcium carbonate were observed on carbonation. Si-rich rims around the clinker grains were observed on carbonation in backscattered electron (BSE) images indicating migration of calcium ions from inner C-S-H and clinker grains. The specific gravity of decalcified C-S-H and alumina gel formed after carbonation was estimated to lie between 2.00 to 2.15 and 2.00 to 2.30 respectively. The implications of carbonation of hydration products was observed on pore structure properties of the hydrated system. Increase in concrete porosity and coarsening of pore structure was observed on carbonation in all the blended cements.

The progress of carbonation in concrete was found to be dependent on numerous material and environmental parameters. The rate of carbonation increased with increase in clinker

replacement level with SCMs. Mixes with similar clinker replacement level but with different types of SCMs showed noticeable difference in carbonation resistance. No direct correlation was observed between the rate of carbonation and compressive strength/porosity of concrete whereas a reasonable correlation was observed between chemical parameters describing carbon dioxide buffer capacity of cement and rate of carbonation in concrete. A numerical model, which uses the basic principles of physics and chemistry, along with the parameters measured using experimental study, to predict the carbonation depth in concrete was developed. The modeled carbonation depth data showed excellent correlation with the experimental data. Reserve alkalinity, porosity, saturation index, drying diffusion coefficient and environmental conditions were found to be the major parameters that influence the rate of carbonation. The model developed can be used for wide range of environmental conditions and cements containing supplementary cementitious materials.

## सार

कंक्रीट में स्टील सुदृढीकरण का संक्षारण कंक्रीट संरचनाओं में गिरावट का प्रमुख कारण है। क्लोराइड प्रवेश और कार्बोनेशन दो प्रमुख प्रक्रियाएं हैं जो मजबूती के जंग को जन्म देती हैं। कार्बोनेशन पर्यावरण में मौजूद कार्बन डाइऑक्साइड के साथ सीमेंट के कैल्शियम असर चरणों की प्रतिक्रिया है। दुनिया भर में उपलब्ध सीमेंट के बहुमत में पूरक इंजीनियरिंग और आर्थिक प्रदर्शन में सुधार करने के लिए पूरक सीमेंटिटियस सामग्री (एससीएम) शामिल हैं। हाइड्रेशन के बाद एससीएम युक्त सीमेंट में मौजूद कैल्शियम हाइड्रॉक्साइड की कुल मात्रा सामान्य पोर्टलैंड सीमेंट (ओपीसी) से कम है, जिससे कमजोर पड़ने वाले प्रभाव और एससीएम की पॉज़ज़ोलैनिक प्रतिक्रिया होती है, जिससे सीओ 2 को बांधने के लिए कंक्रीट की क्षमता कम हो जाती है, जिससे कार्बोनेशन को अधिक संवेदनशील बना दिया जाता है। ।

इस अध्ययन का उद्देश्य विभिन्न पर्यावरण जोखिम स्थितियों के तहत एससीएम युक्त सीमेंटों पर कार्बोनेशन के प्रभाव की जांच करना था। ओपीसी / फ्लाई ऐश और ओपीसी / स्लैग और टर्नरी बाइंडर्स शामिल हैं जिनमें ओपीसी / कैल्सीनड क्ले / चूना पत्थर और ओपीसी / स्लैग / फ्लाई ऐश और केवल ओपीसी के नियंत्रण मिश्रण शामिल हैं, कार्बनेशन प्रदर्शन के लिए जांच की गई थी। एक्स-रे विवर्तन (एक्सआरडी) और थर्मोग्रामिमेट्रिक विश्लेषण (टीजीए) का उपयोग हाइड्रेटेड और कार्बोनेटेड उत्पादों को दर्शाने के लिए किया जाता था। बुध घुसपैठ पोरोसीमेटरी (एमआईपी) और स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम) माइक्रो स्ट्रकचर में होने वाले परिवर्तनों को दर्शाने के लिए इस्तेमाल किया गया था। कार्बनेशन पर ठोस मात्रा में संभावित दीर्घकालिक परिवर्तनों का मूल्यांकन करने के लिए थर्मोडायनामिक मॉडलिंग का भी उपयोग किया जाता था। कार्बनेशन पर कंक्रीट के परिवहन गुणों में परिवर्तन और कंक्रीट में कार्बोनेशन की दर पर भौतिक और रासायनिक मानकों के प्रभाव की भी जांच की गई।

एक्सआरडी परिणाम कैल्शियम हाइड्रॉक्साइड का कार्बोनेशन दिखाते हैं और अन्य हाइड्रेटेड चरण एक साथ होते हैं और कैल्शियम कार्बोनेट के सभी तीन पॉलिमॉर्फों की वर्षा कार्बोनेशन पर देखी जाती है। क्लिंकर अनाज के चारों ओर सी समृद्ध रिम्स बैकस्काक्टेड इलेक्ट्रॉन (बीएसई) छवियों में कार्बोनेशन पर देखा गया था जो आंतरिक सी-एस-एच और क्लिंकर अनाज से कैल्शियम आयनों के प्रवासन को इंगित करता है। कार्बनेशन के बाद क्रमशः 2.00 से 2.15 और 2.00 से 2.30 के बीच निर्णायक सी-एस-एच और एल्यूमिना जेल की विशिष्ट गुरुत्वाकर्षण का अनुमान लगाया गया था। हाइड्रेटेड उत्पादों के कार्बोनेशन के प्रभाव हाइड्रेटेड सिस्टम के पोयर संरचना गुणों पर मनाए गए थे। कंक्रीट पोरोसीटी में वृद्धि और सभी मिश्रित सीमेंट्स में कार्बोनेशन पर छिद्र संरचना की कौर्सनीन्ग देखा गया था।

कंक्रीट में कार्बोनेशन की प्रगति कई सामग्रियों और पर्यावरण मानकों पर निर्भर थी। एससीएम के साथ क्लिंकर प्रतिस्थापन स्तर में वृद्धि के साथ कार्बोनेशन की दर में वृद्धि हुई। इसी तरह के क्लिंकर प्रतिस्थापन स्तर के साथ मिलाता है लेकिन विभिन्न प्रकार के एससीएम के साथ कार्बोनेशन प्रतिरोध में उल्लेखनीय अंतर दिखाई देता कार्बनेशन और संपीड़न शक्ति / कंक्रीट की छिद्रता की दर के बीच कोई प्रत्यक्ष सहसंबंध नहीं देखा गया था, जबकि सीमेंट की कार्बन डाइऑक्साइड बफर क्षमता और कंक्रीट में कार्बनेशन की दर का वर्णन करने वाले रासायनिक मानकों के बीच एक उचित सहसंबंध देखा गया था। कंक्रीट में कार्बनेशन गहराई की भविष्यवाणी करने के लिए प्रयोगात्मक अध्ययन का उपयोग करके मापा गया पैरामीटर के साथ भौतिकी और रसायन शास्त्र के बुनियादी सिद्धांतों का उपयोग करने वाला एक संख्यात्मक मॉडल विकसित किया गया था। मॉडलिंग कार्बोनेशन गहराई डेटा ने प्रयोगात्मक डेटा के साथ उत्कृष्ट सहसंबंध दिखाया। रिजर्व क्षारीयता, पोरोसीटी, संतृप्ति सूचकांक, सुखाने गुणांक और पर्यावरण की स्थिति सुखाने कार्बनेशन की दर को प्रभावित करने वाले प्रमुख पैरामीटर पाए गए थे। विकसित मॉडल का उपयोग पर्यावरणीय परिस्थितियों और पूरक सीमेंटिटियस सामग्रियों वाले सीमेंटों की विस्तृत श्रृंखला के लिए किया जा सकता है।

## GLOSSARY

| | |
|---|---|
| A | Aluminium Oxide $Al_2O_3$ |
| AC | Accelerated Carbonated |
| AFm | Monosulfoaluminate |
| AFt | Ettringite |
| Al/Ca | Ratio of Alumina to Calcium |
| ASR | Alkali Silica Reaction |
| BSE | Backscattered Electron |
| C | Calcium Oxide CaO |
| C$H$_2$ | Gypsum |
| $C_2S$ | Dicalcium Silicate |
| $C_3A$ | Tricalcium Aluminate |
| $C_3S$ | Tricalcium Silicate |
| $C_4AF$ | Tetracalcium Alumino-Ferrite |
| Ca/Si | Ratio of Calcium to Silica |
| CC | Calcium Carbonate |
| CH | Calcium Hydroxide |
| C-S-H | Calcium Silicate Hydrate |
| DTG | Differential Thermogravimetry |
| EDS | Energy Dispersive Spectroscopy |
| F | Iron Oxide $Fe_2O_3$ |
| FTIR | Fourier Transfom Infrared Spectroscopy |
| H | Water $H_2O$ |
| ITZ | Interfacial Transition Zone |
| $LC^2$ | Limestone Calcined Clay |
| $LC^3$ | Limestone Calcined Clay Cement |
| LOI | Loss on Ignition |
| MAC | Mass Absorption Coefficient |
| MIP | Mercury Intrusion Porosimetry |
| N | Natural Carbonated |
| NMR | Nuclear Magnetic Resonance |

| | |
|---|---|
| OPC | Ordinary Portland Cement |
| PCE | Poly-Carboxyl Ether |
| PSD | Particle Size Distribution |
| R.H. | Relative Humidity |
| S | Silicon Dioxide $SiO_2$ |
| SCMs | Supplementary Cementitious Materias |
| SEM | Scanning Electron Microscopy |
| Si/Al | Ratio of Silica to Alumina |
| Si/Ca | Ratio of Silica to Calcium |
| SSD | Saturated Surface Dry |
| TEM | Transmission Electron Microscopy |
| TGA | Thermogravimetric Analysis |
| UC | Uncarboanted |
| w/c | Water to Cement Ratio |
| XRD | X-Ray Diffraction |
| XRF | X-Ray Fluorescence |

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