

HYDRATION AND MICROSTRUCTURE DEVELOPMENT IN LIMESTONE CALCINED CLAY CEMENT

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**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
SEPTEMBER 2019**

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**HYDRATION AND MICROSTRUCTURE DEVELOPMENT IN
LIMESTONE CALCINED CLAY CEMENT**

by

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DEPARTMENT OF CIVIL ENGINEERING

Submitted

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

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

SEPTEMBER 2019

CERTIFICATE

This is to certify that the thesis entitled “**HYDRATION AND MICROSTRUCTURE DEVELOPMENT IN LIMESTONE CALCINED CLAY CEMENT**”, being submitted by **Mr. Sreejith Krishnan**, to the Indian Institute of Technology Delhi, for the award of the degree 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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ACKNOWLEDGEMENTS

I would like to take this opportunity to thank all those who have made my four years of graduate studies a memorable experience. First of all, I would like to express my sincere gratitude to my thesis supervisor Prof. Shashank Bishnoi, for his valuable guidance, constant motivation and discussions throughout these six years. His philosophy towards research, teaching, mentorship as well as life, in general, has been an inspiration. I would like to thank the Swiss Agency for Development and Cooperation for the financial support of my research. I would also like to thank Prof. Karen Scrivener for giving me an opportunity to work in the Laboratory of Construction Materials at EPFL. I would like to thank Julien, Francois, Aurelie, Xuerun, Pawel and Alex for helping to make my stay at EPFL fun and memorable. I would like to thank all the Indian partners (IIT Madras, IIT Bombay and TARA) of the Low Carbon Cement project for their valuable support, suggestions and discussion.

I would also like to take this opportunity to thank all my colleagues and staff of Materials Research Laboratory and Concrete Structures Laboratory. It would be unfair if I do not take this opportunity to thank my friends, who made my life enjoyable at IIT Delhi. First and foremost, I would like to Arun for his constant support, advice, friendship and the many hours of all the pointless discussions. Thanks to Aneeta, Satya, Amarpreet, Meenakshi, Lav, Gopal, and Geetika for your friendship. Thanks to Anuj and Vineet for all the discussions. Thanks to my master's students, Abhishek and Swadesh. I had a great time working with you. Thanks to my family and my sister, who have always encouraged me to follow my dreams. Finally, I would like to thank the most important person in my life without whose support, encouragement and patience this would not have been possible. Thank you Gayathri, you are my rock.

Sreejith

"If I have seen further, it is by standing on the shoulders of giants"

Sir Isaac Newton

ABSTRACT

Cement industry is one of the major contributors of global anthropogenic carbon dioxide (CO₂) emissions. CO₂ is one of the major greenhouse gases that leads to global warming and associated climate change. It is estimated that approximately 7% of the annual CO₂ emissions come from the production of cement. Considering the exponential increase in the global cement demand due to rapid urbanisation and infrastructure development in developing countries such as India and China, finding sustainable alternatives to Ordinary Portland Cement (OPC) is of utmost importance. Ternary blended cements offer such an alternative to OPC, being produced by partially replacing cement with two supplementary cementitious materials (SCMs). Limestone calcined clay cement (LC³) is one such ternary cement where cement is partially replaced using a combination of calcined clay and limestone.

The objective of this study was to understand the hydration and microstructure development in Limestone calcined clay cements (LC³). The primary focus of this study was on an LC³-55 blend having the composition of 50% clinker, 30% calcined clay, 15% limestone and 5% gypsum. Crushed quartz was used as an inert filler to isolate the individual as well as the combined contributions of calcined clay and limestone in the system. Several blend parameters that affect hydration, phase assemblage and strength development in the system (such as purity of clay, type of carbonate used, clinker factor etc.) were identified and individually varied to understand their influence on these characteristics.

The phase assemblage and hydration characteristics of LC³-55 were compared with a ternary cement produced using slag and fly ash (also known as Composite Cement), Portland Pozzolana Cement (PPC) and Ordinary Portland Cement (OPC). The phase assemblage and microstructure in LC³-55 were characterised with the help of techniques such as X-ray Diffraction (XRD), Mercury Intrusion Porosimetry (MIP), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). A significant alumina uptake was observed in the C-A-S-H gel formed in the LC³-55 system due to the presence of calcined clay. The AFt/AFm phase assemblages were seen to vary with the type of SCM in the LC³-55 system, with stratlingite forming in the absence of limestone and calcium monocarboaluminate forming in the absence of calcined clay. The availability of portlandite was seen as the critical parameter affecting the phase assemblage in the LC³ systems. A reduction in the long term hydration of

clinker phases (especially belite) was observed in the LC³-55 which limits the availability of portlandite for the pozzolanic reaction. Therefore, the major strength development in these systems is complete within 28 days. It was found that the reduction in clinker hydration was not due to insufficient availability of sulphate or alkalis. No improvement in clinker hydration trends was observed even after increasing the fineness of clinker. However, the long term clinker hydration was seen to improve when a lower purity clay was used. Alternate sources of carbonates, such as dolomite can be used to produce LC³ cements. In the presence of reactive aluminosilicates from calcined clay, dolomite reacts to form hydrotalcite and carboaluminate phases. Using the knowledge gained from the experimental studies, a numerical model for the hydration and phase development in LC³ systems was developed. Attempts were made to understand the strength development using gel-space ratio calculations. It was found suggests that C-A-S-H formed in the LC³ systems appears to have better space filling capabilities unlike the C-A-S-H formed in the OPC systems. It was also seen that at higher clinker substitution levels, it is advisable to use lower purity clays to ensure optimal consumption of the reactive metakaolin present in the calcined clays.

सार

सीमेंट उद्योग वैश्विक मानवजनित कार्बन डाइऑक्साइड (CO₂) उत्सर्जन के प्रमुख योगदानकर्ताओं में से एक है। CO₂ प्रमुख ग्रीनहाउस गैसों में से एक है जो ग्लोबल वार्मिंग और संबद्ध जलवायु परिवर्तन की ओर ले जाती है। यह अनुमान है कि वार्षिक CO₂ उत्सर्जन का लगभग 7% सीमेंट के उत्पादन से आता है। भारत और चीन जैसे विकासशील देशों में तेजी से शहरीकरण और बुनियादी ढाँचे के विकास के कारण वैश्विक सीमेंट मांग में तेजी के वृद्धि को देखते हुए, ऑर्डिनरी पोर्टलैंड सीमेंट (ओपीसी) के लिए स्थायी विकल्प खोजना अत्यंत महत्वपूर्ण है। टर्नरी ब्लेंडेड सीमेंट्स ओपीसी के लिए एक ऐसा विकल्प प्रदान करते हैं, जो आंशिक रूप से सीमेंट को दो अनुपूरक सीमेंटीय सामग्रियों (एससीएम) से बदलकर बनाया जा रहा है। लाइमस्टोन क्ले सीमेंट (LC3) एक ऐसा टर्नरी सीमेंट है, जहां कैल्साइन्ड क्ले और लाइमस्टोन के संयोजन का उपयोग करके सीमेंट को आंशिक रूप से बदल दिया जाता है।

इस अध्ययन का उद्देश्य लाइमस्टोन कैल्साइन्ड क्ले सीमेंट्स (LC3) में हाइड्रेशन और माइक्रोस्ट्रक्चर डेवलपमेंट को समझना था। इस अध्ययन का प्राथमिक ध्यान एक LC3-55 मिश्रण पर था जिसमें 50% क्लिंकर, 30% कैल्साइन्ड क्ले, 15% लाइमस्टोन और 5% जिप्सम थे। क्वार्ट्ज को एक अक्रिय भराव के रूप में इस्तेमाल किया गया था ताकि कैल्साइन्ड क्ले और लाइमस्टोन के संयुक्त योगदान को अलग किया जा सके। सिस्टम में जलयोजन, पदार्थ संयोजन और शक्ति विकास को प्रभावित करने वाले कई मिश्रण पैरामीटर (जैसे मिट्टी की शुद्धता, कार्बोनेट का प्रकार, क्लिंकर कारक आदि) की पहचान की गई थी और इन विशेषताओं पर उनके प्रभाव को समझा गया।

LC3-55 के पदार्थ संयोजन और जलयोजन विशेषताओं की तुलना स्लैग और फ्लाई ऐश (कम्पोजिट सीमेंट), पोर्टलैंड पॉज़्जोलाना सीमेंट (पीपीसी) और साधारण पोर्टलैंड सीमेंट (ओपीसी) का उपयोग करके उत्पादित एक टर्नरी सीमेंट के साथ की गई थी। LC3-55 में पदार्थ संयोजन और माइक्रोस्ट्रक्चर को एक्स-रे डिफ्रेक्शन (एक्सआरडी), मर्करी इंटरूजन पोरॉमिटर (एमआईपी), थर्मोग्रेविमेट्रिक एनालिसिस

(टीजीए) और स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम) जैसी तकनीकों की मदद से समझा गया था। केल्सीकृत मिट्टी की उपस्थिति के कारण LC3-55 प्रणाली में गठित C-A-S-H जेल में एक महत्वपूर्ण एल्यूमिना अपटेक देखा गया। AFt / AFm असेंबलियों को LC3-55 प्रणाली में SCM के प्रकार के साथ अलग-अलग देखा गया था, जिसमें लाइमस्टोन की अनुपस्थिति में स्ट्रैटलिंगाइट और कैल्शियम मोनोक्रोब्लुमिनेट का गठन केल्सीकृत मिट्टी की अनुपस्थिति में किया गया था। पोर्टलैंडाइट की उपलब्धता को LC3 सिस्टम में चरण असेंबल को प्रभावित करने वाले महत्वपूर्ण पैरामीटर के रूप में देखा गया था। एलसी 3-55 में क्लिंकर पदार्थों (विशेष रूप से बीलाइट) के दीर्घकालिक जलयोजन में कमी देखी गई जो पोज़ोलानिक प्रतिक्रिया के लिए पोर्टलैंडाइट की उपलब्धता को सीमित करता है। इसलिए, इन प्रणालियों में प्रमुख शक्ति विकास 28 दिनों के भीतर पूरा हो जाता है। यह पाया गया कि क्लिंकर जलयोजन में कमी सल्फेट या क्षार की अपर्याप्त उपलब्धता के कारण नहीं थी। क्लिंकर की महीनता को बढ़ाने के बाद भी क्लिंकर जलयोजन में कोई सुधार नहीं देखा गया। हालांकि, कम शुद्धता वाली मिट्टी का उपयोग करने पर दीर्घकालिक क्लिंकर जलयोजन में सुधार देखा गया था। कार्बोनेट के वैकल्पिक स्रोत, जैसे कि डोलोमाइट का उपयोग LC3 सीमेंट का उत्पादन करने के लिए किया जा सकता है। केल्सीकृत मिट्टी से प्रतिक्रियाशील एलुमिनोसिलेट्स की उपस्थिति में, डोलोमाइट हाइड्रोटेल्साइट और कार्बोबिलुमेट चरणों के गठन के लिए प्रतिक्रिया करता है। प्रायोगिक अध्ययनों से प्राप्त ज्ञान का उपयोग करते हुए, LC 3 प्रणालियों में जलयोजन और चरण विकास के लिए एक संख्यात्मक मॉडल विकसित किया गया। जेल-स्पेस अनुपात गणनाओं का उपयोग करके शक्ति के विकास को समझने का प्रयास किया गया। यह पाया गया कि LC3 सिस्टम में गठित C-A-S-H, OPC सिस्टम में गठित C-A-S-H के विपरीत बेहतर स्थान भरने की क्षमता रखता है। यह भी देखा गया कि उच्च क्लिंकर प्रतिस्थापन स्तरों पर, कम शुद्धता वाले क्ले का उपयोग करने की सलाह दी जाती है ताकि केल्सीकृत मिट्टी में मौजूद प्रतिक्रियाशील मेटाकॉलिन की अधिकतम खपत सुनिश्चित की जा सके।

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Glossary

A	Al_2O_3
A/S	Alumina to Silica Ratio in C-S-H
AS ₂	Metakaolin
AFm	$\text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{Mono}$
AFt	$\text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{Tri}$
B	Brucite
BSE	Back Scattered Electron
BW	Bound Water
C	CaO
CC	Composite Cement
C/S	Calcium to Silica Ratio in C-S-H
C ₃ S	$3\text{CaO} \cdot \text{SiO}_2$
C ₂ S	$2\text{CaO} \cdot \text{SiO}_2$
C ₃ A	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$
C ₄ AF	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$
C\$H ₂	Gypsum
CH	Portlandite
C $\bar{\text{C}}$	Calcium Carbonate
C-S-H	Calcium Silicate Hydrate Gel
C-A-S-H	Calcium Alumino Silicate Hydrate Gel
C ₂ ASH ₈	Stratlingite
CMc ₂	Dolomite
CL	Ground Clinker
D	Dolomite
DOH	Degree of Hydration
DTG	Differential Thermogravimetry
EDS	Energy Dispersive X-Ray Spectroscopy
F	Fly Ash
G	Gypsum
H	H ₂ O
Hc	Calcium hemicarboaluminate

Hg	Hydrogarnet
ITZ	Interfacial Transition Zone
KH	Potassium Hydroxide
KS	Potassium Sulphate
L	Limestone
LC ³	Limestone Calcined Clay Cement
K1	Kaolinite clay with approximately 60% kaolinite
K2	Kaolinite clay with approximately 30% kaolinite
OPC	Ordinary Portland Cement
PPC	Portland Pozzolana Cement
PSD	Particle Size Distribution
M	Commercially available metakaolin with approximately 80% metakaolin
Me	Melilite
MAC	Mass Absorption Coefficient
Mc	Calcium monocarboaluminate
MH	Magnesium Hydroxide
M ₄ AH ₇	Hydrotalcite
MK	Metakaolin
MIP	Mercury Intrusion Porosimetry
NH	Sodium Hydroxide
NS	Sodium Sulphate
Q	Crushed Quartz
S	SiO ₂ (Cement Chemistry Notation)
S	Slag
SCM	Supplementary Cementitious Material
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
W	Commercial Portland Cement
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence