

**INFLUENCE OF CURING TEMPERATURE ON
HYDRATION KINETICS, PHASE ASSEMBLAGE AND
STRENGTH DEVELOPMENT OF BLENDED
CEMENTS**

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**DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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CEMENTS**

by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

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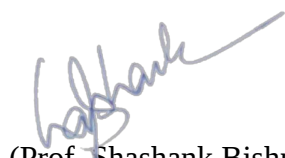


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CERTIFICATE

This is to certify that the thesis entitled **“INFLUENCE OF CURING TEMPERATURE ON HYDRATION KINETICS, PHASE ASSEMBLAGE AND STRENGTH DEVELOPMENT OF BLENDED CEMENTS”**, being submitted by Mr. Arun C. Emmanuel, 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 my supervision and guidance. He has fulfilled the requirements for submission of this thesis, which to the best of my 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.



(Prof. Shashank Bishnoi)

Associate Professor

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Arun

ABSTRACT

There are many cement types available in the market today and several more are under development. The understanding that has been obtained through experience with the conventional cements is not sufficient to update the construction practices for the new cement types that are available in the market. Not only are these new cement types more sustainable, they also offer engineering properties that are advantageous in many situations. Due to the robustness and ease of production of Portland cement, its clinker still makes the majority of most modern cements, with a fraction of the cement being replaced by supplementary cementitious materials (SCMs) that are often more environmentally and economically efficient. Apart from improving the engineering properties of the cements, these SCMs also reduce the CO₂ emissions and the energy consumption in cement production. While sufficient knowledge is available to allow a safe use of cements with clinker fractions as low as 0.7 with fly ash, the further reduction of clinker factors and the advent of ternary cements, which use a combination of SCMs together, necessitates the understanding of the more complex interactions that occur in these cements. This research studies the influence of temperature on the hydration, microstructural development and strength development of cements with 30% and 50% clinker replacement using either single, or a combination of SCMs. In the study, slag-fly ash composite cement and limestone calcined clay cement, which have recently been used as more sustainable alternatives to pozzolanic cements, have especially been focused upon.

Although the characteristics of cements are usually similar from one location to another, their usage occurs in ambient conditions that vary highly, especially in a large and diverse country like India. In India, the temperature, which has been shown to play an important role in hydration and strength development, can vary by almost 50°C at the same location between different weathers. Curing temperatures of 10°C, 27°C and 50°C, which represent usual conditions in the country were chosen for this study. Studies on the rate of hydration and phase development showed that while higher curing temperatures can accelerate early-age development, the long-term development may be hindered. This limiting of hydration and strength development is seen to be more prominent in cements that have a lower clinker content, particularly those that have been replaced with SCMs that contain a higher alumina content.

Microstructural studies have shown that the nature of the hydration products is influenced both by the temperature and the chemical composition of the SCMs. In certain conditions, it is seen that the higher alumina available in the solution at higher temperatures leads to the formation of a more polymerized C-A-S-H, which may repress cement hydration by forming a physical barrier against the reaction, so much so that the hydration nearly stops in some of the blends. This also leads to a reduction in the long-term strength development of these cements and reduces the availability of portlandite, which is required for the hydration of the SCMs. It was found that higher curing temperatures also prevent the formation of hydration products, such as ettringite and carboaluminates, that make an important fraction of the hydrated microstructures of some of the cements. This also influences the strength and microstructural development. The permeability of the pastes and, hence, their durability characteristics are also affected.

The results, however, show that a delay in the exposure of the cements to higher temperatures can lead to an improvement in microstructural and strength development, allowing more of the potential of the SCMs to be utilised. The addition of surplus gypsum is also seen to improve the strength development in some conditions. The results provide important data that can be used in the design and construction of structures that use ternary low clinker cement blends.

सारांश

आज विभिन्न प्रकार के सीमेंट उपलब्ध हैं और कई अन्य विकास के अधीन हैं। ये नए सीमेंट अधिक टिकाऊ होते हैं तथा इनमें अभियांत्रिकी गुण भी होते हैं जो कई स्थितियों में फायदेमंद होते हैं। पोर्टलैंड सीमेंट का क्लिंकर अभी भी अधिकांश आधुनिक सीमेंट बनाने में उपयोग होता है क्योंकि इसका उत्पादन आसान होता है। सीमेंट के एक हिस्से को पूरक सीमेंटेड मटेरियल (एससीएम) द्वारा प्रतिस्थापित किया जाता है जो अक्सर अधिक पर्यावरण अनुकूलित और किफायती होते हैं। सीमेंट के इंजीनियरिंग गुणों में सुधार के अलावा, ये एससीएम कार्बन डाइऑक्साइड उत्सर्जन और सीमेंट उत्पादन में ऊर्जा की खपत को भी कम करते हैं। फ्लाई ऐश के साथ ७०% क्लिंकर वाले सीमेंट्स के सुरक्षित उपयोग की अनुमति देने के लिए पर्याप्त ज्ञान उपलब्ध है। परंतु क्लिंकर को और कम करने के लिए टर्नरी सीमेंट्स, जो एक साथ दो एससीएम के संयोजन का उपयोग करते हैं, के प्रयोग हेतु और अधिक ज्ञान की आवश्यकता है। इस शोध में उन सीमेंट पर अध्ययन किया गया है जिनमें ३०% और ५०% क्लिंकर को एससीएम के द्वारा प्रतिस्थापित किया गया है। अध्ययन में, स्लैग-फ्लाई ऐश कम्पोजिट सीमेंट और लाइमस्टोन कैल्क्लाइंड क्ले सीमेंट, जो कुछ साल पहले ही पॉज़्जोलनिक सीमेंट्स में टिकाऊ विकल्प के रूप से प्रस्तुत करा गया है, पर विशेष रूप से ध्यान केंद्रित किया गया है।

यद्यपि सीमेंट की विशेषताएं आमतौर पर एक स्थान से दूसरे स्थान पर समान होती हैं, उनका उपयोग भिन्न भिन्न स्थितियों में होता है। भारत में, तापमान, जो जलयोजन और मजबूती के विकास में महत्वपूर्ण भूमिका निभाता है, एक ही स्थान पर विभिन्न मौसमों में लगभग ५०° सेल्सियस तक भिन्न हो सकता है। देश में सामान्य परिस्थितियों में पाये जाने वाले तापमान १०°, २७° और ५०° सेल्सियस को इस अध्ययन के लिए चुना गया था। जलयोजन और चरण विकास की दर पर किए गए अध्ययनों से पता चला है कि उच्च तापमान से कम आयु में अधिक मजबूती प्राप्त हो सकती है, तथा दीर्घकालिक विकास में बाधा हो सकती है। यह पाया गया है कि कम क्लिंकर सामग्री वाले सीमेंट्स जलयोजन और मजबूती के विकास को सिमित करती है, विशेष रूप से उन एससीएम के साथ जिनमें एल्यूमिना उच्च मात्रा में होता है।

अध्ययन से पता चला है कि तापमान और एससीएम की रासायनिक संरचना जलयोजन उत्पादों की प्रकृति को प्रभावित करती है। उच्च तापमान पर घोल में उपलब्ध उच्च एल्यूमिना सी-ए-एस-एच को पोलीमराइज कर सकता है, जो एक भौतिक अवरोध बनाकर सीमेंट जलयोजन को कम कर सकता है। इतना कि कुछ मिश्रणों में जलयोजन लगभग रुक जाता है। इससे इन सीमेंटों के दीर्घकालिक शक्ति विकास में भी कमी आती है और पोर्टलैंडाइट की उपलब्धता कम हो जाती है, जो कि एस सी एम के जलयोजन के लिए आवश्यक है। यह पाया गया कि उच्च तापमान भी जलयोजन उत्पादों के निर्माण को रोकते हैं, जैसे कि एट्रिंगाइट और कारबोलुमिनेट्स जो कि सीमेंट्स के जल योजित माइक्रोस्ट्रक्चर का एक

महत्वपूर्ण हिस्सा हैं। यह ताकत और सूक्ष्म विकास को भी प्रभावित करता है। पेस्ट की पर्मीअबिलिटी बढ़ने से उनकी स्थायित्व विशेषताएँ भी प्रभावित होती हैं।

हालांकि परिणाम बताते हैं कि यदि सीमेंट का संपर्क उच्च तापमान से देरी से हो तो माइक्रोस्ट्रक्चरल और ताकत के विकास में सुधार हो सकता है जिससे एससीएम की अधिक क्षमता का उपयोग किया जा सकता है। अध्ययन से पता चला है अधिक जिप्सम भी कुछ स्थितियों में मजबूती को बढ़ाता है। इस शोध के परिणाम का उपयोग उन संरचनाओं के अभिकल्प और निर्माण में किया जा सकता है जिनमें कम क्लिंकर वाले टर्नरी सीमेंट मिश्रणों का उपयोग किया जाता है।

സാരം

ഇന്ന് പല തരത്തിൽ ഉള്ള സിമൻറ് വിപണിയിൽ ലഭ്യമാണ്. കൂടാതെ നിരവധി ഗവേഷണങ്ങൾ പുതിയ തരം സിമൻറ് നിർമ്മാണവുമായി ബന്ധപ്പെട്ടു ഈ മേഖലയിൽ നടക്കുന്നു. ഇത്തരം നൂതന സിമന്റുകളിൽ മിക്കതിലും, ക്ലിങ്കറിന്റെ ഒരു ഭാഗം സപ്ലിമെന്ററി സിമെന്റിഷ്യസ് മെറ്റീരിയലുകൾ (എസ്.സി.എം.) ഉപയോഗിച്ച് മാറ്റി സ്ഥാപിക്കപ്പെട്ടവയാണ്. ഇത്തരം സിമെന്റുകൾ പലപ്പോഴും പാരിസ്ഥിതികമായും സാമ്പത്തികമായും വളരെ കാര്യക്ഷമമാണ്.

സിമന്റുകളുടെ രാസപ്രവർത്തനം, മൈക്രോസ്ട്രക്ചറൽ വികസനം, ശക്തി വികസനം എന്നിവകളിൽ രാസപ്രവർത്തന സമയത്തുള്ള താപനിലയുടെ സ്വാധീനം, 30%, 50% ക്ലിങ്കർ മാറ്റി (എസ്.സി.എം. ഉപയോഗിച്ച്) ഉള്ള സിമെന്റുകളിൽ എങ്ങനെ ബാധിക്കും എന്നത് ഈ ഗവേഷണത്തിൽ പഠിക്കുന്നു. ഇന്ത്യയിലെ വിവിധ കാലാവസ്ഥകളെ പ്രതിനിധീകരിക്കുന്ന 10°C, 27°C, 50°C എന്നീ താപനിലകൾ ഈ പഠനത്തിനായി തിരഞ്ഞെടുത്തു.

രാസപ്രവർത്തനം, ഘട്ട-വികസനം എന്നിവയെക്കുറിച്ചുള്ള പഠനങ്ങൾ കാണിക്കുന്നത് ഉയർന്ന ക്യൂറിംഗ് താപനില ആദ്യകാലഘട്ടത്തിൽ ഉള്ള രാസ പ്രവർത്തനങ്ങളെ ത്വരിതപ്പെടുത്തുമെന്നാണ്. എന്നിരുന്നാലും, ദീർഘകാലത്തിൽ ഉള്ള കാര്യക്ഷമതയും, ശക്തി വികസനവും തടസ്സപ്പെട്ടേക്കാം. കുറഞ്ഞ ക്ലിങ്കർ ഉള്ള സിമന്റുകളിൽ ഈ പ്രത്യാഘാതങ്ങൾ കൂടുതൽ ദൃശ്യമാണ്, പ്രത്യേകിച്ചും ഉയർന്ന അലുമിന അയോണുകൾ അടങ്ങിയിരിക്കുന്ന എസ്.സി. എമ്മുകൾ ഉപയോഗിച്ച് നിർമിച്ച സിമന്റുകളിൽ.

രാസപ്രവർത്തനഘട്ടത്തിൽ ഉള്ള താപനിലയും എസ്.സി.എമ്മുകളുടെ രാസഘടനയും രാസപ്രവർത്തന-ഉൽപ്പന്നങ്ങളുടെ സ്വഭാവത്തെ സ്വാധീനിക്കുന്നുവെന്ന് മൈക്രോസ്ട്രക്ചറൽ പഠനങ്ങൾ തെളിയിച്ചിട്ടുണ്ട്. ചില വ്യവസ്ഥകളിൽ, ഉയർന്ന താപനിലയിൽ ലഭ്യമാകുന്ന ഉയർന്ന അലുമിന, കൂടുതൽ അളവിൽ പോളിമറൈസ്ഡ് ആയ C-A-S-H രൂപപ്പെടുന്നതിലേക്ക് നയിക്കുന്നു, ഇത് അയോണുകളുടെ സ്വതന്ത്രമായ ചലനത്തിനെതിരെ ഉപരോധം സൃഷ്ടിച്ച്, ഇത്തരം സിമെന്റുകളുടെ മുന്നോട്ടുള്ള രാസപ്രവർത്തനത്തെ അടിച്ചമർത്തുന്നു. ഇത് മൂലം സിമന്റുകളുടെ ദീർഘകാല ശക്തി വികസനം കുറയ്ക്കുന്നതിനും കാരണമാകുന്നു. കൂടാതെ,

പോർട്ട്-ലാൻഡ്വിൻറെ ലഭ്യത കുറയുന്നത് എസ്സിഎമ്മുകളുടെ പ്രവർത്തനത്തെയും ബാധിക്കുന്നു. ഉയർന്ന താപനില, രാസ-ഉൽപ്പന്നങ്ങളായ എട്രിംഗെറ്റ്, കാർബോഅലൂമിനേറ്റുകൾ എന്നിവയുടെ രൂപവത്കരണത്തെ തടയുന്നു. ഇത് ശക്തിയെയും മൈക്രോസ്ട്രക്ചറൽ വികസനത്തെയും സ്വാധീനിക്കുന്നു. കൂടാതെ പേസ്റ്റുകളുടെ പ്രവേശനക്ഷമതയെയും അവയുടെ ഈടിനെയും ബാധിക്കുന്നു.

എന്നിരുന്നാലും, ഉയർന്ന താപനിലയിലേക്ക് സമ്പർക്കം ചെയ്യുന്നതിലെ കാലതാമസം മൈക്രോസ്ട്രക്ചറൽ, ശക്തി വികസനം എന്നിവ മെച്ചപ്പെടുത്തുന്നതിന് കാരണമാകുമെന്ന് ഗവേഷണ-ഫലങ്ങൾ കാണിക്കുന്നു. ചില സാഹചര്യങ്ങളിൽ അധികം ജിപ്സത്തിൻറെ സാന്നിധ്യവും ശക്തി വികസനം മെച്ചപ്പെടുത്തുന്നതായി കാണിക്കുന്നു.

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Glossary

AFt	Ettringite
AFm	Monosulphate
A/S	Alumina to Silica Ratio in C-A-S-H
BSE	Back Scattered Electron
Cc	Calcium Carbonate
CH	Portlandite
C/S	Calcium to Silica Ratio in C-A-S-H
DoH	Degree of Hydration
EDX	Energy Dispersive X-Ray Spectroscopy
FH	Ferrous Hydroxide
Hc	Calcium Hemicarboaluminate
Hg	Hydrogarnet
Ht	Hydrotalcite
LC ³	Limestone Calcined Clay Cement
LOI	Loss on Ignition
MAC	Mass Absorption Coefficient
Mc	Calcium Monocarboaluminate
MIP	Mercury Intrusion Porosimetry
OPC	Ordinary Portland Cement
PSD	Particle Size Distribution
Pt	Portlandite
SCM	Supplementary Cementitious Material
SEM	Scanning Electron Microscopy

TGA	Thermogravimetric Analysis
w/b	Water to Binder ratio
w/c	Water to Cement ratio
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence