INFLUENCE OF CALCINATION CONDITIONS ON THE PHYSICO-CHEMICAL CHARACTERISTICS OF CALCINED CLAYS FOR USE AS SUPPLEMENTARY CEMENTITIOUS MATERIALS

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CERTIFICATE

This is to certify that the thesis entitled “Influence of calcination conditions on the physico-chemical characteristics of calcined clays for use as supplementary cementitious materials” being submitted by Ms. Mehnaz Dhar, 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 her under my supervision and guidance. She 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

Reducing the clinker to binder ratio is a key strategy to reduce CO_2 emissions in cement industry. Currently, fly ash, ground granulated blast furnace slag and ground limestone are added to the concrete. However, their availability varies around the world and is expected to decline in the future. This limited supply has led to growing interest in calcined clays, as clay deposits are geographically spread and sufficiently abundant to meet the projected demand of cement. Additionally, their high pozzolanic reactivity enables a higher reduction in clinker to binder ratio.

The properties of the binder depend on the composition and characteristics of the material added to ordinary Portland cement. The calcination process alters the physico-chemical properties of raw clays, making it essential to understand these changes to predict performance in binder system. This thesis investigates the influence of calcination conditions on the physical and chemical characteristics of kaolinite clays for use as supplementary cementitious material. Nine natural clay samples were selected for this work and calcined in a laboratory muffle furnace at 400°C, 500°C, 600°C, 700°C, 800°C, 900°C and 1000°C. The structural changes in the calcined clays were analysed using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Fourier transformation infrared spectroscopy (FTIR). The change in physical properties like specific surface area, density, water demand and morphology upon calcination were studied. The pozzolanic reactivity was assessed using lime reactivity and modified chapelle test methods.

The results show that the conversion of kaolinite to metakaolin significantly changes the degree of crystallinity and bonding between silicates and aluminate layers. This phase transformation governs reactivity without changing the physical properties. The metakaolin becomes unstable around 950°C and transforms into Al-Si spinel phase, as confirmed by differential scanning calorimetry. The spinel phase reduces the pozzolanic reactivity significantly and marks an onset of over-calcination in kaolinitic clays. The associated minerals, such as quartz, iron and 2:1 clay minerals, influence only the temperature at which spinel forms but not the quantity. Highly disordered iron rich clays exhibit spinel formation at temperatures approximately 80°C lower than those of quartz-rich kaolinite.

A combination of methylene blue and density measurement allows the assessment of the quality of calcined clays at an industrial scale in a rapid and cost-effective manner. The degree of conversion of kaolinite to metakaolin can be effectively obtained by measuring the residual kaolinite content and methylene blue reduction of less than 50%, compared to the raw sample, indicates under-calcination. Additionally, the formation of spinel phase, which is the first less reactive product that forms upon over-calcination, can be identified by density measurements as it has a higher density. The associated minerals influence the properties of kaolinite clays as iron-rich kaolinite clays exhibit higher specific surface area and water demand than quartz-rich kaolinite. Moreover, metakaolin formation occurs at lower temperature in iron-rich clays compared to quartz-rich kaolinite. Interestingly, the calcite impurities do not interfere with the calcination of kaolinite and the physical properties and pozzolanic reactivity of the calcined clays containing calcite were similar to the control sample. The environmental impact of additional CO_2 emissions due to partial decomposition of calcite must be taken into consideration. Limited experiments on flash calcination showed that a higher calcination temperature is required to achieve a similar degree of dehydroxylation compared to soak samples. Flash calcined clays exhibit lower specific surface area and higher amorphous fraction than soak calcined clays at similar degree of dehydroxylation. The decomposition of smectite upon calcination temperature was studied in detail and the results show that smectite undergoes two step-mass loss, unlike a single step process observed in kaolinite. The hydroxy groups that are removed in the second step transforms smectite into an amorphous fraction. Although the calcination temperature required for smectite is higher (900°C), the pozzolanic reactivity is similar to kaolinite clays.

Overall, this study provides a comprehensive understanding of the processes that clays undergo upon calcination, and the factors that influence their suitability for use as SCMs. This study also details techniques that can be used to characterise and assess clays and their quality of calcination.

सारांश

सीमेंट उद्योग में CO_2 उत्सर्जन को कम करने के लिए बाइंडर में क्लिंकर की मत्रा को घटाना महत्वपूर्ण है। वर्तमान में, फ्लाई ऐश, ग्राउंड ग्रैन्युलेटेड ब्लास्ट फर्नेस स्लैग (GGBFS) और ग्राउंड चूना पत्थर का उपयोग कंक्रीट में किया जाता है। हालांकि, इनकी उपलब्धता विश्व भर में सीमित है और भविष्य में और घटने की संभावना है। इस सीमित आपूर्ति के कारण कैल्सिन की गई मिट्टी में रुचि बढ़ी है, क्योंकि मिट्टी पूरे विश्व में व्यापक रूप से उपलब्ध हैं और भविष्य की मांग को पूरा करने के लिए पर्याप्त हैं। इसके अतिरिक्त, इनकी उच्च पोज़ोलैनिक क्रियाशीलता क्लिंकर की मत्रा को अधिकतम रूप से घटाने में सहायक है।

बाइंडर की गुणात्मक विशेषताएँ उस सामग्री की संरचना और गुणों पर निर्भर करती हैं जिसे साधारण पोर्टलैंड सीमेंट (OPC) में मिलाया जाता है। कैल्सिनेशन प्रक्रिया कच्ची मिट्टी की भौतिक और रासायनिक गुणों को बदल देती है, इसलिए इन परिवर्तनों को समझने की आवश्यकता है ताकि बाइंडर प्रणाली में उनके अभिनय को समझा जा सके। इस शोध में काओलिनाइट युक्त मिट्टी को सहायक सीमेंटीय सामग्री (SCM) के रूप में उपयोग करने हेतु कैल्सिनेशन स्थितियों के प्रभाव का अध्ययन किया गया है। नौ प्राकृतिक मिट्टी के नमूनों को चयनित किया गया और 400°C से 1000°C तक विभिन्न तापमानों पर प्रयोगशाला की मफल भट्टी में कैल्सिन किया गया। कैल्सिन की गई मिट्टी में संरचनात्मक परिवर्तनों का विश्लेषण थर्मोग्राविमेट्रिक विश्लेषण (TGA), डिफरेंशियल स्कैनिंग कैलोरीमेट्री (DSC), एक्स-रे विवर्तन (XRD) और फूरियर ट्रांसफॉर्म इन्फ्रारेड स्पेक्ट्रोस्कोपी (FTIR) द्वारा किया गया। कैल्सिनेशन से उत्पन्न भौतिक गुणों जैसे विशिष्ट सतह क्षेत्र, घनत्व, जल आवश्यकता और कण संरचना का भी अध्ययन किया गया। पोज़ोलैनिक क्रियाशीलता को लाइम रिएक्टिविटी और संशोधित चैपेल परीक्षण विधियों से परखा गया।

परिणामों से ज्ञात हुआ कि काओलिनाइट से मेटाकाओलिन में रूपांतरण क्रिस्टलीयता की डिग्री और सिलिकेट-अल्यूमिनेट परतों के बीच के बंधन को काफी हद तक बदल देता है। यह परिवर्तन भौतिक गुणों में बदलाव के बिना क्रियाशीलता को नियंत्रित करता है। लगभग 950°C पर मेटाकाओलिन अस्थिर हो जाता है और DSC के अनुसार यह Al-Si स्पिनल चरण में परिवर्तित हो जाता है। यह स्पिनल अवस्था पोज़ोलैनिक क्रियाशीलता को काफी हद तक घटा देता है और काओलिनाइट मिट्टी में ओवर-कैल्सिनेशन की शुरुआत को दर्शाता है। सहायक खनिज जैसे क्वार्ट्ज, लोहा और 2:1 प्रकार की मिट्टियाँ स्पिनल के बनने के तापमान को प्रभावित करती हैं लेकिन उसकी

मात्रा को नहीं। लौह-समृद्ध, अधिक अव्यवस्थित मिट्टियों में स्पिनल का निर्माण क्वार्ट्ज-समृद्ध काओलिनाइट की तुलना में लगभग 80°C कम तापमान पर होता है।

कैल्सिन की गई मिट्टी की गुणवत्ता को औद्योगिक स्तर पर शीघ्र और सस्ती विधि से आँकने हेतु मिथाइलीन ब्लू और घनत्व मापन का संयोजन उपयोगी पाया गया। काओलिनाइट से मेटाकाओलिन में रूपांतरण की डिग्री को अवशिष्ट काओलिनाइट मात्रा द्वारा मापा जा सकता है और यदि मिथाइलीन ब्लू अवशोषण कच्चे नमूने की तुलना में 50% से कम हो, तो यह अंडर-कैल्सिनेशन को दर्शाता है। साथ ही, स्पिनल चरण, जो ओवर-कैल्सिनेशन की पहली कम क्रियाशील उत्पाद है, घनत्व माप से पहचानी जा सकती है क्योंकि इसकी घनता अधिक होती है। सहायक खनिज मिट्टी की अन्य विशेषताओं को भी प्रभावित करते हैं – लौह-समृद्ध काओलिनाइट में क्वार्ट्ज-समृद्ध की तुलना में अधिक विशिष्ट सतह क्षेत्र और जल आवश्यकता पाई गई। इसके अलावा, लौह-समृद्ध मिट्टी में मेटाकाओलिन का निर्माण अपेक्षाकृत कम तापमान पर होता है।

दिलचस्प रूप से, कैल्साइट अशुद्धियाँ काओलिनाइट की कैल्सिनेशन प्रक्रिया में हस्तक्षेप नहीं करतीं, और कैल्साइट युक्त कैल्सिन की गई मिट्टी के भौतिक गुण और पोज़ोलैनिक क्रियाशीलता नियंत्रण नमूने के समान रहे। हालांकि, कैल्साइट के आंशिक विघटन से उत्पन्न अतिरिक्त CO_2 उत्सर्जन का पर्यावरणीय प्रभाव ध्यान में रखना चाहिए।

फ्लैश कैल्सिनेशन पर सीमित प्रयोगों से पता चला कि सोक पद्धति से समान डिग्री की डीहाइड्रॉक्सिलेशन प्राप्त करने के लिए अधिक तापमान की आवश्यकता होती है। फ्लैश कैल्सिन की गई मिट्टी की सतह क्षेत्र कम लेकिन अमोर्फ अंश अधिक होता है। स्मेक्टाइट के विघटन का विस्तृत अध्ययन किया गया जिससे पता चला कि इसमें दो चरणों में भार कम होता है, जबकि काओलिनाइट में यह एक चरण में होता है। दूसरे चरण में हाइड्रॉक्सी समूहों के हटने से स्मेक्टाइट अमोर्फ अंश में बदल जाता है। यद्यपि स्मेक्टाइट की कैल्सिनेशन के लिए तापमान अधिक (900°C) होता है, फिर भी इसकी पोज़ोलैनिक क्रियाशीलता काओलिनाइट जैसी ही होती है।

समग्र रूप से, यह अध्ययन कैल्सिनेशन के दौरान मिट्टी में होने वाले परिवर्तनों का सर्वग्राही ज्ञान प्रदान करता है और उनके सीमेंटीय अनुप्रयोगों के लिए उपयुक्तता को प्रभावित करने वाले कारकों की विस्तृत जानकारी देता है। इसके साथ ही यह अध्ययन ऐसी तकनीकों को भी प्रस्तुत करता है जो कैल्सिन की गई मिट्टी की गुणवत्ता के मूल्यांकन में उपयोग की जा सकती हैं।

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LIST OF ACRONYMS

A	Anatase
BET	Brunauer Emmett Teller
CaO	Calcium oxide
CH	Calcium Hydroxide
FTIR	Fourier Transformation Infrared Spectroscopy
HCl	Hydrochloric Acid
He	Helium
H	Hematite
I	Illite
ICP	Inductively Coupled Spectroscopy
IS	Indian Standard
K	Kaolinite
LOI	Loss on Ignition
LR	Lime Reactivity
MAC	Mass Absorption Coefficient
MB	Methylene Blue
MC	Modified Chapelle
NaOH	Sodium Hydroxide
OPC	Ordinary Portland Cement
Q	Quartz
PSD	Particle Size Distribution
SEM	Scanning Electron Microscopy
Sm	Smectite
SSA	Specific Surface Area
TGA	Thermogravimetric Analysis
TiO_2	Titanium dioxide
XRD	X-ray Diffraction
XRF	X-ray Fluorescence