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Alternative to Low Carbon Cement: Limestone Calcined Clay Cement (LC^3)

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Abstract: Introducing secondary cementitious material (SCM) helps reduce CO_2 emissions in the cement and construction industry, during and performance advantages, including low permeability, resistance to chlorides and sulfates, mitigation of alkali-silica reaction, greater strength, and lower temperatures for mass Concrete and improved workability. Industrial waste such as SCM, such as fly ash, slag, silica fume, volcanic ash, and other by-products from the different process mixing with clinker and gypsum, in varying proportions, at the grinding stage of blended cement manufacturing. A new SCM as Limestone Calcined Clay Cement (LC^3) is a unique material that is also a cementitious material for the future to reduce dependency on industrial waste as SCM. In this paper usage of LC^3 and its impact and benefits are discussed.

Keywords: Clinker, Durability, Hydration, Kaolinite, Pozzolana.

I. Introduction

Cement manufacturing is known for one of the top carbon dioxide (CO_2) emitting processes, and the CO_2 contribution from cement is about 6-7% of the total global CO_2 emission. The primary source of CO_2 emission in the Cement manufacturing process is the calcination of limestone during the heating and burning process and secondly from the fuels used to produce the heat to burn the limestone. There are other indirect sources of CO_2 emission such as electricity, logistics, and support process. It is estimated that cement consumption in India in the next decade will increase up to three to four folds to meet the requirement of infrastructure, housing, and social and economic developments. Given the CO_2 emission rate of 0.6-0.7 t CO_2/t cement, there is a serious and urgent need to reduce the CO_2 emissions in cement manufacturing. In India, produced clinker is currently mixed with supplementary cement materials such as limestone, fly ash, slag, or combination with gypsum to make cement as per Bureau of Indian Standards. Given the exponential growth in cement demand and focus on renewable energy, there may be a scarcity of supplementary cement materials in the near future, and CO_2 abatement in cement manufacturing will be a challenge [1].

There are many strategies to reduce CO_2 emissions are in practice. This paper focuses on developing suitable additional supplementary cement materials (SCM), known as calcined clay. The calcined clay is recognized as a constitute of Portland Pozzolana Cement as per IS 1489 (Part 2).

II. Calcined Clay

It is established that clay with 40% Kaolinite content, after calcination by a thermal process, is found suitable as SCM to mix with clinker, limestone, and gypsum to develop the compressive strength like Ordinary Port land Cement within 7 days or later.

When the clay undergoes the thermal treatment, metakaolin formation takes place from Kaolinite during the dihydroxylation process between 600-700 °C. The disordered structure of metakaolin combined with Penta-coordinated Al (V) gives the pozzolanic reactivity [2].

The reactive aluminates from the calcined clay mixed with calcite rich material limestone or dolomite in the presence of clinker and gypsum, responsible for multiple interactions and produce Limestone Calcined Clay Cement (LC^3). The typical composition of LC^3 is Clinker-50%: Calcined Clay 30%: Limestone 15%: Gypsum 5%. Generally, the calcined clay and limestone ratio is 2:1 and can be optimized subject to product requirements. When LC^3 is mixed with water, additional reactions and interactions occur during the hydration process compared to the Ordinary Portland Cement. The metakaolin from the calcined clay act as pozzolanic materials and forms calcium aluminum silicate hydrate (C-A-S-H). The C_3A from clinker reacts with limestone and forms carboaluminate hydrates. The presence of carboaluminate hydrates promotes the reaction of aluminate from the metakaolin [3].

III. Hydration Mechanism in Presence of Calcined Clay

The interaction in the LC^3 comprises the clinker and pozzolanic reactions, limestone interaction with clinker hydration, and its products. Initially, clinker phases react to produce C-S-H, CH, and ettringite. Then in the presence of excess aluminates from clinker, ettringite converts to monosulphate and addition of aluminosilicate lead to the formation of C-A-S-H subject to the concentration of silica and alumina. Due to this reaction,

porefilling enhances and develops benefits on transport characteristics.

The Pozzolanic Reaction:

$$A_{SCM} + S_{SCM} + CH + H = C\text{-}A\text{-}S\text{-}H$$

The Limestone Reaction with Clinker Phases:

$$C_3A + CaCO_3 + CH + H = C_3A.CaCO_3.H$$

The Limestone Reaction with Calcined Clay:

$$A_{SCM} + xCaCO_3 + 3CH + H = C_3A.xCaCO_3.H$$

The heat of hydration development is significantly lower with calcined clay compared to other SCM such as fly ash. The long-term hydration of clinker phased (C_2S) is slowed down in the LC^3 in the presence of portlandite for pozzolanic reactions. That is the reason major strength development take place in the later stage up to 28 days [5]. The combination of the calcined clay and limestone collectively accelerates the setting characteristics of LC^3 and rises between 3-4 hours; it means LC^3 can have standard-setting time characteristics and can be compared to other blended and masonry cement. The limestone presence is found useful in enhancing the kinetics of heat release rate and correlates to reduce the delayed setting time compared to other SCMs with higher dosages. The strength development in the LC^3 is comparable to Ordinary Portland Cement even with lower clinker content, lower than other blended cement. It is also indicating that concrete product of LC^3, strength with calcined clay and limestone on par with Ordinary Portland Cement [5].

IV. Conclusion

From the various studies, the performance of calciner clay-limestone as SCM has shown improved durability in terms of chlorides and moisture penetration and corrosion resistance. Based on the past and ongoing studies, Limestone Calcined Clay Cement (LC^3) is an encouraging product to fulfill the promise of low carbon cement alternative to other blended products considering the cement demand growth and scarcity of present SCMs in the near future.

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