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Hydration kinetics and mechanisms of carbonates from stone wastes in ternary blends with calcined clay

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HIGHLIGHTS

- Stone dusts can act as a reactive component in cement hydration when combined with calcined clay.
- Carboaluminates are produced by the reaction of stone dust wastes with calcined clay and portland cement.
- Reduction in clinker factor up to 45% is possible by using calcined clay and marble dust.

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ABSTRACT

This study aims to evaluate the feasibility of utilizing marble stone dust and Kota stone dust as carbonate source in the ternary cement blends with calcined clay. In this article, a novel application of these dusts in a system where they contribute to strength development through a chemical reaction is presented. Ternary cement blends were prepared with by replacing 45% of the ordinary portland cement by a combination of calcined clay and stone dust waste. Three stone dust wastes were collected from Rajasthan region in western India for this study. Crushed quartz and laboratory grade calcite were used as a substitute for stone dust wastes to produce control blends. The hydration process of the ternary cement blends with stone dust waste were studied using X-ray diffraction, thermogravimetric analysis and isothermal calorimetry. The mechanical properties were studied by measuring compressive strength at 1, 3, 7, 28 and 90 days. It was found that marble dust and Kota stone dust can be used as a carbonate source in ternary cement blends containing calcined clay, with formation of carboaluminate phases observed during the hydration of the cement. Formation of additional AFm phases such as stratlingite was observed in the absence of carbonate sources. The synergetic effect that exists in the OPC – calcined clay – limestone systems was also found to exist in the OPC – calcined clay – stone dust system, which led to improved compressive strength.

1. Introduction

Marble and Kota stone are two dimensional stones used extensively for construction in India, with an annual production of 17 million tonnes [1]. Marble is formed by the metamorphic transformation of limestone by natural forces. Chemically, marble is made up of various carbonates such as calcite and dolomite. They can be classified as siliceous or non – siliceous based on the presence of quartz [2]. In India, Rajasthan is the largest marble producer, accounting for 95% of the production in the country [3]. Similarly, Kota stone is a variety of siliceous limestone that is mined in Kota, Rajasthan. The waste generated during the quarrying of the marble stone, can vary from 30% to 60% depending up on whether manual or mechanized mining process is employed. Additionally, 10% of the mined marble stone is wasted during the processing [4]. Nearly 6 million tonnes of marble dust waste and 1.2 million tonnes of Kota stone dust waste is generated in India annually [5]. The processing waste is in the form of a slurry, which is dumped openly on available land, leading to a degradation of the environment. In addition to making the productive land unusable, drying up of the waste slurry results in finer particles becoming airborne, causing severe air pollution and associated health risks. High incidence rates of lung diseases such as the silicosis have been reported among the miners working in the stone mines [6].

Utilizing these stone dust wastes in construction industry would be a sustainable solution to a critical environmental problem posed by inadequate stone dust waste disposal practises. Stone waste has been used for replacement of the fine and coarse aggregates in concrete which improved the durability, workability as

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well as mechanical properties of the concrete [7,8]. Gameiro et al. [9] observed an improved resistance to permeability as well as to chloride penetration when marble sand was incorporated into concrete when compared to river sand. Self-compacting concrete produced with natural pozzolan and marble dust additions (up to 30%) has shown improved rheological properties [10,11], but a reduction in compressive strength was observed at higher replacement levels.

Possibility of utilizing the marble dust as a partial cement replacement has been explored by researchers who have suggested that up to 10–15% of cement can be substituted without compromising on the mechanical properties. More than 10–15% replacement with marble dust resulted in the reduction of the compressive strength due to the increased porosity of the hydrated microstructure [12–15]. Higher replacement levels also results in the reduction in the available alite (C_3S) and belite (C_2S) phases, which are the main reactive fractions of the portland cement. The addition of marble dust was observed to have improved the workability of the cement. The improved performance of the marble dust blended cement has been attributed to the filler effect [16]. Therefore, most existing studies attempt to use marble dust and Kota stone dust as filler rather than reactive component in cement hydration process [17].

Ternary cements, in which low clinker factors can be achieved by partially replacing clinker with a combination of two supplementary cementing materials (SCM) have been gaining prominence in the cement industry. Limestone Calcined Clay Cement or LC^3 is one such ternary cement, in which clinker factor of 0.50 was achieved by partially replacing clinker using a combination of calcined clay and limestone. Formation of carboaluminate phases has been observed in LC^3 during early ages of hydration [18]. Calcium hemicarboaluminate and calcium monocarboaluminate are AFm type hydration products that have been reported to form in limestone blended cements, with CO_3^{2-} ions able to combine with C_3A to form carboaluminates [19–21]. During the hydration of ordinary portland cement, the sulphate ions (added to prevent the false setting) react with the C_3A present in the cement to form the ettringite phase. On the complete consumption of sulphate ions, the ettringite formed combines with C_3A phase to form monosulphate. The addition of limestone or calcite introduces CO_3^{2-} ions into the system, resulting in the modification of the final phase assemblage. It has been shown experimentally and with thermodynamic calculations that in the presence of carboaluminate phases, the transformation of the ettringite into monosulphate phase do not take place [22]. The stabilization of water rich, low density ettringite results in reduced porosity and improved strength [23]. Pilot production of LC^3 has been carried out in India and Cuba with promising results [24,25]. The synergetic effect between the calcined clay and carbonate ions results in a refined pore structure in systems LC^3 even at early ages. This refined pore structure as well as lower intrinsic permeability results in improved durability characteristics (against chloride as well as sulphate attack) due to greater resistance against ion transport [26].

Carbonate minerals such as calcite or dolomite are the major constituent of the marble dusts [3,27] making them an ideal replacement for limestone in LC^3 type systems. In this study, the potential of having marble dusts and Kota stone dust as reactive component in ternary blends when combined with clinker and calcined clay was investigated.

2. Experimental program

2.1. Characterization of materials

A 43 grade ordinary portland cement (OPC) conforming to BIS 8112 – 2013 [28] available in the market was used for this study. The cement used did not contain limestone as a filler. This ensured that only source of carbonate in the blends studied is contributed by the stone dusts. The Rietveld quantitative XRD phase analysis of the cement was done using commercially available Rietveld software package (TOPAS v5 from Bruker AXS). Raw kaolinitic clay was collected from a clay mine in Bhuj, Gujarat and was calcined in a rotary kiln. Kaolinite in clays upon heating transforms into amorphous metakaolin, which can then be used as pozzolanic material [29]. The calcination or the dehydroxylation of the kaolinite occurs within the temperature range of 600 °C–900 °C [30,31]. It was ensured that the temperature inside the rotary kiln did not exceed 900 °C to prevent the formation of unreactive crystalline mullite. The XRD of calcined clay (Fig. 1) clearly showed the amorphous "hump" (around 15° and 30°) which confirms the presence of metakaolin and the absence of crystalline mullite phase. At 925 °C, the metakaolin formed gets transformed to silicon spinel. On exposure to higher temperature, the silicon spinel is then transformed to pseudomullite (1100 °C) and finally gets converted to mullite (1400 °C)[32].

Two marble dusts KG and BA were procured from Kishangarh and Banaswara regions in Rajasthan respectively. Kota stone dust (KS) was collected from a stone processing unit in Kota, Rajasthan. Stone dusts were dried at 105 °C for 24 h in an oven to remove any residual moisture present and were crushed with a laboratory grade ball mill to increase the fineness. Marble dust, KG contains calcite and dolomite as the major phases with quartz and other clay minerals being the minor phases whereas marble dust BA has dolomite as the major phase. Quartz and calcite were the major phases present in Kota stone dust. The amount of calcite, dolomite and quartz present in the stone dusts have been measured using Rietveld analysis (Table 1). Industrial grade limestone (LS) (Duracal 15 from Omya) and crushed quartz were used to compare the effect of stone dusts on the hydration process. The chemical as well as the major phase composition of the raw materials used are shown in Table 1.

The particle size distribution of the raw materials are shown in Fig. 2. Ternary cement blends were made by interblending the raw materials together in the following proportions by mass – 55% OPC, 30% calcined clay and 15% stone dust/LS/crushed quartz (Table 2). No additional sulphate correction was carried out in this study. The results were compared with two control blends – O45Q (55% OPC and 45% Quartz) and OPC.

2.2. Tests on cements

2.2.1. X-Ray diffraction

Cylindrical cement paste specimens (2 cm diameter) were cast with a water to binder ratio of 0.45 for carrying out XRD and TGA analysis of the paste. The specimens were cured under lime saturated water till the required testing age. X-ray diffraction was used to identify the hydration products of the blends and was carried out on fresh slices (3mm thickness) taken from cylinders at 1, 3, 7, 28 and 90 days. The tests were carried out with a voltage of 40 mV and current 25 mA with Cu target (Kα = 1.54 Ã...). The scanning angle range was between 5° and 65° at the rate of 0.3 s/step with a step size of 0.019° resulting in a total scanning time of approximately 17 min per sample. The slices were immersed in isopropanol for 7 days to stop the hydration process and subsequently stored in a vacuum desiccator. Quantitative analysis of the hydrated cement was done by using external standard method [33] using rutile (Alfa Aesar 42681) with 97.5% crystallinity as the external standard. Fundamental parameters approach (FPA) [34] was used for calculation of the X-ray diffraction profiles with a chebyshev polynomial with 5 coefficients used for fitting the background in rietveld refinements. The amount of clinker phases reacted at a given age were calculated by first measuring the unre-