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β-Belite cements (β-dicalcium silicate) obtained from calcined lime sludge and silica fume

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The utilization of lime sludge (LS), a pulp and paper industry residue, and silica fume (SF), a ferrosilicon industry by-product, as raw materials for the preparation of β-dicalcium silicate (β-C_2S or β-belite) is investigated. β-phase belite is synthesized in a molar ratio of calcined LS/SF at 2.0 by hydrothermal method followed by calcination at 1000 °C for 2 h, which is lower temperature than conventional production temperature of about 1200 °C, and importantly without any chemical stabilizers. The produced belite cements containing 89.3% of β-belite, the rest being α-belite (5.93%), tobermorite (C–S–H, 1.71%), cristobolite (SiO_2, 1.83%) and free lime (CaO, 1.24%). The micro analytical characteristic of the raw materials and formed belite are examined by means of TG-DTA-DTG, XRF, XRD, SEM with EDAX, FT-IR, BET techniques and isothermal conduction calorimetry. The hydration of pastes and compressive strength of mortars of the formed β-belite blended with ordinary Portland cement are studied with a partial replacement of cement by 10%, 20% and 30%. The reaction of β-belite in combination with Portland cement is comparable up to 10% replacement of cement to the pozzolanic reactions of other materials used in similar ways. However, it is observed that the premature stiffening of belite incorporated cement pastes takes place with low heat of hydration because of higher reactivity of belite cement incorporation.

1. Introduction

β-phase of belite (β-Ca_2SiO_4, β-dicalcium silicate) is one of the major polymorph in industrial Portland cement clinker because of its lowest rate of heat evolution during cement hydration [1]. The rate of change in heat evolution leads to form different type of polymorphs (α, α'_H, α'_L, β and γ) of belite compound that dependent on its reaction mechanism by fastest quenching transformations. The techniques show more reactive and very high surface area of belite cement improves mechanical strength because of slow hydration at early ages [2–5]. The reduction of energy in the cement production is to reduce the lime saturation factor (LSF) by replacement of belite in cement materials [6,7]. Moreover, the belite rich cements are suitable for long term sustainable materials for the infrastructure development [8]. A substitution of a major part of alite (tri-calcium silicate) to curtail more CO_2 emission during cement production can be achieved by belite and the production of belite cements attracted the interest of specialists for a long time in the construction industry [9,10].

Other than construction applications, belite is also used as refractory materials [11], heat resistance coatings [12], bioactive self-setting materials [13], and electrical insulators [14]. Conventionally, belite is readily prepared from CaO and SiO_2 by various methods such as solid state reaction [15,16] at relatively low temperature, hydrothermal-calcination route [9,17,18], sol–gel synthesis [19], Pechini process [20], clinkerization followed by heat treatment at different high temperatures [9] and mechnochemical route of new composites especially for various oxide compounds [10,21–24]. The belite is synthesized from limestone and quartz by solid state reaction at elevated temperature above 1200 °C by using different chemical stabilizing agents that leads to non-homogeneous products with impurity [25,26]. In a recent study, active low-energy reactive belite cement was synthesized by Staněk and Sulovský [7] and this kind of reactive belite can be used in special applications in place of OPC.

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It is well known that the concrete is the most widely used construction materials due to its low cost and long durability. Generally, the production of every ton of Portland cement releases about the same quantity of CO_2, a greenhouse gas in to the atmosphere, which is accounted for 7–8% of total CO_2 emission [27–29]. On the other hand, there is a strong need to develop materials and technologies that utilize various wastes in an effective way for new product development. The manufacture of cement requires 40–50% for production cost and 20–30% of thermal energy [30], and 12–15% of electrical energy [31]. India is the second largest cement producer in the world; currently total capacity utilized is 280 million tons and estimated capacity of 550 million tons by 2020. There are 180 large and 380 small cement plants producing cement throughout India. It is accounted that about 95% of the thermal energy is consumed by Indian cement manufacturing industry (U.S. Geological Survey, 2015; 53rd Annual Report of Indian Cement Industry, 2013–2014). According to Central Pollution Control Board, Government of India (Technical report -POSP/103/2006-200734), nearly 4.6 million tons per annum of lime sludge (LS), a residual solid is generated from the pulp and paper industry during the re-causticizing process of green liquor to white liquor and from petroleum industry in India. Moreover, they are disposed-off by dumping into waste land posing severe environmental pollution. The raw lime sludge, in its natural state is unsuitable for construction engineering applications because of its high moisture content, low density and poor pozzolanic characteristics [32]. It was also observed that the raw LS, up to 10% replacement of cement attained equivalent strength of control concrete, but further increase in replacement reduces the strength [33,34]. The influence of calcined lime sludge blended with cement mortars were studied earlier [35,36]. LS and/or calcined LS (CLS) are not pozzolanic, or slightly due to the presence of small amount of amorphous SiO_2 (but, mainly $CaCO_3$/CaO). But the earlier study by Rodríguez et al. [35] proved that the calcined paper sludge imparted pozzolanic activity in the cement mortar.

Another industrial by-product silica fume (SF), a ferrosilicon industry residue is being studied by various researchers for the partial replacement of cement in concrete due to its high specific surface area and Pozzolanic activity [37–40]. The guideline for the use of SF and its beneficial influence in concrete was reported by many researchers (ACI 234R–06, 2008). ACI committee [41] also suggested the use of SF up to 12% for replacement of cement. Apart from pozzolanic activity of SF, it also acts as filler in concrete, which fills the pores and voids between the cement paste and aggregates leading to more compaction of concrete. Further, Sellevold et al. [4] reported that SF accelerates the hydration of cement during the early stages by providing nucleation sites, where the products of cement hydration can readily precipitate from solution. Hence, it is clear that many inert industrial waste materials can be activated to form valuable supplementary cementitious materials and they are more variable in composition than that of manufactured materials. Properly applied, these wastes can actually improve the performance of cement [42]. In a similar line, an industrial process for stabilizing and evaluating the sewage sludge mediated with lime as raw material for cement industry was carried out by Rodríguez et al. [43], and observed that apart from stabilization, the lime raised the temperature of the mix, which helped in evaporation of water, portlandite formation and oxidation of organic matter present in the sludge.

With this background, an attempt is made to synthesis of belite phase cement by using CLS with highly reactive SF material by hydrothermal method. To the best of authors' knowledge, LS and SF are not employed so far to produce β-belite through hydrothermal synthesis method without using any chemical admixtures, which is a novel study in this field.

2. Materials and methodology

2.1. Materials

The LS is collected from M/s Kalpana Lime House, Porur, Chennai, India. SF is obtained from M/s Corniche India Pvt. Ltd. Mumbai. The ordinary Portland cement (OPC) of 53 grade conforming to IS: 12269-1987 [44] and locally available grade 2 sand conforming to IS: 383-1970 [45] is used. Lignosulfonate, first generation superplasticizer (labelled, SP) having specific gravity of 1.08–1.1 and self life of 6 months is used.

2.2. Experimental methods

The microstructural studies of samples are carried out by using scanning electron microscope (SEM) TESCAN VEGA3 and ZEISS EVO 18 using secondary electron in the accelerating voltage range of 5 kV–10 kV with the probe current from 1 pA to 2 μA.

Linn High Therm GmbH VMK 1400 laboratory furnace is used for calcination of both raw materials and intermediate products and the samples are kept in an alumina crucible and heated to the required temperatures. The samples are prepared in powder/pellet forms for the microanalytical study.

Simultaneous thermal analyses, thermogravimetric – differential thermogravimetric – differential thermal analysis (TG-DTG-DTA) using Netzsch STA & QMS 449F3 with Proteus software are used with alumina crucible fitted with pierced lids. The samples are used in powder form with size less than 25 μm for conducting thermal analysis to identify the phase transition temperature at a uniform heating rate of 10 °C/min under nitrogen atmosphere.

Nicolet 6700 Fourier Transform Infra-Red (FT-IR) system with Omnic Software version 9 is used for the spectroscopic study. Initially, 0.1 mg of the sample is taken and mixed with KBr in the ratio of 1:8 and then the sample is compressed into a pellet form of fine thickness by using a hydraulic pressure pelletizer of 5 Tons load capacity with wave number range of 400–4000 cm^{-1}. The sample is then loaded in the sample holder and placed in the test chamber of FT-IR.

Bruker's D2 PHASER X-Ray Diffraction (XRD) system, equipped with 1-D LynxEye detector is used in the present study, which employs Cu-Kα radiation (30 kV, 10 mA) with Nickel filters. A continuous scan from 10° to 60° 2θ in step width of 0.02° and counting time of 0.5 s per step is performed on less than 25 μm size powder samples.

Surface area and pore radius of the resultant samples are determined by Brunauer-Emmett-Teller (BET) analysis. Powder sample of 0.5 g is taken and degassed for 1 h at 100 °C to remove the moisture. Quantachrom ASiQWin-05090-2.0 series BET analyzer is used for this measurement using Nitrogen gas as adsorbate.

Calmetrix- I CAL 2000 HPC; USA, operating with 110–240V, 50/60 Hz electrical supply is used for heat of hydration studies.

Micro-test Compression Testing Machine (CTM) of 300T capacity is used to determine the compressive strength of mortars.

3. Results and discussion

3.1. Characterization of raw materials

According to authors' earlier study (Maheswaran et al. [33]), it is confirmed that the as-received LS is mainly of prismatic calcite rhombohedral crystal morphology [$CaCO_3$]. The decomposition of raw LS in the calcination temperature range of 700–800 °C gives lime (CaO, calcium oxide). CLS is obtained by calcination of LS at temperature of 800 °C for 2 h. The morphology of the as-received LS and CLS is studied by using SEM and is shown in Figs. 1a and b. The