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Influence of catalytic nano-additive for stabilization of β-dicalcium silicate and its hydration rate with different electrolytes

Sanat Chandra Maiti, Chinmay Ghoroi*

DryProTech Lab, Chemical Engineering, Indian Institute of Technology Gandhinagar, Palaj, Gandhinagar, Gujarat 382355, India

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ABSTRACT

The influence of nano-additives (nano-TiO_2 and nano-MgO) on stabilization of β-dicalcium silicate (β-C_2S) was investigated and compared with corresponding micron size additives. The effectiveness of phase stabilization with different wt% of nano- and micron-additives along with the influence of sintering temperature on stabilization of β-C_2S were studied using Rietveld refinement of XRD data. In addition, hydration study of β-C_2S stabilized by nano-additive was also carried out in the presence of $CaCl_2$, NaCl, NaOH and distilled water. The rate of hydration and influence of different electrolytes were analyzed by TG and DTG curve. The result shows that nano-TiO_2 provides a catalytic effect on phase stabilization even at very low wt%. The hydration result of β-C_2S stabilized by nano-TiO_2 indicates that electrolyte solution and its ion play an important role towards hydration kinetics. The morphology of the C-S-H phase strongly depends on the electrolyte solution used for the hydration.

1. Introduction

Dicalcium silicate, Ca_2 SiO_4 (C_2S) is one of the important cement phases which comprises about 15–30 wt% of Ordinary Portland cement (OPC) [1,2]. Among different polymorphs of C_2S, see Table 1, β-form of C_2S is the major component in OPC due to its high hydraulic properties [3–6]. Therefore, stabilization of β-C_2S phase and its hydration is important for cement industry. At room temperature, the orthorhombic structure of γ-C_2S contains two Ca^{2+} with six regular coordinated oxygen environment [7–9]. In contrast, the monoclinic β-form contains two Ca^{2+} ions with eight oxygen atoms in distorted environments [10]. Thus, at room temperature β-form of C_2S is metastable in nature and is more reactive with water than γ form [11]. However, β-C_2S is stable between the calcination temperature range of 1000–1200 °C and α -phase is dominant at high temperature beyond 1400 °C. However, at room temperature the clinker undergoes phase transformation from β to γ while it is subjected to natural cooling [12]. This phase transformation is associated with ~12 % volume change which is known as "dusting" [13].

There are several techniques reported to prevent γ-C_2S formation such as fast cooling by air or water, doping of micron size additive oxides (Cr_2O_3, B_2O_3, P_2O_5, MgO, Fe_2O_3 and As_2O_5) [1,14-19] and reducing the size of the reactant particle (< 2 μ m) [3].

However, to the best our knowledge use of nano-additive for the purpose is not reported in the literature. Most of the studies with nano-particles are focused to increase the physical properties and hydraulic reactivity of the cement material [12,20-22]. For example, nano-TiO_2 is effective in increasing the hydraulic properties of OPC [22,23]. Recent studies have shown that insertion of nano-materials into the crystal structure is a unique technique to improve the material properties [24–26]. The technique is used for increasing the lithium content in the lithium titanate phase [24]. The study suggests that nano-additive could be an option for effective stabilization of a certain phase due to its higher diffusivity, higher mobility and high surface energy [27]. No such work on β-C_2S stabilization is reported in the literature. Even the explanation of effectiveness of micron-size additives for cement phase stabilization has several discrepancies. In the present form, they are mostly general guidelines in terms of (a) ionic radius (R) [28], (b) charge to ionic radius (C/R) [19] and (c) polarization ability (C^2/R) [29]. These guidelines fail to explain some of the experimental results in the literature. This discrepancy could be due to several other factors like calcination temperature, reactant particle size [3,30,31], reactant ratio, presence of various ions [3,14,32], cooling effect [3] including prevailing experimental conditions [33]. Furthermore, the influence of additive size towards the phase stabilization is not well studied and lacks of proper explanation for β-C_2S stabilization. Moreover, it is believed that hydration rate of calcium silicate in general depends on the electrolytes and there are several studies with tricalcium silicate [34,35]. There have been limited studies reported pertaining to the hydration of β-C_2S. However, hydration of β-

* Corresponding author.
E-mail address: chinmayg@iitgn.ac.in (C. Ghoroi).

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Table 1
Polymorphic transformation of di-calcium silicate (Ca_2SiO_4) at different temperature.

Polymorphic transformation	Temperature (°C)
$\alpha_H^{'}$ (orthorhombic) $\leftrightarrows$ α (hexagonal)	1425
$\alpha_L^{'}$ (orthorhombic) $\leftrightarrows$ $\alpha_H^{'}$ (orthorhombic)	1177
β (monoclinic) $\overset{\triangle V=+1\%}{\leftrightarrows}$ $\alpha_L^{'}$ (orthorhombic)	675
β (monoclinic) $\xrightarrow{\triangle V=+12\%}$ γ (orthorhombic)	490
γ (orthorhombic) $\rightarrow$ $\alpha_L^{'}$ (orthorhombic)	850

Table 2
Particle size of reactants and the additives.

Reactants		Micron-additive		Nano-additive	
$CaCO_3$ (μm)	SiO_2 (μm)	MgO (μm)	TiO_2 (μm)	MgO (nm)	TiO_2 (nm)
12	30	12	14	45	20

Table 3
Notation of the different samples.

Type	Notation	Sample name
Pure mixture	A	$2CaCO_3 + SiO_2$
Mixture with micron-additive	B	$2CaCO_3 + SiO_2$ + 3.0 wt% micron-MgO
	C	$2CaCO_3 + SiO_2$ + 3.0 wt% micron-TiO_2
	D	$2CaCO_3 + SiO_2$ + 0.25 wt% micron-MgO
	E	$2CaCO_3 + SiO_2$ + 0.25 wt% micron-TiO_2
Mixture with nano-additive	F	$2CaCO_3 + SiO_2$ + 3.0 wt% nano-MgO
	G	$2CaCO_3 + SiO_2$ + 3.0 wt% nano-TiO_2
	H	$2CaCO_3 + SiO_2$ + 0.25 wt% nano-MgO
	I	$2CaCO_3 + SiO_2$ + 0.25 wt% nano-TiO_2

C_2S stabilized by nano TiO_2 has not been explored. Thus an organized investigation is required to understand the behavior of β-C_2S hydration kinetics and the morphology of the hydrated phase with different electrolytes.

In the present study, different percentage of nano and micron size TiO_2 and MgO were used as additives and its effectiveness towards the β-C_2S stabilization was investigated. Qualitative and quantitative phase analysis were performed using X-ray diffraction (XRD). The morphology was examined by field emission scanning electron microscopy (FESEM). Finally, the hydration of β-C_2S stabilized by nano-TiO_2 (3 wt %) was studied in the presence of $CaCl_2$, NaCl, NaOH and compared with the hydration rate in distilled water. The degree of hydration was measured by observing the mass loss in thermogravimetry (TG) experiment. Morphology of the corresponding hydrated samples was analyzed with the help of FESEM.

2. Experimental

2.1. β-C_2S stabilization

2.1.1. Preparation of sample

Dicalcium silicate with and without additives were synthesized from 2:1 mole ratio of AR grade $CaCO_3$ (SRL India) and SiO_2 (Sigma Aldrich). The nano-size additives (TiO_2 and MgO) were procured from Sigma Aldrich and corresponding micron size particles were obtained from SRL India. The size of the nanoparticles (TiO_2 and MgO) reported by the manufacturer was approximately 20 and 45 nm, whereas for the micron sized particles it was determined by employing laser diffraction particle size analyzer (Cilas, Model 1190) under dry analysis mode (as tabulated in Table 2). Both nano and micron-size additives were mixed with the raw materials separately in two different weight ratios (0.25 wt% and 3 wt%). 9 samples were prepared to investigate the β-phase stabilization (listed in Table 3). The mixture of raw materials and additives were homogenized with the help of magnetic stirrer in anhydrous acetone medium for 15 min. After mixing, the solutions were dried at 100 °C in hot air oven. The powder samples were then pressed into a pellet under 1 ton load and fired in a chamber furnace (Electroheat-EN170QT/Naskar & Co, India) at different temperatures (1200, 1350, 1400 and 1450 °C) for 1 h. After the reaction all samples (with and without additive) were quenched in air. After quenching, the reaction mixture was grounded in mortar and pestle and was passed through a 75 micron sized sieve. The final samples were stored in a desiccator for characterization (SEM and XRD analysis). To establish the effect of temperature on β-C_2S stabilization, similar experiments with TiO_2 (both micron and nano-size) were carried out for 1 h at 1350 °C and 1400 °C.

2.1.2. FESEM and XRD study

The quality of mixing and morphology of the reactants as well as products were examined by field emission scanning electron microscopy (JEOL-JSM-7600F).

XRD patterns were collected on a Bruker-D8-Discover X-ray diffractometer with Cu-Kα source, operating at 30 mA and 40 kV. The step size of the scan was kept as 0.005 and the scan speed as 0.2 s /step. To analyze the composition of the reaction mixture, Rietveld refinement was carried out with the help of TOPAS 4.2 from Bruker AXS, UK. The quality of fitting was assessed using the R weighted factor (R_{wp}) and the goodness of fitting (GOF) [36,37].

2.2. Hydration study

β-C_2S stabilized by 3 wt% nano-TiO_2 was milled in planetary ball mill (insmart Systems-MBM, India) and then used for hydration study. Approximately 50 g of β-C_2S was milled in ethanol medium for an hour at 400 rpm using 5 mm ZrO_2 milling balls to get the uniform particle size.

To investigate the hydration at different medium, 1 M solutions of $CaCl_2$, NaCl and NaOH were prepared. For this purpose the paste of β-C_2S was prepared with corresponding medium keeping the liquid to solid mass ratio 1. Each type of pastes were stored in four different plastic vials and sealed for long term hydration study (28 days). At the end of the designated time intervals (3, 7, 14 and 28 days), the samples were crushed and washed with acetone to stop the further reaction. Finally, the samples were dried in the oven at 60 °C for 24 h and stored in desiccator for further study. Thermogravimetric analysis (TGA) was performed for each samples at 10 °C/min in constant N_2 environment upto 800 °C. The morphology of the hydrated samples for each intervals were examined with the help of FESEM and different phases were analyzed by XRD. The surface area of the different samples was measured by BET method (Micrometrics-3Flex 3500).

3. Results and discussion

3.1. β-C_2S stabilization

3.1.1. FESEM studies

Scanning electron micrograph of pure sample as well as samples with different additives before the reaction are shown in Fig. 1. The morphology of pure material is shown in Fig. 1A. It can be seen that