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Research Article

Effect of Na_2SiO_3 and Na_2CO_3 on hydration properties of dicalcium silicate prepared from black rice husk ash

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Abstract

This research aims to investigating the effects of sodium silicate (Na_2SiO_3) and sodium carbonate (Na_2CO_3) on the hydration properties of dicalcium silicate prepared from black rice husk ash (BRHA). BRHA is a waste residue from rice milling plant. The major composition and crystalline phase of SiO_2 were determined by X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively. The SiO_2 content of BRHA was 93.7% and therefore was used as silica source for the synthesis of dicalcium silicate by firing with $CaCO_3$ at 1100 ºC for 1 hr. XRD results revealed that β-dicalcium silicate or Larnite is the major phase formed. This indicated that BRHA is a potential source of silica and can be used in the as-received from for the synthesis of dicalcium silicate. The obtained dicalcium silicate was reacted with water. The hydration reaction of dicalcium silicate was activated using Na_2SiO_3 and Na_2CO_3 at the level of 1, 2 and 3 wt%. The changes in the properties of the hydrated cement products were monitored by several techniques such as X-ray diffraction (XRD), gravimetry/differential thermal analysis (TG/DTA), and Compressive strength. Results showed that the 1% of Na_2SiO_3 is suitable activator in this work. It's gave the amounts of $Ca(OH)_2$ of 41.91% at 28 days of hydration and highest amorphous CSH gel was present. Moreover, the compressive strength development of hydrated cement with 1% of Na_2SiO_3 is higher than without activator. Results found that the optimal 1% of Na_2SiO_3 gave the compressive strength of 154 kg/cm^2 at 28 days.

Keywords: dicalcium silicate, belite, black rice husk ash

Introduction

Portland cement manufacturing industry produces about 5% of the total global man-made CO_2 production (Scrivener & Kirkpatrick, 2008). The environmental demand for reduction of CO_2 emissions, the increment of energy cost, the cost and equirement of raw materials, reinforce the need for the development of alternative, more environmentally friendly cements. Recently, the synthesis of dicalcium silicate has received much attention due to lower carbonate content and burning temperature resulting in a reduction of CO_2 emission. Dicalcium silicate is one of the major components and was present about 15-30 wt% of Portland cement. Dicalcium silicate can be prepared by burning at 800-1200 °C which consumes energy around

1350 kJ/kg in comparison with tricalcium silicate which is around 1810 kJ/kg (Kurdowski et al., 1997). However, the drawback of dicalcium silicate is that the hydration reaction at the early age is slow compared to tricalcium silicate. As a result, a lower rate of strength development was usually obtained.

Nowaday, many reseaches have interested in the synthesis of dicalcium silicate at low temperature. Several industrial wastes such as rice husk ash (Romano et al., 2007), lignite fly ash (Pimraksa et al., 2009) and silica fume (Maheswaran et al., 2016) were used as alternative raw materials. Previous researches recommended that the use of industrial by-products is not only a waste reduction in the environmental mean, but also enhancement the synthesis of dicalcium silicate. In Thailand, a large quantity of rice husk ash is generated from the rice milling plant and biomass powerplant. These ashes lead to serious environmental and health impacts. According to Rodrigues & Monteiro (1999), rice husk ash was successfully used as a raw material for the preparation of β-dicalcium silicate at low temperature (700°C). The problem of hydration reaction can be overcome by using various activators, for example calcium chloride ($CaCl_2$) and sodium hydroxide (NaOH). Recently, the alikali-activators (Na_2SiO_3 and Na_2CO_3) has been more attention for this due to its most effective for hydration reaction even though innert matarails (Piyapanuwat & Asavapisit, 2011).

This article aims to investigate the synthesis of dicalcium silicate prepared from black rice husk ash (BRHA) which was obtained from steam rice milling plant and calcium carbonate ($CaCO_3$) in the presence of two acitivators, sodium silicate and sodium carbonate. The effect of acitivators on hydration of dicalcium silicate was investigated using X-ray driffarction and scanning electron microscopy (SEM) analyses.

Materials and methods

Black rice husk ash (BRHA) was obtained from the Thanakij Rice Mill, Thailand. The ash was pretreated with hot HCl at 80 °C for 1 hr and washed with distilled water to remove impurities and dried at 80 °C for 48 hr. The dried ash was ground and screened to pass a 200 sieve mesh. Dicalcium silicate sample was prepared from BRHA and laboratory grade $CaCO_3$ with Ca/Si ratio of 2:1. The dry mixtures of $CaCO_3$ and BRHA were mixed in an alumina crucible. All samples were fired by electric furnace at 1100 ºC for 1 hr and ground until throughout a 200 sieve mesh. The chemical compositions of ground BRHA was investigated by X-ray fluorescence using a Bruker AXS S4Pioneer spectrometer. The crystalline phases of ground BRHA and dicalcium silicate sample were characterized by X-ray diffraction using a Bruker AXS D8Discover diffractometer with Cu K α radiation at a voltage of 40 kV and 40 mA and a step size of 0.02° 2θ, scanning rate of 3°/min from 10° to 60° 2θ. Quantitative analysis of the crystalline phases was carried out on the X-ray data using the computer program TOPAS 2.1. The microstructure of BRHA and dicalcium silicate sample were observed by scanning electron microscopy coupled with energy-dispersive spectroscopy (EDS) using JEOL JSM-IT300 Link OXFORD X-MAX (IE-350). The content of free lime of ground sample was determined by the chemical method as following ASTM C114-07.

Hydration reaction of this study was performed on cement pastes. Dicalcium silicate samples were mixed with Na_2SiO_3 or Na_2CO_3 at 1, 2 and 3 wt% as activators and water to solid ratio of 0.5 was used for all mixtures. Each activator firstly was dissolved in the water, and then added into the ground sample. The slurry was thoroughly mixed and then poured into a cylindrical plastic mold and wrapped with cling film for curing. The hydrated samples were cured at 7 and 28 days and measured according to the standard testing protocol C109/C

109M-95 (ASTM C109-95). The changes in the properties of the hydrated cement were monitored by several techniques such as X-ray diffraction (XRD), gravimetry/differential thermal analysis (TG/DTA), and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS). The development of $Ca(OH)_2$ was investigated using TG/DTA (Netzsch-409) with four replicates for each sample. Subsamples with weights of 15 mg, ground to < 150 μm, were heated to 600ºC in alumina crucibles under an N_2 atmosphere at rate of 5ºC/min. The TG/DTA data were calibrated by analyzing varying amounts of $Ca(OH)_2$ (Univar) mixed with Al_2O_3 (Riedel-deHaen) (Asavapisit et al., 1997).

Results and discussion

Properties of BRHA

The chemical compositions and properties of BRHA were analyzed by XRF, XRD and SEM, as shown in Table 1. It is found that the percentage of SiO_2, Na_2O, K_2O, Al_2O_3, CaO, Fe_2O_3, TiO_2 and SO_3 were 93.70, 0.03, 2.55, 0.40, 0.92, 0.28, 0.02 and 0.40 by weight, respectively. It is found that the main composition is SiO_2 which supported Rahim et al. (2015), they reported the purity concentration of silica in the range of 82.79-97.00 % of BRHA.

Table 1. Chemical compositions of BRHA.

Compound (wt%)	SiO_2	Na_2O	K_2O	Al_2O_3	CaO	Fe_2O_3	TiO_2	SO_3	LOI
BRHA	93.70	0.03	2.55	0.40	0.92	0.28	0.02	0.40	4.40

XRD pattern in Figure 1 shows critobalite peaks at 2θ ≈ 22°-36° (one form of stable crystalline phase of SiO_2 at high temperature) as the main phase (JCPDS file number 82-1403), which indicated the nature of the silica. This result supported by Rozainee et al., 2008; Rodrigues, 2003 and Pimraksa et al., 2009, the major phase of black rice husk ash contains cristobalite phase along with amorphous material. The physical appearance of BRHA shows an angular in shape with a rough surface and the internal porous structure, as shown in Figure 2. It might effect on the hydration reaction. So, this work tried to improvement the properties of BRHA before synthesized dicalcium silicate.

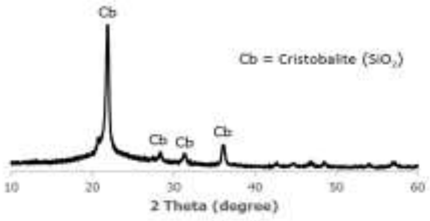


Figure 1. The XRD pattern of the BRHA.

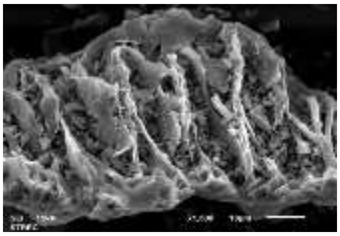


Figure 2. Scanning electron micrographs of BRHA.

Characterization of dicalcium silicate

The synthesized dicalcium silicate was characterized by SEM and XRD as shown in Figure 3 and 4, respectively. In SEM technique, the spherical particle on the surface corresponds to the belite crystalline (Pimraksa et al., 2009) which is in agreement with the XRD pattern. The β form of belite was present at the highest percentage of Lanite (40.9%), as determined by TOPAS 2.1 programe. The remaining peaks were Portlandite, Lime, Cristobalite and Calcite, respectively. Moreover, the free lime content of this sample was 21.92%.

The effect of Na_2SiO_3 and Na_2CO_3 on the hydration properties

The microstructures of the hardened cement paste containing various amounts of Na_2SiO_3 and Na_2CO_3 at the age of 7 and 28 days are shown in Figure 5-6 (from SEM technique). The control samples without activators at the age of 7 (Figure 5(a)) and 28 days (Figure 6(a)), the spherical and irregular shape particles were observed. When 3% Na_2SiO_3 and 3% Na_2CO_3 (Figure 5(b)-(c)) were added, the spherically shaped and some fine hexagonal like crystals of $Ca(OH)_2$ appear at the age of 7 days, and subsequently some tiny fibrous crystals were precipited on the surface of a 28-day sample (Figure 6(b)-(c)).

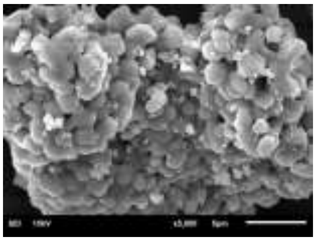


Figure 3. Scanning electron micrographs of dicalcium silicate from BRHA.

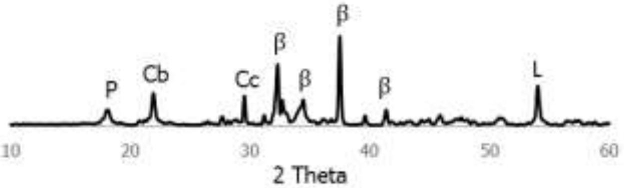
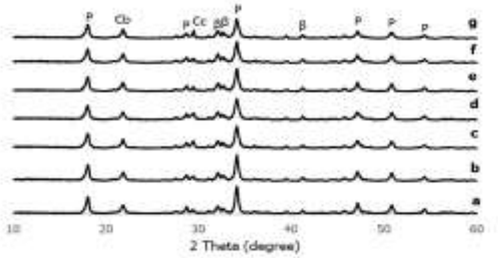


Figure 4. The XRD pattern of dicalcium silicate. (P = Portlandite, Cc = Calcite, Cb = Cristobalite (SiO_2), β = Lanite (Ca_2SiO_4), L = Lime (CaO)).

Figure 5. SEM micrographs of hydrated cements for 7 days: (a) without activator, (b) 3% Na_2SiO_3 and (c) 3% Na_2CO_3.

Figure 6. SEM micrographs of hydrated cements for 28 days: (a) without activator, (b) 3% Na_2SiO_3 and (c) 3% Na_2CO_3.

These fibrous crystals have been reported to be calcium silicate hydrate (CSH) (Radwan et al., 2013). SEM micorgraphs revealed that the formation of CSH is enhanced at the age of 28 days. In addition, these observations were confirmed by EDS analysis on a 28-day sample. The percentages of the following elements: Ca, Si, O, C and Na in the sample with 3% Na_2SiO_3 were 19.02, 2.50, 56.20, 22.16 and 0.12, respectively, and in the sample with 3% Na_2CO_3 are 14.62, 2.86, 60.60, 21.08 and 0.84, respectively. XRD patterns of hydrated cement with and without activators after 7 and 28 days of hydration are shown in Figure 7-8. The sample without activator presents Portlandite, Cristobalite Calcite and Lanite peaks at $2\theta \approx 34^{\circ}$, 22°, 29°, and 33° for 7 and 28 days, respectively and also found the percentage of Portlandite were 49.10% and 44.86% for 7 and 28 days. The occurrence of peaks from the samples with activators represented as similar the control sample. However, the intensity of Portlandite peak decreased with increasing percent of activators (1-3%). This relative decreasing of Portlandite phase of sample can be derived from the increasing of calcium silicate hydrate phase during hydration process (Piyapanuwat et al. , 2011) and consequent contribute the strength improvement (Lea, 1970). This investigation agreed with the SEM results.



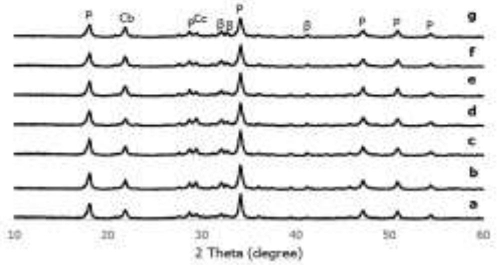


Figure 7. The XRD pattern of cement paste hydrated for 7 days: (a) without activator, (b) with 1% Na_2SiO_3, (c) with 2% Na_2SiO_3, (d) with 3% Na_2SiO_3, (e) with 1% Na_2CO_3, (f) with 2% Na_2CO_3 and (g) with 3% Na_2CO_3.

Figure 8. The XRD pattern of cement paste hydrated for 28 days: (a) without activator, (b) with 1% Na_2SiO_3, (c) with 2% Na_2SiO_3, (d) with 3% Na_2SiO_3, (e) with 1% Na_2CO_3, (f) with 2% Na_2CO_3 and (g) with 3% Na_2CO_3.

(P = Portlandite, β = Lanite (Ca_2SiO_4), Cc = Calcite, Cb = Critobalite

Table 2 shows the amount of $Ca(OH)_2$ present in hydrated cement containing 1, 2 and 3wt% of Na_2SiO_3 and Na_2CO_3. Results showed that the amount of $Ca(OH)_2$ present in the sample without activator hydrated for 28 days was 37.49%. In the present of 1, 2 and 3wt% of Na_2CO_3, the amount of $Ca(OH)_2$ detected during 28 days of hydration decreased to 33.08, 30.88 and 22.06 %, respectively. In case of hydrated cement containing 1, 2 and 3wt% of Na_2SiO_3, the amount of $Ca(OH)_2$ were 41.91, 35.29 and 24.26%, respectively. So, results showed that the 1% of Na_2SiO_3 is suitable activator in this work. It's gave the amounts of $Ca(OH)_2$ of 41.91% at 28 days of hydration and highest amorphous CSH gel was present.

Table 2. The percentage of $Ca(OH)_2$ in the hydrated cement at 28 days of hydration.

Results	Control	Na_2CO_3			Na_2SiO_3		
		1%	2%	3%	1%	2%	3%
Area of Peak	85	75	70	55	95	80	50
% of $Ca(OH)_2$	37.49	33.08	30.88	22.06	41.91	35.29	24.26

We also found that all samples with Na_2CO_3 had the lowest strength due to the low content of siliga and alkalinity (Figure 9). However, the hydrated cement with 1% of Na_2SiO_3 increased the 28-day strengths to 154 kg/cm^2 at 28 days. Because of Na_2SiO_3 dissociation is higher than Na_2CO_3. It’s might be effect on the formation of $Ca(OH)_2$ and CSH gel. In addition, sodium silicate was found to be a silica compound. So, it's supported the silica content in the system. As a result, the development becomes more CSH gel compared to the control. However, if the amount of silica exceeds the balance, it may result in the inhibition of hydration to other compounds.

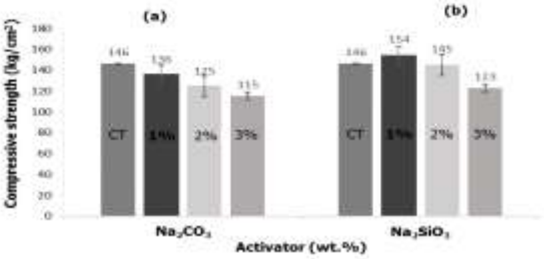


Figure 9. Compressive strength of hydrated cements for 28 days: (a) with 1-3% Na_2CO_3 and (b) with 1-3% Na_2SiO_3.

Conclusion

This research works showed that black rice husk ash residue can be used as an alternative raw material for the synthesis of cement clinker namely dicalcium silicate. The optimum conditions for the formation of dicalcium silicate is obtained by firing the ash with $CaCO_3$ at 1100 °C for 1 hr in an electric furnace and larnite was found to occur as high as 40.9%. The reactivity of the synthesized dicalcium silicate was assessed through the hydration reaction with water in the presence of two activators: Na_2SiO_3 and Na_2CO_3. Results indicated that 1% of Na_2SiO_3 showed a positive effect on the formation of $Ca(OH)_2$ and CSH gel, at the age of 28 days. Moreover, the compressive strength development of hydrated cement with 1% of Na_2SiO_3 is higher than without activator. It's found that the optimal 1% of Na_2SiO_3 gave the compressive strength of 154 kg/cm^2 at 28 days.

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