



## Research article

## Synthesis of belite cement from nano-silica extracted from two rice husk ashes



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## ABSTRACT

Nano-silicas extracted from a pure rice husk ash calcined in the laboratory (RHA) and ash from an impure industrial rice husk waste (BRHA), were used to form belite cement by firing with two different calcium sources (calcium carbonate and calcium nitrate). The nano-silica extracted from RHA was highly reactive due to its high pore volume and low activation energy of dehydration. The formation of belite cement from both nano-silicas was studied by firing with two different calcium sources,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CaCO}_3$  at 800–1100 °C. Both nano-silicas formed the principal phase in belite cement (Iarnite or  $\beta\text{-C}_2\text{S}$ ) at temperatures as low as 800 °C, especially with calcium nitrate as the calcium source. Thus, highly impure BRHA is shown to be very suitable as a starting material for the low-temperature production of belite cement, especially in conjunction with calcium nitrate as the calcium source.

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## 1. Introduction

Portland cement clinker manufacture requires a large amount of energy (3100 MJ/ton clinker) and produces large amounts of  $\text{CO}_2$  (Hendriks et al., 2004; Norchem, 2011). Some of the strategies that have been developed to solve these problems include the use of alternative fuels and supplementary cementitious materials (Bentz et al., 2011; Chen et al., 2010; Matschei et al., 2007; Mineral Products Association (MPA), 2012; OECD/IEA and the World Business Council for Sustainable Development, 2009). Recently, the synthesis of belite cement ( $\text{Ca}_2\text{SiO}_4$  or  $\text{C}_2\text{S}$ ) has received attention as a means of saving energy and raw materials. The theoretical of energy necessary to produce belite is about 1350 kJ/kg, whereas alite ( $\text{Ca}_3\text{SiO}_5$  or  $\text{C}_3\text{S}$ ) requires approximately 1810 kJ/kg (Kurdowski et al., 1997). However, a major disadvantage of belite cement is its low reactivity and very poor strength in the early ages of hydration due to its high thermodynamic stability and dense

structure which hinders its attack by water (Diamond and Lopez-Flores, 1981).

Numerous methods and raw materials have been proposed to produce highly reactive belite cement at low temperature. Hydrothermal methods have often been considered for preparing highly reactive belite cement from low-cost raw materials such as rice husk ash, aerosols and fly ash (Pimraksa et al., 2009; Singh, 2006; Singh et al., 2002). El-Didamony et al. (2012) reported the use of nano-materials such as nano-calcium and nano-silica, and compared these with conventional raw materials (calcium carbonate and quartz) to produce belite cement by a non-hydrothermal method. They showed that smaller particle size of the starting material reduced the calcination temperature compared with the conventional process.

Nano-silica is known to have high porosity and surface area, making it widely useful as fillers, pharmaceuticals, catalysts, chromatography, and fiber-cement composites (Bakaev and Pantano, 2009; Cabrillac and Malou, 2000; Ge et al., 2008; Morpurgo et al., 2010; Hamzeh et al., 2013). Traditionally, nano-silica is produced from sodium silicate, a product of reacting quartz sand and sodium carbonate at 1300 °C (Affandi et al., 2009). This process requires a large amount of energy. Thus, nano-silica produced from biomass waste such as rice husk ash has many

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economic and environmental advantages. Recent studies have shown that rice husk ash (RHA) can be used as a precursor for the preparation of nano-silica with a porous structure and a particle diameter of 5–60 nm (Liou, 2004; Liou and Yang, 2011). However, the RHA from which this nano-silica was prepared was calcined in the laboratory, and did not contain the impurities such as  $K_2O$ ,  $CaO$ ,  $MgO$ , etc. (Houston, 1972) that occur in industrial rice husk ashes (designated BRHA) which are black in color due to the presence of a high carbon content. Since these impurities might affect the purity and reactivity of the extracted nano-silica. Some researchers focus on the application of BRHA on cement and concrete technology (Chatveera and Lertwattanaruk, 2009, 2011, 2014). However, the aim of the present research is to compare the reactivity of nano-silica extracted from pure RHA prepared in the laboratory with black rice husk ash (BRHA) and investigate their suitability for producing belite cement by reaction with  $(Ca(NO_3)_2)$  and  $(CaCO_3)$ . The effect of the surface area and reactivity of the two calcium sources was also studied to provide important information for the improvement of belite cement synthesis from waste materials.

## 2. Experimental

### 2.1. Extraction of nano-silica from RHA and BRHA

Rice husk (RH) and black rice husk ash (BRHA) were obtained from the Thanakij Rice Mill, Thailand. Rice husk ash (RHA) was produced in the laboratory by calcining rice husks in air at 650 °C for 1 h. Commercially-produced black rice husk ash (BRHA) was pretreated with hot HCl and washed with distilled water. Both the RHA and pretreated BRHA were then used as precursors to extract nano-silica by the precipitation method as follows: the RHA precursors were added to 1.5 M NaOH solution in a solid/liquid ratio (S:L) of 1:6, with constant stirring and heating at 100 °C for 1 h. The resulting sodium silicate solution was then centrifuged to remove any solid residue and filtered several times to obtain a clear and colorless solution. This sodium silicate solution was adjusted to pH  $7 \pm 0.1$  by the addition of 1.0M HCL and the resulting aquagels were cured at 50 °C for 12 h, centrifuged with distilled water to remove salts and dried at 80 °C for 48 h. The dried solids were ground and screened to pass a 200 sieve mesh to obtain the nano-silica grains.

The compositions of the nano-silicas extracted from RHA and BRHA were investigated by X-ray fluorescence using a Philips model WDXRF PW2400 spectrometer. The crystalline phases of all the samples were characterized by X-ray diffraction using a Miniflex diffractometer with  $Cu K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at a voltage of 40 kV and 40 mA and a step size of  $0.02^\circ 2\theta$ , scanning rate of  $3^\circ/\text{min}$ , from  $10^\circ$  to  $90^\circ 2\theta$ . In view of the nanometric size of these silicas, they were investigated by transmission electron microscopy (TEM) using a JEM2100 microscope at an accelerating voltage of 80 kV. The samples were prepared by ultrasonically dispersing 0.2 g in ethanol, placing a drop of the suspension on a copper grid and coating with a carbon film. The surface area and porosity were measured by the BET method using a Quantachrome autosorb automated gas sorption analyzer, on 5 replicates of the  $N_2$  adsorption isotherms. The thermal decomposition kinetics of both nano-silicas were determined by thermogravimetric analysis (Pyris 1 TGA, Perkin Elmer, USA) at heating rates of 10, 15 and 20 °C/min under  $N_2$  and  $O_2$  atmospheres. At each heating rate, the samples were first heated to 110 °C, held at 110 °C for 10 min, then heated to 900 °C and held at this temperature for 10 min before cooling. The activation energy of the thermal decomposition was determined by the Ozawa method (Ozawa, 1965, 1970).

### 2.2. Preparation of belite cement

Belite cement was prepared from the nano-silicas extracted

**Table 1**  
Compositions of the belite cement mixes.

Sample	Mixtures (g)			
	Nano-silica		$Ca(NO_3)_2$	$CaCO_3$
	RHA	BRHA		
R1	16.3	–	83.7	–
R2	31.5	–	–	68.5
B1	–	16.3	83.7	–
B2	–	31.5	–	68.5

from RHA and BRHA (section 2.1) by reaction with laboratory grade  $Ca(NO_3)_2$  and  $CaCO_3$  at a Ca/Si ratio of 2:1, (Table 1). The dry ingredients were mechanically mixed for 5 min, placed in an alumina crucible and fired in air for 60 min at 800, 900, 1000 and 1100 °C. The resulting belite cements were analyzed by XRD for crystalline belite using a step size  $0.02^\circ$ , scan rate of  $3^\circ$  per min and scan range of  $10^\circ$ – $60^\circ 2\theta$ . Free lime was determined by the chemical method as follow ASTM C114-07 (American Society for testing and Materials, 2007).

## 3. Results and discussion

### 3.1. Characteristics of nano-silica extracted from RHA and BRHA

#### 3.1.1. Physical and chemical properties

Table 2 presents the chemical compositions of raw rice husk ashes RHA and BRHA and the nano-silicas extracted them.  $SiO_2$  is the major component of both nano-silicas, but the LOI of raw BRHA is relatively high compared with RHA, which was determined as followed ASTM C311 (American Society for testing and Materials, 2012), due to the presence of carbon impurities resulting from incomplete firing; these impurities are removed by the nano-silica extraction process which also removes  $K_2O$  and  $CaO$  and carbon (Table 2) (Kamath and Proctor, 1998; Liou and Yang, 2011). This result is consistent with Monshizadeh et al. (2011), who reported that the LOI is removed by extraction with NaOH.

The XRD patterns (Fig. S1) show that the  $SiO_2$  ( $2\theta \approx 22^\circ$ ) in raw RHA is amorphous, whereas in raw BRHA it occurs as cristobalite (JCPDS file number 82-1403) resulting from burning the rice husk at high temperature (900–1000 °C). However, this crystalline silica becomes amorphous after alkaline extraction.

The crystalline size of the nano-silicas extracted from both siliceous materials, determined by TEM analysis, were 20–50 nm

**Table 2**  
Chemical composition of nano-silica extracted from RHA and BRHA.

Compound	% weight			
	RHA		BRHA	
	Raw	Nano-silica	Raw	Nano-silica
$SiO_2$	92.80	97.10	93.70	98.90
$Na_2O$	0.08	2.26	0.03	0.63
$K_2O$	3.35	0.21	2.55	0.13
$Al_2O_3$	0.15	0.06	0.40	0.15
$CaO$	0.70	0.08	0.92	0.06
$Fe_2O_3$	0.17	0.02	0.28	0.02
Cl	–	0.19	–	0.01
TiO	–	–	0.02	–
$SO_3$	–	–	0.40	–
MgO	0.79	–	–	–
$P_2O_5$	1.07	–	–	–
LOI*	2.44	–	4.40	–

LOI\*: Loss on ignition, which was determined as followed ASTM C311 (American Society for testing and Materials, 2012).

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