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Evaluation of cement retarding performance of cellulosic sugar acids

Weiliang Hou, Jie Bao *

State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

HIGHLIGHTS

- Cellulosic sugar acids as cement retarder additive were detailedly evaluated.
- Excellent retarding setting of cellulosic sugar acids was demonstrated.
- Addition of cellulosic product did not impact cement strength and soundness.
- Cellulosic product was competitive as cement retarder with starch-based product.

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ABSTRACT

Cellulosic sugar acids from lignocellulose biomass are composed of gluconic acid, xylonic acid, arabonic acid, galactonic acid and mannonic acid. The major application of cellulosic sugar acids is cement retarder additive. This study experimentally investigated the performance of cellulosic sugar acids on cement hydration and compared with the commercial sugar acid from crop starch feedstock. The excellent retarding efficiency of cellulosic sugar acids was demonstrated while cement strength and soundness maintained similar to that of starch based sugar acid product. X-ray diffractograms, thermograms, and microstructure analyses showed that the hydration of cement reactions and the formation of cement products were significantly delayed by the addition of cellulosic sugar acids. This study indicates that cellulosic product from low-cost agriculture residue is a promising alternative of commercial product from crop starch feedstock as cement additive.

1. Introduction

Lignocellulose biomass is composed of cellulose, hemicellulose, and lignin [1,2]. Hydrolysis of cellulose and hemicellulose releases various monosaccharides such as glucose, xylose, arabinose, galactose, and mannose. Utilization of these sugars from lignocellulose biomass could convert to the corresponding sugar acids including: gluconic acid, xylonic acid, arabonic acid, galactonic acid and mannonic acid [3–6]. Ikeda et al. [7] firstly reported cellulosic gluconic acid production using waste office paper as feedstock. Zhou et al. [8] produced xylonic acid using hemicellulose hydrolysates from corn stover. Yao et al. [9] completely converted all pentose and hexose sugars (glucose, xylose, arabinose, galactose, and mannose) into the corresponding sugar acids in corn stover enzymatic hydrolysate. The techno-economic analysis showed that the minimum cellulosic sugar acids selling price was competitive with that of commercial gluconic acid from starch feedstock [10].

This study experimentally evaluated the performance of cellulosic sugar acids as cement additive. The impact of cellulosic sugar acids on setting time, fluidity, strength and soundness of cement paste was analyzed and excellent performance of cellulosic sugar acids was demonstrated comparing to starch-based sugar acid. X-ray diffractograms, thermograms, and microstructure indicated that cellulosic sugar acids significantly delayed the hydration of cement reactions (such as alite and belite) and the formation of cement hydration products (such as $Ca(OH)_2$). This study indicates that cellulosic product from low-cost agriculture residue could significantly prolong cement setting time while cement ruggedness, durability and stability were well maintained. This product provided a promising alternative of commercial product from crop starch feedstock as cement additive.

2. Material and methods

2.1. Materials

Cellulosic sugar acids were prepared by a dry acid pretreatment and biodetoxification approach according to Hou et al. [11] and Liu

* Corresponding author.
E-mail address: jbao@ecust.edu.cn (J. Bao).

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et al. [12]. Briefly, corn stover was dry acid pretreated at 2.0% (w/w) of sulfuric acid ratio at 175 °C for 5 min for conversion of hemicellulose to xylose, then biodetoxified to remove inhibitors generated by pretreatment [13–15]. The pretreated and detoxificated corn stover was hydrolyzed by cellulase for conversion of cellulose to glucose and then fermented by *Gluconobacter oxydans* DSM 2003 for complete conversion of sugars to the corresponding sugar acids [16]. Cellulosic product was obtained simply by solid-liquid separation and decoloration of fermentation slurry.

Portland cement was purchased from Shandong cement Co., Shandong, China. Polycarboxylate QS8020 was from Qishuo Industry Co., Shanghai, China. Commercial gluconic acid was from Shangdong Xiwang Group, Shandong, China. Cellulosic mixed sugar acids (mainly containing gluconic acid and xylonic acid) as cement retarder was added into cement at the same percentage ratio with commercial gluconic acid.

2.2. Setting time

The consistency of cement paste was measured by Vicat apparatus (Luda Construction Co., Shanghai, China) and adjusted by water addition into standard range. The setting time of cement paste was also determined by Vicat apparatus according to Chinese Standard Protocol GB/T 1346-2011. Briefly, 500 g of cement was mixed by required amount of water into cement paste mixer (NJ-160, Wuxi Construction Co., Jiangsu, China). The cement paste was mixed by the rotation at 140 rpm for 120 s, then stopped for 15 s; again mixed at the rotation at 285 rpm for 120 s.

2.3. Fluidity

The fluidity of cement paste was determined according to the Chinese Standard Protocol GB/T 2419-2005. Briefly, 300 g of cement was mixed with 87 mL of water and 0.18 g polycarboxylate as water reducer into cement paste mixer and mixed by the rotation at 140 rpm for 180 s. Cement paste was fully filled into a standard copper conical cylinder (60 mm in height, 50 mm in top circle diameter and 75 mm in bottom circle diameter), then the cylinder was lifted up promptly to let cement paste flowing on a glass plate for 30 s. The circle diameter of cement paste slurry on the glass plate was measured as the indicator of the fluidity of cement paste.

2.4. Strength analysis

The flexural and compressive strength of cement mortars were measured according to Chinese Standards Protocol GB/T17671-1999. Briefly, the cement mortar was prepared using standard sand with the weight ratio of cement, sand and water at 2:6:1 for obtaining standard specimens (40 × 40 × 160 mm). The flexural strength was conducted on the long surface of cement mortar specimen using a cement bending tester (300KN, Jinan Kaine Testing Mechanics Co., Shandong, China) and three specimens were tested for each sample. The compressive strength was conducted on cement pressure tester (DKZ-5000, Jinan Kaine Testing Mechanics Co., Shandong, China) and six specimens were tested for one sample.

2.5. Soundness

The soundness of cement paste was determined by Le-chatelier apparatus according to Chinese Standard Protocol GB/T 1346-2011. Briefly, the Le-chatelier (30 mm in height, 10 mm in circle diameter) was fully filled by the prepared standard consistency cement paste, sealed by two pieces of lightly oiled glass sheet, and stored in a curing box with temperature of 20 °C and humidity of 95% for 1 day. Then the whole assembly was submerged in water bath with room temperature, and boiled within 30 min then kept boiling for 3 h. After cooled down to room temperature, the expansion distance of Le-chatelier was measured as the indicator of the soundness of cement paste.

2.6. Scanning electron microscopy

Microstructure of cement paste was analyzed after 24 h hydration. Briefly, cement and aqueous solution with cellulosic or commercial product (water to cement ratio 0.5) were co-fed into cement paste mixer and mixed for 2 min by rotation at 285 rpm. The fresh paste was poured into plastic bottles and sealed, then stored in a curing box at 20 °C and 95% of humidity for 24 h. Then cement paste was fractured as small pieces, submerged in alcohol for 7 day and dried in an oven. The microstructure of dried cement paste pieces was observed by scanning electron microscopy (JSM-6360 LV, JEOL, Tokyo, Japan).

2.7. X-ray diffraction and TG/DSC

Some pieces of cement pastes were ground and stored for phase identification and thermal analysis. The phase identification was analyzed by using X-ray diffractograms (XRD) with a CuKα radition D/Max 2550 V (Rigaku, Tokyo, Japan). Each sample was scanned from 10° to 70° with a step in $2\theta = 0.02°$ at 40 kV (100 mA).

The thermal analysis was performed on a TGA/DSC1 1600HT (Mettler-Toledo International Inc, Zurich, Switzerland) equipment with simultaneous thermogravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) system. Each sample was carried out at a heating rate of 10 °C/min from 25 °C to 1000 °C under N_2 atmosphere.

3. Results and discussion

3.1. Assay of setting time and fluidity

Cellulosic sugar acids mainly contained 112 g/L of gluconic acid and 57 g/L of xylonic acid were prepared by a dry acid pretreatment and biodetoxification biorefinery approach [11,12]. Cement additive assay of cellulosic sugar acids product was firstly conducted by testing essential retarding setting (such as setting time and fluidity) and compared with commercial sugar acid (gluconic acid) as control. The addition was based on the weight ratio of sugar acids to cement.

Setting time is an important index to evaluate retarding setting of cellulosic product as retarder additive. The initial setting time of cement paste increased from 185 min, 207 min to 236 min with the addition dosage of cellulosic sugar acids from 0.01%, 0.02% to 0.03%, leading to 14%, 28% and 46% increase than that of cement paste control without sugar acid addition, respectively (Fig. 1a). The final setting time improved by 7%, 18% and 29% at the increased addition dosages than that of cement paste control, respectively (Fig. 1b). Furthermore, setting time (initial or final) with cellulosic sugar acids addition was consistent with commercial sugar acid control at the same dosage.

The fluidity indicates the uniformity of cement paste. The addition of cellulosic sugar acids product slightly increased the fluidity comparing with commercial control at high addition (Fig. 2). The fluidity was 274 mm after the addition of cellulosic sugar acids at the dosage of 0.03% (w/w), while it was only 247 mm by adding commercial control and 214 mm without sugar acid addition, indicating that cellulosic sugar acids product increased the cement workability by providing better fluidity.

These results elucidated that cellulosic sugar acids could efficiently prolong cement setting time and improve cement fluidity,

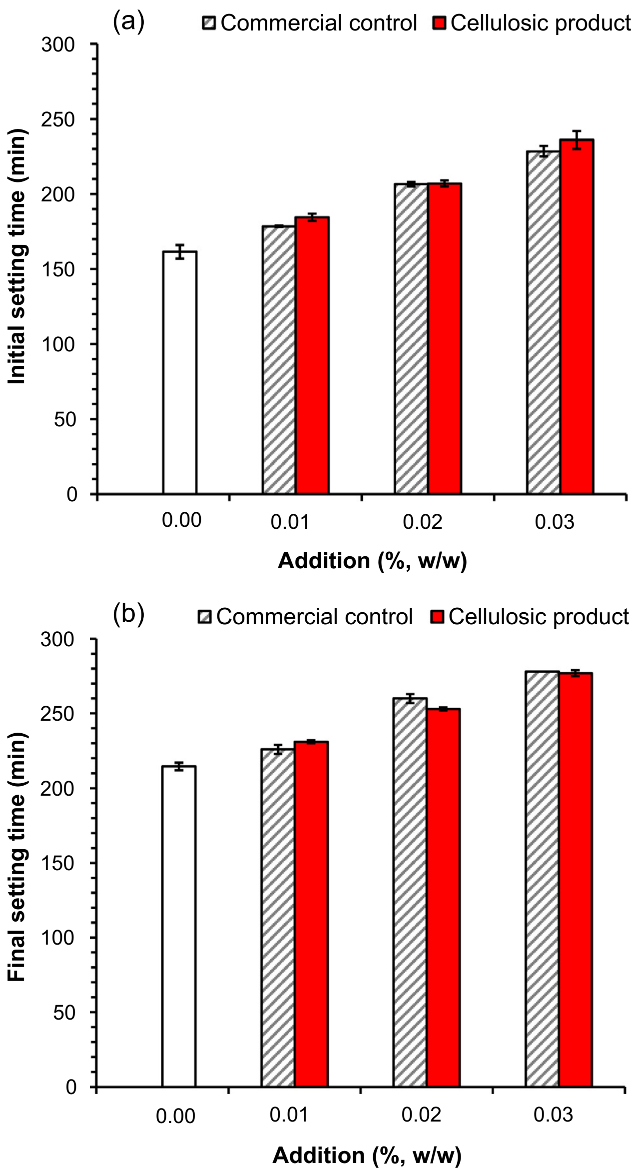

Fig. 1. Setting time of cement paste with cellulosic product as cement retarder additive. (a) Initial setting time; (b) Final setting time.

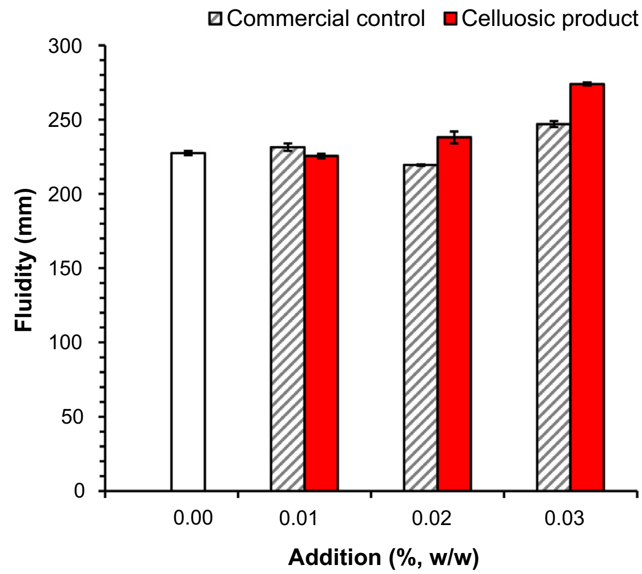

Fig. 2. Fluidity of cement with cellulosic product as cement retarder additive.

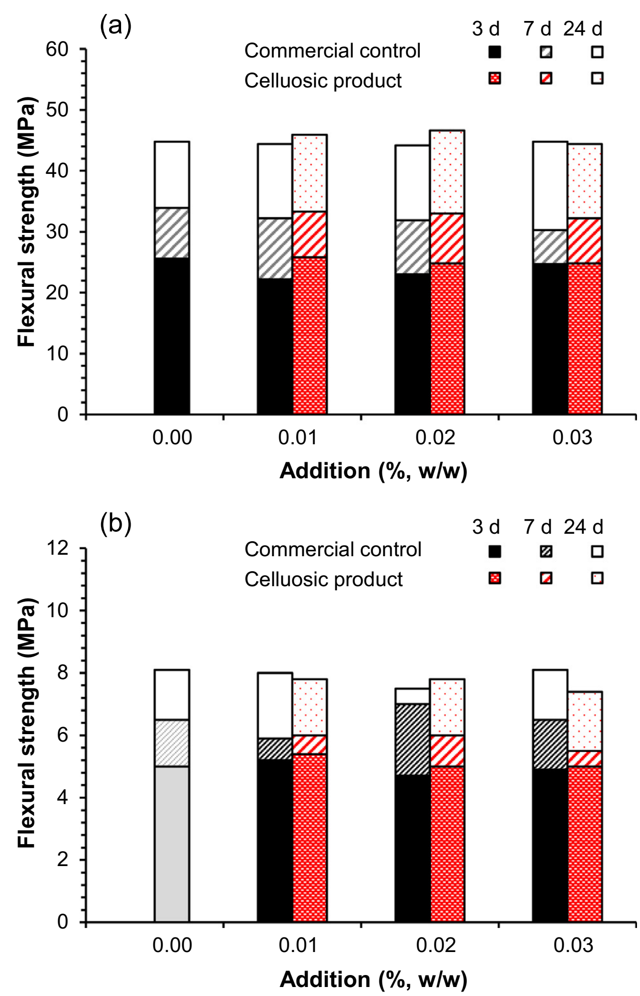

Fig. 3. Compressive strength (a) and flexural strength (b) of cement paste with cellulosic product as cement retarder additive.

indicating that fresh concrete could maintain plasticity for longer time to facilitate pouring and construction.

3.2. Assay of strength and soundness

Cement strength and soundness were evaluated when cellulosic sugar acids product was added. The addition of cellulosic sugar acids product after hydration for 3–28 days showed the similar compressive strength and flexural strength with that of cement paste control without sugar acid addition, as well as commercial sugar acid control (Fig. 3), indicating the addition of cellulosic sugar acids did not deliver negative impact on ruggedness and durability of infrastructures such as buildings and bridges.

Soundness is the ability to resist volume expansion of cement paste. The addition of cellulosic sugar acids product showed slightly better effect comparing to commercial control at the same dosage by reducing the expansion distance (Fig. 4). The expansion of cement mortar was significantly below to the threshold value of 5 mm according to Chinese Standard Protocol GB/T 1346-2011,

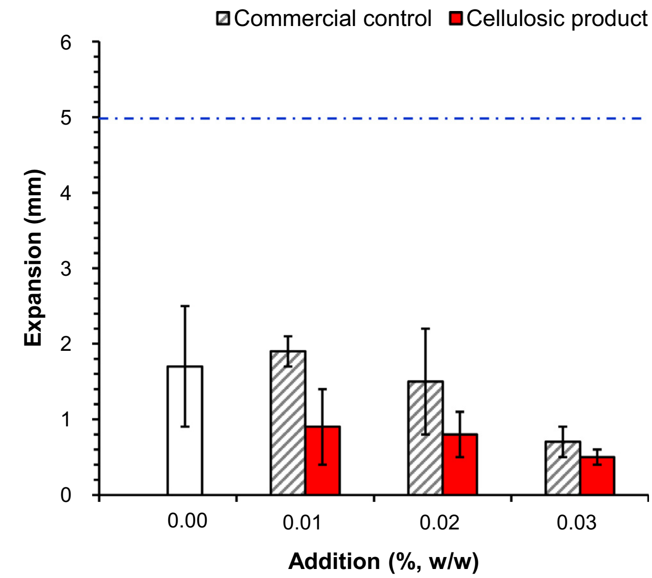

Fig. 4. Soundness of cement paste with cellulosic product as cement retarder additive.

indicating that the addition of cellulosic sugar acids behaved the sufficient reliability and stability of infrastructures built by concrete structure.

3.3. Assay of X-ray diffractograms and thermograms

The cement formation involves hydration reactions of alite (C_3S) and belite (C_2S) with water to form $Ca(OH)_2$, as well as the hydration of aluminite (C_3A) [17,18]. The hydration reaction of cement paste was evaluated by X-ray diffractograms (Fig. 5) for hydrated cement composition and thermogravimetric analysis (TG) for degree of cement hydration (Fig. 6). When 0.03% (w/w) of cellulosic sugar acids was added into cement, the retardation of alite hydration was slightly prolonged than that of commercial control (Fig. 5a) and the retardation of aluminite hydration was similar to that of commercial control (Fig. 5b). The formation of hydration product $Ca(OH)_2$ added by cellulosic product was significantly delayed at the same dosage, indicating the better retardation than that of commercial control (Fig. 5c).

Thermogravimetric analysis was used to determine the amount of water into the hydrated products of cement [19–21]. The mass loss by dehydroxylation of $Ca(OH)_2$ emerged at 400 to 500 °C, while free water and chemically combined water lost at room temperature to 400 °C (Fig. 6). At the dehydroxylation temperature section of 400–500 °C, the mass loss of cement with cellulosic sugar acids addition was respectively 9.1% and 25.8% smaller than that of the addition of commercial control and blank cement, demonstrating the less amount of $Ca(OH)_2$ in cement added by cellulosic sugar acids. Heat flow during mass loss was monitored by Differential Scanning Calorimetry (DSC). The endothermic peak caused by dehydroxylation of $Ca(OH)_2$ showed that 19.8% of heat loss was reduced by cellulosic sugar acids addition than that of blank cement and 2.1% reduction to commercial control.

3.4. Microstructure assay

Ettringite forms from the hydration of aluminite (C_3A) in early hydration stage [22] and could be directly observed from cement microstructure by scanning electron microscope (SEM) micrographs [23]. In blank cement without sugar acids added, aluminite

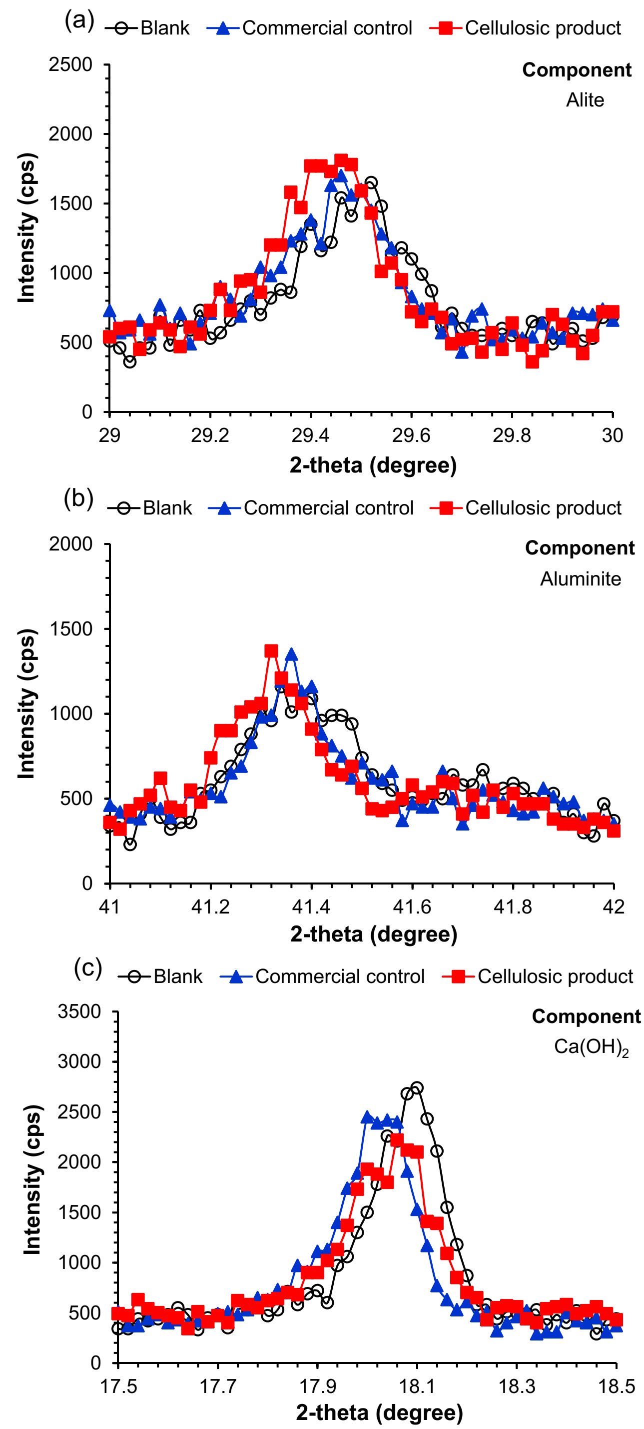

Fig. 5. X-ray diffractograms of cement paste with cellulosic product as cement retarder additive. (a) X-ray diffractograms of alite; (b) X-ray diffractograms of aluminite; (c) X-ray diffractograms of $Ca(OH)_2$.

was quickly hydrated to ettringite with the formation of fine needlelike crystals in the initial hydration (8 h) (Fig. 7 and Fig. S1). With the crystals grow (24 h), a densely packed structure was formed and only few free crystals could be observed. When cellulosic sugar acids product were added into cement as retarder additive, more needlelike crystals were observed than that of blank cement and commercial control during the hydration (24 h). The result indicates that cellulosic sugar acids not only inhibited hydration rate of cement reactants (such as alite, belite and aluminite),

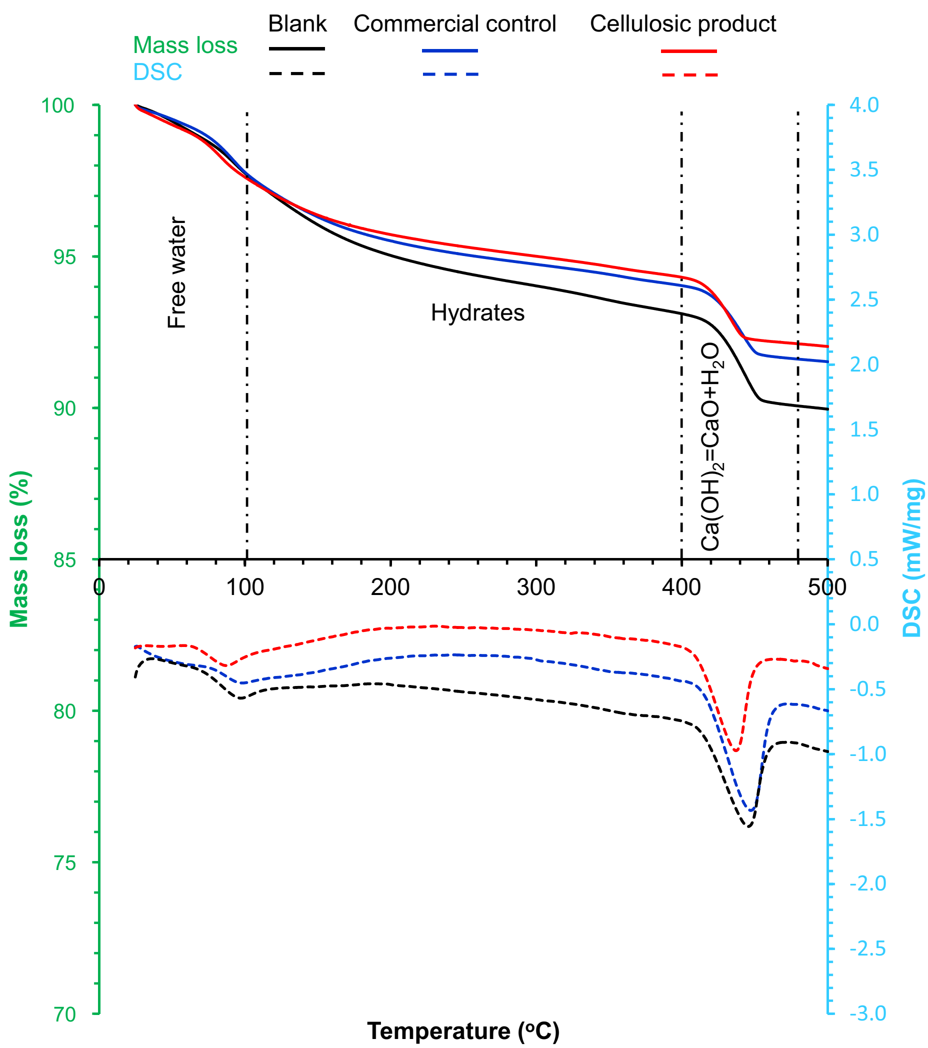

Fig. 6. Thermogravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) analysis of cement paste with cellulosic product as cement retarder additive.

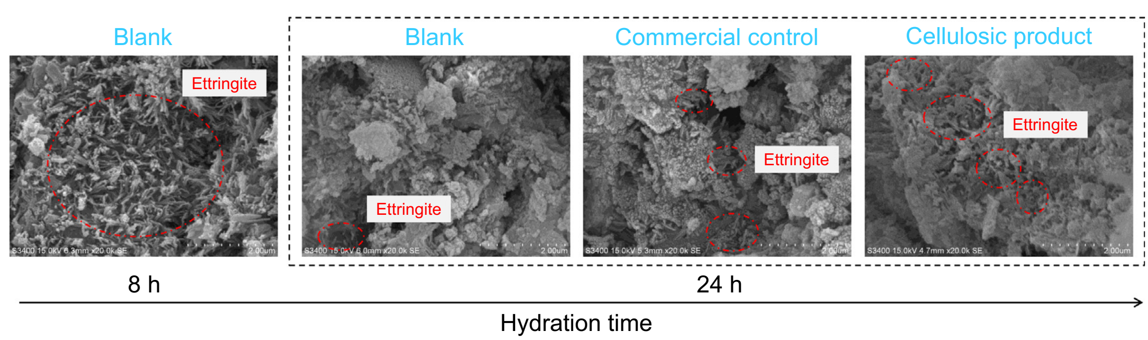

Fig. 7. Scanning electron microscope micrographs (SEM) of cement paste with cellulosic product as cement retarder additive.

but also reduced the further conversion of hydration intermediate product (such as ettringite).

4. Conclusion

The study analyzed retarding setting of cellulosic sugar acids as cement additive and compared with commercial gluconic acid. The results indicate that cellulosic sugar acids efficiently delayed cement setting time, hydration of cement reactions (such as alite and belite), and the formation of cement hydration products (such as $Ca(OH)_2$). The study provides an important basis for the industrialized application of cellulosic sugar acids product as cement retarder additives.

Conflict of interest

None.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.conbuildmat.2019.01.025.

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