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The hydration and microstructure characteristics of cement pastes with high volume organic-contaminated waste glass powder

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HIGHLIGHTS

- Filter glass contains saccharides and high dosages of Na^+ and Cl^-.
- The addition of filter glass can significantly retard the hydration process of cement.
- $CaCl_2$, nanosilica or microsilica or a washing treatment can reduce retardation.
- The organic contamination contributes to the lower calcium hydroxide consumption.
- A high gel porosity was observed in filter glass paste samples.

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ABSTRACT

This study investigates the influence of the organic-contaminated waste glass powder-filter glass on cement hydration and the microstructure characteristics of the hydration products. In order to study the influences of organic contamination, treated (washed) glass powder was used as reference addition. The incorporation of filter glass powder results in longer induction periods and lower reaction intensity compared to the samples with washed glass. The addition of chemical accelerators such as $CaCl_2$, nanosilica and microsilica can significantly improve the hydration of samples containing high volumes of filter glass powder. The organic contamination shows a negligible effect in terms of hydration products identified by XRD analysis. In mixtures with high volume filter glass powder (70%), the formation of calcium hydroxide was delayed at 3 and 7 days. Samples containing more than 50% waste glass present a higher pore volume in pore sizes lower than 15 nm and lower pore volume between 20 and 50 nm. It was observed from the SEM analysis that the organic contamination may slow the pozzolanic reaction of glass particles in mixes with 70% filter glass.

1. Introduction

In recent years, the recycling ratio of waste glass has increased in many countries due to the concerns towards the protection of natural resources; for instance an increasing amount of the waste glass are collected from urban wastes and reused to produce containers like bottles and jars. However, some recycled glass fractions cannot be used in the manufacturing of new glass products, either because they are contaminated, or because some recycled glass pieces are too small to meet the manufacturing specifications. Such recovered glass is then used for producing non-container glass products. One ideal application for these glass fractions is to be used as concrete ingredients such as aggregates and supplementary cementitious material, because the amorphous glass has the potential to exhibit pozzolanic reactivity [1,2].

As a municipal waste with pozzolanic reactivity, waste glass has been widely applied as supplementary cementitious material and aggregate replacement in concrete [3–6]. Using waste glass as aggregates in concrete could improve the workability because of the smooth surface [7,8]. Some researchers also developed waste glass aggregates based self-compacting concrete [9]. As a material with a high content of amorphous silica and sodium, alkali silica reaction (ASR) is a serious challenge for using large size glass cullet in concrete [10]. However, the ASR could be inhibited after the addition of fine pozzolanic materials such as slag and metakolin [11], and even fine glass powder can be used to suppress the expansion [12–15]. When the waste glass is ground fine enough, there is no significant ASR exhibition [16]. Therefore, many studies investigated using fine waste glass powder to partly replace cement as supplementary cementitious materials. Glass fractions

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can exhibit higher pozzolanic activity than fly ash when the particles are fine enough [6,17]. A mortar sample containing 25% soda lime glass powder and 75% cement as binder was reported to reach approx. 60 MPa in compressive strength after 90 days, which was almost equal to the 100% cement samples [18,19]. Nathan investigated the durability of concrete containing low dosages of fine glass powder; the results showed that the glass powder addition can improve the compressive strength, reduce the ASR expansion and enhance the resistance to rapid chloride penetration [20]. The enhancement of durability also was observed through tests such as water absorption, and the resistance to chloride and to freeze-thaw cycles [21]. In most studies, the addition of glass powder as cement replacement is limited to below 30% [21,22], since a higher content may induce the reduction of mechanical performance. Moreover, applications of high volume waste glass powder with replacements up to 60% were also developed: high volume glass powder containing concrete exhibited compressive strength over the plain sample and better resistance for chloride penetration after 1 year of curing [23].

Recent studies about influences of contamination in waste glass usually focused on heavy metal contaminated waste glass, such as glass from cathode ray tubes (CRT), where cement could be used to immobilize the heavy metal in CRT glass [24,25]. However, the waste glass fractions contaminated by organics (sugar, fiber) received less attention. This kind of waste glass usually combines with very fine particles and is mixed with organic matters, making it difficult to clean and recycle for re-producing new glass products. For the sustainable use of this kind of organic containing glass fractions, it is desirable to use such filter glass as building material. However, the organic contamination will influence the application of the waste glass fractions in concrete. The waste glass in this study is a filter glass powder, which is filtered out of the furnace while drying the glass fraction during the manufacturing of glass products. It has a very fine particle size and contains considerable amounts of organic matters such as fibres and saccharides from labels and glue. Organic matter such as wood fibres and recycled waste paper fibre could be used to improve the performance of cement composites [26,27], but as an organic addition, fibres act as an inhibitor and show a negative effect on the cement hydration, because of the sugars, starches and tannins [28]. Saccharides are mainly responsible for the inhibition of cement hydration in fibre-cement composites [29]. Different organic compounds show different influences on retardation of cement hydration [30]. Saccharides could be absorbed on the surfaces of cement particles and hydration products, which inhibits the hydration process and hydration products growth [31,32]. The zeta potential of hydrating cement particles is positive and changed to negative after the incorporation of saccharides, which could explain the absorption of sugar on the cement particle surface [33].

The present study aims to perform a comprehensive evaluation and to have a better understanding of the influencing of filter glass as supplementary cementitious material on cement hydration, products and microstructure, providing some theoretical basis for its application.

2. Materials and methods

2.1. Materials

The cement applied in this study is CEM I 42.5N supplied by ENCI, Netherlands. The used glass powder is a filter glass which was filtered out in a glass drying furnace, provided by a glass recycling plant. The microsilica in this study was provided by Elkem, nanosilica was provided by AkzoNobel with a concentration of 50% and the calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) was provided by VWR international. The filter glass powder after washing was used as references, they were washed by distilled water with the L/S 2 and 250 rpm for 24 h. Then these two glass powders were milled, sieved and utilized as supplementary cementitious materials in present study. The specific surface area of milled filter glass powder is 0.65 m^2/g.

2.2. Methods

Different pastes were prepared with the water/binder ratio of 0.3, where cement was replaced by the filter glass or washed filter glass with 0%, 30%, 50% and 70% by mass. The mix designs are shown in Table 1.

The particle size distribution of materials were determined by laser particle size analyzer, Mastersizer 2000. The specific density of materials were conducted by the gas pycnometer micrometrics, AccuPyc II 1340.

The sugar content of filter glass and ion concentration of filter glass and washed filter glass were conducted by the high-performance anion exchange chromatography (HPAEC) and ion chromatography (IC).

The calorimetry test was performed using an isothermal calorimeter (TAM Air, Thermometric). Cement was replaced by filter glass powder or washed filter glass with 0% to 70% by mass. Solid raw materials were firstly mixed with distilled water, then the mixed paste was injected into the ampoule and sealed by a lid and loaded into the calorimeter. All measurements were conducted for 160 h under a constant temperature of 20 °C. The duration of the calorimetry test for samples containing 70% waste glass was increased to 378 h because the induction period was relatively long. To study the influences of different chemical addition and treatment methods on the hydration of sample containing high volume of filter glass, additional samples for calorimeter were prepared as shown in Table 2.

The X-ray diffraction test was conducted by Bruker D2 PHASER with a Co tube to study the hydration products of the paste samples. All samples were cured in ambient temperature and tested after 3, 7 and 28 days. After curing, all samples were crushed and immersed in acetone to cease further hydration. At last, all samples were milled into powder (<300 μm) for the XRD test.

The thermal-gravimetric (TG) analysis was conducted in a STA 449 F1 instrument, as follows: ground powder containing samples after 28 days and 90 days of ambient curing were heated up to 1000 °C from 40 °C at the rate of 10 °C/min with nitrogen as the carrier gas.

Nitrogen sorption analysis was performed using a Brunauer-Emmett-Teller (BET)specific surface area and porosity instrument (TriStar II 3020, Micrometrics). Samples were milled (<400 μm) and dried at 105 °C in an oven until the mass was constant. The surface area was calculated by the Brunauer-Emmett-Teller method [34] using the adsorption branch. The pore size distribution was determined by the Barrett–Joyner–Hallenda method [35] from the adsorption branch.

The microstructure of samples were observed by Scanning Electron Microscope with EDX detector (Phenom Pro). The EDX analyses were conducted at 10 kV accelerating voltage. Crushed samples were immersed in acetone and then dried in the oven at 40 °C to cease further hydration. After that, samples were used for SEM observation.

3. Results and discussion

3.1. Materials characterization

The chemical composition of raw materials are presented in the Table 3. It can be seen that the filter glass mainly contains sodium

Table 1
Mix proportions (wt%).

Sample label	Filter glass powder (%)	Washed filter glass powder (%)	Cement (%)	Water/ binder ratio
C0	0	0	100	0.3
C3	30	0	70	0.3
C5	50	0	50	0.3
C7	70	0	30	0.3
CW3	0	30	70	0.3
CW5	0	50	50	0.3
CW7	0	70	30	0.3

CF 100% cement + filtrate (L/S 2) filtrate/cement 0.3.

Table 2
Chemical addition and treatment methods for high volume filter glass powder containing sample.

Sample ID	Treatment Methods
B7	30% cement + 70% heat treated filter glass powder (550 °C for 4 h)
DW7	30% cement + 70% second washing filter glass powder (L/S 2-L/S 10)
5% $CaCl_2$ dihydrate	C7 + 5% $CaCl_2$ dihydrate (by mass of binder)
5% nano silica	C7 + 5% nanosilica (by mass of binder)
5% micro silica	C7 + 5% microsilica (by mass of binder)

Table 3
Chemical composition of raw materials.

Chemical composition	Filter glass (%)	Washed filter glass (%)	CEM I 42.5N (%)
Na_2O	11.382	11.47	/
MgO	1.424	1.389	1.553
Al_2O_3	2.749	2.577	3.443
SiO_2	66.971	68.294	14.382
SO_3	0.249	0.133	4.424
K_2O	0.844	0.799	0.449
CaO	14.247	13.613	69.243
TiO_2	0.195	0.144	0.382
Cr_2O_3	0.15	0.147	0.015
MnO	0.032	0.028	0.097
Fe_2O_3	0.955	0.788	3.857
ZnO	0.058	0.043	0.107
BaO	0.069	0.065	0.016
PbO	0.042	0.036	0.008
P_2O_5	/	/	0.306
Cl	0.207	0.061	0.073

Table 4
Sugar and ion content of filter glass powder.

Filter glass			Filter glass	Washed filter glass
Sugar	mg/kg	Ion	mg/kg	mg/kg
Arabinose	12	Na^+	1549	766
Galactose	67.8	K^+	84	50
Glucose	91.8	Ca^{2+}	109	32
Xylose	14.8	Mg^{2+}	11	3
Mannose	67.7	NH_4^+	48	36
Galacturonic acid	31.3	Cl^-	540	191
Glucuronic acid	37	PO_4^{3-}	107	38
		SO_4^{2-}	235	72
		Organic Mass[a]	4.5%	2.0%
		pH	9.807	9.704
		LOI1000°C[b]	2.5%	1.5%

[a] 550 °C in oven with air for 4 h.

[b] by TG in N_2 protective atmosphere.

oxide, calcium oxide and silica with proportion of 11.4%, 14.2% and 67.0%, respectively, while a small quantity of MgO, Al_2O_3, K_2O and Fe_2O_3 can be observed. To wash out the contamination in filter glass, the washing treatment of 24 h with L/S 2, 250 rpm was conducted. As can be seen that the filter glass contains 4.5% organic matter from the ignition loss at 550 °C, after the washing treatment, only 2.0% of organic is retained in the washed filter glass powder. Comparing the chemical composition of washed filter glass with untreated sample, a slight reduction of MgO, Al_2O_3, SO_3, CaO and Cl can be found. From the particle size distribution results shown in Fig. 1, washing treatment results in the slight decrease of volume around 40 μm, the d_{50} particle size of filter glass powder, washed filter glass powder and cement is 33.2, 31.4 and 22.1 μm, respectively. The specific density of cement, waste glass powder and washed glass powder are 3091 kg/m^3, 2421 kg/m^3 and 2429 kg/m^3, respectively.

The results of leaching test are presented in Table 4. Apparently, many kinds of saccharides are presented in the filter glass, such as galactose, glucose and mannose with leaching of 67.8 mg/kg, 91.8 mg/kg and 67.7 mg/kg, respectively. Additionally, high content of soluble salt also can be found, it can be observed that filter glass contains a relatively high leaching of Na^+ and Cl^- with a dosage of 1549 mg/kg and 540 mg/kg, respectively. After washing treatment, the residual Na^+ and Cl^- are 766 mg/kg and 191 mg/kg.

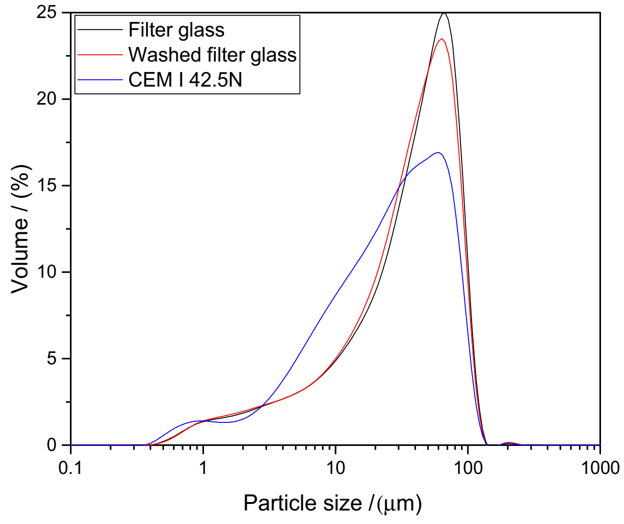


Fig. 1. Particle size distribution of material.

Fig. 2 exhibits the morphology of filter glass particles and cement particles. The glass particles show smoother surface and sharp edges compared with the cement particles.

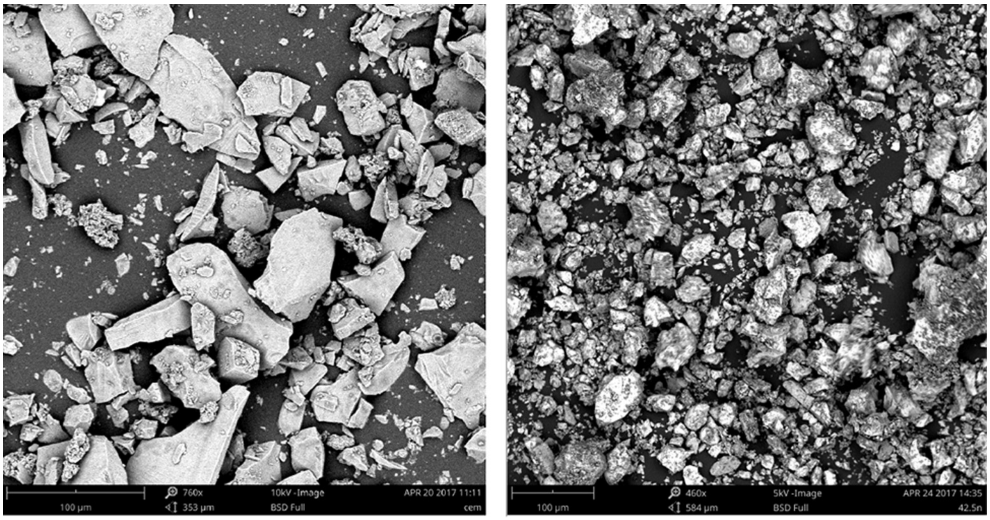
3.2. Early age hydration

The results of isothermal calorimetry test of pastes containing different amount of filter glass powder (C3, C5 and C7) and washed filter glass (CW3, CW5 and CW7) are shown in Figs. 3 and 4. It is apparent that all samples have the same general shape of heat flow curve as cement which contains five stages including initial reaction stage, induction stage, acceleration stage, reduction stage and long term reaction stage [36].

As shown in Fig. 3(a), samples containing filter glass powder show longer induction periods than the reference sample (C0), and the intensity of heat flow was also reduced. It can be seen that the sample mixed with filtrate shows a weak delay effect on hydration. The addition of filter glass powder results in obviously reduced heat flow and prolonged hydration. Especially for the sample containing 70% filter glass powder (C7), it shows no obvious reaction after 160 h of hydration. The increasing of the filter glass content obviously increases the time to achieve the peak of heat flow and reduces the intensity of hydration heat generation. Therefore, the cumulative heat was also decreased, which can be observed in Fig. 3(b). Because no heat release was observed in the sample containing 70% filter glass powder, the cumulative heat of C7 shows almost no increase after 160 h hydration.

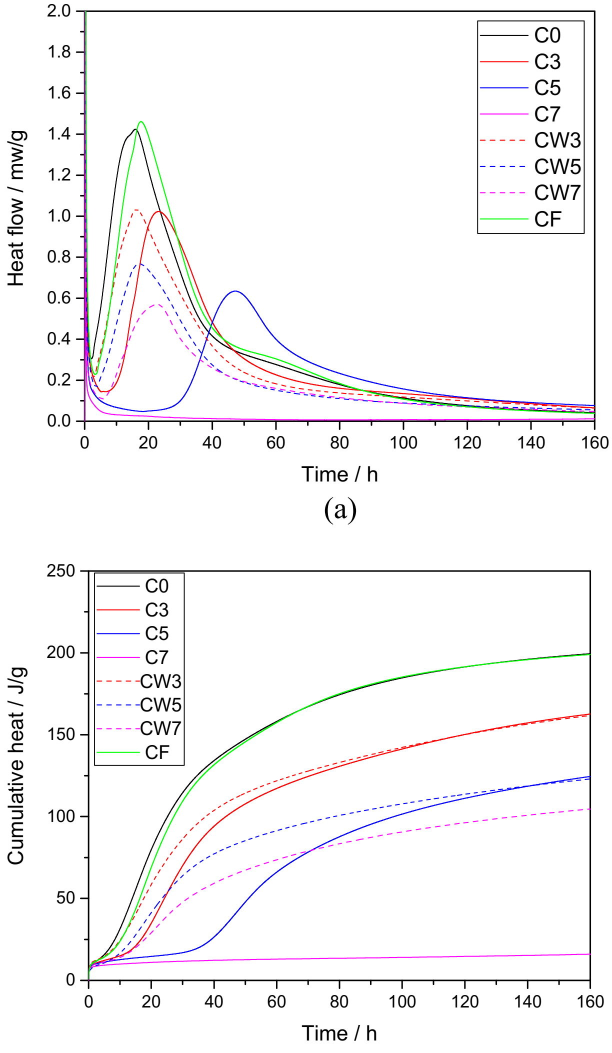
As shown in Fig. 3(a), samples containing washed filter glass show a lower intensity of heat flow than the reference sample. No significant delay in terms of the heat flow peak location is observed. The sample incorporating 70% washed filter glass powder shows the reaction peak around 20 h, which is slightly delayed compared to the reference. With the increasing of washed filter glass amount in the mixture, the intensity of reaction and the cumulative heat decreases continuously. It is noticeable that the cumulative heat of sample containing 30% filter glass (C3) presents at the same level as the washed contained sample (CW3) after 160 h hydration, which also are presented by C5 and CW5, which indicates that the organic contamination in filter glass just increasing the induction period during the hydration but shows no effect on the cumulative heat of hydration.

In order to better understand the hydration process of mixtures with 70% filter glass powder, the testing duration was increased to 378 h and the results are shown in Fig. 4. It is noticeable that the reaction starts from 170 h and the peak of the acceleration stage is at 275 h, so the hydration is delayed by almost 250 h compared



(a) (b)

Fig. 2. SEM picture of waste glass particle (a) and cement particle (b).



(a)

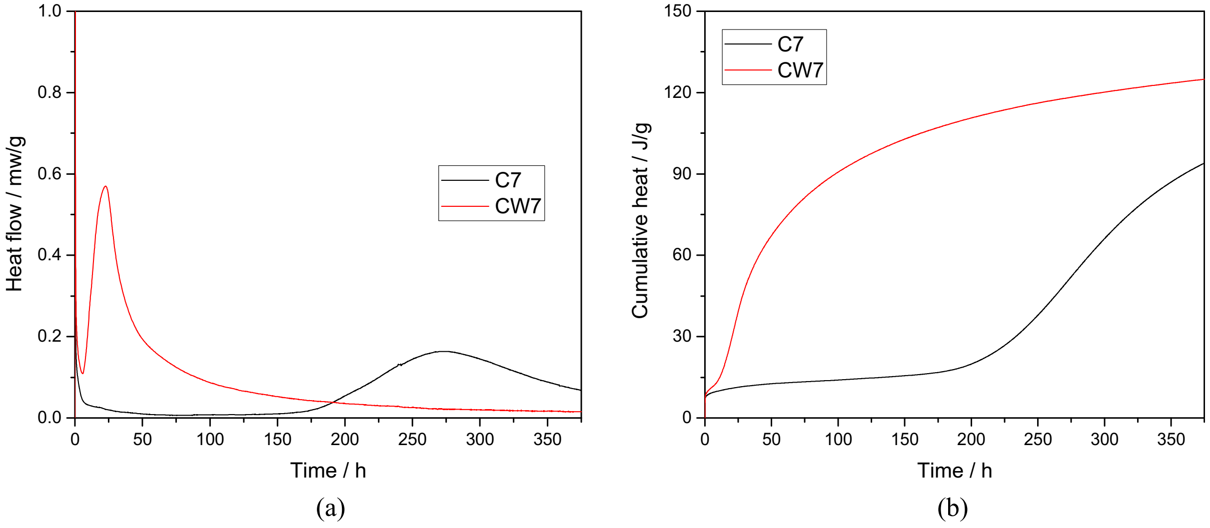
(b)

Fig. 3. Calorimetric results of different pastes: (a) heat flow and (b) cumulative heat.

to the mixtures with washed filter glass. The duration of the main reaction stage is longer, with lower reaction intensity.

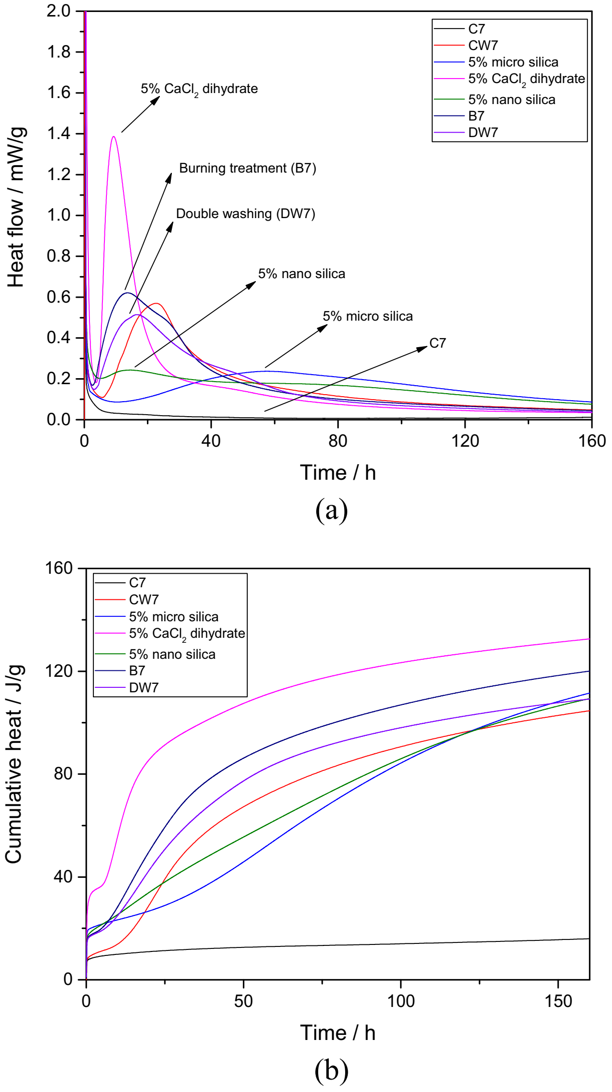
It is believed that the fine glass powder can partially dissolve in the high pH environment and exhibit pozzolanic activity due to the high amorphous silica content [1,19,37,38]. The pozzolanic reaction presents limited influence on early cement hydration, as it is a long-term reaction. With the increasing replacement of glass powder in pastes, less cement particles result in a lower concentration of ions due to the dilution effect [23]; as a consequence the intensity of hydration will be reduced but no influence will be shown concerning the reaction rate. When filter glass is incorporated, the sugars in it are responsible for the delay of the heat flow peak during the hydration. As an inhibitor of cement hydration, the sugars absorb on the surface of cement particles and the surface of hydration products, which slows down the growth of CH and C-S-H gels and inhibits the hydration of cement particles [39–41]. The sugar in filter glass increases the duration of the induction stage, and the higher content of filter glass in pastes, the longer the induction period is. Eventually, the reaction suddenly begins again owing to the fact that the increasing number of nucleation sites overcome the barrier of limited sugar present in the pore solution [32].

To improve the hydration of sample containing filter glass powder, different chemical additions were used to accelerate the reaction in C7, which can be seen in Fig. 5. It is clear that chemical additions improves the hydration of C7 significantly. The addition of 5% calcium chloride dihydrate by mass of binder enhances the reaction rate and cumulative heat, the peak of heat flow is brought forward to 9 h compared the 275 h of C7. The CaCl$_2$ can be used to improve the hydration of cement and the early strength of concrete. It is stated in literature that a dosage up to 3% to 4% could be used [42]. The incorporation of microsilica and nanosilica also improve the hydration of C7 with a dosage of 5% by mass of binder, and the peaks of heat flow take place after 56 h and 18 h respectively. Calcium chloride is a widely used chemical addition for the hydration acceleration of C$_3$S and Portland cement, as it can significant decrease the setting time and increase the early age strength. The Ca^{2+} from calcium chloride can absorb on the surface of C$_3$S and increase the zeta potential [43,44]. The additional Ca^{2+} from calcium chloride can form complexes with saccharides, which may reduce the effect of saccharides on cement particles surface [45]. This is different from the addition of nanosilica and



(a) (b)

Fig. 4. Calorimetry results of 70% filter glass and 70% washed filter glass powder containing samples (a) heat flow (b) cumulative heat.



(a)

(b)

Fig. 5. Influences of different chemical addition on hydration of sample containing 70% filter glass (a) heat flow (b) cumulative heat.

microsilica, which produce more nucleation sites for the cement hydration. As can be seen in Fig. 5(a), the addition of microsilica and nanosilica show no obvious influence on the reaction intensity but decrease the time to reach the heat flow peak. It was found that nanosilica shows more effective on accelerating hydration than microsilica with the same dosage (5%). The source of nanosilica used in this study is a slurry with 50% concentration, which can fully disperse during the mixing, while microsilica usually aggregates together. These result in different performances in the acceleration of hydration. The sample containing 70% double washing treatment filter glass (DB7) and sample containing 70% heating treatment filter glass (B7) also show no significant delay in hydration. After the double washing treatment, more saccharides can be removed, as it can be observed that the heat peak of CW7 is slightly delayed compared with the DB7. After the heating treatment, the organic matter including saccharides were totally removed by burning at 550 °C for 4 h, while the salts were still kept which explains why B7 exhibits higher intensity and an earlier heat peak than CW7 and DB7 during the hydration.

Table 5 illustrates the cumulative heat (normalized by the mass of cement) after 160 h hydration and the cumulative heat (normalized by mass of cement) change compared the plain sample (C0). It can be seen that when the dosage of glass powder is less than 50%, there is no large difference between the samples containing filter glass and washed filter glass. This means the saccharides just retard

Table 5
Summary of cumulative heat of samples at 160 h.

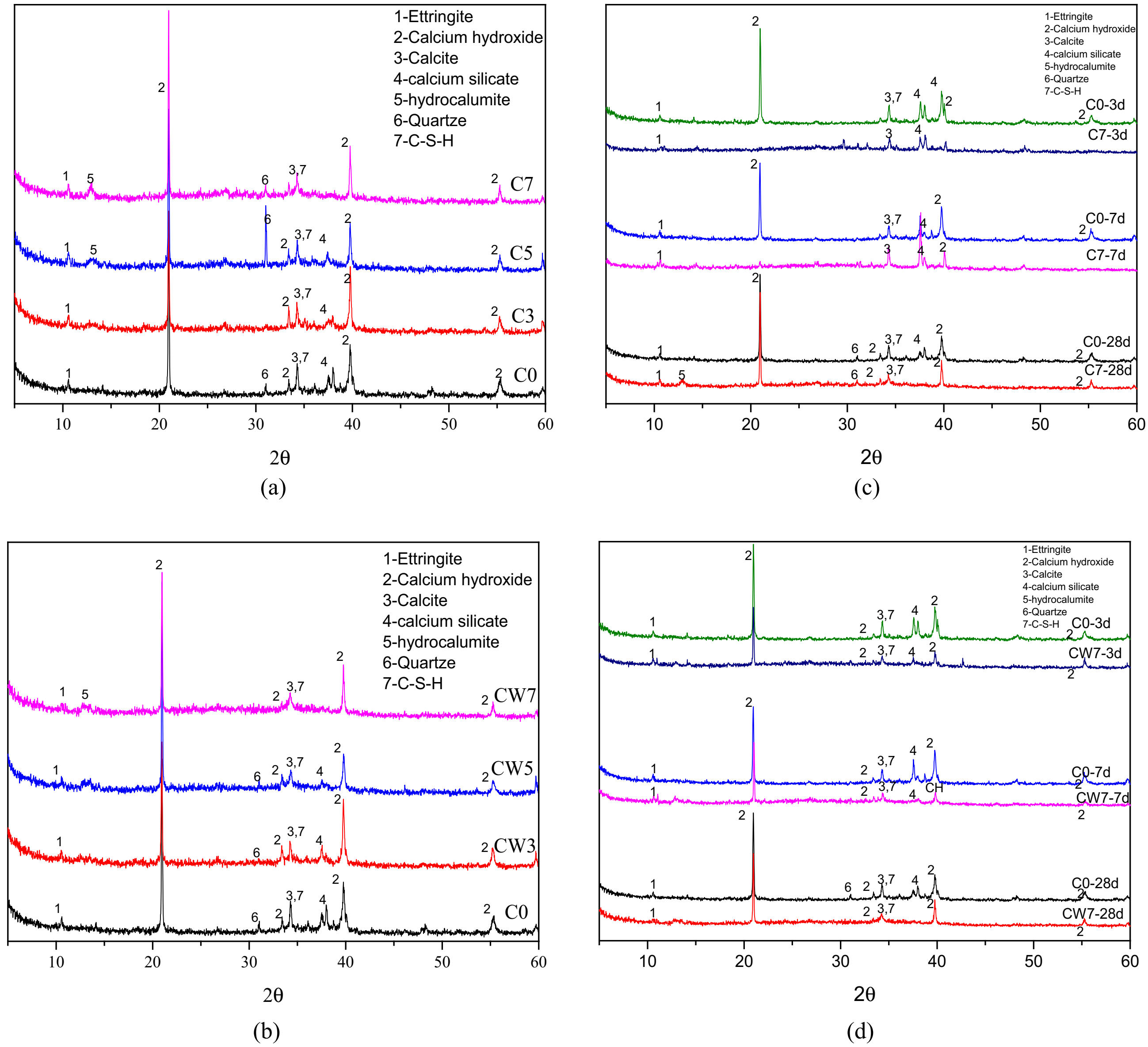
Sample	Cumulative heat at 160 h/(J/g cement)	Heat change/ (J/g cement)
C0	199.5	/
CF	199	−0.5
C3	232.37	32.87
CW3	231.04	31.54
C5	249.08	49.58
CW5	245.94	46.44
C7	53.3	−146.17
CW7	348.83	149.33
C7 + 5%CaCl$_2$·2H$_2$O	441.73	242.23
C7 + 5% microsilica	371.17	171.67
C7 + 5% nanosilica	363.93	164.43
B7	399.97	200.46
DW7	363.87	164.37

the hydration, but have limited influence on the cumulative heat with the glass powder dosages of 30% and 50%. C7 shows a cumulative heat with 53.3 J after 160 h hydration, which is due to the serious delay caused by the saccharides. It can be seen that the increasing cement replacement ratio results in higher heat change, which may due to the increasing effective water/cement ratio. After the addition of accelerator such as nanoparticles and calcium chloride, the cumulative heat of samples are enhanced significantly. The burning treatment and the second washing treatment of the filter glass also can enhance the hydration of samples, which show higher cumulative heat than the CW7. More saccharides and organic matter can be removed during the treatment procedure, so consequently, less retardation is seen in B7 and DW7.

3.3. X-ray diffraction

Fig. 6 illustrates the X-ray diffraction results of paste mixtures with different compositions and curing ages. The XRD patterns results of samples containing 30%, 50% and 70% filter glass powder and washed filter glass powder are shown in Fig. 6(a) and (b) respectively; these mixes were tested after 28 days of curing. It can be seen that after 28 days of hydration, typical hydration products are presented in all samples, such as ettringite that mainly from hydration of C_3A; quartz from the impurities; C-S-H and calcium hydroxide from the hydration of alite and belite; and calcium carbonate from the carbonation process during the cement hydration or curing. It should be noticed that the peak of hydrocalumite only shows in the samples with more than 50% waste glass. The intensity of the peak of unreacted calcium silicates decreases with the increasing amount of waste glass in the mixture, which is due to the dilution effects of glass powder addition.

The effect of curing age on samples containing 70% filter glass powder and washed filter glass powder are presented in Fig. 6(c) and (d). It can be observed from Fig. 6(c) that the peak intensity of calcium hydroxide shown in mixes containing 70% filter glass is lower compared to the reference sample (C0) after 3 days curing. A similar behavior is also found in the same mixture after 7 days curing. After 28 days, the peaks of ettringite, calcium hydroxide,



(a)

(c)

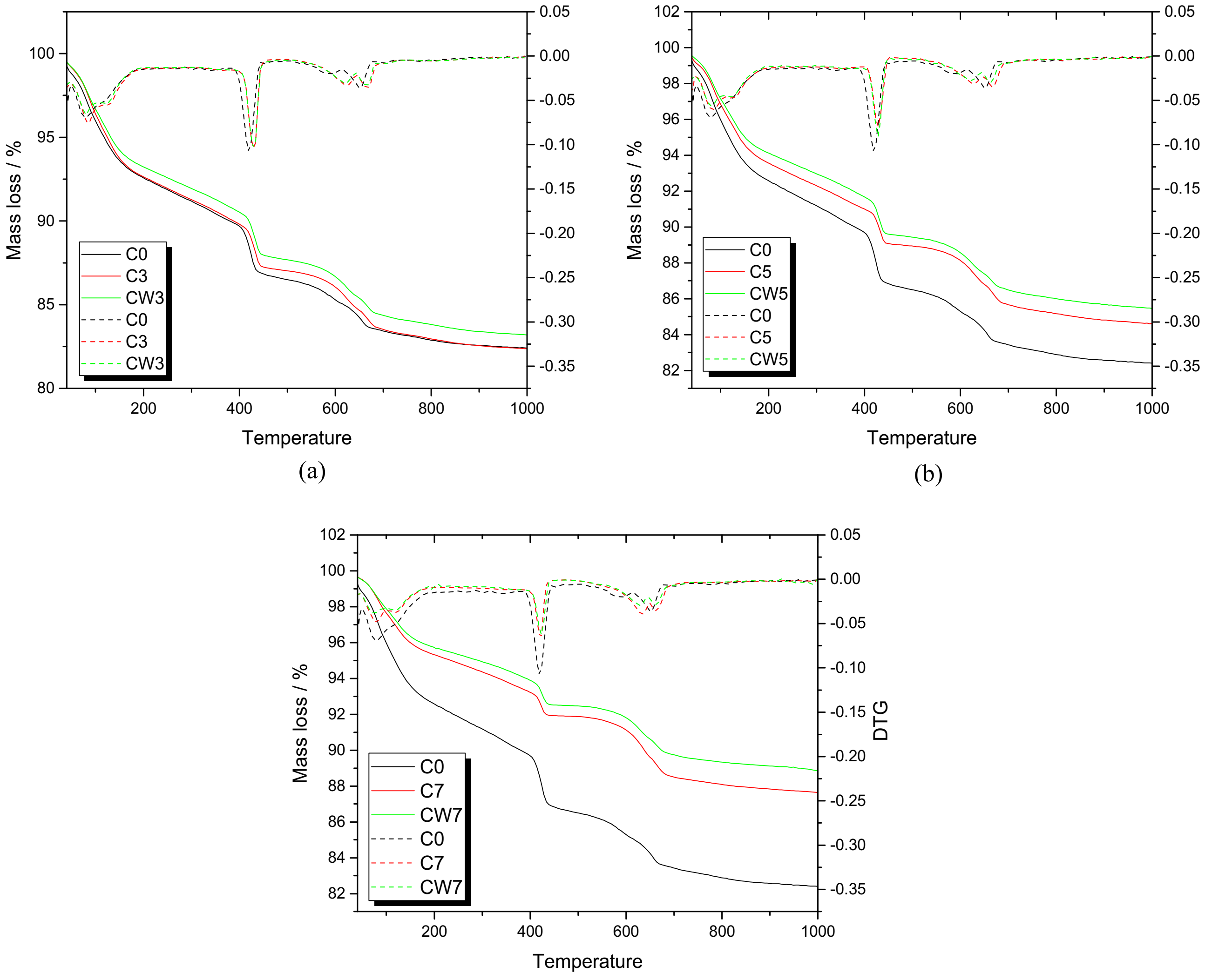
(b)

(d)

Fig. 6. The XRD patterns of pastes mixtures: (a) with filter glass powder (b) with washed filter glass powder (c) 70% filter glass powder with age (d) 70% washed filter glass powder with ages (1-Ettringite, 2-calcium hydroxide, 3-calcite, 4-calcium silicate, 5-hydrocalumite, 6-quartze, 7-C-S-H).

quartz and calcium carbonate are obviously observed in the XRD results, and the peaks of alite and belite show relatively low intensity. Compared to the filter glass powder based mixtures, the XRD results of 70% washed filter glass powder containing sample (CW7) show similar hydration products as the reference after 3 days of curing. As the curing aging increases, the peaks of alite and belite gradually decrease. After 28 days of curing, C7 and CW7 show a similar composition in terms of hydration products, which shows high intensity of calcium hydroxide peaks and relatively low intensity of alite and belite peaks.

The addition of filter glass as cement replacement shows significant effect on the hydration process. As shown in Table 2, the filter glass powder contains various kinds of saccharides such as galactose, glucose and mannose. The incorporation of large amount of filter glass powder (for instance C7) results in a high content of incorporated organic contaminations such as paper fibre and sugar. During the hydration, degradation also takes place on the paper fibre under the alkaline environment, which results in more released saccharides. As shown in Fig. 6(c), the saccharides from filter glass exhibit a weaker effect on formation of ettringite and stronger effects on the formation of calcium hydroxide during hydration. The mechanism of saccharides on cement hydration was investigated in detail in previous research, which indicates that the presence of saccharides results in the retardation of cement hydration, due to surface absorption of retarders directly on the anhydrous surface; resulting in the nucleation and growth poisoning of hydrates including portlandite [39]. Actually the effect of saccharides is more evident on the hydration of C_3S and C_2S than C_3A [39,40,30,46]. This explains why only the ettringite formation is not delayed from the XRD results. The increasing content of waste glass powder in the mixture leads to the reduced peak intensity of C_2S and C_3S. When the glass powder was used as cement replacement, the filler effects and heterogeneous nucleation [47,48] can be shown, similar to the role of applying fly ash or slag as cement substitute, thus more surface is available during the hydration. Besides, glass powder has a high content of amorphous silica, which will be dissolved in the alkaline environment and releases the silicates to the solution [49], increasing the consumption of C_3S and C_2S, and thus resulting in the reduced peak intensity of calcium silicate in high volume glass powder containing samples [17]. Additionally, the peak of hydrocalumite is observed from the XRD results, especially in samples with high filter glass contents such as C5 and C7 after 28 days curing, while the hydrocalumite is also shown in the sample containing 70% washed filter glass powder, which may relate to the residue of chloride after the washing procedure. Ordinary Portland cement can bind chloride



(a)

(b)

(c)

Fig. 7. TG results of samples with different filter glass and washed filter glass content: (a) 30% (b) 50% (c) 70%

through physical adsorption and chemical substitution [50]. Hydrocalumite is a product from the hydration of calcium aluminate phase, with a layered structure [51]. In ordinary cement paste, the ettringite will react with hydrocalumite to a calcium monosulfoaluminate hydrate. In the presence of Cl^-, SO_4^{2-} in the layered structure will be replaced by the Cl^- [52,42]. The chloride content in the filter glass powder is 0.540 mg/g, which contributes to the formation of the double layered hydroxide.

3.4. Thermogravimetric analysis

The thermogravimetric results of different mixtures are shown in Fig. 7. The TG and DTG curves of samples containing 30%, 50% and 70% filter glass and washed filter glass powder are presented in Fig. 7(a)–(c) respectively. It can be seen that all samples present a significant mass loss from 40 °C to 105 °C. This mass loss is assigned to the physical bound water in mixtures. As the temperature increases, the mass loss is obviously increasing before 200 °C. After the evaporation of physically bound water, the C-S-H and AFm begin to lose the chemically bound water gradually at higher temperatures [53]. The following two significant mass losses are attributed to the decomposition of calcium hydroxide (400 °C–460 °C) and calcium carbonate (600 °C–700 °C). During the testing temperature range of 40 °C to 1000 °C, samples with waste glass powder show less total mass loss than the reference sample (C0). Additionally, the highest content of filter glass powder sample (C7) shows the least mass loss, which is also observed in washed filter glass containing samples. It is noticeable that washed filter glass samples show less total mass loss than the filter glass samples with the same replacing level after 28 days curing.

The calcium hydroxide content that normalized by mass of cement are shown in Fig. 8. The content of calcium hydroxide is calculated from the TG results by applying the following equation:

$$W_{CH} = \frac{W_{400} - W_{460}}{M_{H_2O}} \times M_{CH} + \frac{\Delta W_{CO_2}}{M_{CO_2}} \times M_{CH} \qquad (1)$$

W_{400} – Mass loss at 400 °C
W_{460} – Mass loss at 460 °C
M_{H_2O} – Molar mass of water
M_{CH} – Molar mass of calcium hydroxide
M_{CO_2} – Molar mass of carbon dioxide

Fig. 8 shows the calcium hydroxide content (normalized by cement) after 28 days and 90 days curing in different samples.

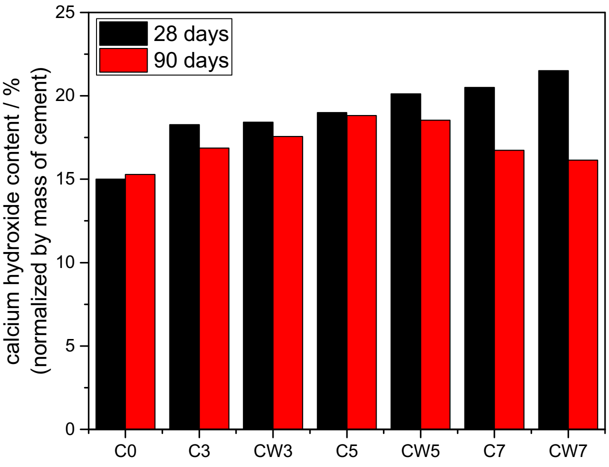


Fig. 8. Calcium hydroxide contents.

The addition of both filter glass and washed filter glass promotes the formation of calcium hydroxide. Filter glass powder containing samples, especially for high volume filter glass incorporation sample, present a slightly lower calcium hydroxide content after 28 days curing but higher after 90 days than samples containing washed filter glass. For the sample containing washed filter glass, calcium hydroxide consumption can be observed in all samples. Apparently, more calcium hydroxide is consumed in washed filter glass containing samples with the increasing of the replacement ratio compared with the sample containing filter glass powder. The lower calcium hydroxide consumption after 28 days and the delay of calcium hydroxide formation in samples with filter glass addition may indicate that the pozzolanic reaction of glass powder is partially influenced by the retardation effect of saccharides.

3.5. N_2 adsorption analysis

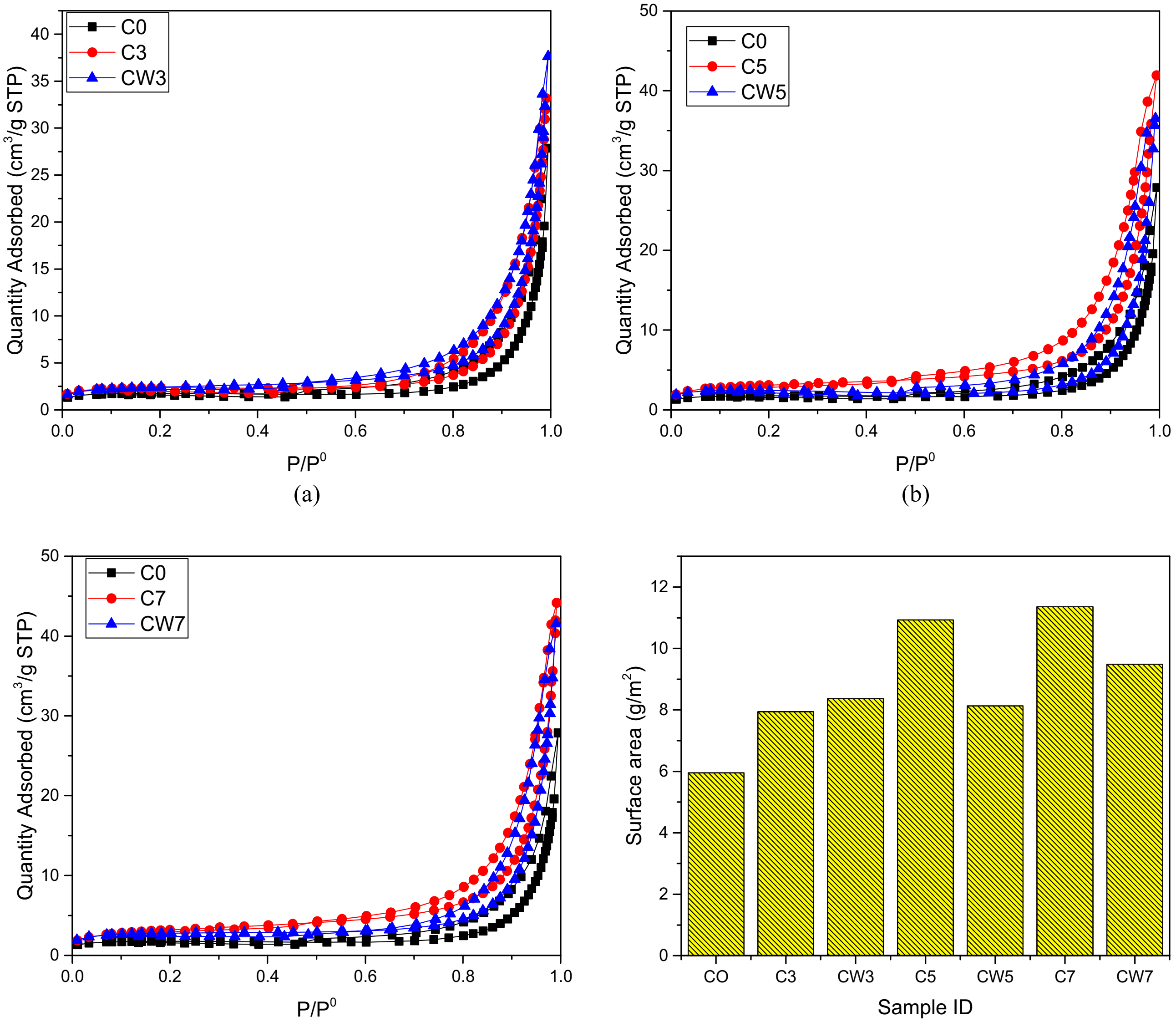
Fig. 9(a–c) present the nitrogen sorption and desorption isotherms of samples containing different dosage of filter glass powder and washed filter glass powder at various relative pressures (p/p^0). It is clear that the isotherm curves show similar type loop. A summary of the specific surface area results from the BET (Brunauer–Emmett–Teller theory) calculation is shown in Fig. 9(d).

It can be seen that samples with filter glass and washed filter glass powder show higher quantity of adsorbents than the reference (C0) from the nitrogen adsorption branch. The washed filter glass containing sample (CW3) absorbs slightly higher absorbents than the sample containing filter glass powder (C3) under the same replacement ratio of 30%, after the relative pressure reaches 0.4. When the dosage of filter glass and washed filter glass powder increased to 50% and 70%, samples containing filter glass powder show higher absorption ability than the washed filter glass powder incorporated samples, from the very low relative pressure to high relative pressure.

It can be seen from Fig. 9(d) that mixtures show different surface areas. The addition of filter glass and washed filter glass powder increases the specific surface area when compared with the reference (C0). It is noticeable that 70% filter glass powder containing sample (C7) presents the highest surface area around 11.36 m^2/g, while this value is 9.49 m^2/g in washed filter glass based samples. In addition, no significant difference in surface area is observed between filter glass and washed filter glass containing samples at low replacement level (30%).

The nitrogen sorption isotherm analysis was conducted through pore size distribution calculation by BJH (Barrett-Joyner-Halenda) method. The results of pore size distributions of mixtures are shown in Fig. 10. As can be seen, the addition of filter glass and washed filter glass powder leads to different pore structure changes on the hydration products. For samples containing 30% washed glass powder (CW3), a slightly higher volume of pores that less than 15 nm and relatively larger volume of pores from 2 nm to 50 nm is observed in Fig. 10(a), when compared with filter glass powder containing samples (C3). Further increasing the filter glass powder dosage to 50% and 70% leads to high porosity at low ranges (<15 nm), and low porosity at high ranges (>20 nm) when compared with washed filter glass powder containing samples, as shown in Fig. 10(b) and (c).

The addition of both filter glass and washed filter glass powder increase the surface area and results in reaction products with higher porosity. It is well known that the higher hydration degree of cement pastes contributes to the high specific surface area [54]; and the water/cement ratio show limited influence on the surface area [55]. As a consequence, the addition of glass powder could be the main reason for the increased surface area. On the one hand, the incorporation of glass powder lowers the overall Ca/Si atom ratio and increases Al/Ca in the pore solution, which causes the



(a) (b)

(c) (d)

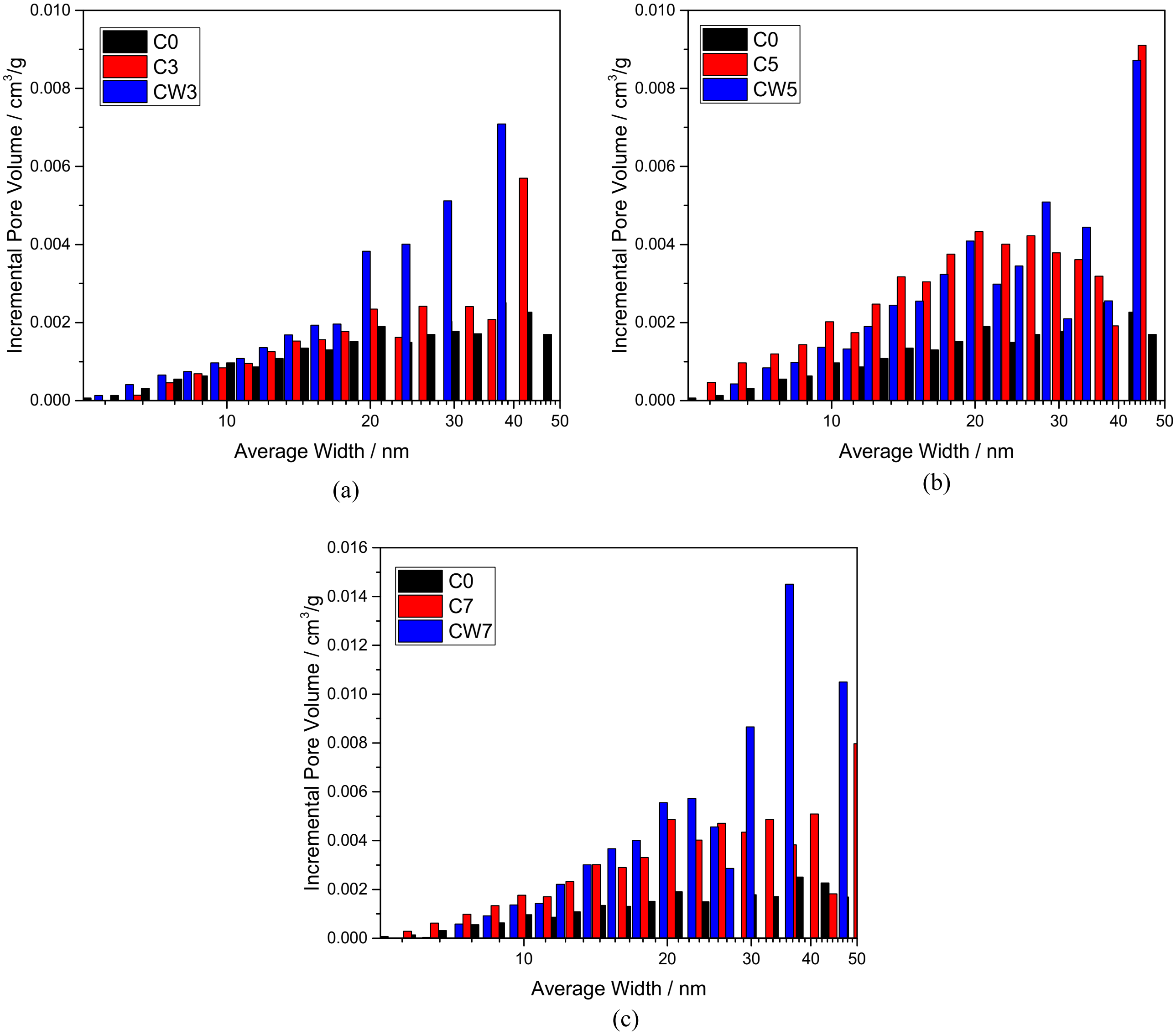
Fig. 9. Nitrogen sorption isotherm curves (a) (b) (c) and (d) Bet surface areas.

producing of C-S-H gel with low density as fly ash in early age [56]; on the other hand, the dissolving of glass powder in alkali environment releases silicate, which also promotes the hydration of the cement particle [57]. Comparing filter glass containing samples with washed filter glass containing ones, filter glass containing samples present higher surface area and larger pore volume. This indicates that the incorporation of filter glass produces C-S-H gels with lower density than washed filter glass incorporating samples. The retardation of the saccharide in filter glass powder containing samples induces the high initial dissolution of ions [29,31], while the long delay period demonstrates that the many ions could migrate to the sites far from the reaction particle [32]. These result in the formation of C-S-H gel in the open pore spaces [58] and higher surface area in terms of the microstructure, which is also due to the more porous structure.

3.6. SEM

The SEM- EDX are used together to determine the microstructure and chemical composition of hydration products of pastes containing filter glass powder and washed filter glass powder. The results are shown in Fig. 11.

It can be observed that the plain cement paste (C0) shows a relatively dense microstructure. The hydration products ideally fill the space between the unreacted cement particles and show a homogeneous structure. The result of EDX obtained around the unreacted cement particle shows a Ca/Si ratio of 2.02, which is a typical C-S-H produced by cement hydration [59,60]. The filter glass and washed filter glass incorporation leads to a more porous structure at micro scale. As can be seen in Fig. 11(d) and (e) that 30% filter glass (C3) and washed filter glass (CW3) samples shows more porosity than the plain sample, and EDX and SEM images with 8000 × exhibit that the glass particles around 10 μm are covered by the C-S-H gel with a low Ca/Si ratio. For example, Ca/Si with 1.09 and 1.67 are observed in C3 and CW3, respectively. At the same time, most of the glass particles around 10 μm in C7 show clean and smooth surface with a Ca/Si with 0.14, which is due to the largely unreacted glass particles. These may indicate that a limited pozzolanic reaction occurred on the surface of these glass particles, and the products from cement hydration fill the pores between glass particles with weak binding forces. The EDX



(a)

(b)

(c)

Fig. 10. BJH pore distributions.

result of the glass particles surface in sample C7 also presents high Si and O content, which can be referred to the raw glass phase, while the morphological image of sample containing 70% washed filter glass powder exhibits a rough surface of glass particle. As can be seen from the SEM picture Fig. 11(b) and (c), the glass particles in CW7 are covered by the reaction products. The EDX result of the gel on the surface of glass particle shows a low Ca/Si of 0.93, which can be considered as the products from the pozzolanic reaction of glass powder.

Compared with the glass particles in high volume filter glass and washed filter glass containing samples, it is obviously that the washed filter glass particles show a clear sign of pozzolanic reaction. The glass particle could be dissolved in the alkaline environment and the silicate released from glass phase reacts with the calcium hydroxide from cement hydration. The filter glass powder contains organic matter and saccharides contamination, which poisons the surface of cement particle and the growth of calcium hydroxide. Consequently, the dissolution of glass particles is inhibited, which limits the pozzolanic reaction on the surface of glass particles. Combining with the results of BET, it can be suggested that the samples containing washed filter glass show higher volume pore between 20 and 50 nm, which is related to the C-S-H from pozzolanic reaction.

4. Conclusions

This paper studies the influences of high volume filter glass powder on cement early age hydration, reaction products, mechanical properties and microstructure properties. The following conclusions can be addressed:

(1) The leaching results indicate that the filter glass contains saccharides and high dosage of Na^+ and Cl^-. After washing treatment, the soluble salts and organic matter can be removed efficiently.
(2) The addition of filter glass powder significantly retards the hydration process. The incorporation of filter glass powder also decreases the heat flow peak and cumulative heat during hydration. After washing, filter glass powder shows

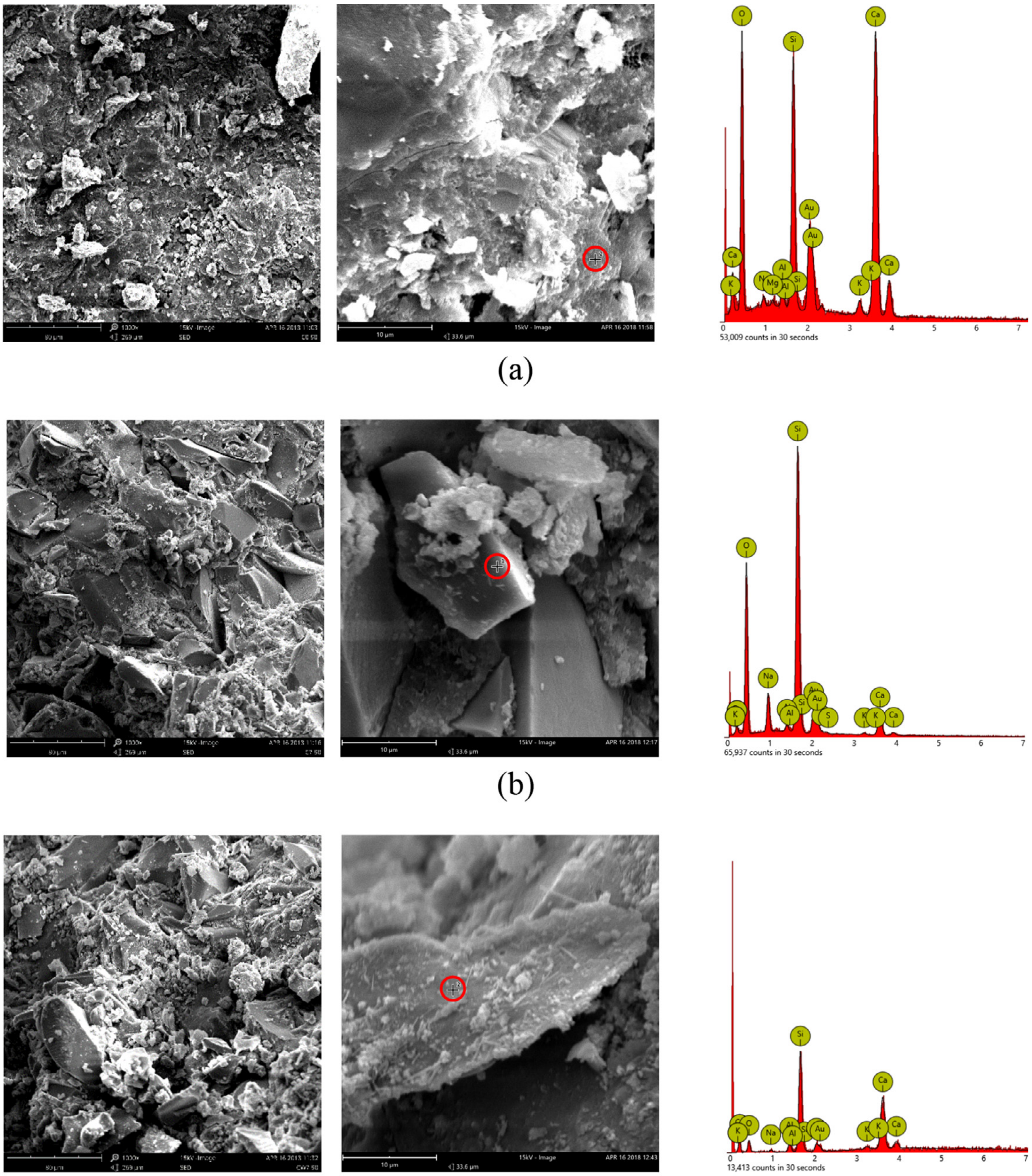
a limited influence of retardation on the cement hydration, which indicates that the organic contamination in filter glass is the main reason for the retardation of hydration.

(3) The addition of the hydration accelerator such as $CaCl_2$, nanosilica and microsilica can significantly improve the hydration process and reduce the retardation of sample containing high volume filter glass. Burning treatment and second washing treatment for filter glass also can obviously reduce the retardation effect.

(4) The saccharides in filter glass powder show significant influence on the hydration of high volume filter glass containing samples during different ages. After 28 days curing, the high volume filter glass powder containing samples show peaks of hydrocalumite which is related to the chloride in raw material. Also, the high volume filter glass powder and washed filter glass powder incorporation improve the consumption of tricalcium silicate and dicalcium silicate.

(5) The filter glass powder containing samples show lower calcium hydroxide consumption than washed filter glass powder containing samples. However, the amount of generated portlandite suggests that the glass undergoes a pozzolanic reaction.

(6) The filter glass powder incorporation increases the specific surface area, which is attributed to the increasing pore volume. The saccharides in filter glass powder contributes to



(a)

(b)

(c)

Fig. 11. SEM images and EDX results: (a) plain sample C0 (b) 70% filter glass sample C7 (c) 70% washed filter glass sample CW7.

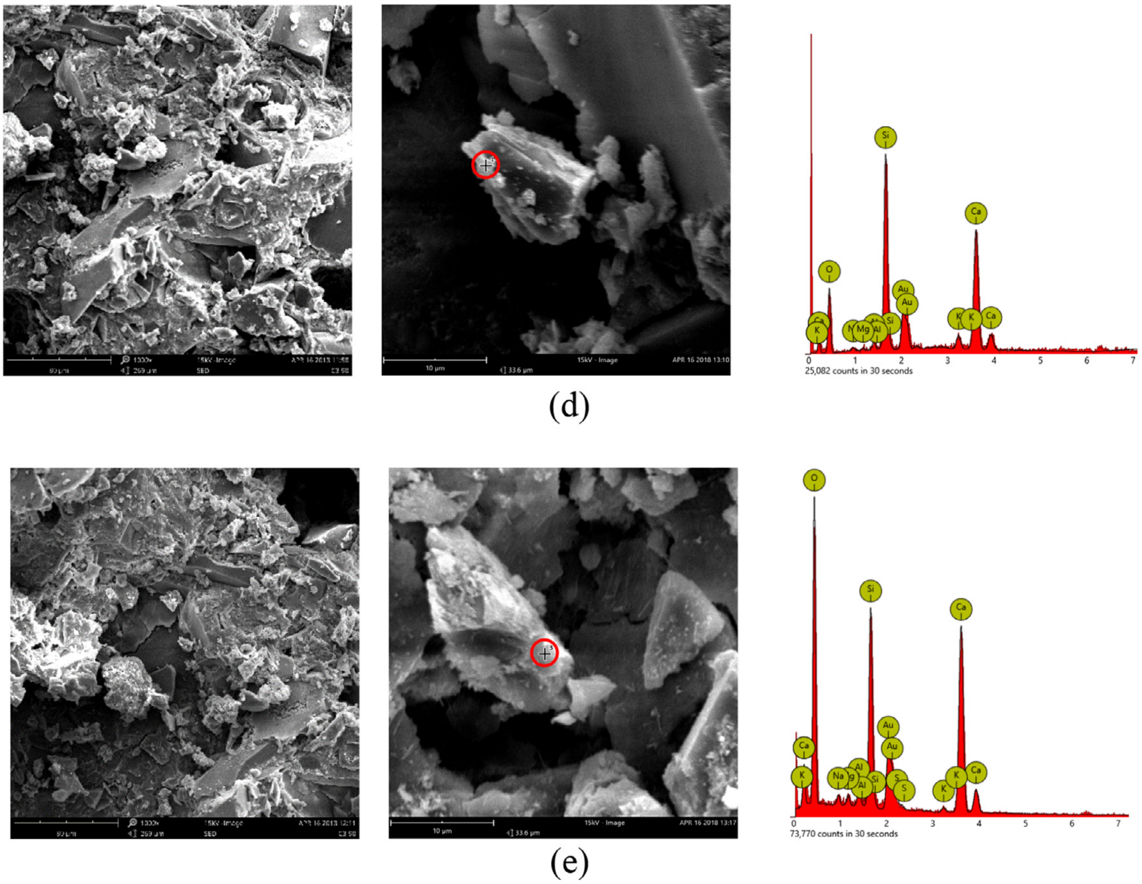


Fig. 11 (*continued*)

the higher pore volume of less than 15 nm and lower pore volume of more than 20 nm when compared to the filter glass after washing.

(7) High volume filter glass powder and washed filter glass powder containing samples result in porous microstructure. From the SEM images, the washed filter glass powder shows higher activity of pozzolanic reaction than the filter glass powder.

5. Declarations of interest

None.

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References

[1] A. Shayan, A. Xu, Performance of glass powder as a pozzolanic material in concrete: a field trial on concrete slabs, Cem. Concr. Res. 36 (3) (2006) 457–468.

[2] H. Du, K.H. Tan, Waste glass powder as cement replacement in concrete, J. Adv. Concr. Technol. 12 (11) (2014) 468–477.

[3] G. Lee, C.S. Poon, Y.L. Wong, T.C. Ling, Effects of recycled fine glass aggregates on the properties of dry-mixed concrete blocks, Constr. Build. Mater. 38 (2013) 638–643.

[4] H. Zhao, C.S. Poon, T.C. Ling, Utilizing recycled cathode ray tube funnel glass sand as river sand replacement in the high-density concrete, J. Clean. Prod. 51 (2013) 184–190.

[5] T.C. Ling, C.S. Poon, Use of recycled CRT funnel glass as fine aggregate in dry-mixed concrete paving blocks, J. Clean. Prod. 68 (2014) 209–215.

[6] T.C. Ling, C.S. Poon, Properties of architectural mortar prepared with recycled glass with different particle sizes, Mater. Des. 32 (5) (2011) 2675–2684.

[7] S.B. Park, B.C. Lee, J.H. Kim, Studies on mechanical properties of concrete containing waste glass aggregate, Cem. Concr. Res. 34 (12) (2004) 2181–2189.

[8] İ.B. Topçu, M. Canbaz, Properties of concrete containing waste glass, Cem. Concr. Res. 34 (2) (2004) 267–274.

[9] S.C. Kou, C.S. Poon, Properties of self-compacting concrete prepared with recycled glass aggregate, Cem. Concr. Compos. 31 (2) (2009) 107–113.

[10] S. Multon, M. Cyr, A. Sellier, P. Diederich, L. Petit, Effects of aggregate size and alkali content on ASR expansion, Cem. Concr. Res. 40 (4) (2010) 508–516.

[11] M. Thomas, The effect of supplementary cementing materials on alkali-silica reaction: a review, Cem. Concr. Res. 41 (12) (2011) 1224–1231.

[12] R. Idir, M. Cyr, A. Tagnit-Hamou, Use of fine glass as ASR inhibitor in glass aggregate mortars, Constr. Build. Mater. 24 (7) (2010) 1309–1312.

[13] H. Du, K.H. Tan, Use of waste glass as sand in mortar: Part II – alkali-silica reaction and mitigation methods, Cem. Concr. Compos. 35 (1) (2013) 109–117.

[14] F.P. Cota, C.C.D. Melo, T.H. Panzera, A.G. Araújo, P.H.R. Borges, F. Scarpa, Mechanical properties and ASR evaluation of concrete tiles with waste glass aggregate, Sustainable Cities Soc. 16 (C) (2015) 49–56.

[15] A. Saccani, M.C. Bignozzi, ASR expansion behavior of recycled glass fine aggregates in concrete, Cem. Concr. Res. 40 (4) (2010) 531–536.

[16] Y. Shao, T. Lefort, S. Moras, D. Rodriguez, Studies on concrete containing ground waste glass, Cem. Concr. Res. 30 (1) (2000) 91–100.

[17] N. Schwarz, N. Neithalath, Influence of a fine glass powder on cement hydration: comparison to fly ash and modeling the degree of hydration, Cem. Concr. Res. 38 (4) (2008) 429–436.

[18] M.C. Bignozzi, A. Saccani, L. Barbieri, I. Lancellotti, Glass waste as supplementary cementing materials: the effects of glass chemical composition, Cem. Concr. Compos. 55 (2015) 45–52.

[19] K. Zheng, Pozzolanic reaction of glass powder and its role in controlling alkali-silica reaction, Cem. Concr. Compos. 67 (2016) 30–38.

[20] N. Schwarz, H. Cam, N. Neithalath, Influence of a fine glass powder on the durability characteristics of concrete and its comparison to fly ash, Cem. Concr. Compos. 30 (6) (Jul. 2008) 486–496.
[21] A. Omran, A. Tagnit-Hamou, Performance of glass-powder concrete in field applications, Constr. Build. Mater. 109 (2016) 84–95.
[22] J.-X. Lu, B.-J. Zhan, Z.-H. Duan, C.S. Poon, Using glass powder to improve the durability of architectural mortar prepared with glass aggregates, Mater. Des. 135 (Dec. 2017) 102–111.
[23] H. Du, K.H. Tan, Properties of high volume glass powder concrete, Cem. Concr. Compos. 75 (2017) 22–29.
[24] Z. Hui, C.S. Poon, T.C. Ling, Properties of mortar prepared with recycled cathode ray tube funnel glass sand at different mineral admixture, Constr. Build. Mater. 40 (2013) 951–960.
[25] T.C. Ling, C.S. Poon, Utilization of recycled glass derived from cathode ray tube glass as fine aggregate in cement mortar, J. Hazard. Mater. 192 (2) (2011) 451–456.
[26] X. Lin, M.R. Silsbee, D.M. Roy, K. Kessler, P.R. Blankenhorn, I. Materials, Approaches to improve the properties of wood fiber reinforced cementitious composites, Cem. Concr. Res. 24 (8) (1994) 1558–1566.
[27] J.L. Pehanich, P.R. Blankenhorn, M.R. Silsbee, Wood fiber surface treatment level effects on selected mechanical properties of wood fiber-cement composites, Cem. Concr. Res. 34 (1) (2004) 59–65.
[28] Y.M. Wei, Y.G. Zhou, B. Tomita, Hydration behavior of wood cement-based composite {I}: evaluation of wood species effects on compatibility and strength with ordinary Portland cement, J. Wood Sci. 46 (2000) 296–302. Copyright (C) 2015 American Chemical Society (ACS). All Rights Reserved.
[29] N.L. Thomas, J.D. Birchall, The retarding action of sugars on cement hydration, Cem. Concr. Res. 13 (6) (1983) 830–842.
[30] K. Kochova, K. Schollbach, F. Gauvin, H.J.H. Brouwers, Effect of saccharides on the hydration of ordinary Portland cement, Constr. Build. Mater. 150 (2017) 268–275.
[31] J.F. Young, A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures, Cem. Concr. Res. 2 (4) (1972) 415–433.
[32] M.C. Garci Juenger, H.M. Jennings, New, insights into the effects of sugar on the hydration and microstructure of cement pastes, Cem. Concr. Res. 32 (3) (2002) 393–399.
[33] C.M. Neubauer, M. Yang, H.M. Jennings, Interparticle potential and sedimentation behavior of cement suspensions: effects of admixtures, Adv. Cem. Based Mater. 8 (1) (1998) 17–27.
[34] E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, J. Am. Chem. Soc. 73 (1) (1951) 373–380.
[35] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (2) (1938) 309–319.
[36] J.W. Bullard, H.M. Jennings, R.A. Livingston, A. Nonat, G.W. Scherer, J.S. Schweitzer, K.L. Scrivener, J.J. Thomas, Mechanisms of cement hydration, Cem. Concr. Res. 41 (12) (2011) 1208–1223.
[37] V. Vaitkevičius, E. Šerelis, H. Hilbig, The effect of glass powder on the microstructure of ultra high performance concrete, Constr. Build. Mater. 68 (2014) 102–109.
[38] L.A. Pereira-De-Oliveira, J.P. Castro-Gomes, P.M.S. Santos, The potential pozzolanic activity of glass and red-clay ceramic waste as cement mortars components, Constr. Build. Mater. 31 (2012) 197–203.
[39] M. Bishop and A. R. Barron, Cement Hydration Inhibition with Sucrose , Tartaric Acid , and Lignosulfonate : Analytical and Spectroscopic Study, 2006, pp. 7042–7049.
[40] F.F. Ataie, M.C.G. Juenger, S.C. Taylor-Lange, K.A. Riding, Comparison of the retarding mechanisms of zinc oxide and sucrose on cement hydration and interactions with supplementary cementitious materials, Cem. Concr. Res. 72 (2015) 128–136.
[41] B.J. Smith, L.R. Roberts, G.P. Funkhouser, V. Gupta, B.F. Chmelka, Reactions and surface interactions of saccharides in cement slurries, Langmuir 28 (2012) 14202–14217.
[42] S. Kourounis, S. Tsivilis, P.E. Tsakiridis, G.D. Papadimitriou, Z. Tsibouki, Properties and hydration of blended cements with steelmaking slag, Cem. Concr. Res. 37 (6) (Jun. 2007) 815–822.
[43] J.J. Thomas, A.J. Allen, H.M. Jennings, Hydration kinetics and microstructure development of normal and CaCl2 – accelerated tricalcium silicate pastes, J. Phys. Chem. C 113 (46) (2009) 19836–19844.
[44] V.K. Peterson, M.C. Garci Juenger, Hydration of tricalcium silicate: effects of CaCl2 and sucrose on reaction kinetics and product formation, Chem. Mater. 18 (24) (2006) 5798–5804.
[45] A.C.F. Ribeiro, M.C.F. Barros, V.M.M. Lobo, A.J.F.N. Sobral, S.I.G. Fangaia, P.M.G. Nicolau, F.A.D.R.A. Guerra, M.A. Esteso, Interaction between calcium chloride and some carbohydrates as seen by mutual diffusion at 25 °C and 37 °C, Food Chem. 124 (3) (2011) 842–849.
[46] H. Hong, S. Xiao-dong, Interaction effect of triisopropanolamine and glucose on the hydration of Portland cement, Constr. Build. Mater. 65 (2014) 360–366.
[47] P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars Effect of inert materials on short-term hydration, Cem. Concr. Res. 33 (2003) 1939–1947.
[48] G. Xu, Q. Tian, J. Miao, J. Liu, Early-age hydration and mechanical properties of high volume slag and fly ash concrete at different curing temperatures, Constr. Build. Mater. 149 (2017) 367–377.
[49] M. Torres-Carrasco, J.G. Palomo, F. Puertas, Sodium silicate solutions from dissolution of glass wastes., Stat. Anal. Mater. Constr. 64 (314) (2014) 1–14.
[50] M.V.A. Florea, H.J.H. Brouwers, Chloride binding related to hydration products part I: ordinary Portland cement, Cem. Concr. Res. 3 (2) (2012) 125–131.
[51] P. Zhang, G. Qian, H. Cheng, J. Yang, H. Shi, R.L. Frost, Near-infrared and mid-infrared investigations of Na-dodecylbenzenesulfate intercalated into hydrocalumite chloride (CaAl-LDH-Cl), Spectrochim. Acta - Part A Mol. Biomol Spectrosc. 79 (3) (2011) 548–553.
[52] B. Yu, H. Bian, J. Plank, Self-assembly and characterization of Ca-Al-LDH nanohybrids containing casein proteins as guest anions, J. Phys. Chem. Solids 71 (4) (2010) 468–472.
[53] L. Alarcon-Ruiz, G. Platret, E. Massieu, A. Ehrlacher, The use of thermal analysis in assessing the effect of temperature on a cement paste, Cem. Concr. Res. 35 (3) (Mar. 2005) 609–613.
[54] R.S. Mikhail, L.E. Copeland, S. Brunauer, Pore structures and surface areas of hardened Portland cement pastes by nitrogen adsorption, Can. J. Chem. 42 (2) (Feb. 1964) 426–438.
[55] M.C. Garci Juenger, H.M. Jennings, The use of nitrogen adsorption to assess the microstructure of cement paste, Cem. Concr. Res. 31 (6) (2001) 883–892.
[56] S. Goñi, M. Frias, I. Vegas, R. García, R. Vigil De La Villa, Effect of ternary cements containing thermally activated paper sludge and fly ash on the texture of C-S-H gel, Constr. Build. Mater. 30 (2012) 381–388.
[57] M. Ben Haha, G. Le Saout, F. Winnefeld, B. Lothenbach, Influence of activator type on hydration kinetics, hydrate assemblage and microstructural development of alkali activated blast-furnace slags, Cem. Concr. Res. 41 (3) (2011) 301–310.
[58] H.M. Jennings, Model for the microstructure of calcium silicate hydrate in cement paste, Cem. Concr. Res. 30 (1) (2000) 101–116.
[59] S.A. Rodger, G.W. Groves, Electron microscopy study of ordinary Portland cement and ordinary Portland cement-pulverized fuel ash blended pastes, J. Am. Ceram. Soc. 72 (6) (1989) 1037–1039.
[60] I.G. Richardson, G.W. Groves, Microstructure and microanalysis of hardened ordinary Portland cement pastes, J. Mater. Sci. 28 (1) (1993) 265–277.