ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 22, No. 4. 2016

The Role of Waste Glass Powder During the Hydration Process of Composite Cementitious Materials

Shuhua LIU^{1,2*}, Weiwei HAN¹, Wei ZHOU¹

¹ State Key Laboratory of Water Resources and Hydropower Engineering Science, Wuhan University, Wuhan 430072, China

² Department of Civil, Environmental and Geomatic Engineering, University College London, Gower Street, London, WC1E 6BT, U.K.

crossref http://dx.doi.org/10.5755/j01.ms.22.4.13210

Received 24 September 2015; accepted 19 December 2015

The role of waste glass powder (GP) during the hydration process of composite cementitious materials was investigated by using mercury intrusion porosimetry (MIP), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The compressive strength was also tested. The results indicate that the chemical activity of GP is low. But the pozzolanic reactivity of GP greatly improves with its fineness and the elevated curing temperature, which contributes to improving the mechanical strength. The hydration process of composite cementitious material containing GP is similar to that of pure cement. With the increase of GP content in the composite cement, the occurring time of second exothermic improves, but the value of second exothermic peak and the cumulative hydration heat reduce. The characteristic pore size of pastes containing GP decreases over curing age, which significantly improves their strength. GP does not modify the type of hydration products of composite cementitious material. The microstructure of hardened pastes containing GP is dense due to the generation of C-S-H gel with a low Ca/Si ratio. There is a reaction ring along GP with high fineness, which can enhance the interfacial transition zone to avoid ASR.

Keywords: waste glass powder, hydration properties, compressive strength, microstructure.

1. INTRODUCTION

Waste glass are largely generated from bottles, jars, windows and windshields, bulbs, cathode ray tubes, etc. In 2005, approximately 12.8 million tons of waste glass was disposed in the United States, yet only 2.75 million tons were recycled [1]. In China, approximately 4.7 million tons of waste glass is discharged every year [2]. However, not all waste glass can be recycled to produce new glass because of impurities, high cost, and various colors [3]. For instance, 1.65 million tons of waste glasses are abandoned in U.K. every year because of unsuitability for recycling [4]. Approximately 4500 tons of waste glass were recycled annually, the recycled percentage was 3.3 % and the remaining 96.7 % was sent to landfill for direct dumping [5]. The landfill treatment is carried out at tremendous cost, e.g. the New York City pays Material Recycling Facilities up to \$45 per ton for the disposal of the glass, and the annual amount of waste glass generated exceeds 100,000 tons [6].

The amount of waste glass is gradually increased with the growth in number or quantity of glass products, which calls for more landfill sites. Furthermore, waste glass is an unbiodegradable material, thus landfill cannot provide an environmental friendly solution. It is imperative to figure out an efficient and environmentally friendly way to dispose waste glass. Cement-based materials, which are largely used in civil engineering, have little restriction on the quality of raw materials, thus providing an efficient way to massively recycle industrial solid waste. Since

1970s, many researchers have studied the incorporation of waste glass as aggregate or cementitious material in concrete [7]. Kou et al. [8] focused on the use of waste glass as aggregate to produce self-compacting concrete. They found that the chloride penetration resistance improved and the air content of concrete increased with the increase of glass aggregate replacement rate. However, a major concern regarding the use of glass as aggregate in concrete is the chemical reaction between the silica-rich glass particles and the alkali in the pore solution of concrete, which may cause alkali-silica reaction (ASR) expansion and thus reduce the stability and the durability. Rachida et al. [9] revealed that only glass particle with the size more than 1 mm could lead to harmful expansion related to ASR. Other study indicated [10] that glass powder with an average size of 300 µm did not show any pozzolanic behavior. Shao et al. [11] and Rachida et al. [12] stated briefly that ground glass powder with the size less than 38 µm exhibited a pozzolannic behavior. The smaller glass particle led to higher reactivity with lime, higher compressive strength and lower ASR expansion of concrete. It means that the ASR can be reduced or even eliminated if the particle size of GP is small enough. Because of high content of SiO₂ and CaO, waste glass can exhibit a remarkably pozzolanic behavior if ground finely enough. It can substitute partial cement and act as a supplementary cementitious material [13]. Rachida et al. [14] revealed that pozzolanic reaction of waste glass powder led to the formation of C-S-H gel with a low Ca/Si ratio. This C-S-H gel could increase the density of the paste microstructure and lead to the decrease of porosity and permeability.

^{*} Corresponding author. Tel.: +86-27-68772233; fax: +86-27-68772310. E-mail address: *shliu@whu.edu.cn* (S. Liu)

This paper mainly focuses on figuring out the hydration activity and the strength development of paste and mortar containing GP with different fineness and under various curing conditions. Besides of the strength, microstructure of the mortars is investigated by using XRD, SEM as well as MIP. The hydration heat evolution rate and cumulative hydration heat of composite cementitious material containing GP were also measured by an isothermal calorimeter (TAM Air).

2. EXPERIMENTAL

42.5 Ordinary Portland cement which complies with the Chinese standard GB175-2007 is used in this study. GP is made of waste glass bottles which are crushed and ground in a ball mill after being washed and dried. In contrast with spherical fly ash particles, most GP particles with smooth surface morphology are irregular angular, blocky and clastic. The chemical compositions of cement and GP used are listed in Table 1.

Table 1. Chemical composition of cement and GP/mass, %

Compositions	SiO ₂	Al_2O_3	CaO	Fe ₂ O ₃	MgO	SO_3	K ₂ O	Na ₂ O
Cement	24.55	4.66	58.77	3.36	0.04	3.33	0.99	0.24
GP	69.17	2.94	10.25	1.47	1.16	0.11	1.26	12.13

From Table 1, GP contains large quantities of active SiO_2 which contributes to the pozzolanic activity when ground to certain fineness. As for the effect of fineness on the strength of mortar, this work selects the GP with two finenesses whose specific surface area are $325 \text{ m}^2/\text{kg}$ and $658 \text{ m}^2/\text{kg}$ as coarse glass powder (CGP) and fine glass powder (FGP) respectively. The hydration process of composite cementitious materials was studied under standard (20 °C) and 40 °C steam curing conditions.

The mix proportions of the pastes and mortars are illustrated in Table 2 and Table 3 respectively. Pastes with water-to-binder ratio of 0.5 were prepared for hydration heat test, MIP, XRD and SEM analysis. As the mechanical strength of the pastes is unsteady, mortars with binder-to-sand ratio of 1:3 and water-to-binder ratios of 0.5 and 0.3 were prepared for compressive strength test. In accordance with GB/T17671-1999, 100 mm cubic specimens were prepared with the only modification in the fineness and curing temperature. They were cured under higher than 90 % RH and 20 ± 1 °C for 24 hours before demolded. Each half of the specimens were cured under standard and 40 °C steam curing conditions.

Table 2. Mix proportion of the pastes/mass, %

Samples	Cement	FGP	Water
Cement	100	0	50
GP20	80	20	50
GP40	60	40	50

A battery solution type compression testing machine WAY-2000 was used to measure compressive strength at 3 and 90 days. And the cores from the crushed paste specimens were collected and stored in absolute ethylalcohol in order to terminate the hydration. Then, in order to be used for XRD analyses, the samples were ground in an agate mortar and dried under 60 °C drying condition for 3 hours to avoid carbonization. MIP and SEM techniques were also employed to characterize the

pore structure of pastes and morphology of mortars containing different dosages of waste glass powder under different curing conditions.

Table 3. Mix proportions of the mortars/g

W/B	GP /%	Cement	GP	Water	Sand
0.3	0	450	0	135	1350
0.3	20	360	90	135	1350
0.3	40	270	180	135	1350
0.5	0	450	0	225	1350
0.5	20	360	90	225	1350
0.5	40	270	180	225	1350

3. RESULTS AND DISCUSSION

3.1. Hydration heat evolution

The hydration heat evolution rate and cumulative hydration heat of the composite cementitious materials containing GP at 20 $^{\circ}$ C are shown in Fig. 1.



Fig. 1. a – hydration heat evolution rate; b – cumulative hydration heat of the composite cementitious materials

The hydration process of composite cementitious materials incorporating GP is similar to that of the pure cement. The initial hydration heat evolution rate of GP pastes which corresponds to the first peak of the curve is higher than that of the pure cement. This may attribute to that the water content in the system is relatively higher when GP partially replaces cement, thus there is more water participating in the initial hydration with cement. The reaction between water and cement releases the surface energy and promote the fast reaction of aluminates, leading to the improvement of hydration rate of the system within a short time. Then the hydration heat evolution rate decreases rapidly, and the reaction enters the second stage, i.e. dormant period. For pure cement pastes and the pastes containing 20 % and 40 % GP, the durations of the induction period increase from 1.678 h to 1.858 h and 1.874 h, respectively, and it also postpones the appearance of the second exothermic peak (9.345 h, 12.62 h, 13.114 h) (Fig. 1 a). Furthermore, a reduction in the total hydration heat with increasing dosage of GP can be also observed (Fig. 1 b). This may be caused by the increase of effective water due to increase of the replacement ratio of GP, which results in relatively decreased concentration of Ca2+ in pore solution. Therefore, the dormant period in which the concentration of Ca²⁺ need to reach saturation state before further hydration of GP is prolonged and the occurring time of the second exothermic peak is delayed.

Compared with pure cement, the hydration heat evolution rate and total hydration heat of the cementitious system containing GP reduce, which weakens the intensity of hydration reaction as a whole. The similar curves illustrate that GP is inert and the activity is very low in the early hydration stage. But the hydration reduces the ASR risk, and hereby improves the durability of hardened cement paste in the long run.

3.2. Compressive strength

Table 4 shows the compressive strength development of mortars with different content and fineness of GP under two curing conditions.

 Table 4. Compressive strength of mortars under standard and 40 °C steam curing conditions /MPa

Sample	W/B	Standa	rd curing	Steam curing		
		3 days	90 days	3 days	90 days	
GP-0	0.3	44.02	64.11	44.48	67.66	
FGP-20	0.3	33.61	67.25	43.69	73.99	
FGP-40	0.3	21.65	61.32	30.83	74.23	
CGP-20	0.3	31.58	60.29	40.06	70.36	
CGP-40	0.3	16.39	53.63	26.85	64.23	
GP-0	0.5	31.09	61.43	34.48	58.36	
FGP-20	0.5	18.58	42.36	26.74	44.64	
FGP-40	0.5	13.48	38.77	19.91	41.73	
CGP-20	0.5	14.67	39.60	17.09	41.30	
CGP-40	0.5	8.82	34.35	12.14	37.25	

The control sample has a higher strength than those containing GP at all curing ages under standard curing conditions. This phenomenon can be attributed to the low GP reaction level and the increase in water to binder ratio at normal temperature. Elevated temperature can advance and improve the reactivity of GP and accelerate its pozzolanic reaction, leading to the generation of more C-S-H gel, which contributes to the strength development. GP is less reactive than cement, thus the latter is prior to reacting. The prior hydration of cement could make the pH value a little higher than 13.0 in a short time [15]. The high alkalinity in matrix breaks down the silica structure of the glass, and more silica and aluminum dissolve and participate in the pozzolanic reaction [16].

As for the fineness, small particles can dissolve in the pore solution, and then participate in the pozzolanic reaction to form stable C-S-H gel with low alkalinity [17]. With respect to large GP particles, hydroxide ions generally erode and dissolve the particles, then the released SiO_2 reacts with calcium hydroxide and high alkali C-S-H to form new hydration products until they all have been consumed. Then the generated low alkali C-S-H gel gradually cumulate around the GP and firmly link GP and the matrix to improve the strength.

3.3. Mercury intrusion porosimetry (MIP)

GP can significantly influence porosity, pore size distribution and pore shape of cement paste. Fig. 2 shows that the total pore volume of GP pastes is a little higher than that of pure cement paste. The hydration reactivity of GP is lower than that of cement (especially at early ages), thus generating fewer hydration products to fill the pores. But, GP changes the pore distribution of the paste. According to the pore size distribution, the pores in the paste are divided into four categories: aerogel pores (< 5 nm), mesopores (5-50 nm), medium capillary pores (50-95 nm) pores and large capillary pores (>95 nm) [18]. Fig. 3 shows the pore size distribution percent of three samples at 28 and 90 days. With the increase of curing age, the capillary pores decrease and turn into mesopores. The increase of total volume and the decline of capillary pores suggest that the rise of porosity attribute to the increase of pores smaller than 50 nm and thus improves the pore size distribution effectively, which will be beneficial to the strength and durability of the cementbased materials.

3.4. X-ray diffraction (XRD)

Fig. 4 and Fig. 5 show the hydration products of pastes under different curing conditions. Compared with the pure cement, no new diffraction peaks appears for the pastes containing GP, illustrating that GP does not modify the hydration products of the binder. The intensity of calcium hydroxide diffraction peak falls significantly with the increase GP content [19]. This may be caused by the pozzolanic reaction of GP, which consumes some Ca(OH)₂ [1]. In addition, cement content, which plays a dominant role in the generation of Ca(OH)₂ in the hardened pastes, decreases with the increase of GP content, contributing to the decline in number of generated calcium hydroxide.

When composite cementitious materials containing GP contacts with water, the clinker reacts preferentially and forms C-S-H gel, Ca(OH)2 and C-A-H etc. [20]. GP dilutes the concentration of cement, relatively improving the effective water for the cement hydration in the system. So, the reaction rate of pastes containing GP exceeds the pure cement at early hydration stage. In addition, the concentration of Ca²⁺ decreases because of the relative increase of effective water, which delays the saturation of Ca^{2+} and the induction period of hydration. As $Ca(OH)_2$ generates constantly, the pH value of the liquid phase increases. The dissociated hydroxide ions destruct and dissolve the silica vitreous, rupturing Si-O-Si to form Si-OH, leading to disaggregation caused by rupture of oxobridged oxygen bond in vitreous with irregular network structure. The process is as follows.

$$\equiv Si - O - Si \equiv +OH^{-} \longrightarrow \equiv Si - O^{-} + HO - Si \equiv.$$
(1)



Fig. 2. Effect of waste glass powder on pore size distributions of pastes at 28 days: a - cumulative curves; b - differential curves



Fig. 3. Effect of GP content on pore size distribution of the pastes at: a – 28 days and b – 90 days

Simultaneously, SiO_4^{4-} , Ca^{2+} and Na^+ are accumulating to reach a new saturation state, the process must be long enough to make the products interplay of various ions precipitate to realize the nucleation, growth of hydrates and the formation of a mesh structure. The process can be illustrated by Eq. 2:

$$xCa(OH)_2 + SiO_2 + mH_2O \rightarrow xCaO \cdot SiO_2 \cdot nH_2O.$$
 (2)

When the concentration of Ca^{2+} is relatively insufficient for SiO_4^{4-} , the cement hydrates C-S-H gel which has high pH value may participate in reaction to form hydrates with a low Ca/Si ratio [21]:

$$x (1.5 - 3.0) \operatorname{CaO}_2 \cdot \operatorname{SiO}_2 \cdot n\operatorname{H}_2 O + y\operatorname{SiO}_2 \rightarrow$$

$$z(0.8 - 1.5)\operatorname{CaO} \cdot \operatorname{SiO}_2 \cdot n\operatorname{H}_2 O.$$
(3)

According to the principle of chemical equilibrium and the dissolution equilibrium theory, the precipitation of low alkali C-S-H gel consumes large quantities of ions from liquid phase, which promotes the hydration of cement and the dissolution of GP to ensure the persistence of the reaction.

The intensity of the characteristic diffraction peak of $Ca(OH)_2$ in pure cement paste increases obviously after steam cured, which shows that high temperature can promote the hydration of cement effectively [22]. But the characteristic diffraction peak of CAH near 12° for pastes with and without GP almost disappears. This may be attributed to the conversion of calcium aluminate hydrates under high temperature. When the content of gypsum in Portland cement is low, it's possible to discern unhydrated

 C_3A in the system. The existing unhydrated C_3A can react with satureted sodium hydroxide solution [23]:

$$C_3A+CH_{12}+H=C_4AH_{13}.$$
 (4)

 C_4AH_{13} can exist in alkalescent medium containing CH in ambient temperature. However, the metastable C_4AH_{13} inclines to translate into C_3AH_6 under high temperature [23]. The transformation process is as follows: $C_4AH_{13}+C_2AH_8=2C_3AH_6+9H.$ (5)

From Fig. 4 and Fig. 5, it is obvious that the intensity o f the calcium hydroxide diffraction peak for samples cured $40 \,^{\circ}$ C is higher than that cured at normal temperature.



Fig. 4. XRD patterns of the pastes with and without glass powder at 28 days under standard curing condition

Elevated temperature can accelerate both pozzolanic reaction of GP that consumes CH and the hydration of cement which can generate CH. The amount of CH in blended binder incorporating GP depends on aformentioned two processes. All of these possible reasons cause the variation of Ca(OH)₂ characteristic diffraction peak, and the total Ca(OH)₂ content in the systerm.



Fig. 5. XRD patterns of the pastes with and without glass powder at 28 days under 40 °C steam curing condition

3.5. Scanning electron microscopy (SEM)

Fig. 6 a shows hydration products of the pure cement paste. Calcium silicate hydrate possesses a fibrous morphology, presenting itself radiated and agglomerated. It's hard to discern the needle-like ettringite from C-S-H. These hydrates overlap and connect with each other, binding unhydrated particles to form a mesh structure, which forms the skeleton of the system. The microstructure of the pure cement pastes at 28 days is porous and loose. Unlike Fig. 6 a, Fig. 6 b shows that pastes containing 20 % GP are a little denser, and it's difficult to identify hydrates in some parts. This may be attributed to that the smaller particles and wider grading distribution of GP could increase the stacking density of binders, decreasing void content in hydrates. Moreover, C-S-H gel generated from the pozzolanic reaction of GP decreases the pores volume. The shape of the C-S-H gel in pastes containing GP is abnormal short column and lamelliform, which differs from those in pure cement specimens. Fig. 6 c displays that the microstructure of the pastes containing 40 % GP is much denser. There is an obvious reaction ring along the GP. Different from ASR, there is no crack in or near the reaction ring. Pozzolanic reaction is found at the edge of particles. The generated C-S-H gel constantly fills the interfacial transition zone to ensure the consolidation of GP particles within the hydrate matrix.

4. CONCLUSIONS

- 1. GP can be used as mineral admixture in the cementbased materials. Compared with pure cement paste, the early strength of pastes containing GP is low. GP is temperature sensitive and has a higher tendency to participate in pozzolanic reaction under high temperature. GP with lower average particle size exhibits higher pozzolanic reactivity, thus improves the strength of the paste matrix.
- 2. The hydration process of composite cementitious material containing GP is similar to that of pure cement. With the increase of GP content in the composite cement, the occurring time of second exothermic improves, but the value of second exothermic peak and the cumulative hydration heat reduce.
- 3. The pore structure of pastes containing GP is much denser. The pores in the pastes containing GP become finer.
- 4. GP does not modify the type of the hydration products. GP pastes contain less $Ca(OH)_2$ because of pozzolanic reaction, but elevated temperature can promote the generation of CH in the early stage.
- 5. GP pastes contain much more C-S-H gel, resulting in a denser matrix and higher strength. The reaction ring along hydrated GP can be discerned in paste containing 40 % GP. The pozzolanic reaction of GP with high fineness enhanced the interfacial transition zone to avoid ASR.

Acknowledgments

This project is funded by the National Natural Science Foundation of China (51208391), Technology Project of Hubei Highway Administration (2013-731-2-3), and the Opening Funds of Guangxi Key Laboratory of New Energy and Building Energy Saving (15-J-22-4-001).



Fig. 6. a-SEM image of cement at 28 days; b-SEM image of GP20 at 28 days; c-SEM image of GP40 at 28 days

REFERENCES

- Schwarz, N., Cam, H., Neithalath, N. Influence of a Fine Glass Powder on The Durability Characteristics of Concrete and Its Comparison to Fly Ash *Cement and Concrete Composite* 30 (3) 2008: pp. 486–496.
- Qu, C., Gao, Z.Y., Liu, S.H., Zhao, D., Zeng, J.C., Huang, C.M. Application Research of Obsolete Glass Dust Used in RPC *Concrete* 55 (08) 2011: pp. 82–84.
- Liu, S.H., Xie, G.S., Wang, S. Effect of Curing Temperature on Hydration Properties of Waste Glass Powder in Cement-Based Materials *Journal of Thermal Analysis and Calorimetry* 119 (1) 2015: pp. 47–55. http://dx.doi.org/10.1007/s10973-014-4095-6
- Meyer, C. Recycled Glass-From Waste Material to Valuable Resource *Proceedings of the International Symposium: Recycling and Reuse of Glass Cullet* 2001: pp. 1–10.
- Ling, T.C., Poon, C.S., Wong, H.W. Management and Recycling of Waste Glass in Concrete Products: Current Situations in Hong Kong *Resources Conservation and Recycling* 70 (1) 2013: pp. 25-31. http://dx.doi.org/10.1016/j.resconrec.2012.10.006
- Shi, C.J., Zhen, K.R. A Review on the Use of Waste Glass in the Production of Cement and Concrete Resources *Resources Conservation and Recycling* 52 (2) 2007: pp. 234–247.
- Kim, J., Yi, C.K., Zi, G. Waste Glass Sludge as a Partial Cement Replacement in Mortar Construction and Building Materials 75 (2) 2015: pp. 242–246.
- 8. **Kou, S.C., Poon, C.S.** Properties of Self-Compacting Concrete Prepared with Recycled Glass Aggregate *Cement and Concrete Composite* 31 (1) 2009: 107–113.
- Rachida, I., Martin, C., Arezki, T.H. Use of Glass as ASR Inhibitor in Glass Aggregate Mortars *Construction and Building Materials* 24 (12) 2010: pp. 1309–1312.
- Nwaubani, S.O., Poutos, K.I. The Influence of Waste Glass Powder Fineness on the Properties of Cement Mortars International Journal of Applied Innovation Engineering Management 2 (2) 2013: pp. 110–116.
- 11. Shao, Y.X., Lefort, T., Moras, S., Rodriguez, D. Studies on Concrete Containing Ground Waste Glass *Cement and Concrete Research* 30 (1) 2000: pp. 91–100.

- Rachida, I., Martin, C., Arezki, T.H. Pozzolanic Properties of Fine and Coarse Color-Mixed Glass Cullet *Cement and Concrete Composite* 33 (1) 2011: 19–29. http://dx.doi.org/10.1016/j.cemconcomp.2010.09.013
- Federico, L.M., Chidiac, S.E. Waste Glass as a Supplementary Cementitious Material in Concrete – Critical Review of Treatment Methods *Cement and Concrete Composite* 31 (5) 2009: pp. 606–610.
- Rachida, I., Martin, C., Arezki, T.H. Use of Fine Glass as ASR Inhibitor in Glass Aggregate Mortars *Construction and Building Materials* 24 (12) 2010: pp. 1309–1312.
- Taylor, H.F.M. Cement Chemistry (2nd edition). Thomas Telford, London, 1997. http://dx.doi.org/10.1680/cc.25929
- Mohammadreza, M., Kyle, A.R. Effect of Curing Temperature and Glass Type on The Pozzolanic Reactivity of Glass Powder *Cement and Concrete Research* 58 (1) 2014: pp. 103–111.
- Rachida, I., Martin, C., Arezki, T.H. Pozzolanic Properties of Fine and Coarse Color-Mixed Glass Cullet *Cement and Concrete Composite* 33 (1) 2011: pp. 19–29. http://dx.doi.org/10.1016/j.cemconcomp.2010.09.013
- 18. Metha, P.K., Monterio, P.J. Concrete, Microstructure, Properties and Materials. McGraw-Hill, London, UK, 2003.
- Dyer, T.D., Dhir, R.K. Chemical Reactions of Glass Cullet Used as Cement Component *Journal of Materials in Civil Engineering* 13 (6) 2001: pp. 412–419.
- 20. **Yuan, R.Z.** Cementitious Material Science. Wuhan University of Technology Press. Wuhan, 1996.
- 21. Lothenbach, B., Scrivener, K., Hooton, R.D. Supplementary Cementitious Materials Cement and Concrete Research 41 (12) 2011: pp. 1244–1256. http://dx.doi.org/10.1016/j.cemconres.2010.12.001
- 22. Shi, C.J., Wu, Y.Z., Riefler, C. Characteristics and Pozzolanic Reactivity of Glass Powders *Cement and Concrete Research* 35 (5) 2005: 987–993. http://dx.doi.org/10.1016/j.cemconres.2004.05.015
- 23. Yuan, R.Z. Cementitious Material Science. Wuhan university of technology press, Wuhan, 1996.