CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 9, No. 2, 2015 Chemical Technology

Viktor Shevchenko and Galyna Kotsay

PROSPECTIVE OF GLASS POWDER AS ACTIVE ADDITIVE TO PORTLAND CEMENT

Department of Engineering, Mechanic and Petrochemistry,
Warsaw Polytechnic, Plock, Poland

Received: May 12, 2014 / Revised: May 28, 2014 / Accepted: June 25, 2014

Abstract. The usage of fine grinded silicate glass as an active additive to Portland cement has been considered in order to substitute neat cement in the cement composition, just as it is in EN 197-1 European standard by the example of active mineral additives of natural and artificial origin.

Keywords: glass powder, cement, glass grains surface, activation energy, compressive strength.

1. Introduction

The composites based on Portland cement are part of the composites widely used in modern building. EN 197-1 European standard represents 26 composites, where neat cement CEM I is partially substituted for active additives of natural and artificial origin, *e.g.* puzzolane materials, beaded slugs, *etc*. Silicate glass, including glass container wastes as the most widespread wastes, may be referred to them as well. Nowadays a great amount of crushed glass is accumulated throughout the world. It is an artificial material for the production of which considerable material and power resources were already used. That is why it is necessary to use such material effectively. One of the possible directions is using recycling glass as an active additive capable to substitute neat cement in the composites.

Recently a great number of works in this field has been published. Majority of them deals with the effect of fine grinded glass on the mechanical strength of Portland cement and products on its basis, as well as on the cement expanding after long keeping under various conditions. The latter property is very important because the increase in volume of the products formed by the reaction between glass and alkali in hardened cement may result in the appearance of cracks and damage of building constructions [1]. Taking this fact into account we consider it necessary to examine it separately from the mechanical strength.

The decrease in mechanical compressive strength of the samples made from cement paste was observed in [2]. For example, if the content of glass powder increases from 10 to 30 % in one-day samples, their strength decreases by 26 and 63 %, respectively, compared with that of the samples without additives. After 28 days the decrease is 19 and 54 %, respectively. While using glass for LCD screens, the chemical composition of which considerably differs from that of the container glass, the decrease in strength of one-day samples is 10 and 30 %, respectively (under the mentioned conditions); after 28 days – 6 and 25 %, respectively [3]. K. Sobolev *et al* [4] studied the effect of neat cement substitution for glass powder of different composition in the composition with gypsum and supersilica. For the composite composed of glass (50 %), cement (35 %), gypsum (5 %) and supersilica (10 %) the early strength (after 2 days) decreases by 40 % for window glass, by 55 % – for LCD-screen glass, by 50 % – for brown container glass and by 57 % – for green container glass. After 28 days the compressive strength achieves the corresponding values of the control samples. At the same time Z. Zainab *et al*. [5] show that mechanical compressive strength increases by 8 % after 3 days for concrete with 10 % of glass powder, and by 2.6 % – for concrete with 20 % of glass. After 28 days the decrease in strength by 8.5 % is observed for concrete with 10 % of glass powder and the increase by 4.3 % – for concrete with 20 % of glass. According to [6] the addition of 10 and 20 % of glass powder increases the strength of concrete by 16 and 25 %, respectively.

2. Experimental

Portland cement CEM I 32.5 R produced in accordance with European standards EN197-1 was used for the investigations. The chemical composition of cement and container glass is represented in Table 1. The strength of samples in the form of arms was determined according to the standard EN 196-1 and represented as the index of active strength (IAS). It is determined as a ratio between compression strength of the sample with additive and without it (check sample).

3. Results and Discussion

The analysis of publications shows that there is no agreement concerning fine grinded glass used as an additive or substitute for Portland cement. The first reason is that there are various types of container glass which sometimes considerably differ by their compositions. Moreover, in most cases the aspect of chemical interaction between glass and alkali at early and late stages of hydration is not taken into consideration. Actually every type of glass reacts with alkali in its own manner depending on its composition, especially the mix of glasses usually found while storing domestic wastes. The second important factor determining the possibility of glass wastes usage is its optimal quantity in the composition of cement composite. Literature data do not show a single opinion. In some publications [7] the maximum quantity of glass is limited by 0.1–1.0 % relative to cement weight, some references [8] allow using even 90 %. Such different estimations force to change the approach for solving problem.

To our mind, taking into account all above mentioned, it is necessary to base on glass behavior under cement hydration conditions. If we speak about container glass, we have multi-component alkali-silicate glass (Table 2).

The total content of alkaline oxides in the container glass is within 13–14 wt %. Taking into account that R_2O content in CEM I (EN 197-1) exceeds 1 %, as a rule (Table 3), the special procedure is necessary allowing to estimate the glass contribution into general alkalinity to prevent the intensification of alkaline corrosion at later stages of hardening [13].

Table 1

Chemical composition of Portland cement and container glass

Materials	Oxides, wt %								
	$Si0_2$	Al_2O_3	CaO	MgO	Na_20	K_20	Fe_2O_3	Cr_2O_3	SO_3
Cement	21.2	5.8	64.4	1.9	0.2	0.4	3.6	–	2.5
Colorless glass	72.2	1.8	10.10	1.65	13.19	0.61	0.04	0.01	0.4
Brown glass	72.15	1.75	10.0	1.55	13.79	0.16	0.25	0.03	0.32
Green glass	71.8	1.8	10.97	1.00	12.72	0.63	0.45	0.25	0.38

Table 2

Chemical composition of container glass based on different literature data

Glass	Ref.	Oxide (wt %)										
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Cr_2O_3	TiO_2	BaO
Colorless	[9]	72.50	0.16	0.20	9.18	3.65	13.20	0.12	0.39	–	–	–
	[10]	72.50	0.40	0.20	9.70	3.30	13.70	0.10	–	–	–	–
	[1]	72.17	1.35	0.07	10.92	1.10	13.13	0.61	0.09	<0.05	0.06	<0.05
	[3]	64.74	–	–	20.19	–	0.30	0.23	–	–	–	–
	[11]	73.04	1.81	0.04	–	10.75	–	13.94	0.22	–	–	–
Green	[11]	71.30	2.18	0.59	–	12.18	–	13.07	0.05	0.44	–	–
	[1]	71.24	1.61	0.32	10.79	1.57	13.12	0.63	<0.05	0.22	0.07	<0.05
	[12]	72.38	1.49	0.29	11.26	0.54	13.52	0.27	0.07	0.13	0.04	–
Brown	[11]	72.10	1.74	0.31	–	11.52	–	14.11	0.13	0.01	–	–
	[1]	72.08	2.19	0.22	10.45	0.72	13.71	0.16	0.05	<0.05	0.10	<0.05
	[12]	72.21	1.37	0.26	11.57	0.46	13.75	0.20	0.10	0.026	0.04	–
	[4]	71.19	2.38	0.29	10.38	1.70	13.16	0.70	0.04	–	0.15	–

Table3

Chemical composition of CEM I based on different literature data

Ref.	Oxide (wt %)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Cr_2O_3
[9]	20.33	4.65	3.04	61.78	3.29	0.24	0.59	3.63	–
[11]	21.24	5.97	3.34	62.72	2.36	0.13	0.81	1.97	–
[10]	20.20	4.70	3.00	61.90	2.60	0.19	0.82	3.90	–
[3]	21.65	6.50	3.20	63.70	1.90	0.01	0.62	–	–
[5]	21.14	5.78	3.59	64.43	1.52	–	–	2.35	–
[14]	20.40	5.68	2.85	64.50	1.09	0.18	0.64	–	>0.05
[15]	20.20	4.70	3.00	61.90	2.60	0.19	0.82	3.90	–
[12]	20.84	5.52	3.61	65.57	2.13	0.82	0.19	0.91	0.03

The variant when crushed glass is introduced into raw material while cement production is also possible. In such a case the alkaline oxides of glass transfer into cement composition increasing its alkali content. For example introducing 1.3 % of crushed glass the alkali content of cement is doubled (from 0.2 to 0.4 wt %) [16].

The situation is quite different if we add glass powder to cement. In such a case only Na^+ and K^+ ions participate in the chemical process. Ions are on the glass surface in no equilibrium state and their activation energy of leaching is 7 times (for K^+) and 13 times (for Na^+) less compared with activation energy of these ions diffusion in glass volume [17].

The preliminary estimate based on comparison of alkaline components quantity on the surface and in the volume of glass grains showed to minimize the effect of alkali content in glass powder on that in the cement composite, the content of glass powder in the composite should not exceed 1%.The similar conclusions were obtained by us on the basis of investigations about ASR-effect [7].

In the opinion of authors [18] the excess of alkali content above 0.4 mol/g increases the cement hydration rate in the early period that is a positive phenomenon in the case of glass powder addition. However the considerable excess of alkali in the cement composition with glass has a negative influence during late period of hardening because of increasing alkaline corrosion due to the following reaction with active SiO_2 of fillers:

$$SiO_2 + Na_2O + nH_2O \rightarrow Na_2SiO_3 \cdot nH_2O$$

As a result, sodium metasilicate absorbs the surplus water, washed out from the cement as gel and generates dangerous breaking stresses.

In the state of cement “false” setting till the moment of real setting the cement-glass system is in an active state, where chemical reactions take place affecting the structural matrix formation of future hydrated cement and its properties [19]. Without going too much into the chemical process mechanism let us note that the role of glass (content < 1 % in the composite) is only the insignificant increase of total alkalinity of the cement-glass system. Glass serves also as a crystallization nucleator of primary crystalline phase of Portland cement. The increase in R_2O content due to the increase in glass content (> 1 %) results in the glass additive transformation into a fine-grinded filler. While long-term hydration, especially under increased humidity the transformed filler becomes the potential danger for concrete constructions due to ASR-effect [1].

In the majority of investigations dedicated to the glass powder used as an active additive to Portland cement the quantity of introduced glass varies from 20 to 50 % [3, 4, 9-11]. However, taking into account the alkaline factor, the glass quantity should not exceed 1 %. Therefore we studied the compression strength of the samples with different quantity of glass powder of different types (Fig. 1) in order to determine the effect of glass powder quantity on the mechanical strength of cement products.

One can see that the early strength (after 2 days of hardening) increases by 5–17 % depending on glass type. This result is observed only for the samples with 1 % of glass powder. However after 28 days of hardening their strength is lower by 20–30 % compared with that of the check sample. It means that glass powder is the active additive only during early stages of hardening. Further the glass is non-effective and serves as an ultradispersed filler.

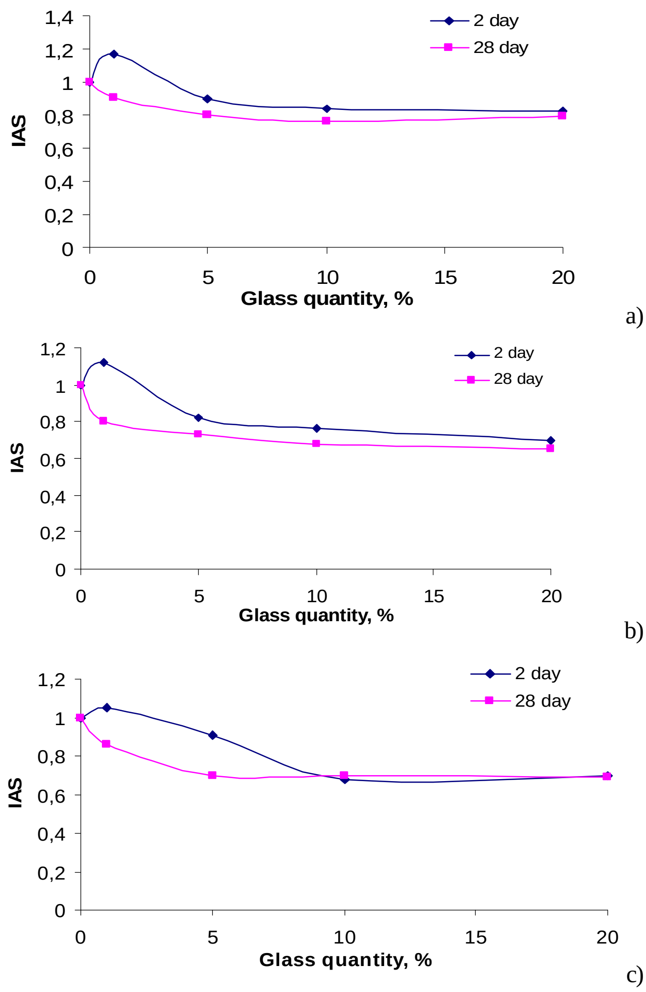

Fig. 1. Dependence of glass quantity in cement composite on IAS for different types of glass: colorless (a); brown (b) and green (c)

Taking into account that water-cement ratio (W/C) for the majority of cement products is within the range of 0,4-0,6 and the activity of glass component in the composite depends on W/C [7] we may assert that this ratio should be 0.6 for real influence on mechanical strength of cement with glass maximum allowable content of 1 % (Table 4).

Table 4

Dependence of cement strength on water-cement ratio and glass type

Glass type	Glass quantity	CEM I 32.5R* IAS** after 28 days	
		Concrete C20 W/C = 0.60	Concrete C20 W/C = 0.50
Colorless***	1 % over 100 %	1.32	0.86
Brown***	„–„	1.37	0.96
Green***	„–„	1.43	0.98

* According to EN197-1 European standard

** IAS-index of active strength; it is determined from the ratio of compression strength of the sample with glass to the compressive strength (Rcs, MPa) of control sample

*** Chemical composition of glasses are represented in Table 2, pos. [7]

Table 5

Dependence of standard samples strength on W/C and glass content

Glass quantity	W/C ratio	CEM I 32.5R IAS Rcs (MPa) after 2 days of hardening	CEM I 32.5R IAS Rcs(MPa) after 28 days of hardening
1.0 % over 100%	0.50	1.18	1.08
1.0 % over 100%	0.60	1.35	1.00

For C20 concrete based on neat Portland Cement at W/C = 0.5 we observe the insignificant decrease of mechanical strength for all types of glass (Table 4). The increase of W/C ratio to 0.60 increases the strength by 30–40 % depending on glass type. Hence, the main factor affecting the glass additive activity is a water-cement ratio, ***i.e.*** the increase of glass-liquid phase ratio. It favors the effective proceeding of the reaction between glass and liquid phase and as a result increases mechanical strength and terms of setting beginning and ending [20].

To check the assumption about influence of W/C ratio on the compressive strength of cement with green glass additive (as the most effective type of glass) we investigated cement standard samples. The results are given in Table 5.

The presented results also confirm the increase in mechanical strength with the increase of W/C ratio. It should be also stressed that glass powder favors the increase of early strength (after 2 days of hardening). After 28 days we observe some decrease in strength but it is at the level of control samples. So, in our opinion, the glass grains in the composition of cement composite serve as crystallization nucleators of main crystalline phase of cement and increases strength while early hardening. But when crystallization process is going stronger, the glass role is hidden. Thus, glass powder in small quantity (0.1–1 % relative to cement weight) is an accelerator of setting and hardening at early stage of cement composite hydration.

4. Conclusions

On the basis of literature data and our own investigations we may assert that optimum quantity of glass powder additive is 0.1–1.0 % relative to Portland cement weight. In such a case the powder plays a role of the active additive and accelerates cement hydration at early stages. However if the content exceeds 1 %, the glass powder transforms into the fine-grinded filler capable to intensify the alkaline corrosion of cement. Therefore it is hardly to expect the wide application of glass wastes as the additives to the cement composites similar to European EN 197-1.

The important factor determining the additive activity is water/cement ratio. Its increase to 0.6 leads to the increase of glass-liquid ratio intensifying ASR-effect. Among three main types of recycling glass the green glass is the most active. It additionally contains Cr_2O_3 which catalyzes the conversion of calcium hydro silicate CSH(I) into 1,4-tobermorite as one of the primary crystalline phases of post induction period of Portland Cement hydration [21-23].

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ПЕРСПЕКТИВИ ВИКОРИСТАННЯ СКЛЯНОГО ПОРОШКУ ЯК АКТИВНОГО ДОДАТКУ ДО ПОРТЛАНДЦЕМЕНТУ

Анотація. *На основі проведеного аналізу літератури показано значний вплив лужної складової скла на загальний луговміст цементних композитів. Встановлено, що при заміні 1 % цементу на скляний додаток спостерігається збільшення міцності цементних розчинів тільки на початкових стадіях твердіння. Встановлено, що дрібномелене скло є прискорювачем процесу твердіння цементних розчинів, при цьому важливу роль відіграє водоцементне відношення.*

Ключові слова: *скляний порошок, цемент, питома поверхня, енергія активації, міцність на стиск.*