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A MECHANISM OF PORTLAND CEMENT HARDENING IN THE PRESENCE OF FINELY GRAINED GLASS POWDER

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Abstract. Glass wastes as a cullet are used in the production of building materials mainly as an inert aggregate. However, finely grained glass powder with its well developed surface can not be regarded as passive toward cement solutions whish has actually been proven in practice. Literary sources provide no information about chemical influence of finely grained glass on the process of hardening, especially in its early pre-induction hydration period – the period which considerably conditions the cement stone structure formation and its properties.

Key words: finely grained glass powder, cement, binding, hardening, hydration, modifier

1. Introduction

Glass industry wastes and glassware cullet are widely used in the production of different building materials mainly as an inert aggregate. This is due to the fact that glass is an ecologically safe material and has an artificial origin. It is important to distinguish two types of glass wastes: fine filling agent (1–5 mcm) and finely grained powder (10–50 mcm). The first one is ineffective as an additive to concretes, whereas the second one in certain amounts may be used as an artificial active additive to cement [1].

According to the literary sources [2] the use of the grinded glass (10 to 40 %) of different chemical structures instead of cement decreases compression strength of samples by 42 %. However, exchange of sand as a fine filling agent for the same amount of grinded glass has practically no impact on the compression strength. Therefore, in a great amount finely grained glass is not an active additive to cement.

As it has been shown in our previous investigations [3], addition of finely grained glass to cement even in an amount of 0.5–1 % increases the strength of cement solution and concrete samples. This fact corroborates an active role of finely grained glass in the process of hardening and cement stone structure formation. Moreover, such negligible amount is capable of affecting the duration of the binding process and thus can be an accelerating or retarding agent of the hydration process.

The aim of this work is establishing the role of finely grained glass powder in the cement hydration process from the moment of water adding to the end of the hardening process depending on chemical and fractional composition of the glass powder, as well as assessing the role of the powder as an active additive to the formation of cement stone structure.

2. Experimental

The following investigation methods have been used: microcalorimetry, X-ray diffractometry, IR-spectroscopy, thermoanalysis. CEM I 32.5R cement complying with the EN 197-1 European standard has been used as an initial material. Container glasses of different chemical compositions (green, brown and colorless) have been used as additives. The chemical compositions of different glasses are shown in [1]. It should be noted that these glasses differ by the content of alkaline oxides and R_2O_3. In the previous investigations it had been established that 1 % of finely grained glass powder is an optimum amount of additive, which was added to the cement mass in solution or concrete. In all the cases water:cement ratio was 0.5.

3. Results and Discussion

It is well-known that glass is a material with an amorphous structure, characterized by a large supply of free energy. At comminution and grinding plenty of disrupt structural unsaturated bonds are being formed, which explains considerable activity of glass powder. Multicomponent glass – the glass that has been used in our investigations –contains approximately 14 mass % of Na_2O and K_2O. In the glass structure the ions of these metals have considerably less binding energy as compared to covalent bond of Si-O in the structural fragment of $Si\text{-}O^{-+}Na$ or $Si\text{-}O^{-+}K$.

In water solution Na^+ and K^+ ions are easily diffused from glass to the solution and form sodium and potassium hydroxides in the solution, correspondingly. They are displaced by H^+ ions from water and thus hydrate the surfaces of glass grains. This is a so called ion-exchange mechanism of interaction between glass and water. Since the area of glass grain surface is very large, comparable to the area of cement grain surface, ionic exchange is very active. Titration analyses show that alkalinity of cement solution without glass additives is near 6 ml of 0.1N HCl. Separate glass powder in water under normal conditions has alkalinity in the range from 0.15 (colourless glass) to 0.55 ml of 0.1N HCl (green glass). Thus, the total alkalinity has to increase, however alkalinity of cement mixture with glass additives is 35-40 % less. In our opinion, it is connected with high content of SiO_2 in the glass (near 70 %), which results in the formation of calcium hydrosilicate (CSH), see reaction (1):

$$\underset{\text{cement}}{Ca(OH)_2} + \underset{\text{glass}}{SiO_2} + (n-1)H_2O = \underset{\text{a phase in a cement stone}}{CaOSiO_2 \cdot nH_2O} \quad (1)$$

As a result of reaction (1) the amount of calcium hydroxide in the cement solution decreases. Consequently, the alkalinity of solution with glass powder additives decreases as well and additional amount of CSH crystal phase in a cement stone is formed. This fact is confirmed by the decrease of intensity of lines d = 4.90 E (see Fig. 1).

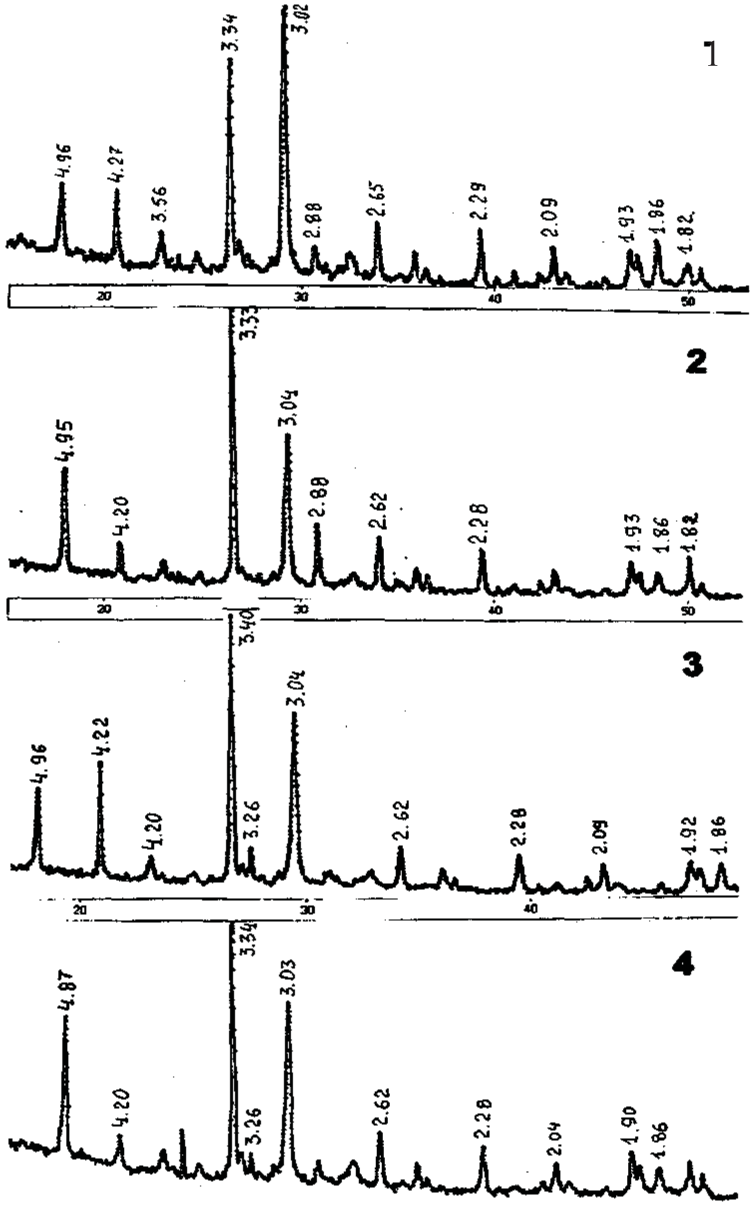
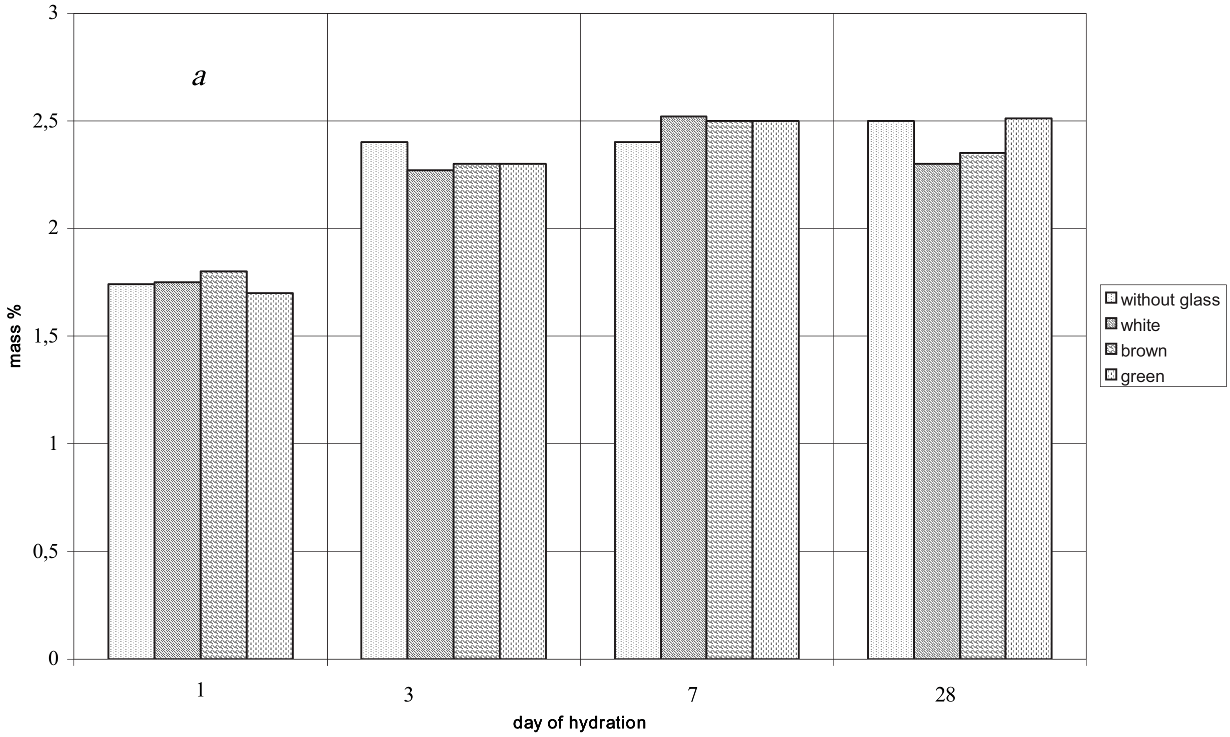


Fig. 1. X-rays of cement stone with glass powder additives: control sample without glass (1), sample with 1 % of colourless glass (2), sample with 1 % of brown glass (3), sample with 1 % of green glass (4)



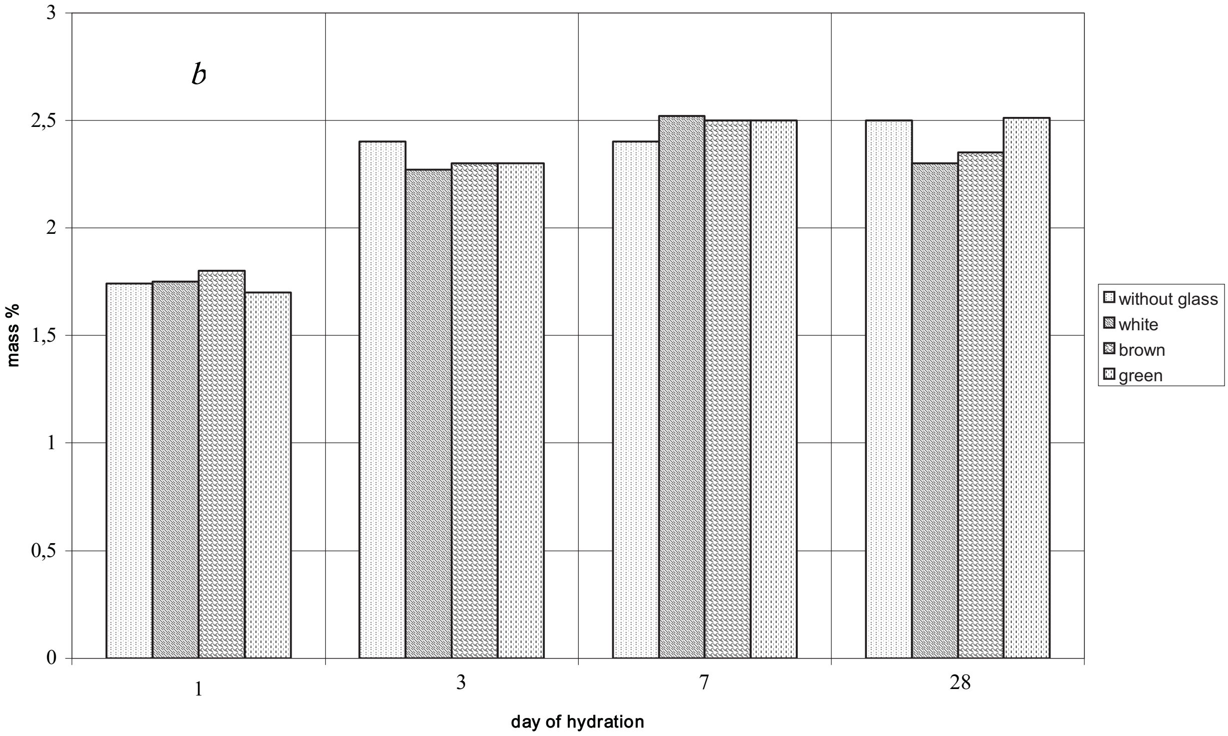


Fig. 2. Mass losses of cement stone within temperature interval up to 723 K determined by thermoanalysis: up to 683 K (a), up to 723 K (b)

The results of differential thermoanalyses of cement stone samples (Fig. 2) also confirm the abovementioned supposition. It is known that mass losses of cement stone samples in the interval up to 683 K are connected with water separation from hydrates of CSN type. After the first day of hydration the mass losses of the samples with green glass increase. The mass losses of other samples, including control sample, are around 8 %. After three and seven days of hydration mass losses of the samples with glass are higher by 0.2-0.4 % than of those without glass, which indicates the increase in CSN amount in the samples with glass. Mass losses in the range of 683–723 K are caused, first of all, by $Ca(OH)_2$ decomposition. As the increase in CSN amount and concomitant hydrates in the presence of glass powder should be accompanied with reduction of $Ca(OH)_2$ amount, mass losses of samples with glass should be less than mass losses of the control sample. We observed this phenomenon after 3 and 28 days of hydration.

The obtained results allow explaining the reasons of mechanical strength increase in the samples with glass powder. It is connected, first of all, with the increase of CSN amount and appearance of accompanying hydrates, which quasi additionally link the structure of cement stone as bundles of short crystals-fibers oriented in different directions [4-5]. It means that finely grained glass powder modifies the structure of cement stone via leaching process, i.e. chemically. As a result, the cement stone properties, first of all its mechanical strength, are changed. If we consider the effect of glass chemical composition on the modification process, we can conclude the following: the lower chemical stability of the glass, i.e. the greater amount of alkalis in the glass composition, the greater effect on the modification of glass.

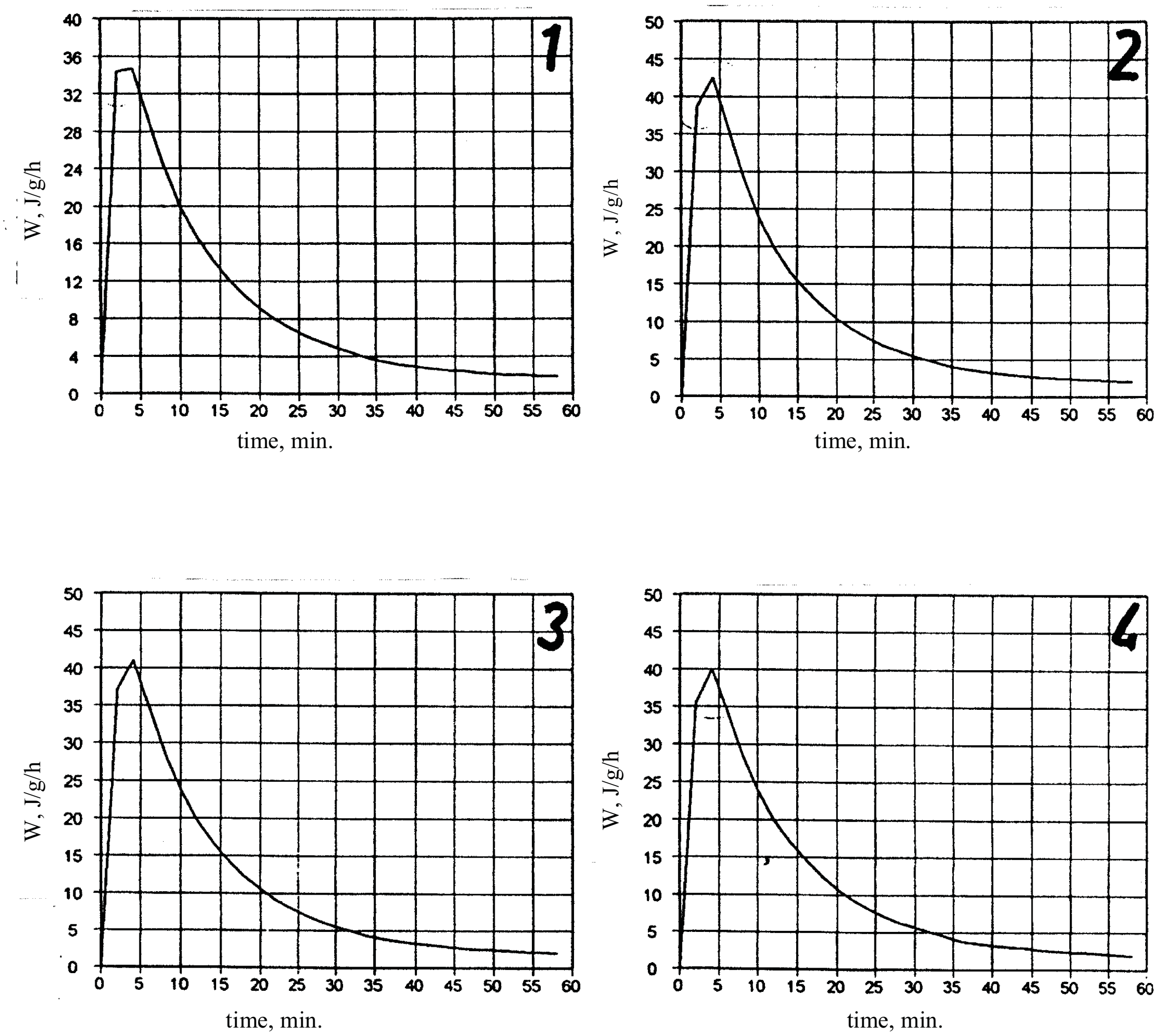


Fig. 3. Thermal balance of cement solution during preinduction period of hydration process [7]: control sample without glass (1); sample with 1 % of colorless glass (2); sample with 1 % of brown glass (3); sample with 1 % of green glass (4)

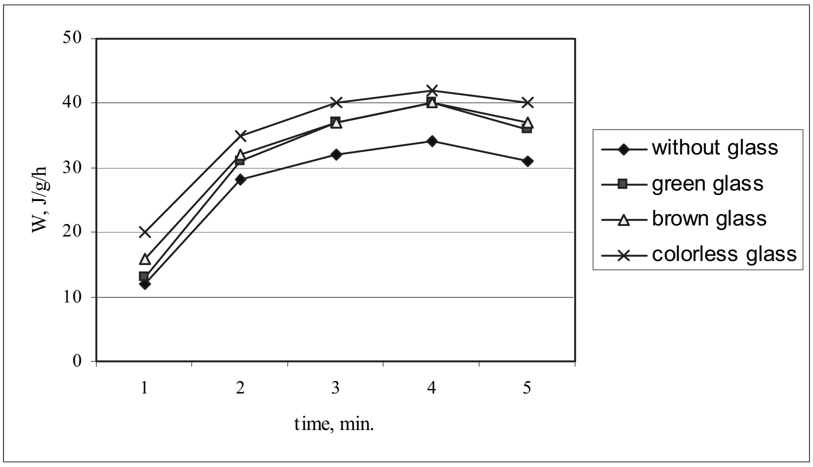


Fig. 4. The change of heat evolution rate during preinduction period at Portland cement hydration

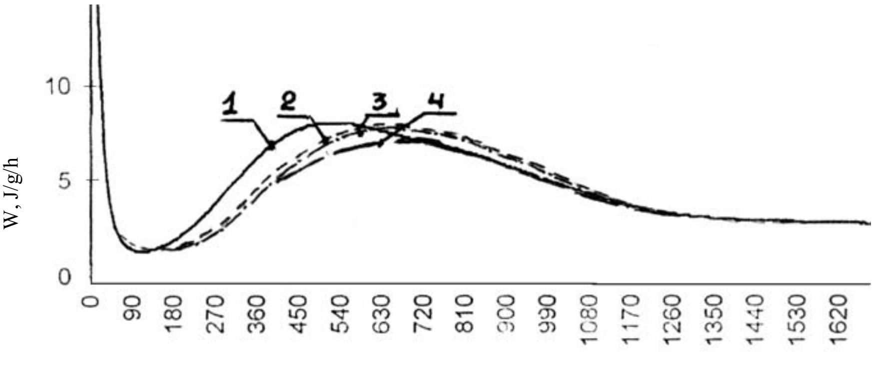


Fig. 5. Microcalorimetric curve of cement hydration determined for 48 hours: Cem-1 control sample (1); Cem-1 + 1 % of colorless glass (2); Cem-1 + 1 % of brown glass (3); Cem-1 + 1 % of green glass (4)

In view of the chemical action of finely grained glass over the hydration process, the problem of such influence from the moment of water addition to preliminary mixed cement and glass powder in corresponding proportions, is of great interest.

In terms of the modern theory of solutions [6], the determination of thermodynamical characteristics of hydration process is very important. Calorimetric methods are used for this purpose. In our case we have used microcalorimeter capable of measuring thermal effects under isothermal conditions. Heat evolution rate *W*(*J/g/min*) has been used as an estimation criterion. The dependence of heat evolution rate in the cement solution upon hydration time during 60 minutes is represented in Fig. 3.

In Fig. 4 we can see a sharp increase in heat evolution rate during the first two minutes for all samples. During the period from minute 2 to 3 the rate increases slightly and achieves its maximum after 4 minutes of hydration. Then the rate decreases. It is connected with the output of Ca^{2+} ions from cement to water solution, as the process is exothermic [8]. It should be noted that during the whole explored period the values of the control sample are 20 % less than those of the samples with glass. Finely grained glass is an additional source of Na^+ and K^+ ions, which results in heat evolution rate rise. Hence, during preinduction period (2–4 min.) the glass additives accelerate cement hydration process. However, heat evolution rate decreases for the samples with glass after two hours of hydration. Such difference lasts for almost 17 hours and then disappears (Fig. 5).

Thus we can conclude that after two hours glass additives retard hydration process as glass takes away part of water for its own hydration instead of cement hydration.

4. Conclusions

It has been established that addition of finely grained glass to portland cement or to portland cement based concrete accelerates the binding process during preinduction period of hydration (2–4 min.) but retards it during after-induction period. However, this does not affect the mechanical strength of the concrete samples after the first day of hardening. The strength of samples with glass is higher as compared to the control samples, because, as has been stated above, glass additives modify cement stone structure.

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МЕХАНІЗМ ТВЕРДІННЯ ПОРТЛАНДЦЕМЕНТУ В ПРИСУТНОСТІ ДРІБНОЗМЕЛЕНОГО ПОРОШКУ СКЛА

Анотація. *Відходи скла у вигляді скляного бою досить широко використовуються для виробництва будівельних матеріалів переважно як інертний наповнювач. Однак дрібнозмелений порошок скла має дуже розвинену поверхню, і, в зв'язку з цим, не може вважатися пасивним відносно цементних розчинів, що і було підтверджено на практиці. В літературі відсутні відомості про хімічний вплив дрібнозмеленого скла на тверділня, особливо на початку передіндукційного періоду гідратації, який значною мірою зумовлює формування структури цементного каменю та його властивості.*

Ключові слова*: дрібнозмелений порошок скла, цемент, зв'язування, тверділня, гідратація, модифікатор.*