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Pozzolanic reactivity of recycled glass powder at elevated temperatures: Reaction stoichiometry, reaction products and effect of alkali activation

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ABSTRACT

Use of glass powder as concrete SCM or in development of lime–pozzolan binders could provide environmental and economical benefits. In exposure to an alkaline pore solution, glass powder (GP) dissolves and reacts pozzolanically with calcium hydroxide (CH). In this paper, the stoichiometry and products of this reaction are studied using a CH–GP binder system cured at 60 °C. TGA, selective acid dissolution, SEM/EDS, and QXRD methods are used to quantify the stoichiometry, and characterize the reaction products as a function of age. It is determined that approximately equal masses of CH and GP react with each other and with water to produce C–S–H. Both crystalline and amorphous C–S–H are formed, but the crystalline C–S–H is favored at later ages and higher alkalinities. NaOH-activation accelerates the reactions. However when high alkalinity is maintained, GP continues to dissolve after complete consumption of CH, and forms alkali–silicate gels, which could be expansive and deleterious.

1. Background on using recycled glass in concrete

Application of recycled soda-lime glass (bottles, window plates) as a concrete constituent has been studied in the last two decades [1–13]. While one approach is to use glass cullet as fine aggregate replacement, it is more economically and environmentally attractive to use finely ground glass powder (GP) as a supplementary cementitious material (SCM) [14]. Also, the consistency in composition and mineralogy of glass powder, specifically in locations where good quality SCMs are not available, adds to the value of GP as a SCM. Another potentially valuable approach could be to use GP in combination with hydrated lime ($Ca(OH)_2$, also abbreviated as CH) in a portland cement-free lime–pozzolan binder [15,16].

In our previous studies [1–3], it was shown that soda-lime glass can undergo both alkali silica reaction (ASR) and pozzolanic reaction in concrete. While the exterior surface of glass particles – where $Ca(OH)_2$ precipitates – undergoes a pozzolanic reaction, the internal surfaces of particles (i.e., internal micro-cracks) undergo ASR deterioration (Fig. 1). These internal micro-cracks form initially during crushing glass bottles to obtain aggregates. It was also determined that the degree of cracking and crack widths within glass particles significantly impact the ASR reactivity of glass [3]. Glass powder has been shown not to cause ASR since it only has a small number of thin internal microcracks. In addition, it was shown that wider cracks of larger particles can be healed through thermal annealing before using glass aggregates in concrete to obtain recycled glass sand with lower risk of ASR [3]. The present work focuses on pozzolanic reaction of soda-lime glass powder.

A pozzolanic reaction is the result of interactions between amorphous siliceous materials (e.g., glass powder, silica fume, fly ash, etc.) and calcium hydroxide, leading to formation of calcium silicate hydrates (C–S–H) as the main product. It is known that utilization of pozzolanic SCMs in concrete leads to superior long-term durability performance. Yet, there are some challenges; for example, lower early age strength of concrete containing SCM in comparison with 100% ordinary portland cement (OPC) concrete. This is due to the slower rate of pozzolanic reaction comparing to the hydration of portland cement. There are different factors determining the rate of pozzolanic reaction: composition and crystallinity of the SCM, particle size of SCM, pore solution pH, and curing conditions (i.e., temperature and relative humidity). The dissolution rate of amorphous silica is known to be the rate-determining step during pozzolanic reaction [17].

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The strength of concretes containing glass powder has been studied with different particle sizes of glass powder and different replacement dosages of portland cement. While Shayan and Xu [4,5] found that the early and long term strengths (up to 404 days) of concretes with glass powder of smaller than 10 μm is lower than a control plain concrete, Shao et al. [6] have found higher strength at 90 days for concretes containing 30% glass powder of smaller than 38 μm. Also, Shi et al. [7], have shown that the compressive strength of mortars containing 20% fine glass powder (specific surface area = 467 m^2/kg) is higher than the control mixture at 28 days based on ASTM C311 strength activity index. In addition, they have reported that increasing the curing temperature to 65 °C results in a higher strength of 20% GP mortars even at 3 days comparing to the control mortar. More recent studies [18,19] also documented the effectiveness of increasing the curing temperature on accelerating the pozzolanic reaction of glass powder. The study by Idir et al. [8] showed that replacing cement with soda-lime glass powder of specific surface area 540 m^2/kg (particles smaller than 41 μm) results in strength of glass powder concrete catching up to a 100% OPC concrete at about 90 and 210 days for cement replacement levels of 10% and 40%, respectively. Dyer and Dhir [9] studied the effect of glass powder (GP) replacing up to 40% mass of OPC, and concluded that GP does not have a significant effect on the hydration rate of portland cement itself. Schwarz and Neithalath [20] reported higher pozzolanicity of soda-lime glass powder comparing to fly ash, and also suggested that glass powder releases only a small fraction of its alkalis into the pore solution. Shi and Zheng [10] and Federico and Chidiac [11] have published review papers on using recycled glass in concrete, and the latter has suggested the use of alkali activation to enhance the pozzolanic performance of glass powder; an approach which is further studied in this work. It should be noted that, as documented by the results of the present study, alkali activation can improve the kinetics of pozzolanic reaction of glass powder and could be very useful for lime–pozzolan binders [16]. At the same time, alkali activation may be harmful to hydration of portland cement. As such, further research is needed to evaluate the feasibility of using alkali activation in OPC concrete to enhance the pozzolanic reaction of SCMs.

2. Research objectives

To develop concrete materials containing glass powder SCM, it is important to know the correct proportioning and materials processing procedures that result in optimum mechanical, durability, and environmental performance. Past studies [4–11] have used arbitrary dosages of glass powder and curing methods, and evaluated their impact on concrete properties. To provide a better understanding of the pozzolanic reaction of glass powder (GP) with calcium hydroxide (CH), this paper for the first time:

- Measures the quantitative stoichiometry of CH–GP–water (or 1 M NaOH solution) pozzolanic reaction.
- Identifies the composition and mineralogy of reaction products.
- Evaluates the effect of alkali activation on the rate of pozzolanic reaction.

The pozzolanic reaction is studied using a CH–GP binder system (no portland cement) instead of a more complex OPC–GP binder, to allow for a more accurate characterization of the reactions by eliminating the effects of simultaneous OPC hydration. In addition, the experiments are performed at 60 °C to accelerate the rate of pozzolanic reaction and allow a more conclusive study within a feasible time span. Increasing the temperature primarily influences the reaction kinetics, but it may also affect the degree of crystallinity of the resulting C–S–H. The authors acknowledge that, the quantitative results obtained are the most precise for the exact experimental conditions studied (e.g., in development of heat cured lime–pozzolan binders activated by water or NaOH). In addition, these findings could be valuable, at least qualitatively, for a more general case of using glass powder SCM in portland cement binders that are cured at room temperature.

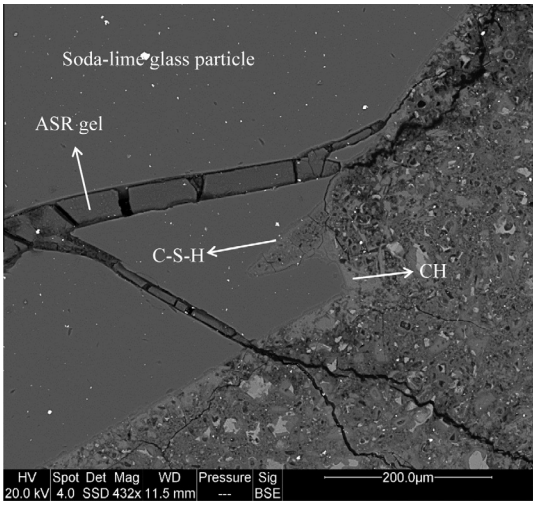

Fig. 1. Alkali silica reaction occurring in the interior of a soda lime glass particle, while the particle surface undergoes a pozzolanic reaction.

3. Theoretical considerations on stoichiometry of the pozzolanic reaction

The chemical reaction between a pozzolan and calcium hydroxide results primarily in formation of calcium silicate hydrates (C–S–H) that could have various compositions and structures. A large number of calcium silicate hydrates have been identified in the literature; Richardson [21] has tabulated many types of C–S–H materials with their exact compositions and crystal structure. One important factor which influences the composition and properties of the resulting C–S–H is the concentrations of the reactants in pore solution, specifically the relative availability of Ca and Si. For example, it is known that in a calcium-rich system (e.g., during hydration of portland cement), C–S–H that is compositionally similar to jennite (Ca/Si = 1.5) can precipitate [22]:

$$9Ca(OH)_2 + 6SiO_2 + 2H_2O \leftrightarrow (CaO)_9(SiO_2)_6(H_2O)_{11} \quad (1)$$

However, in systems with lower availability of calcium or high Si concentration (e.g., during a pozzolanic reaction), formation of C–S–H that is similar to tobermorite (Ca/Si = 0.83) is more likely:

$$5Ca(OH)_2 + 6SiO_2 + 3H_2O \leftrightarrow (CaO)_5(SiO_2)_6(H_2O)_8 \quad (2)$$

Eqs. (1) and (2) provide stoichiometric information. For example, in Eq. (1), 1 g SiO_2 reacts with 1.85 g $Ca(OH)_2$ and 0.1 g water to form 2.95 g jennite; while in Eq. (2), 1 g SiO_2 reacts with 1.03 g $Ca(OH)_2$ and 0.15 g water to form 2.18 g tobermorite. It should be noted, however, that these stoichiometric values are approximate as (a) solid solutions of different C–S–H types or of C–S–H and CH can form, and (b) the water content can vary widely, specifically when the material is exposed to external drying or self-desiccation. Also, the curing temperature influences the crystallinity of the resulting C–S–H, with high temperatures favoring a higher degree of crystallinity [23].