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The effect of CaO/SiO₂ molar ratio of CaO-Al₂O₃-SiO₂ glasses on their structure and reactivity in alkali activated system

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ABSTRACT

The influence of CaO/SiO₂ molar ratio of calcium aluminosilicate glasses on resulting structure and reactivity was investigated. Chemical compositions of glasses were chosen to mimic the composition of the fly ash and slag amorphous phase. Understanding the reactivity of these materials is of high importance allowing further development of the composite cements to limit the environmental footprint of cement industry. Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were employed to examine the structure of glasses. Reactivity of the glasses was analyzed on paste samples after 1, 2, 7, 28 and 90 days of curing by means of thermogravimetry (TGA), X-ray diffraction (XRD) and FTIR. Spectroscopic results emphasize dependence of the structure on the chemical composition of the glasses. The higher CaO/SiO₂ the more depolymerized the glass network is, though there is no direct correlation with the reactivity. Significant differences in reactivity is observed primarily between the glasses of peraluminous (CaO/Al₂O₃ < 1) and percalcic region (CaO/Al₂O₃ > 1). Amongst the pastes made of glasses of percalcic region a higher degree of reaction at later ages is observed for the paste containing glass of lower CaO/SiO₂ molar ratio. This is due to both degree of depolymerization and the nature of these glasses (pozzolanic and hydraulic materials). No difference of degree of reaction has been observed within the glasses of CaO/SiO₂ lower than 1.

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1. Introduction

Nowadays due to economic and environmental reasons production of composite cements containing supplementary cementitious materials (SCMs) is common [1,2]. SCMs constitute large group of cement components that show pozzolanic or hydraulic behavior [3], or are little reactive like limestone [3,4]. SCMs such as fly ashes (FA) or granulated blast furnace slag (GBFS) are industrial by-products of manufacturing processes which are produced in higher temperatures (~1300–1600 °C). Rapid quenching results in vitrification of the majority of these materials. Chemically they are characterized by the reduced CaO but increased content of Al₂O₃ as compared to PC clinker [3]. Composite cements blended with high quality FA or GBFS show improved long term strength and durability features [5–7]. Hence they relatively quickly become a commodity deficit because of their availability and cost [8,9]. In consequence, industry is forced to search for newer solutions which is usually obtained by looking for other materials having similar properties or introducing more advanced multi-component systems. In recent years utilization of waste glass [10–13] as well as use of

laboratory synthesized glasses [14,15] as SCMs has been an object of the researchers study. Moreover many studies have proved that addition of limestone induce a positive impact on the early compressive strength of the FA [4,16] and GBFS [17,18] containing composite cements, i.e. so called filler effect [19]. Additionally, limestone reacts with alumina bearing clinker phases from clinker and with SCMs like fly and slag glass [20,21] leading to formation of carbonate-AFm (hemi- and monocarbonate) phases that is accompanied by the stabilization of ettringite content. These modification of the phase assemblage results decrease in porosity and in a consequent increase in strength [4,21,22].

Phase composition has an important impact on SCMs performance [23–27] amongst the other characteristics. It has been established that the amorphous phase is the most reactive phase in SCMs like GGBFS and fly ashes [26]. Except of some reactive crystalline components that can be found in calcareous fly ashes, crystalline phase (e.g. quartz, mullite) are consider to be inert (or react imperceptibly slowly) constituent that do not take part in hydration processes. Structure of the amorphous phase of SCMs is composed of Si and Al tetrahedra joined by bridging oxygen (BO) in two ways Si—O—Si and Si—O—Al. These aluminosilicate framework is characterized by varying degree of polymerization [23]. Due to charge balancing requirement of the [AlO₄]⁵⁻ units structural role of Al is more complex and is a function of CaO/Al₂O₃ (C/A) ratio [28]. When the charge compensating cation exist

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enough for Al in percalcic glasses ($C/A > 1$) all Al act as a network former for the formation of $[\text{AlO}_4]^{5-}$ tetrahedra. An excess of the non-frame-work cations (Na^+ or Ca^{2+}) can depolymerize the aluminosilicate networks by forming NBO (non-bridging oxygen). On the other hand in peraluminous join ($C/A < 1$) not enough Ca atoms are available for charge compensation of $[\text{AlO}_4]^{5-}$ tetrahedra, therefore Al may occur in five- and six-fold coordination [29,30]. Degree of depolymerization of $[\text{SiO}_4]^{4-}$ limits dissolution rate of glass upon contact with the highly alkaline solution present over the cement hydration [31]. Taking into account that chemical composition determines degree of depolymerization of $[\text{SiO}_4]^{4-}$ anions significant differences in reactivity of slag and fly ash glasses with different structure is certain. This in turn determines the overall rate of hydration of cement and its characteristics [32,33]. Understanding of the reactivity of the glasses is important for the cement industry because it enables the further progress in the clinker reduction and use of the full potential of SCMs. The parametric approach in cement development fails because the cement composition is complicated and interaction between the cement components multiple. The generic models are needed to optimize the cement composition. That is why authors undertaken the effort to progress in the understanding the correlation between the chemical composition, glass structure and the reactivity in cement conditions. The simplified system has been chosen to show the effect of CaO/SiO_2 on the structure and reactivity of the presented glasses as well as to understand the specific role of alumina under changing $\text{CaO}/\text{Al}_2\text{O}_3$ molar ratio. Presented approach allows to develop the research by systematic addition of other constituents of SCMs glasses (e.g. Fe_2O_3 , MgO). The effect of other network modifiers such as Na^+ , K^+ on the network modification was neglected on purpose as they induce comparable changes in the glass network as Ca^{2+} , are present in minor extent in FA and GBFS and may volatilize at higher temperature.

In this paper we present comprehensive study on the structure of four $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses along the percalcic and peralkaline joins. Chosen compositions are important especially when concerning chemistry of Portland cement. Three of them represents variability of chemical composition of siliceous and calcareous fly ash (F and C type acc. to ASTM C618) glasses and one glass introduce granulated blast furnace slag (GBFS) composition. The far-infrared (FIR), middle-infrared (MIR) and Raman spectroscopy were employed to obtain detail information on the structure of the synthesized glasses. X-ray fluorescence (XRF) allows to compare targeted chemical composition with acquired one. Thermogravimetry analysis (TGA), powder X-ray diffraction (XRD) were used to characterize hydration product and to determine reactivity of the glasses. Finally MIR spectroscopy allowed to establish the nature of bonds occurred in the studied hydrated pastes.

2. Materials and Methods

2.1. Synthesis of Glasses

Due to complex chemical composition of amorphous phases of fly ashes (FA) and granulated blast furnace slags (GBFS) commonly used in cement industry a description of the structure and their potential reactivity in the cementitious environment is complicated. Therefore model glasses were examined with compositions consisting of three oxides, namely CaO , Al_2O_3 and SiO_2 which FA and GBFS are principally abundant in. Consequently G1 glass was prepared with composition within primary field of crystallization of mullite, G2 and G3 of anorthite and G4 of gehlenite (Fig. 1). Chosen approach allow to examine the influence of calcium on the structure and properties of glasses in two regions: peraluminous where molar ratio of $\text{CaO}/\text{Al}_2\text{O}_3$ (C/A) is lower than 1 (G1 and G2) and percalcic where C/A molar ratio is > 1 (G3 and G4).

Glass batches were prepared by melting analytically pure components: $\text{Al}(\text{OH})_3$, amorphous SiO_2 and CaCO_3 . Compounds proportions were chosen to acquire final composition of the glasses shown in the

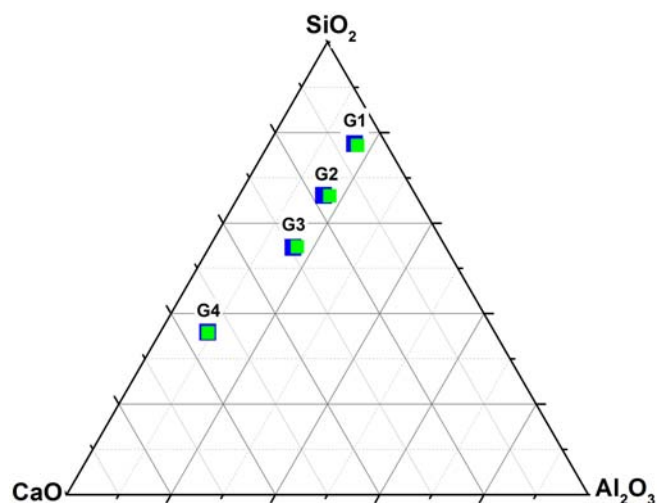


Fig. 1. Targeted (blue squares) and nominal measured by means of XRF (green squares) chemical composition of the glasses (in mol %) in the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1. Batches of about 2.3 kg were first homogenised for 24 h in plastic barrels with valves inside. Ten rubber stoppers in different size were placed into the barrel to improve mixing process. Subsequently homogenised batches were calcinated in ceramic crucibles in electric furnace in temperature $1000\text{ }^\circ\text{C}$ (temperature rise $300\text{ }^\circ\text{C}/\text{h}$) for two hours. The calcinated material was placed again into the barrel and homogenised for another 4 h. Last step was to sieve the lot through a mesh of 1 mm. Finally batches were melted in graphite crucibles in induction furnace in about $1800\text{ }^\circ\text{C} \pm 50\text{ }^\circ\text{C}$ and held constant for 30 min at targeted temperature. In order to produce vitreous structure molten glasses were rapidly quenched in water ice bath. Finally, after drying 200 g of glass were grind for 2 h in ceramic mill and then sieved through $63\text{ }\mu\text{m}$ mesh. Oversized material was returned to the mill. Chemical composition of the synthesized glasses was determined by X-ray fluorescence (XRF). The results of the analysis are presented in Table 1 as well as depicted in Fig. 1.

2.2. Experimental Mix

Synthetic mixes of glasses, portlandite and limestone were prepared to study the reactivity of the glasses. $1\text{ mol}/\text{dm}^3$ NaOH solution was used (pH 14) to accelerate the reaction. Mixes of the following composition were prepared:



Clinker was excluded on purpose to simplify the working system. Resulting mixes are named after the kind of glass incorporated into the paste therefore MG1, MG2, MG3 and MG4 are discussed.

Table 1
Nominal glasses composition analyzed by means of XRF and molar ratios of individual oxides.

Type of glass	Chemical composition						Molar ratio of oxides	
	[wt%]			[mol %]			C/S	C/(A + S)
	Al_2O_3	SiO_2	CaO	Al_2O_3	SiO_2	CaO		
G1	26.3	69.1	4.7	17.3	77.1	5.6	0.07	0.1
G2	26.7	59.4	13.9	17.5	66.0	16.6	0.25	0.2
G3	26.1	49.8	24.1	16.9	54.7	28.4	0.52	0.4
G4	15.3	34.8	49.9	9.3	35.7	55.0	1.54	1.2

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