

WASTE GLASS POWDER-BASED ALKALI-ACTIVATED MORTAR

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Abstract

The global warming ensues from the emission of large amount of greenhouse gases in the atmosphere. The part of the carbon footprint attributed to the concrete becomes more and more important due to the cement content and the increase of the worldwide demand for concrete. Although much is done to reduce the environmental impact of concrete with the use of supplementary cementitious materials, the best alternative can be the development of new Portland cement-free binder through alkali-activation of waste products. This paper deals with the development of waste glass powder (GP) based alkali-activated mortar. Metakaolin (MK) is used to replace a part of glass powder in order to introduce Al and also to stabilize alkali ions in the system. The effect of NaOH concentration and MK content on the mechanical and microstructural properties of mortars are studied. Results show a gradual increase in the mechanical properties of the mortar with more cohesion between the paste and sand aggregates when MK is added up to 8%. In contrast, without MK or with less than 3% of MK content, the compressive strength decreases with the time with a poor cohesion between the paste and aggregates. Moreover, the NaOH concentration of 5M is enough to activate the studied system as a high level of concentration induces a delay in the geopolymer gel formation. According to the first results, this glass powder based geopolymer seems promising and further studies need to be carried out.

Keywords: carbon footprint, glass powder, geopolymer concrete, cementitious material, alkali-activation

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1. INTRODUCTION

Concrete is one of the most widely used building materials in the world. The cement constitutes the main element that provides the binding and the good mechanical properties of concrete. The demand in cement keeps on increasing due to the global population growth particularly in the emerging and developing countries [1]. The demand of cement for 2010 was estimated at 3310 million metrics [2]. However, the cement industry produces 5 to 8% of the atmospheric CO₂ in the world [3]. The production of one tonne of clinker, which accounts for 95% of the Portland cement composition, generates about one tonne of CO₂. The carbon dioxide (CO₂), largely responsible for the increase in greenhouse gas effect, contributes significantly to climate change [4] resulting in the rise of the global average surface and sub-surface ocean temperatures [5]. Although much is done to reduce the environmental impact of concrete with the use of supplementary cementitious materials in replacement of part of the cement, the carbon footprint of concrete remains high. One of the best alternative can be the development of new Portland cement-free binder through alkali-activation of waste products. These binders known as alkali-activated materials have been studied for the first time and patented in 1908 by Kühl [6] who, by combining a vitreous slag and an alkali sulfate or carbonate with or without added alkali earth oxides or hydroxides obtained a good performance materials comparable to Portland cement. Purdon [7,8] is the first one who developed in more detail the scientific basis for these binders in 1940 by testing several different blast furnace slags activating by sodium hydroxide or by the combination of Ca(OH)₂ and different sodium salts. However, it is only in the last decades

especially since the 1990s that alkali activation research has grown significantly in the world due to the environmental issues related to the Portland cement. The advantage of these binders is that large variety of alumino-silicate material sources often industrial by-products such as fly ashes, slag with an amorphous phase can be activated. Several activators such as alkali sulfate, carbonate, hydroxide or silicate can be used. Alkali (especially Na or K) silicates are by far the activators that lead to the formation of materials with higher performances [9,10] and show the greatest industrial relevance in alkali activation [11].

Furthermore, non-recycled glass constitutes one of the most wastes produced in some countries and sets a major environmental issue. Unlike other forms of waste including paper or organic constituents, waste glass bottles will remain stable after their disposal in landfills. Although, this mineral material can be used several times without significant changes in its chemical and physical properties, the recycling of glass except for clear one, remains negligible. The use of GP in alkali activated system can be useful due to its alkali and silicate content. Actually the GP contains almost 13% of Na₂O. The high Na content of GP could allow to reduce the concentration of NaOH solution used as activator.

This paper deals with the development of waste glass powder based alkali-activated mortar. MK is used to replace a part of glass powder in order to introduce Al and thus form geopolymer gel. The microstructural and mechanical properties of mortars were investigated.

2. EXPERIMENTAL PART

2.1 Materials

Table 1: Chemical composition of GP and MK

| Materials | Chemical composition | | | | | | | | | |
|--------------|----------------------|--------------------------------|--------------------------------|-------|------|-----------------|------------------|-------------------|------|---------------------------------|
| | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O | LOI | Na ₂ O _{eq} |
| Glass Powder | 72.66 | 1.57 | 0.39 | 11.41 | 1.24 | 0.07 | 0.54 | 12.89 | 0.38 | 13.24 |
| Metakaolin | 49.92 | 27.61 | 12.28 | 3.71 | 0.93 | 0.30 | 1.82 | 0.35 | 1.90 | 1.54 |

Table 2: Mix designs of geopolymer mortars.

| No | Sol.NaOH/ PV+MK | E/L* | Slump (mm) | PV (%) | MK (%) | NaOH (M) | Si/Al | Al/Na |
|----|--------------------|------|---------------|-----------|-----------|-------------|-------|-------|
| 1 | 0.60 | 0.45 | 210 | 100 | 0 | 5 | 39.29 | 0.05 |
| 2 | 0.60 | | 210 | 97 | 3 | 5 | 21.33 | 0.09 |
| 3 | 0.60 | | 210 | 95 | 5 | 5 | 16.29 | 0.12 |
| 4 | 0.60 | | 210 | 92 | 8 | 5 | 11.98 | 0.16 |
| 5 | 0.70 | | 230 | 95 | 5 | 8 | 16.29 | 0.09 |
| 6 | 0.76 | | 230 | 95 | 5 | 10 | 16.29 | 0.08 |

* Calculated considering the total water and the total solids (glass powder+metakaolin+NaOH)

The glass powder obtained by milling mixed recycled bottle glass is provided by a sorting center. The mean diameter of particle size is about 13 μm with a density of 2.56 g/cm^3 and a fineness of 4400 cm^2/g . Its chemical composition shown in Table 1 is determined by X-ray fluorescence by means of Axios-Advanced apparatus. The so-called soda-lime silicate glass powder is mainly composed of 72 % SiO₂, 13% Na₂O and 11% CaO. The metakaolin provided by a local company is obtained by calcining kaolin at 700°C (Table 1). Its density and fineness are 2.67 g/cm^3 and 21400 cm^2/g respectively. GP and MK are both amorphous. However, MK contains a crystalline phase such as quartz. NaOH solutions with concentrations of 5, 8 and 10 M prepared by dissolving NaOH pellets (99%) in distilled water were used to activate the glass powder containing 0, 5 and 8% of MK as replacement.

2.1 Mortars Mixed and Methods

Mortars composed of 1 part binder and 2.75 parts of sand were made in accordance with the ASTM C 109 standard using Ottawa normalized sand. The water to binder ratio was 0.45 for all samples. In order to dissolve a part of amorphous silica, the glass powder was mixed with NaOH solution during 2 minutes. MK was immediately added and the procedure for mixing mortar recommended by the ASTM C305 standard was followed. Flow of geopolymer mortars was measured under the fixed designation according to the ASTM C 1437 standard and the results are showed in Table 2 along with the mix designs. Mortars samples were

thermally activated at 60°C during 2 days and cured at 20 °C and 50% humidity until the compressive strength tests at 7, 28 and 91 days. Compressive strength were conducted on the 50x50x50 mm cubes in accordance with the ASTM C109 standard. Microstructural changes were also studied according to the MK content and NaOH concentration at 28 days using a scanning electron microscopy coupled with energy dispersive X-ray microanalysis (SEM/EDS).

3. RESULTS AND DISCUSSION

3.1 Compressive Strength

3.1.1 Effect of Metakaolin Content

Fig. 1 shows the effect of the MK content on the compressive strength of mortar. The incorporation of MK in the glass powder leads to a decrease in the compressive strength at 7 days. This can be explained by the formation of Si-O-Al bonds which are less strong than Si-O-Si present in the activated GP without MK. The compressive strength decreases with time for mortars that contain up to 3% (samples 1, 2) of MK. However, when the MK content is superior or equal to 5 % (samples 3, 4), the compressive strength which was initially low increases with the time. The decrease in the compressive strength of mortars that contain low MK could be due to the high free alkali content. As MK is well known to possess good capability to fix alkali ions [12]. The fixation of alkali ion within the geopolymer matrix make denser and compacter the gel leading to a progressive increase in the resistance. Therefore, a decrease in the silica

content, i.e. from Si/Al ratio of 39.29 (sample 1, 0%MK) to 11.98 (sample 4, 8%MK) leads to an improvement of the compressive strength that increases gradually. These results are in accordance with those observed by Lee et al [13]. According to these authors, an increase in the silica content or the rise in Si/Al modulus makes difficult the formation of the gel by reducing the bonds between particles inducing a decrease in the resistance with the time.

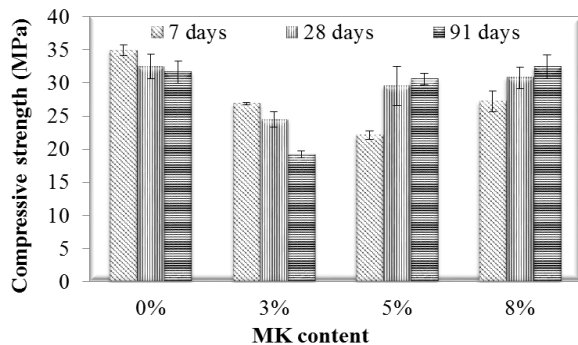


Fig. 1: Effect of the MK content (samples 1-4) on the compressive strength of mortars activated with NaOH 5M.

3.1.2 Effect of NaOH Concentration

The effect of NaOH concentration was also studied and the results are presented in the Fig.2 for samples containing 5% of MK (samples 3, 5 and 6). The compressive strength decreases with increasing NaOH concentration. This result suggests a delay in the geopolymerization process when the concentration is too high due to the limitation of the ion mobility and the stability of ions species [12]. In fact, the rate of dissolution of aluminosilicates in alkaline solutions increases with the hydroxide ion concentration. Alonso and Palomo [12] pointed out that a high concentration of the activator fosters the dissolution process of the solid network but delays the geopolymerization due to the low mobility of alkali ions and thus limiting their diffusion through the solution. The excess of NaOH could induce the formation of a non-uniform reaction product resulting in a reduction of the gel resistance. These results suggest the existence of a threshold concentration beyond which a higher concentration of sodium hydroxide may cause an increase in the amount of dissolved species, and their great difficulty to diffuse into the aqueous phase. In addition, the Na content of the glass powder induces an increase in such an ion in the system. Therefore, for glass powder-based geopolymer, low concentrations of activator will be sufficient to obtain good mechanical properties especially in the conditions of our study.

3.2 Microstructural Study

3.2.1 Effect of Metakaolin Content

Fig. 3 gathers the microstructures of GP mortar activated with and without MK after 28 days of reaction. The activator used is a NaOH solution of 5 M. A denser matrix can be observed in the presence of metakaolin with more cohesion between the sand grains and the paste.

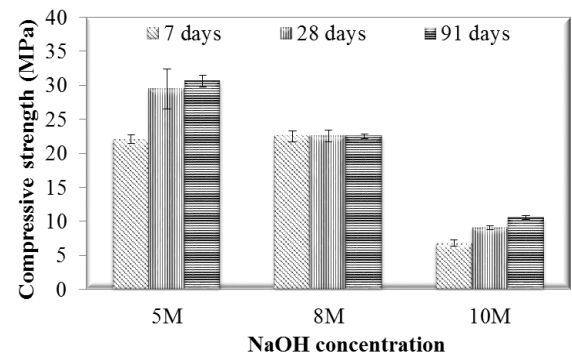


Fig. 2: Effect of NaOH concentration (samples 3, 5, 6) on the compressive strength of GP mortars containing 5% MK.

In contrast the GP mortar activated without metakaolin shows low cohesion between the paste and aggregates. These results are in accordance with the gradual enhancement of the compressive strength when MK was added unlike its decrease without or with low ($\leq 3\%$) MK content. The improvement of the microstructure features of mortars containing 8% MK can be attributed to the stabilization of some alkali ions in the NASH gel formed due to the introduction of aluminum from MK. Since it is well known that in the framework of geopolymer gels, the Si^{4+} and Al^{3+} cations are tetrahedrally coordinated and linked by oxygen bridges and the negative charge on the AlO_4^- is charge-balanced with alkali cations (Na^+ or K^+) [14]. Thus, in such a system, alkalis are fixed and constitute part of the gel network unlike in the mortar without metakaolin where unbound alkali can weaken the gel network resulting in low cohesion and the decrease in the compressive strength.

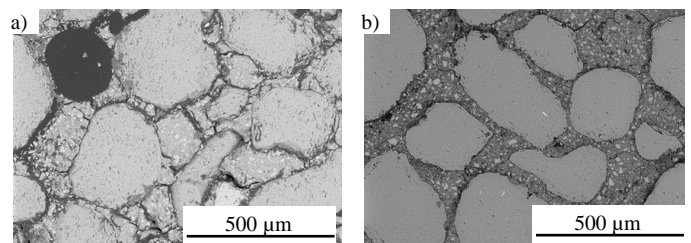


Fig. 3: Microstructure of the mortar activated with NaOH 5M after 28 days: a) 0 % of MK (sample 1) and b) 8% of MK (sample 4).

The energy dispersive spectroscopy (EDS) microanalysis of the gel reveals the presence of calcium silicate hydrate (C(N)-S-H) type gel in the GP mortar activated without MK (Fig 4, a (A)). This gel has almost the same composition as the glass powder (Table 1) with similar $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio (~ 0.18). However, the calcium content in the gel seems to be high, as $\text{Na}_2\text{O}/\text{CaO}$ decreases from 1.2 in the glass particle to 0.79 in the gel confirming the formation of C-S-H type gel with very low C/S (0.23) ratio allowing the incorporation of a high amount of sodium cations. Furthermore, in the presence of MK, both C-S-H and N-A-S-H are present (Fig 4, b). The formation of both gels indicates the glass powder dissolution and also the participation of metakaolin in the gel formation resulting in the reduction of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from almost infinity to

approximately 8%. In addition, the decrease in Na₂O/Al₂O₃ ratio to 1.90 confirms the fixation of a large amount of alkali ions by aluminum atom from the metakaolin and the stability of ions species through the charged-balance with Na⁺ cations inside the gel structure further to the substitution of Si⁴⁺ atoms by Al³⁺ atoms [14,15].

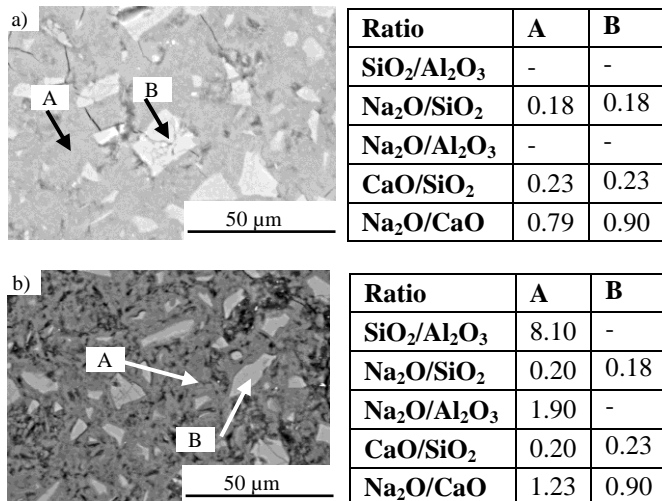


Fig. 4: EDS of the mortar activated with NaOH 5M after 28 days: a) 0 % of MK (sample 1) and b) 8% of MK (sample 4), A: gel and B: unreacted glass particle.

3.2.2 Effect of NaOH Concentration

The changes in the microstructure of mortars according to the NaOH concentration is shown in Fig.5. The increase in the concentration of NaOH solution from 5 M to 10 M induces the formation of a heterogeneous gel resulting in a significant carbonation (dark part) due to the high amount of unbound alkali ions. This is in line with the decrease in the compressive strength when the NaOH concentration increases. Moreover, the cohesion between the paste and aggregates lowers with NaOH concentration.

In addition, for the NaOH concentration of 10 M (Fig 5c), the gel seems to be absent confirming the delay in the geopolymerization process with high NaOH concentration. Therefore, the increase in the NaOH concentration promotes the dissolution process instead of geopolymerization [12]. As already observed with samples containing various amount of metakaolin, the EDS results corroborate the presence of both C-S-H and N-A-S-H gel for NaOH concentration of 5M and 8M (Fig 6a & b). However, no gel can be observed with NaOH concentration of 10M (Fig. 6c) Instead, the chemical analysis reveals high level of carbonation for the 10MNaOH samples resulting in a strong concentration of carbon (70.7%). This result is in accordance with the prevalence of the dissolution over the geopolymerization. Thus, in such a system, low NaOH concentration (~5M) is enough to form geopolymer gels with good performance.

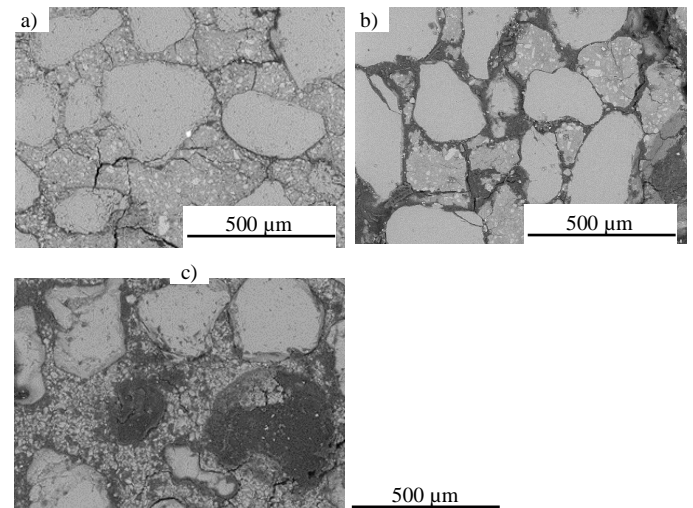


Fig. 5: Microstructure of the mortar containing 5% MK activated with: a) 5 M (sample 3), b) 8M (sample 5) and c) 10M (sample 6) of NaOH after 28 days of reaction.

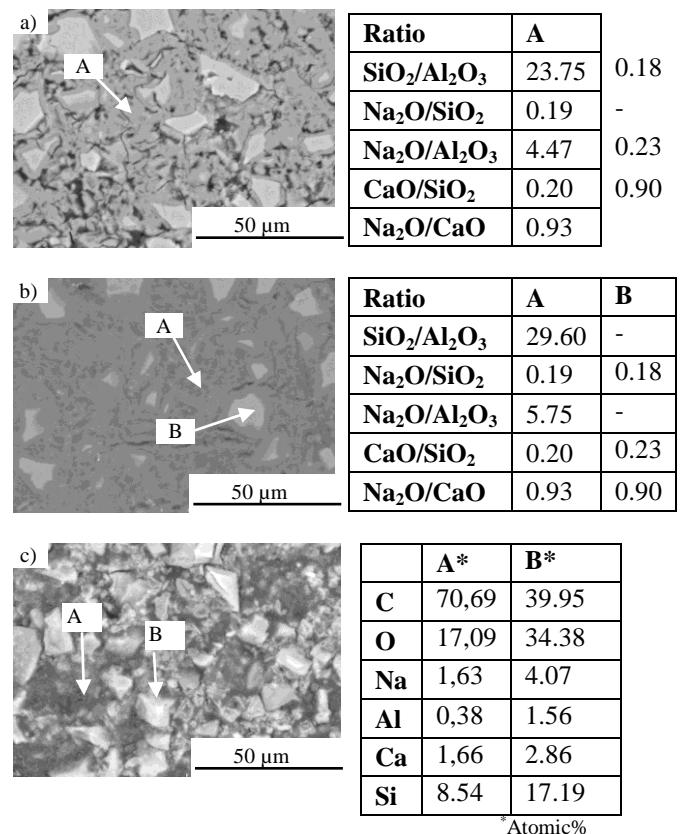


Fig. 6: EDS of the mortar containing 5% MK activated with: a) 5 M (sample 3), b) 8M (sample 5) and c) 10M (sample 6) of NaOH after 28 days of reaction. A: gel and B: unreacted glass particle

4. CONCLUSIONS

This study shows the possibility to use glass powder as material source and activator precursor. Indeed, the activation of glass powder allow the use of less concentrated sodium hydroxide (5M). The addition of aluminum source such as metakaolin is necessary to fix alkali ions in the matrix and thus form a denser gel. The activation of glass

powder reveals the presence of calcium silicate and sodium silicate hydrate (C(N)-S-H) type gel while in the presence of MK, both C-S-H and N-A-S-H are present. The presence of N-A-S-H type gel due to the addition of MK, allows the stabilization of alkali ions. In this work, only up to 8 % of MK can be added, which is not enough to stabilize all alkali ions. But, above 8 % of MK, the workability is worst due its high fineness.

Therefore, the next step of this work will be focused on the study of the effect of superplasticizer on the workability of GP mortar containing high amount of MK in order to find a suitable dispersant agent.

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