WASTE GLASS REUSE IN GEOPOLYMER BINDER PREPARED WITH METAKAOLIN

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Abstract

This work involves valuing residual waste from a glass coming from a recycling station in a geopolymer matrix. This type of waste contains mineral impurities called "infusibles" characterized by a very high melting temperature compared to traditional glass which makes it difficult to use it as glass cullet. The objective of this study is to use this waste as a source of silicates in a geopolymer reaction in combinations with aluminosilicates sources such as Metakaolin (MK).

For that, the first step was to characterize the different raw materials used. A quantitative chemical analysis was carried out by X-Ray Fluorescence and crystallography was determined by X-ray diffraction. The second step focuses on the dissolution of the WG structure. For that, three treatment programs have been realized modifying factors such as temperature (20°C and 90°C) and alkalinity (with sodium hydroxide 10M). After attack of WG, the elements Si^{4+}, Al^{3+}, Ca^{2+} and Mg^{2+} were quantified by ICP-OES analysis. In the last step, the reactivity of glass after the different treatment programs was evaluated by the study of the mechanical behavior of mortars including the glasses and metakaolin (MK), which is a source of aluminosilicates.

Keywords:

Waste glass, alkaline activation, glass treatment, mechanical properties

1 INTRODUCTION

Numerous studies deal with recycling of waste glass. Some of them concern the development of an alternative material for construction in order to minimize the use of natural resources, and so, reduce economic and environmental impacts of these wastes. The alkali-activation and geopolymerisation are important routes for the fabrication of a new binder very friendly for the Earth, in which Ordinary Cement Portland is totally replaced by geopolymer binder. This type of binders allows to decrease the emission of greenhouses by 45 to 64% [Torres 2015].

In this work, waste glass was treated and incorporated as activator in a geopolymer matrix. Metakaolin (MK) was chosen as aluminosilicate source. Moreover, a comparison was made with different glass treatment in order to select the best silica source. A lot of analysis were performed in this study for characterizing raw materials and 4x4x16 specimens, like helium pycnometer (absolute density), gas adsorption method (specific surface), particle-size distribution performed in dry route, X-ray crystallography and X-ray Fluorescence (chemical composition of major elements), and mechanical tests. The soluble fraction of elements was analyzed by FTIR (Fourier Transformed Infrared Spectroscopy) for the modifications of solid structure.

2 CHARACTERIZATION OF MATERIALS

Glass is a non-porous material. Its external surface is in contact with the environment. That's why the fineness of the glass plays a key role in its reactivity. The finer the glass particles and the greater specific area, the higher is its contact surface with the reaction medium. This relationship has also been verified in several types of reactions, including pozzolanic and alkali-silica reactions [Idir 2011][Idir 2010]. Similarly, in other applications such as geopolymerisation and alkaline attacks, fineness remains an important factor [Torres 2015][Al-Sibahy 2012][Dron 1993]. This is the reason why the glass should be crushed finely to increase the reaction power of this type of waste. Another interest of grinding is to limit the alkali-silica reaction of glass aggregates with alkaline medium in case the aggregate attack is partial, since the concentration of NaOH leads to the formation of gel with the glass aggregates. This

gel is large and leads to the swelling of the structures [Idir 2010]. The glass waste was crushed using an air jet disposer (NETZSCH). Grinding parameters are optimized in order to reach the target size of d50 = 6.5µm. Figure 1 shows the fineness of the materials used in this study. The MK has a particle-size distribution similar to the one of the Cement Portland with d50 = 16µm and d90 = 27µm.

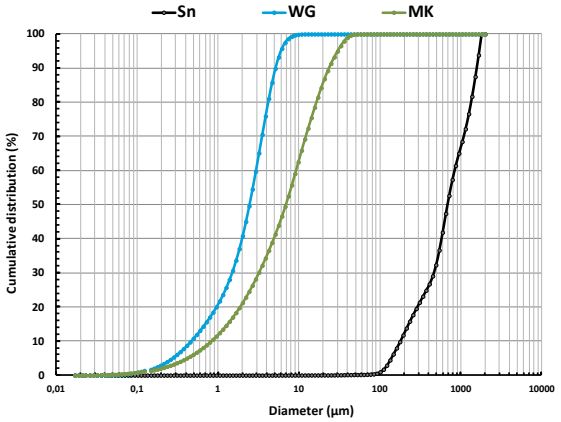

Fig. 1: Particle-size distribution of Normalized Sand Sn, WG and MK

Analysis by x-ray diffraction and x-ray fluorescence were performed at powder state (d50 = 8µm and d90 = 16µm). The chemical composition and crystallography are the main factors influencing the reactivity of the waste glass in the matrix geopolymer. The chemical analysis given in Tab.1 indicates that WG has a mineral nature, is rich in silicon, and contains calcium and sodium in non-negligible quantities. The main elements are silicon (71%SiO_2), calcium-(12%CaO) and sodium (13%Na_2O). In other hand, mineralogical crystallography performed by X-Ray Diffraction (XRD) highlights the amorphous structure of waste glass (Fig. 2).

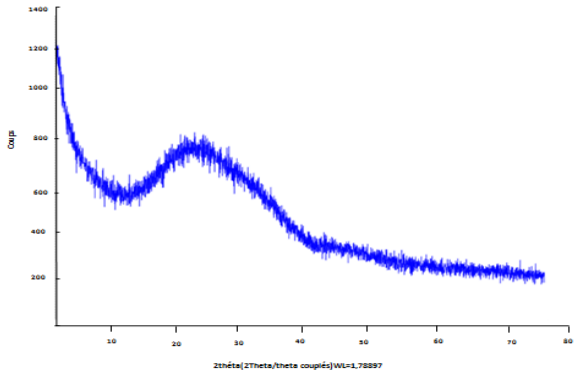

Fig. 2: XRD Analysis of WG

An appropriate chemical composition and an amorphous structure are two key parameters to hope to have a good reactivity of the glass in cementitious matrix as pozzolanic element in partial replacement of Portland Cement [Bouchikhi 2019]. Another possibility to add glass in the matrix is by geopolymerisation [El Hafid 2018][Duxson 2007] after activation since waste glass can represent a source of Si, Ca and Na.

3 ACTIVATION OF WG BY NAOH TREATMENT

3.1 Method of activation

Treatment of glass powder by sodium hydroxide leads to deconstruction of glass structure and liberation of the majority of elements which reorganize themselves in other phases very soluble in water. This new structure brings more reactivity for these elements and precisely for Si, Al, Ca and Na in the geopolymerisation. The program for heat treatment was chosen according to the study of Torres and al. [Torres 2014], study in which treatment is made at 90°C during 6 hours and d90 of powder is lower than 45µm. In order to reduce the duration of treatment from 6 to 4 hours, d90 was fixed to 16µm. Fig. 3 presents the global experimental protocol for the treatment and analysis of powder WG.

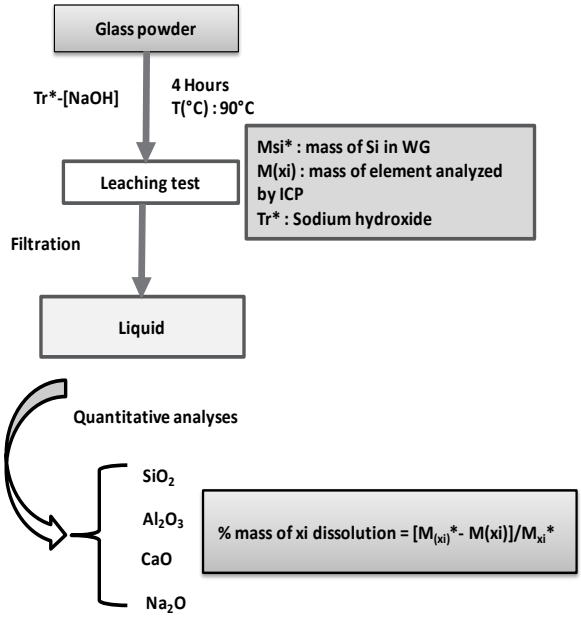

Fig. 3: Experimental protocol

3.2 Quantity of major elements

The ICP-AES analysis (Inductively Coupled Plasma – Optical Emission Spectrometer) allows to quantify the chemical elements in solution. In this study, a focus was made on four elements responsible for the geopolymerisation (precisely Si, Al, Ca and Mg) leached by treated glass.

Tab.1: Chemical composition of WG and MK

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	Fe_2O_3	CaO	Cr_2O_3	TiO_2
WG	13.18	1.76	0.95	71.07	0.44	0.15	12.38	0.06	-
MK	-	0.28	22.43	73.73	0.20	0.99	1.27	0	1.09

Tab.2: Leaching test after treatment of WG

(mg/kg)	SiO_2	Al_2O_3	CaO	Na_2O
TG0M22	3	2	0	3
TG0M90	3	8	3	3
TG10M90	172270	4513	280	Excess

*TG0M22: Glass only treated at 22°C during 4H
*TG0M90: Glass only treated at 90°C during 4H
*TG0M90: Glass treated with NaOH 10M and at 90°C during 4H

Three programs of treatment were realised to compare the effect of the temperature and the effect of sodium hydroxide.

- Program 1 (P1): treatment of reference with an ambient temperature (22°C) and no use of NaOH
- Program 2 (P2): powder in suspension in water (without NaOH) and heated at 90°C during 4h
- Program 3 (P3): powder in suspension in NaOH 10M and heated at 90°C during 4h.

Leaching tests on each material were performed according to the standard NF EN 12457. Tab. 2 presents the quantities of elements leached after each treatment. Results show that a very low content of studied elements was leached for P1 and P2. On the other hand, significant quantity of elements (Si, Al, Ca) is leached by treated glass at 90°C in NaOH 10M (P3). This program is considered as the most efficient in this study.

3.3 Structural comparison of treatments by FTIR

FTIR spectra (Fourier Transformed Infrared Spectroscopy) in transmittance mode have been used to study the structure of the main samples. Fig. 4 shows that no modification is noticed for samples WG and TG0M90. It can be noted the presence of strips characteristic to the glass, especially the large strip between 1400 and 900 cm^{-1} and other peaks around 600 and 400 cm^{-1}. In FTIR spectra of WG and TG0M90, it can also be identify a strip at 3600-3400 cm^{-1} typically due to the presence of water.

On the other hand, a large modification of structure is observed for TG10M90. This result highlights the fact that sodium hydroxide has the capacity to destroy the glass structure and to form other bonds. During the reaction between NaOH and WG, it can be noticed the destruction of Si-O-Si and Si-O-Al bonds to produce other structure more reactive (Equations (1) and (2)).

$$\text{-Si-O-Si--} \xrightarrow[nH_2O]{10NaOH} 2\,(\text{-Si-O}^-, Na^+), nH_2O \quad \textbf{(1)}$$

$$\text{-Al-O-Si-} \xrightarrow[nH_2O]{10NaOH} (\text{-Si-O}^-, Na^+ + \text{-Al-O}^-, Na^+), nH_2O \quad \textbf{(2)}$$

These new chemical bonds are visible by FTIR with the apparition of peaks near to 1450-1400 cm^{-1} and at 900 cm^{-1}.

3.4 Effect of treatment on the aggregates morphology

SEM-EDS observations of the samples coupled with qualitative analyses of the different phases observed have given an approximate relation between the morphology of WG aggregates and the efficacy of the treatment program.

Fig. 5 shows the morphology modification for TG10M90 and the apparition of needles-form phases made of Na, Si and Ca, with the presence of other elements contained in WG. On the other hand, no change of morphology of the samples TG0M22 and TG0M90 is visible. This can be explained by the absence of influence of the temperature alone on the dissolution of glass structure.

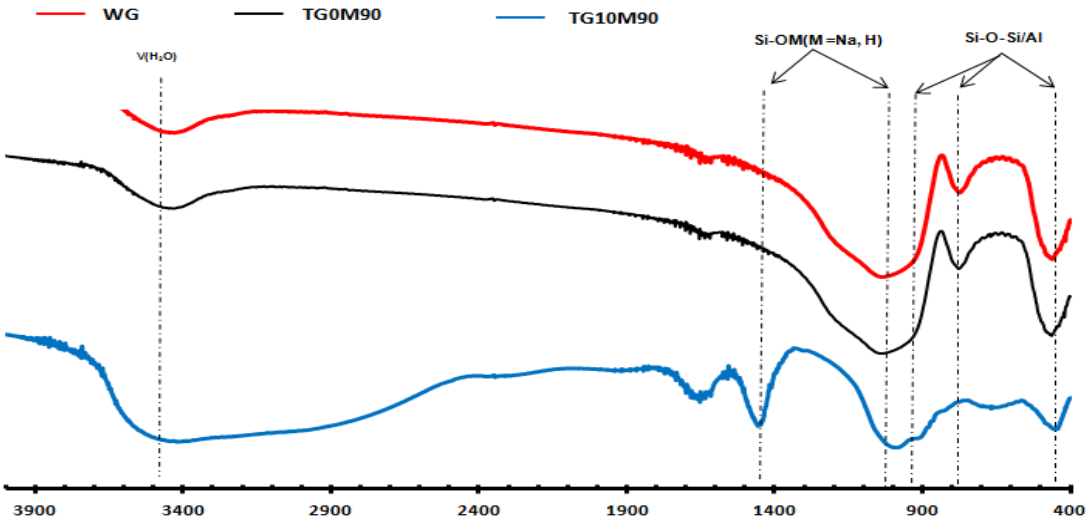

Fig. 4: FTIR Spectra of treated and untreated waste glass

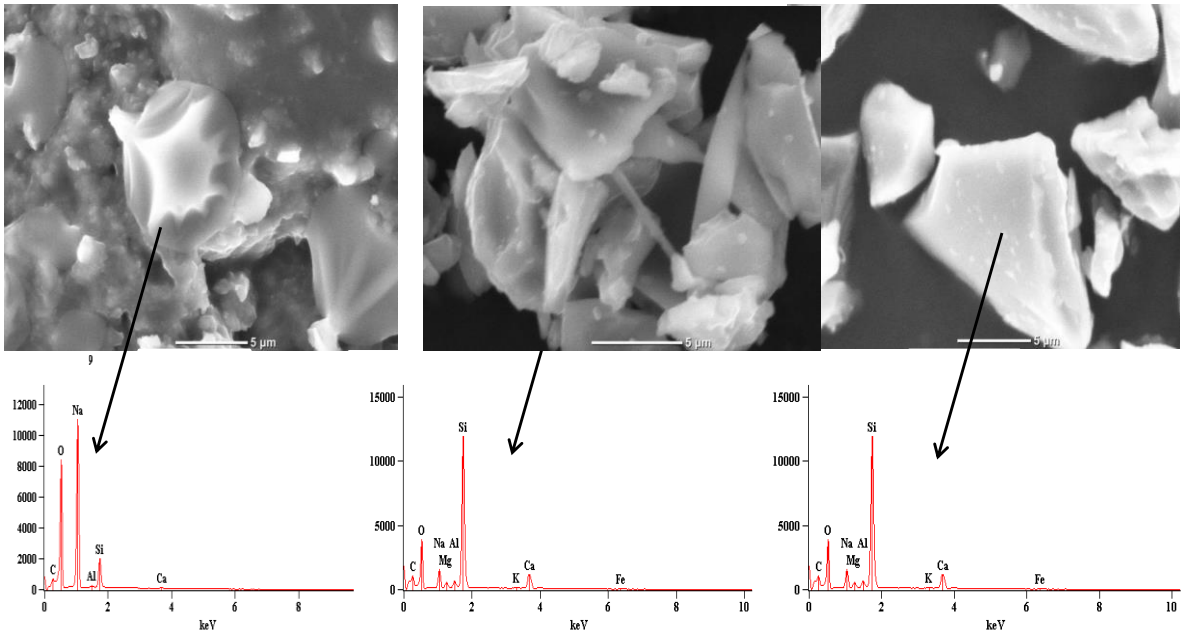

Fig. 5: SEM-EDS observations of WG after treatment TG10M90, TG0M90 and TG0M22 (from left to right)

The results obtained by SEM-EDS remain compatible with the results of the structural comparison given by FTIR (with TG0M90 and TG0M22 which only contain peaks characteristic of the glass structure).

In the other hand, SEM observations confirm the existence of, at least, two types of morphologies on TG10M90: one characteristic of WG structure and the other characteristic of the new structure rich in sodium and with presence of Si, Ca, Al, Mg. This indicates that the attack of WG has not totally succeeded.

The efficacy of attacks is related to the germination around aggregates and the viscosity of the environment. The dissolution of a part of WG causes the liberation of Ca^{2+} in the reaction environment, which leads to the apparition of $Ca(SiO_{5/2})_2$ phases, more stable than $Na(SiO_{5/2})$ according to the steps hereinbelow:

- Intermediate phases between Na+ and $(SiO_{5/2})$:

$$(SiO_{5/2})^- + Na^+ \longrightarrow Na(SiO_{5/2}) \quad (3)$$

- Reaction between $Na(SiO_{5/2})$ and Ca^{2+}

$$2Na(SiO_{5/2}) + Ca^{2+} \longrightarrow Ca(SiO_{5/2})_2 + 2Na^+ \quad (4)$$

The presence of water in the system allows to facilitate the transport and the reaction of the different elements in solution.

4 FORMULATION

4.1 Mixture compositions

In order to perform mechanical tests, the three types of treated glass were incorporated into three formulations prepared in a mixer bowl in accordance with the standard NF EN 196-1 and put in prismatic moulds 4x4x16cm according to the standard NF EN 196-6. Tab. 3 gives the composition of mortars.

In order to compare the different treated glass (and so the effect of the attack), hydroxide sodium was added in mixes 1 and 2 to keep the same quantity of alkali elements.

The temperature of curing has an important impact on geopolymerisation reaction, and especially on the setting time and the development of geopolymer phases. At ambient temperature, the reaction is globally very slow. To accelerate it, it's necessary to increase the temperature [KHA 2007]. In order to activate the geopolymerisation reaction and avoid the cracking of mortars, the curing temperature was fixed at 50°C during 28 days.

4.2 Mechanical properties

Mechanical tests were performed on prismatic moulds. The used device was a 15 tons press type INSTRON. The flexion in three points was realised with a speed of 3000N/min, and compressive test was performed with a speed of 144 kN/min. Tests were made at 7 days of curing. The results are presented in Tab. 4.

Compressive and flexural strengths highlight that formulation containing treated glass with NaOH 10M at 90°C have better mechanical properties than other formulations. This formulation raises 53 MPa in compression and 7.5 MPa in flexion. For the formulations 1 and 2, compressive and flexural strengths are around 20MPa and 3.5MPa respectively.

The attack of WG by sodium hydroxide at 90°C leads to an increase of Si available in the matrix, allowing to reach high compressive strengths. On the other hand, the other treated WG (TG0M22 and TG0M90) do not undergo any dissolution of structure, and so any Si in the matrix. Consequently, the mechanical performances are lower. Compressive strengths obtained are mainly due to reactions between alkaline elements added in the mixes and Si and Al provided by MK.

Tab.3: Composition of mortars

Designation	Quantity of materials (g)				
	MK	Water	Sand	Glass	NaOH
MTG0M22	150	60	450	80	10M[a]
MTG0M90	150	60	450	80	10M[a]
MTG10M90	150	60	450	80	10M[*]

Tab.4: Compressive and flexural strengths

(MPa)	Compressive strength	Flexural strength
MTG0M22	19	3.5
MTG0M90	23	4
MTG10M90	53	7.5

4.3 Dynamic modulus

Another test used for the study of cementitious matrix durability is the measurement of dynamic modulus by determination of resonant frequency obtained by Grindo Sonic MK5. The evolution of elastic modulus of mortars is related to solidification and microstructuralchange (linked to volumic change and geopolymerisation degree) [Verma 2013][Azenha 2010] in the mortars. The evaluation of dynamic modulus of prismatic specimens was performed on a V-E-400 Emodumeter according to NF EN 14146. Fig. 3 presents the evolution of dynamic modulus of mortars at 28 days of curing.

The mortar MTG10M90 has a value of 34 GPa compared to 16 and 20 GPa for respectively MTG0M22 and MTG0M90. The mortar containing TG10M90 has interconnections between constituents stronger than the other mortars. This highlights that waste glass treated with sodium hydroxide and heated is able to react for participating to matrix solidification, and so, to increase the mechanical performances of mortar.

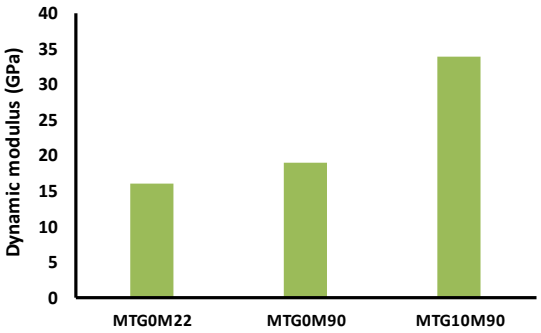

Fig. 3: Evolution of dynamic modulus of mortars at 28 days of curing

4.4 SEM Observations

SEM observations of different mortars present the major phases detected in each formulation (Fig. 4). The presence of TG10M90 and MK leads to formation of an homogeneous gel equivalent to N-A-S-H bonds responsible for the solidification of the matrix [MON 2015]. For the other mortars, two major phases can be noted. The first one is characteristic of presence of gel compatible with the gel present in mortar MTG10M90. The second one is a product of a reaction between sodium hydroxide and carbonates of air: Chabazite-Na.

5 CONCLUSION

This study shows that it can be useful to use the glass in geopolymer reaction as source of silica.

The main conclusions are:

- Chemical composition of glass is interesting for

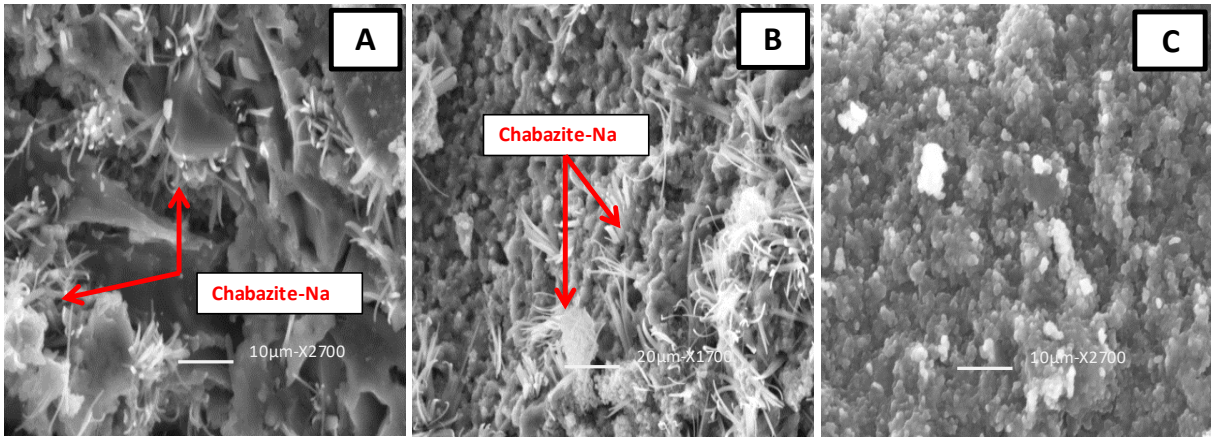

Fig. 4: SEM-EDS observations of mortars MTG0M22, MTG0M90 and MTG10M90 (from left to right)

cement geopolymer but an alkaline activation is necessary.

- After treatment in alkaline media, glass leaches a higher quantity of silica which explains its reactivity with aluminosilica sources (metakaolin). Mechanical properties confirm the importance of silica liberation.
- The geopolymerisation appears like a new route in order to integrate waste glass in construction matrix, but it requires intermediate steps (crushing, drying…).
- Finally, treated glass can replace sodium silica as activator in a geopolymerisation reaction, which can be economically interesting (sodium silica is expensive) and can present environmental advantages (preservation of natural resources and recycling of industrial waste).

6 ACKNOWLEDGMENTS

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