



Physico-chemistry of consolidated material from alkaline activation of waste powder glass

Séka Simplicie KOUASSI^{1*}, Atolé Brice Bienvenu KEDI¹, Tohoué Monique TOGNONVI², Roland Charles NAHO¹, Yapi Yao Jonas ANDJI³

¹Laboratory of Environmental Science and Technology, University of Jean Lorougnon Guédé, Daloa, Côte d'Ivoire

²Unit for Training and Research of Biological Sciences, University of Peleforo Gon Coulibaly, Korhogo, Côte d'Ivoire

³Laboratory of Chemistry of Inorganic Materials, University of Felix Houphouët-Boigny, Abidjan, Côte d'Ivoire

Received 15 Oct 2019,
Revised 27 Dec 2019,
Accepted 29 Dec 2019

Keywords

- ✓ Glass powder,
- ✓ Sodium silicate,
- ✓ Calcium silicate hydrated,
- ✓ Consolidated material,

sekasimplice@ujlg.edu.ci
Phone: +22559808957

Abstract

The present work aims to develop a geopolymer (consolidated material) by alkaline activation of waste glass. A glass bottle sample from the city of Abidjan was crushed and several particle sizes were retained (< 40 μm, 100-250 μm and 250-800 μm). A consolidated material was obtained by activation in sodium hydroxide of the glass powder at 70°C. Several techniques (Chemical Analysis, Thermal Analysis (DTA, GTA), X-Ray Diffraction Analysis, Infrared (IR), Scanning Electron Microscope (SEM), and Mechanical Test) were used to characterize the consolidated material. The results have shown that due to the chemical composition of the glass used (Ca, Si and Na), there is formation of sodium silicate and calcium silicate hydrate which are both at the origin consolidation of the material. These two binders formed in situ contribute to the strong consolidation of the material and to the improvement of its compressive strength. The overall results have led to the conclusion that it is possible to develop non-recycled glass bottles from the city of Abidjan (Ivory Coast) through the manufacture of prefabricated materials.

1. Introduction

Concrete remains today one of the most indispensable materials in the world. It serves in fact, the construction of infrastructure and housing. Its global production is growing exponentially due to ever-increasing needs.

However, the production of concrete has a negative impact on the environment because of its binding component which is cement. Although cement represents only about 7-15% of the concrete, it is the element responsible for the binding properties of concrete. The cement industry contributes 5 to 8% of CO₂ emissions (greenhouse gases) to the atmosphere and consumes about 1.6% of the world's electricity needs [1]. In fact, the production of one ton of clinker (95% in portland cement composition) generates about one ton of CO₂ in the atmosphere [2] which is largely responsible for the destruction of the ozone layer, a direct consequence of global warming.

To reduce the carbon footprint, studies have been undertaken over the last twenty years to develop high-performance and environmentally friendly concretes through the use of additional cementitious materials or cementitious industrial residues (silica fume, slags, fly ash) or glass waste as partial replacement of cement [3–6]. But this technique of partial replacement of the cement by the glass debris also has an environmental and economic impact in the world. A total substitution of cement with glass waste in concrete would contribute to drastically reducing the carbon footprint of cement manufacturing.

Thus, research on new mineral binders with low production costs and less energy consumption has recently been developing, with negligible ecological impact. Among these alternatives, there is the development of new binders by alkaline activation of recovery products [3,7]. We can cite new materials such as geopolymers and the role of sodium silicate solutions finding applications in binders and in some habitat materials.

In Abidjan (Ivory Coast), about 5,000 tons of glass waste from industrial sources is generated annually [8] some of which comes from an unquantified urban source found in aerial dumps. One possible valuation is to use this waste glass for the development of new consolidated materials with particular properties.

2. Material and Methods

To make samples of consolidated materials, waste glass bottles were used and crushed. The elemental chemical composition in molar percentage of the equivalent oxides of the glass used is presented in Table 1.

Table 1 : Mass percentage of the equivalent oxides of the elements present in the waste glass.

	Al₂O₃	CaO	Fe₂O₃	K₂O	MgO	Na₂O	SiO₂	TiO₂
Glass (%)	1.64	9.19	0.23	0.56	0.84	13.89	73.37	0.28

To eliminate any contamination, waste bottle have been washed in water several times. Samples after washing are then air dried and crushed. Several granular fractions are considered. The less than 40 μm fraction called SB₄₀ will be used as part of the mineral binder while the granular fractions between 100 and 250 μm or between 250 and 800 called SB_G will be considered as granular. In alkaline solution (NaOH 5N), an identical amount of SB₄₀ to the mass of NaOH is added. The mixture is stirred for about 10 minutes and then SB_G is added in a proportion of SB_G / SB₄₀ = 15 to respect the content of 70 % by weight of granulate as in concrete. After 5 minutes of homogenization, the mixture is placed in cylindrical tubes of polyethylene of size ($\Phi = 3.45$ cm and H = 6.60 cm) and brought to a temperature of 70°C for 28 days.

The X-ray diffraction patterns were obtained using a diffractometer dedicated to the characterization of polycrystalline plane samples. Its configuration is Debye-Scherrer type. It is equipped with a localized curved detector (INEL CPS 120° Curved Position Sensitive Detector) in the center of which is placed the sample. The exposure time for each sample is 20 minutes and the measured angular range is from 0 to 90 °. The infrared measurements were performed using a Fourier transform spectrometer (NICOLET 380) in the range of 4000-400 cm^{-1} wavenumbers, with a resolution of 4 cm^{-1} , a scanning number of 64 and a mirror speed of 0.4747.

In order to follow the mass evolution of our sample and to know the various thermal accidents which take place during its heating, differential thermal and thermo-gravimetric analysis measurements were carried out between 0 and 500°C with a coupled system DTA-TGA of type SETSY 24 SETARAM. The inert reference material is calcined alumina at 1500 ° C.

The compression tests were performed from a Lloyd Instrument EZ20 test machine (AMETEK, UK). Cylindrical specimens, which extremities have been ground to ensure the flatness of the surfaces, are subjected to increasing load until they break with a speed of displacement of 1 $\text{mm}\cdot\text{min}^{-1}$.

To study the morphology of our samples, a STEREOSCAN 260 scanning electron microscope was used. The principle of this type of microscopy is based on the strong interaction between the secondary electrons emitted and backscattered which make it possible to reconstitute the image of the object.

3. Results

3.1. Presentation of consolidated materials

At the end of the material development protocol described in the experimental part, highly consolidated samples were obtained. Figure 1 shows the photograph of two consolidated materials produced with different sizes of aggregates. These samples are completely rigid and have no apparent crack shape.

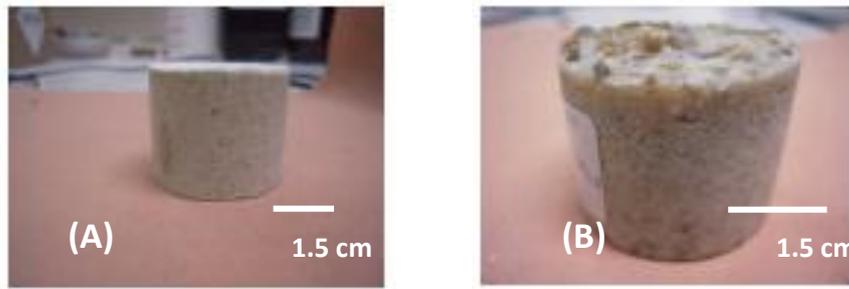


Figure 1. Photograph of 2 consolidated materials developed with aggregate sizes of 100-250 μm (A) and 250-800 (B)

3.2. X-ray diffraction

The X-ray diffraction (XRD) diagrams of raw glass samples and consolidated material pre-baked at 100 °C for 24 hours and made with an exposure time of 15 hours are shown in Figure 2. While diffractogram of the raw glass has a quasi-amorphous structure (characteristic of glasses), that of the consolidated material reveals the presence of characteristic peaks of a poorly crystallized compound that could be attributed to the presence of new phases: calcium carbonate (CaCO_3), hydrated calcium silicate (C-S-H) probably containing sodium (C- (N) -S-H) and hydrated sodium aluminosilicate (S-A-S-H). The presence of calcium carbonate is due to the solution of NaOH recognized for its rapid carbonation in air. The CO_2 thus captured in the air by the NaOH solution will form calcite with the calcium of the glass. Despite the low aluminum content of the glass, hydrates incorporating aluminum have been formed, contributing to the stability of the materials.

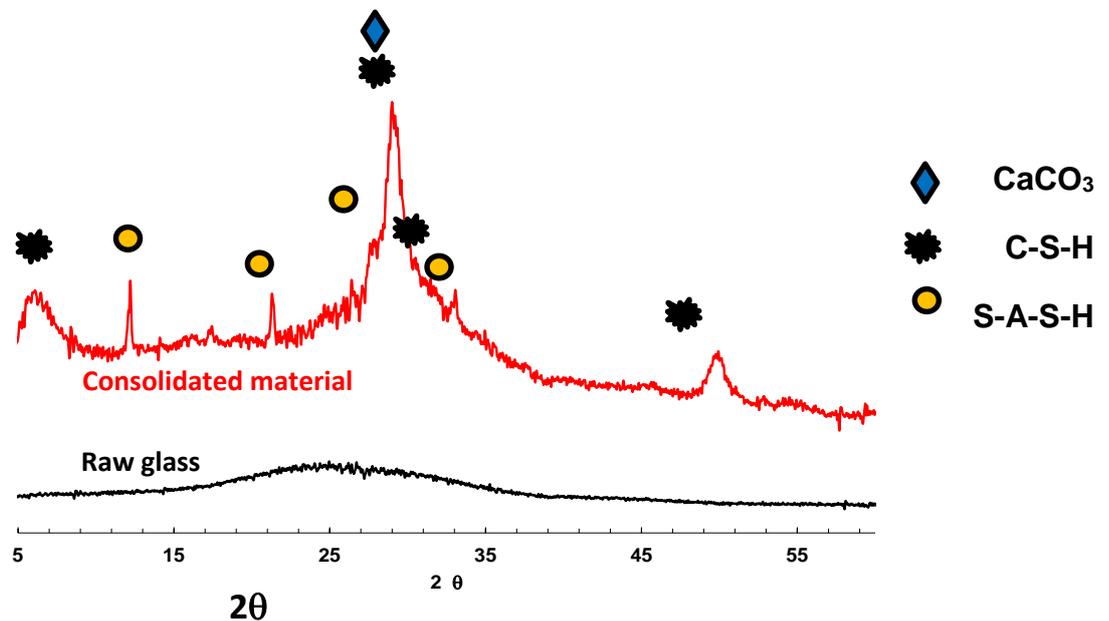


Figure 2: X-ray diffraction of raw glass and consolidated material

3.3. Infrared spectra of raw glass and consolidated material

The IR spectra of the raw glass samples and the consolidated material, previously steamed at 110 °C for 24 hours, are given in Figure 3. For the raw glass, the main vibration bands centered on 3500, 1010, 770 and 463 cm^{-1} can be attributed respectively to the Si-O-H elongation vibration [9–11], to asymmetric elongation vibration of Si-O-Si [12,13], to the symmetrical elongation vibration of Si-O-Si [12,14,15], and the Si-O-Si and O-Si-O deformation vibration [12,16,17]. These same vibration bands are also observed

for the consolidated material which additionally contains vibration bands at 1634, 1494, 1423, 870 and 684 cm^{-1} . While the 1494, 1423 and 870 cm^{-1} bands of this spectrum could be attributed to the vibration of the C-O bond of calcite [12,18–20], broad absorption bands at 463, 684, 1634 and 3500 cm^{-1} are typical of the presence of C-S-H phases [11,14,18]. These results confirm the presence of CaCO_3 and C-S-H in the consolidated material observed in XRD.

3.4. Thermal analyzes of the consolidated material

Differential thermal analysis (DTA) and thermo-gravimetric analysis (GTA) were performed on the raw glass and on the consolidated material to determine the different thermal phenomena as well as the mass losses that can be observed in these samples according to the temperature. The two thermal analysis curves of the raw glass (Figure 4A) show no thermal accident and no loss of mass in the temperature range studied, which is from 0 to 500 °C.

The raw glass is therefore thermally stable in this temperature range. However, the DTA curve of the consolidated material (Figure 4B) in the same temperature range has several thermal accidents. From 50 to 200 °C, we observe an endothermic phenomenon accompanied by a loss of mass of about 10% that we attribute to the decomposition of hydrates (C-(N)-S-H) [18,21] and / or evaporation of the free water present in the pores (dehydration process).

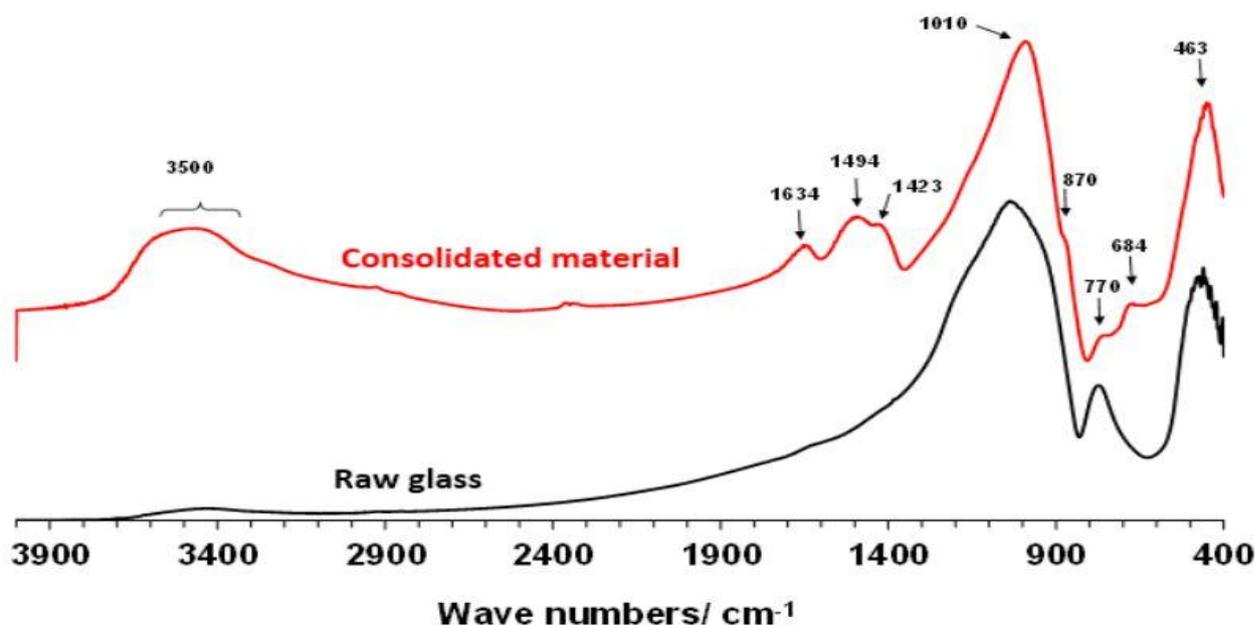


Figure 3: IR spectra of raw glass and consolidated material

At 370 °C, we have a small endothermic peak accompanied by a slight loss of mass of about 1.5% that would be attributed to the dehydroxylation of our sample. It is known in geopolymers that at temperatures ($T > 200$ °C), dehydroxylation occurs by condensation of the surface hydroxyl groups of the structure [22]. By analogy with these materials, the endothermic phenomenon corresponds to the reorganization of the structure by polycondensation. These results indicate that most of the water present in the material is in evaporable form. This is consistent with the observations of Duxon and al. [23]. Indeed, according to these authors, most water in the structure of geopolymeric materials, is present in the form of easily evaporable water, while the rest of the water is tightly adsorbed in small pores or on hydroxyl groups on the surface of the gel.

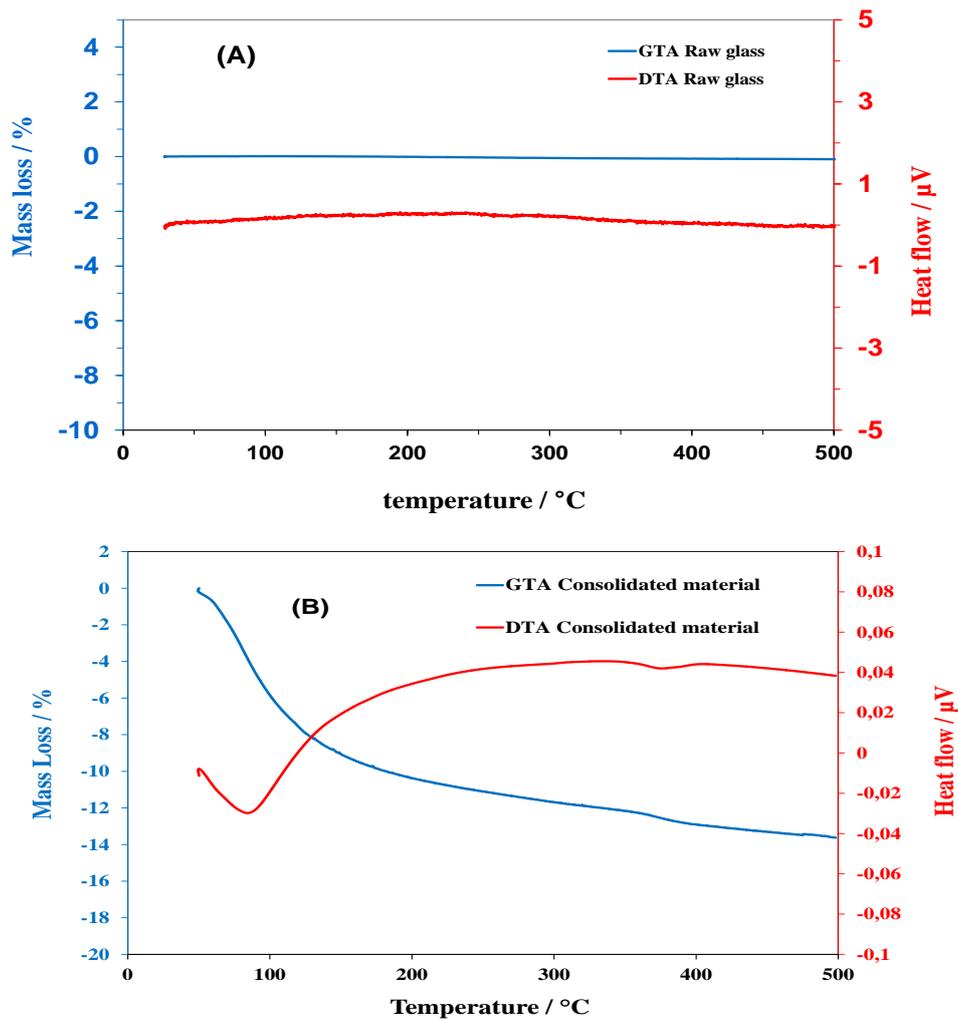


Figure 4: Differential Thermal Analysis (DTA) and Gravimetric Thermal Analysis (GTA) Curves for Raw Glass (A) and Consolidated Material (B)

3.5. Mechanical test: compressive strength

In order to determine the mechanical properties of the material prepared after 28 days in an oven at 70 $^{\circ}\text{C}$, the compressive strength was performed on these samples and Figure 5 gives the compressive strength as a function of the size of the samples aggregates.

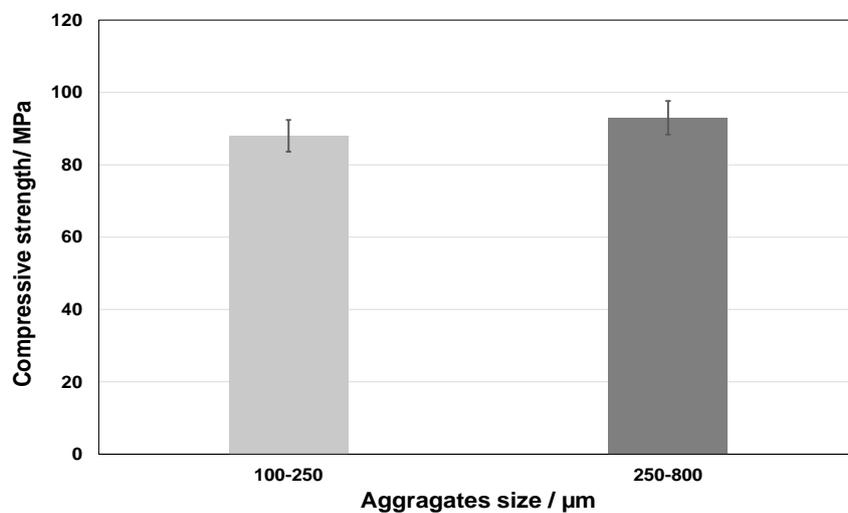


Figure 5: Evolution of the compressive strength according to the size of aggregates

The average value of the compressive strength of materials with aggregates of size between 100 and 250 μm is 88 MPa while that of materials with a particle size of between 250 and 800 μm is 93 MPa. Compression strength is higher for materials with a high aggregate size. In addition, these values of the compressive strength are very high and are close to the value of 100 MPa which is intended to be the reference value for cement-based concretes on specimens with a slenderness of 2.

3.6. Microstructural characterization

Scanning electron microscopy analysis was performed on the consolidated material (Figure 6).

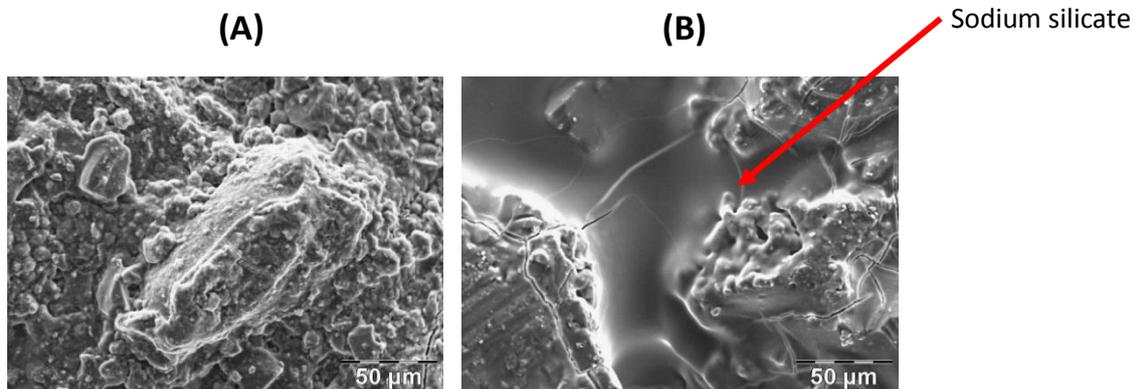


Figure 6: SEM images of consolidated material after 28 days in an oven at 70 ° C with a coated glass grain (A) and a grain boundary (B).

The SEM image shows a highly densified material with a glass grain (granulate) in A completely coated with the binder formed by the decomposition of SB₄₀ and the alkaline solution used. The intergranular space (Figure 6B) shows the cohesion between the glass grains is ensured by the dissolution of the SB₄₀ glass by sodium hydroxide (sodium silicate), which is an adhesive to agglomerate the aggregates of the glass. When we observe the core of the material (Figure 7) after fracturing, we notice that there is no swelling gel (no ASR: Alkali Silicate Reaction) at the origin of the cracking of the material in the long term. The morphology also shows a very dense microstructure with a glass grain of a very smooth surface indicating the good reaction of the glass in basic medium. We also observe a C-S-H film all around the attacked glass grain.

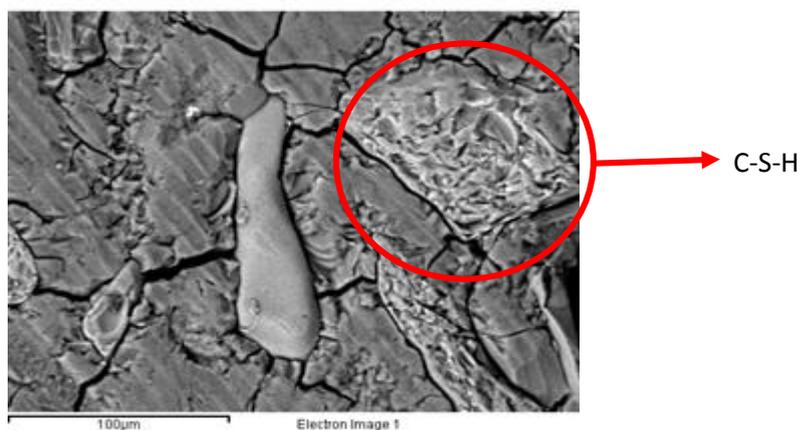


Figure 7: SEM image showing the core of the material after fracturing

In order to know the real nature of the compounds in the consolidated material, the surface of a glass grain was observed at high magnification and compared with C-S-H. Thus, Figure 8 shows the microstructures of the surface of a glass grain in the consolidated material and synthetic C-S-H [24]. We observe a strong similarity between the two microstructures. This could confirm the presence of C-(N)-S-H gel in the materials during this study.

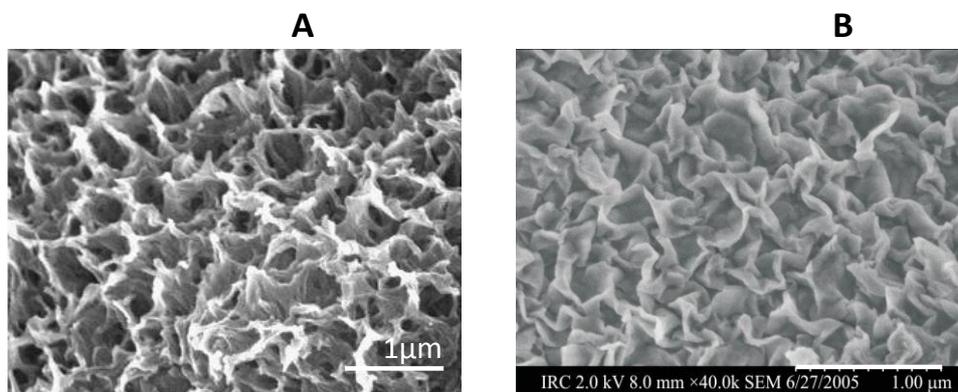


Figure 8 : Microstructure of the surface of consolidated material (A) and synthetic C-S-H (B) [24].

4. Discussion

The results of the four characterization tests (DTA-GTA, XRD, IR and SEM) performed on the developed material indicate the presence of hydrates comparable to those found in ordinary cements and carbonates as phases appearing in the consolidated material.

The origin of the presence of hydrates is related to the hydration of the chemical species in the glass. Indeed, the chemical species (Si, Na and Ca) in the SB glass are hydrated in the presence of water in a basic medium by an activation process comparable to the geopolymeric materials. This mechanism can be summarized as follows: when the glass powder is brought into contact with the basic medium, the siliceous network undergoes a dissolution. This dissolution leads to dissolution of the silicon, sodium and calcium, it is called depolymerization of the glass powder. The solvated chemical species interact with each other to form oligomers. When the solution saturates with oligomers, the latter become polycondensed in geopolymers, we then speak of polycondensation [14]; Although the formation process is different from that of ordinary cement, hydrates similar to those formed during the hydration of cement such as hydrated calcium silicate incorporating sodium (C-(N)-S-H) are observed due to the presence of calcium in the medium. There is also formation of hydrate (S-A-N-H) containing aluminum (sodium aluminosilicate hydrate) which is present in the glass but in small quantities (1.64% Al_2O_3). This confirms the attack of the siliceous network of glass.

In the case of cements, these chemical species are at the origin of the setting reaction therefore the hardening of the cement. These chemical species help to improve the mechanical properties of the cementitious material.

Concerning carbonates, their presence in the materials comes from the soda solution used for its production and the calcium present in the glass. In addition to hydrates, x-ray diffraction reveals the presence of calcium carbonate. The dissolution of the siliceous network implies, as we had previously pointed out, passage of species in solution, including calcium. Being in basic solution (NaOH), calcium in the presence of hydroxide ions in addition to forming C-(N)-S-H, will also react with the CO_2 of air to form calcium carbonate in a two-step process as described in equations 1 and equation 2.

The soda solution is known for its rapid carbonation in contact with air following the reaction:



Once Na₂CO₃ is formed, the latter in the presence of the Ca²⁺ ions present in the mixture will react with these ions to give the calcium carbonate following the reaction:



This reaction occurs because calcium carbonate is more stable than sodium carbonate.

In addition to the presence of hydrates and carbonates, there is also sodium silicates.

The attack of the glass by a solution in a very basic medium leads to the dissolution of the siliceous amorphous network by breaking the Si-O-Si bonds and this dissolution leads to the formation of a solution of sodium silicate which will contribute to improve the mechanical strength of our material.

In the end, the consolidation of our material is due to both the presence of calcium-hydrated sodium silicate gel that is known to be strong binders and sodium silicate, which would explain the high compressive strength obtained for our materials (90 MPa) after 28 days of reaction which is similar to those obtained in concrete based concrete (100 MPa).

Conclusion

A consolidated material was developed from the alkaline attack of bottle glass waste from the city of Abidjan. These bottles, previously crushed, made it possible to obtain a fine granulometry powder after sieving.

This powder with different particle sizes in contact with alkaline solution of concentrated sodium hydroxide (5 N) gives a consolidated material when it is subjected for 28 days to a temperature of 70°C. The materials thus obtained are characterized by means of several techniques.

Les résultats de l'essai mécanique présentent un matériau à forte performance car sa résistance à la compression de l'ordre de 90 MPa est comparable à la valeur caractérisant un matériau de bonne résistance à la compression.

The results of the DTA-GTA analysis, the X-ray diffraction and the infrared, showed the presence during the chemical reaction, of the inorganic binders C-S-(N)-H and the sodium silicate that would cause the hardening of the material obtained. The results of the DTA show us a material sensitive to the thermal effect.

The results of the scanning electron microscopy of the microstructure of the surface of a glass grain in the consolidated material and the synthetic C-S-H show a strong similarity in their structure.

All of these results make it possible to highlight the SB bottles of the city of Abidjan (Ivory Coast) in the field of industries producing compression-resistant materials as well as concrete made from cement.

In perspective, a chemical analysis on the consolidated material in different solutions will study its chemical stability and to improve the compressive strength, additions of pozzolanic compounds will be made.

References

1. K.L. Scrivener, R.J. Kirkpatrick. Innovation in use and research on cementitious material". *Cement and Concrete Research*. 38 (2008). 128–136.; doi:10.1016/j.cemconres.2007.09.025.
2. F. Pacheco-Torgal, D. Moura, Y. Ding, S. Jalali. Composition, strength and workability of alkali-activated metakaolin based mortars. *Construction and Building Materials*. 25 (2011) 3732–3745. doi:10.1016/j.conbuildmat.2011.04.017.
3. R. Idir, M. Cyr, A. Tagnit-Hamou. Pozzolanic properties of fine and coarse color-mixed glass cullet. *Cement and Concrete Composites*. 33 (2011) 19–29. doi:10.1016/j.cemconcomp.2010.09.013.
4. K. Zheng. Pozzolanic reaction of glass powder and its role in controlling alkali–silica reaction. *Cement and Concrete Composites*. 67 (2016) 30–38. https://doi.org/10.1016/j.cemconcomp.2015.12.008.
5. A. Hendi, D. Mostofinejad, A. Sedaghatdoost, M. Zohrabi, N. Naeimi, A. Tavakolinia. Mix design of the green self-consolidating concrete: Incorporating the waste glass powder. *Construction and Building Materials*. 199 (2019) 369–384. doi:10.1016/j.conbuildmat.2018.12.020.
6. V. Gokulnath, B. Ramesh, S. Suvesha. Influence on flexural properties of glass powder in self compacting concrete. *Materials Today: Proceedings*. (2019). doi:10.1016/j.matpr.2019.10.153.
7. A.B. Pascual. Élaboration de nouveaux liants minéraux pour la formulation de bétons écologiques et durables. [Mémoire de Maîtrise en génie civil]. Université Sherbrooke, Canada, 2014.

8. S.S. Kouassi. Etude de la dissolution d'un réseau silicaté en présence d'une solution alcaline. [Thèse de Doctorat en physicochimie des matériaux]. Université de Limoges, France, (2011).
9. R.F. BARTHOLOMEW, B.L. BUTLER, H.L. HOOVER, C.K. WU. Infrared Spectra of a Water-Containing Glass. *Journal of the American Ceramic Society*. 63 (1980) 481–485. doi:10.1111/j.1151-2916.1980.tb10748.x.
10. P. Innocenzi. Infrared Spectroscopy of Sol-Gel Derived Silica-Based Films: A Spectra-Microstructure Overview. *Journal of Non-Crystalline Solids*. 316 (2003) 309–319. doi:10.1016/S0022-3093(02)01637-X.
11. P. Yu, R.J. Kirkpatrick, B. Poe, P.F. McMillan, X. Cong. Structure of Calcium Silicate Hydrate (C-S-H): Near-, Mid-, and Far-Infrared Spectroscopy. *Journal of the American Ceramic Society*. 82 (1999) 742–748. doi:10.1111/j.1151-2916.1999.tb01826.x.
12. E.S. Park, H.W. Ro, C.V. Nguyen, R.L. Jaffe, D.Y. Yoon. Infrared Spectroscopy Study of Microstructures of Poly(silsesquioxane)s. *Chem. Mater.* 20 (2008) 1548–1554. doi:10.1021/cm071575z.
13. J.F. Brown. “The Polycondensation of Phenylsilanetriol”. *Journal of the American Chemical Society*. 87 (1965) 4317–4324. doi:10.1021/ja00947a017.
14. K. Baltakys, R. Jauberthie, V. Kasperaviciute. Formation and stability of C-S-H (i) in Ca(OH)₂/CaO-thermal silica densified-H₂O system. *Ceramics Silikaty*. 53 (2009) 81–87.
15. P. Makreski, G. Jovanovski, B. Kaitner. Minerals from Macedonia. XXIV. Spectra-structure characterization of tectosilicates. *Journal of Molecular Structure*. 2009. 924–926: 413–419. doi:10.1016/j.molstruc.2009.01.001.
16. R. HANNA. Infrared Absorption Spectrum of Silicon Dioxide. *Journal of the American Ceramic Society*. 48 (1965) 595–599. doi:10.1111/j.1151-2916.1965.tb14680.x.
17. D. SNELL. Review of Synthesis and Properties of Tobermorite, C-S-H(I), and C-S-H Gel. *Journal of the American Ceramic Society*. 58 (2006) 292–295. doi:10.1111/j.1151-2916.1975.tb11478.x.
18. I. Pajares, S. Martínez-Ramírez, M.T. Blanco-Varela. Evolution of ettringite in presence of carbonate, and silicate ions. *Cement and Concrete Composites*. 25 (2003) 861–865. [https://doi.org/10.1016/S0958-9465\(03\)00113-6](https://doi.org/10.1016/S0958-9465(03)00113-6).
19. P. Cromme, C. Zollfrank, L. Müller, F. Müller, P. Greil. Biomimetic mineralisation of apatites on Ca²⁺ activated cellulose templates. *Materials Science and Engineering C*. 27 (2007) 1–7. doi:10.1016/j.msec.2005.11.001.
20. C. Li, H. Sun, Z. Yi, L. Li. Innovative methodology for comprehensive utilization of iron ore tailings: part 2: The residues after iron recovery from iron ore tailings to prepare cementitious material. *Journal of hazardous materials*. 174 (2010) 78–83. doi:10.1016/j.jhazmat.2009.09.019.
21. A. Hidalgo, S. Petit, C. Domingo, C. Alonso, C. Andrade. Microstructural characterization of leaching effects in cement pastes due to neutralisation of their alkaline nature. *Cement and Concrete Research*. 37 (2007) 63–70. doi:10.1016/j.cemconres.2006.10.002.
22. D. Dimas, I. Giannopoulou, D. Papias. Polymerization in sodium silicate solutions: A fundamental process in geopolymerization technology. *Journal of Materials Science*. 44 (2009) 3719–3730. doi:10.1007/s10853-009-3497-5.
23. P. Duxson, G. Lukey, J. Van Deventer. Physical Evolution of Na-Geopolymer Derived From Metakaolin Up to 1000°C. *Journal of Materials Science*. 42 (2007) 3044–3054. doi:10.1007/s10853-006-0535-4.
24. S. Mojumdar, L. Raki. “Preparation, thermal, spectral and microscopic studies of calcium silicate hydrate–poly(acrylic acid) nanocomposite materials”. *J. Therm. Anal. Calorim.* 85 (2006) 99–105. doi:10.1007/s10973-005-7353-9.

(2020) ; <http://www.jmaterenvirosci.com>