Preparation and characterization of a composite material based on a geopolymer binder and quartzite aggregates

A.Aboulayt[1], H. Hannache[2], A. Idrissi Adib[2], M. Gomina[3] and R. Moussa[1]
[1] Université Hassan II Casablanca, Faculté des Sciences Aïn Chock , LPCMI, Casablanca, Maroc
[2] Université Hassan II Mohammedia, Faculté des Sciences Ben M'sick, LIM, Casablanca, Maroc
[3] ENSICAEN, CNRS, UMR 6508 CRISMAT, Caen, France.
Corresponding author: redmoussa@yahoo.fr

Summary. We have developed a geopolymer material by alkaline reaction on thermally activated kaolin. Initially we characterized the geopolymer by different methods (rheology, DTA-TGA, etc.) and we mixed it with different amounts of natural sand to obtain a granular composite.

The structural characterization of this material was undertaken by several techniques (XRF, XRD and microscopic observations). A rheological study was implemented to determine the influence of the aggregate rate on the setting kinetic. Three-point bending and compression tests were conducted for mechanical characterization. We also conducted microindentation tests to study the influence of quartzite rate on the hardness of the material.

The results indicate that the integration of quartzite (up to 15 wt. %) did not alter the setting kinetic. We noted a small degradation of the mechanical behavior when the quartzite rate is increased; this effect is due to a higher density of microcracks. However, adding the aggregate has a beneficial effect on the hardness of the material.

These attractive features make this material a plausible matrix whose reinforcement with plant fibers will provide a ternary composite suitable for multiple applications.

Introduction

Geopolymers are inorganic polymers with a three-dimensional and amorphous structure resulting from a process of condensation of monomers of aluminum and silicon obtained by an alkaline attack on SiO_2 and Al_2O_3-rich powder [1].

The alkaline solution is generally composed of the sodium and /or potassium hydroxide and sodium or potassium silicate.

Aluminosilicate powders can come from several natural sources (kaolin, pozzolan...) or industrial (fly ash, blast furnace,slags...) [2] [3].

The phenomenon of geopolymerization is complex. Studies suggest that this process occurs in four stages: (1) a dissolution of the solid phase, source of silicon and aluminum in alkaline solution, (2) the diffusion of Al and Si monomers resulting from the attack, (3) the formation of a gel and (4) the hardening of gel phase [4] [5].

Relatively to conventional construction materials such as portland cement, geopolymers have good physical and chemical properties in terms of shrinkage after setting, mechanical holding and especially resistance to acid attack and fire [6-9].

The elaboration of geopolymers at temperatures close to the ambient constitutes certainly both economical and ecological advantages (low energy cost and low CO_2 emissions of greenhouse).

The use of silica sand, as an additive to improve the performances of a geopolymer matrix has been the subject of recent works [10] [11], these studies have shown that the nature of the added silica has a great influence: the contribution of a reactive amorphous silica promotes polycondensation and increases the Si/Al ratio in the matrix while the inert crystalline silica tends to cause degradation of the material by the lack of cohesion matrix-additive.

However studies have shown that the Si/Al ratio improves the strength of materials in aggressive environment (acids).

In this work, we propose to study the effect of the introduction of natural quartzite on the performance of a matrix geopolymer obtained by alkaline attack of thermally active kaolin.

Quartzite is naturally occurring and the studied properties are the setting mechanisms and the mechanical resistance of the material.

1 Materials and experimental methods

1.1 Starting materials

The geopolymer material is synthesized by the reaction of an alkaline solution on previously active kaolin and quartzite additives. The solution consists of:

- Sodium and potassium hydroxides from Cadilhac Company, 98.5% and 90% purity, respectively.
- An alkaline solution of sodium silicate from Cadilhac Company with 45 wt.% of dry matter, a SiO_2/AlO_2 molar ratio of 2 ± 0.1 and density = 1.54 .

The dry matter is composed of :

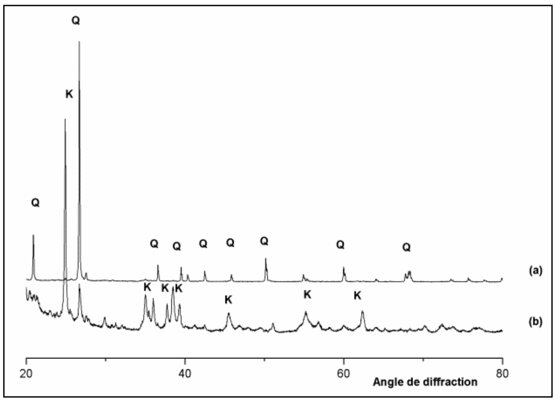
- Commercial kaolin (SIBELCO).
- Natural quartzite, originally from the region of Marrakesh, (Assif lmal). This mineral is mainly used as additive degreasing in ceramic tiles industry [12].

Kaolin and quartzite were characterized by quantitative chemical analysis (XRF,Magixpro, Panalytical) (table 1), and mineralogical analysis (XRD,Panalytical X'Pert Pro), (Fig. 1).

Table 1. Quantitative chemical composition of powders in wt.%

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5	MnO	P.F
Kaolin	47.54	35.49	0.89	0.18	0.43	0.33	0.09	2.15	0.02	0.05	0.01	12.61
Quartzite	90.70	4.10	0.80	0.30	0.80	0.50	0.10	1.20	---	---	---	1.50

Fig. 1. X-ray diagram of the quartzite powder (a) and the kaolin powder (b). K: kaolinite, Q: quartz



The XRD spectrum of kaolin presents characteristic peaks of kaolinite and free quartz . Quartzite spectrum presents only the characteristic peaks of quartz.

Characterization results permits us to estimate that the kaolin is composed of a 89.5 wt.% of kaolinite and 6 wt.% of free quartz while the quartzite is mainly composed of free silica (89.3 wt. %).

The synthesis of geopolymers necessitates the use of activated kaolin. Metakaolin is obtained by thermal treatment in order to amorphising clay particles, sources of aluminum by dehydroxylation [13].

Figure 2 represents the kaolin XRD spectrum before (a) and after heat treatment at 750 °C for two hours. We observe the quasi total disappearance of characteristic peaks of kaolinite.

We also determined the particle size distributions of metakaolin and quartzite powders using a laser particle size analyzer (Coulter LS 230) (fig. 3).

Metakaolin presents a unimodal distribution with a very fine grain population of average size of about 4µm, while quartzite presents a very large multi-modal distribution of grain sizes wish reach 2 mm.

Fig. 2. XRD diffraction pattern of the kaolin before (a) and after heat treatment (b). K: kaolinite, Q: quartz

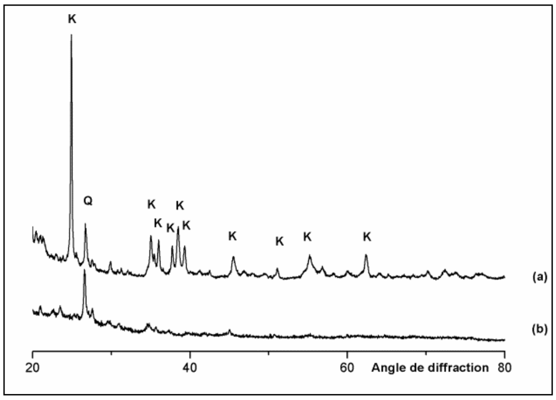
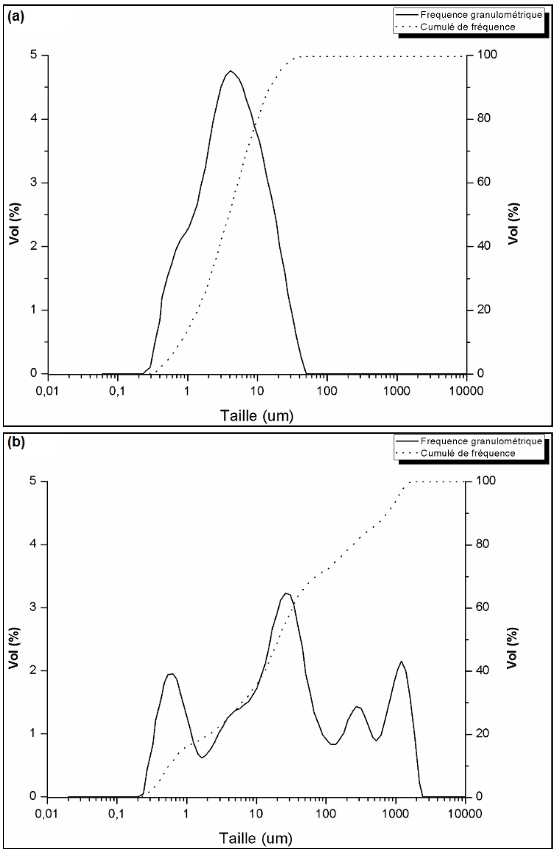


Fig. 3. Grain size distribution of the metakaolinite (a) and the quartzite (b) powders



1.2 Synthesis of the geopolymer

The composition of the alkaline solution then used for the synthesis is shown in Table 2.

To elaborate the geopolymer matrix, we prepare an equal quantity of alkaline solution and metakaolin mixture. We also prepare mixtures consisting of alkaline solution, metakaolin and quartzite. The formulations are shown on table 3 wt.%..

The suspensions are poured into a parallelepiped molds (20 × 20 × 80 mm3) posed on a vibrator to promote the elimination of gas bubbles, molds are then placed in a drying oven at 40 °C for 12 hours.

Table 2. Composition of the alkaline solution in wt.%.

Constituent	H2O	KOH + NaOH	silicate de sodium (solution)
wt.%.	33.5	22.5	44

Table 2. Formulations of prepared geopolymers.

Quartzite/liant (%)	0	5	8	10	13	15
Alkaline solution (g)	100	95	92.5	90	88.5	85
Metakaolin (g)	100	95	92.5	90	88.5	85
Quartzite (g)	0	10	15	20	25	30

1.3 Characterization methods

The investigation of the physical and structural characteristics of the materials required the implementation of several techniques:

-We used rheology to determine the evolution of the viscosity of the mixtures from the first stages of the polycondensation in order to study the setting as a function of temperature (30 to 60 ℃) and composition. The tests were carried out on a Haak Rheostress type I rheometer, in the plane-plane configuration (PP60Ti). Mixtures previously undergo stirring for two minutes prior to be injected into the rheometer.

-The mechanical characterization of samples (aged 28 days) was performed by determining the three-point bending (samples of size 2 × 2 × 8 cm3) and compression (2 × 2 × 3 cm3) strengths.The fracture tests were run on a universal tensile testing machine (Istron type 5566) equipped with a 10 KN load cell capacity at a cross-head displacement rate of 1 –mm/min.

-The observation of the microstructure was performed on the gold-sputtered fracture surfaces using a scanning electron microscope (Carl Zeiss SEM Supra 55 type, Oberkochen, Germany).

- The hardness of the material is measured by the Vickers method with a tester under a load of 2 kg (Clemex).

2 Results and discussion

2.1 Rheological comportment.

The study of the rheological behavior of geopolymers turns on a valuable approach for the determination of the influence of several parameters (composition, temperature...) on the mechanism and kinetic of setting.

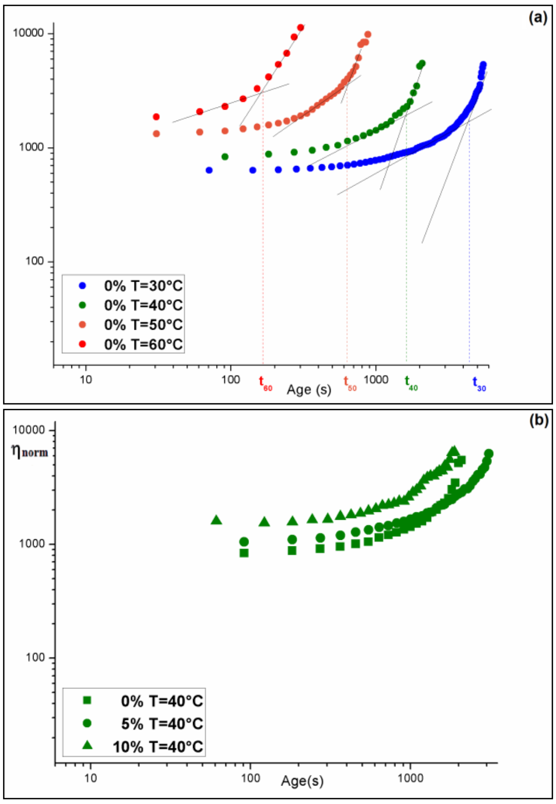
We studied the effect of two parameters namely the composition of the starting pastes (the mass percentage of quartzite) and temperature (30 to 60 ℃) on the evolution of viscosity from the young age until the geopolymer setting.

A recent study showed that at the first age of the mixture between alkaline solution and powder dry (metakaolin with or without additives) the suspensions viscosity depends strongly on the alkaline solution. This study has shown that it is more judicious to work in terms of normalized viscosity [14].

$$\eta_{norm} = \eta / \eta_{sol}(T) \qquad (1)$$

Figures 4 a and b illustrates changes in the normalized viscosity according to the age of the paste with 0 wt.% quartzite at temperatures ranging from 30 to 60 ℃ (a) and the evolution of η_{norm} of pastes from 0 to 15 wt. % of quartzite tested at 40 °C.

Fig. 4. Normalized viscosity of the pastes with 0 wt.% quartzite vs. time for different temperatures (a) and the evolution of η_{norm} of pastes from 0 to 15 wt. % of quartzite tested at 40 °C (b). (Shear rate $\gamma' = 5s^{-1}$)



We note that:

-Whatever the compositions and temperatures studied, the evolution of viscosity vs. time follows the same allure: a slight increase in the first ages of the mixture followed by a rapid increase due to the hardening of the material.

A graphical approach allows to estimate a setting time that corresponds to the inflexion of the evolution of viscosity [14].

-The temperature has an accelerator effect on the setting. The increase in temperature seems to favour the dissolution phenomena of soluble oxides, diffusion of complex Al and Si complexes dissolved, the formation of a gel resulting from polymerization and finally the hardening of the gel [15].

- The addition of the quartzite increases significantly the viscosity of mixtures.

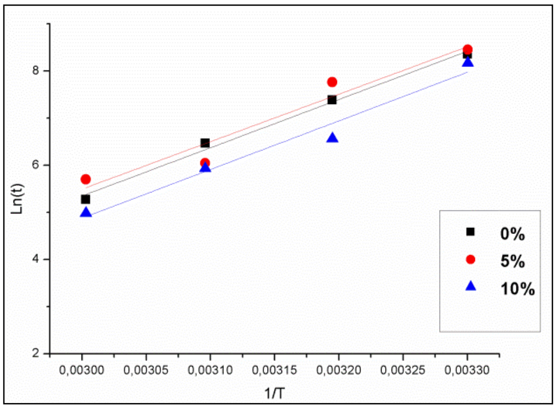
The same experimental protocol for the determination of the setting time has been applied to compositions ranging from 0 to 15 wt.% of quartzite.

-The variation of Ln(t) versus 1/T (Fig. 5) shows a perfect correlation with Arrhenius law:

$$t_{prise} = A\, e^{-Ea/RT} \qquad (2)$$

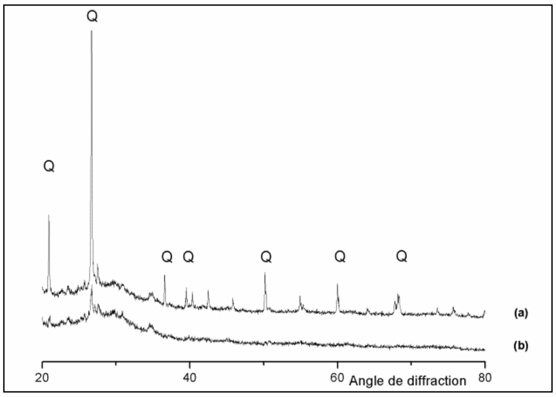
The calculation of the slope of the rights (-Ea/R, Ea is the activation energy of polymerization and R is the ideal gas constant) provides access to an average value of the order of 84 kJ/mol for Ea for all of the compositions explored. This value is of the same order of magnitude as that reported in the literature for similar compositions [14].

Fig. 5. Time sitting vs. sitting temperature of 0, 5 and 10 wt.% of quartzite.



In the light of this result, it appears that the quartzite added to metakaolin plays no major role in the setting process of geopolymers. This mineral has only a role of inert aggregate in the material. This observation is confirmed by XRD analysis (Fig. 6). We note that the spectrum of the material containing 15 wt.% of quartzite presents mainly representative amorphous phase dome of the geopolymer and characteristic peaks of quartz.

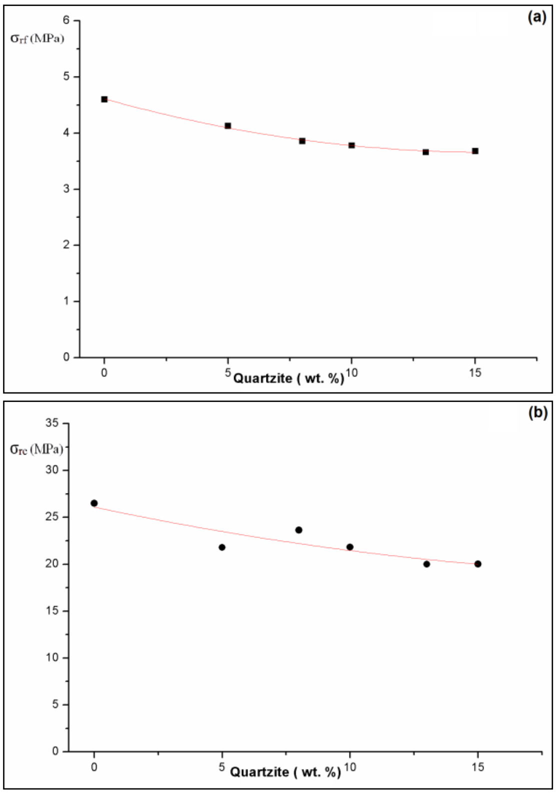
Fig. 6. X-ray diagram of geopolymer containing 0 (a) and 15wt.% of quartzite) (b),(Q: quartz)



2.2 Mechanical characterization

Mechanical characterization was studied by the study of the evolution of flexural and compressive strengths versus rate of quartzite on samples elaborated at 40 °C 28 days aged (Fig.7 a and b respectively).we note that the introduction of quartzite decreases both materials strength in inflexion and compression of about 20%.

Figure. 7. Three point bending (a) and compression (b) strengths vs. the amount of quartzite (wt.%).



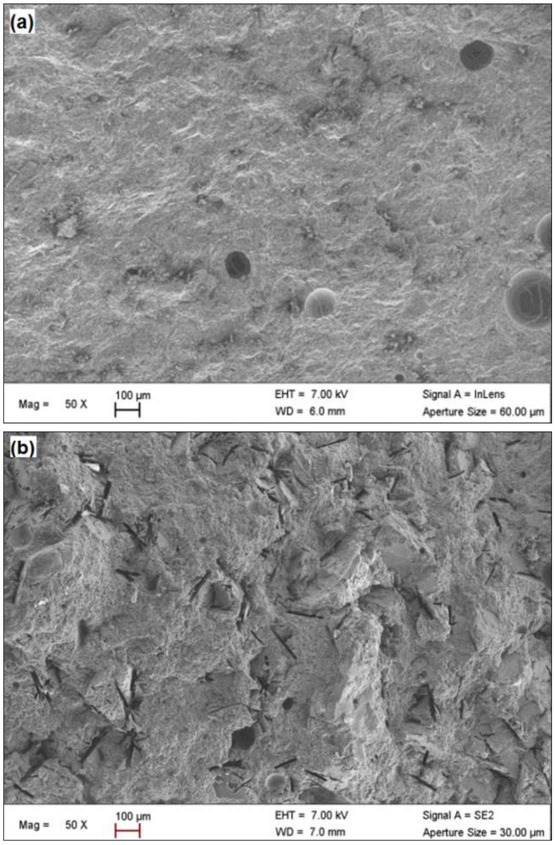
The mechanical performance of the geopolymer matrix with (0 wt.% of quartzite), which presents fragile type of the comportment at break although acceptable, are limited by the presence of intrinsic defects. These defects are spherical macrocracks likely caused by gas release during the curing and the drying (Fig.8. a).

The degradation observed in the presence of quartzite can be explained by:

- The decrease in the volume of the geopolymer phase responsible of the cohesion of the material.

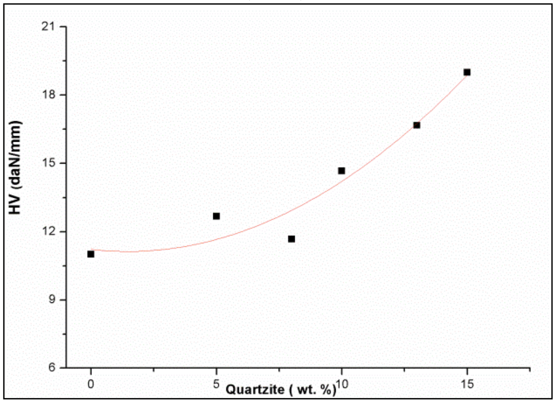
-The lack of cohesion between the matrix and the grains of chemically inert quartzite, and which has a very wide size distribution (fig. 3.b), resulting in the phenomena of decohesion clearly visible on surfaces of ruptures (Fig.8.b).

Fig.8. SEM micrographs of the surfaces of rupture



On the other hand, the addition of the quartzite has a beneficial effect on the surface properties such as the hardness. Addition of 15% of quartzite (hard mineral) increases significantly the hardness of the material (Fig. 9)

Fig. 9. Vickers microhardness vs. the amount of Quartzite (wt.%).



Conclusion

Good mechanical performances of a geopolymer synthesized by alkaline reaction on a metakaolin, prompted us to use it as a matrix for the elaboration of composite materials. we chose a natural aggregate, the quartzite.

The rheological study and XRD characterization show that the aggregate acts as a chemically inert charge and has no influence on the setting characteristics of the matrix. The addition has an impact on the mechanical resistance of the material. We note a degradation of the order of 20% for a rate introduction of 15 wt. %

On the other hand, there is a sensible improvement of a surface property, the hardness, an essential characteristic for a material that can be used for coating.

Acknowledgements

The authors wish to thank the SCAC (Service of Cooperation and Cultural Action) of France Embassy in Morocco for its financial help under the Competitive Clusters Program (2009-2011).

This work was also supported by the Hassan II Academy of Science and Technology (V2GV Project).

Authors would like to thank Pr. M. El Ouazzani and Mr. M. Riahi (Mechanical Laboratory., science Faculty of Casablanca) for their contribution on rheological tests.

References

1. J. Davidovits,Chemistry of Geopolymeric Systems Terminology, *Proceedings of Geopolymer, International Conference, France* (1999).
2. J.W Phair, J.S.J. van Deventer, Characterization of fly-ash-based geopolymeric binders activated with sodium aluminate, Industrial & Engineering chemistry Research, **41**, 4242-4251 (2002).
3. T.W. Cheng, J.P. Chiu,. Fire-resistant geopolymer produced by granulated blast furnace slag, Minerals Engineering, **16**,205–210 (2003).
4. K. Komnitsas, D. Zaharaki, Geopolymerisation: a review and prospects for the minerals industry, Minerals Engineering, **20**, 1261–77 (2007)
5. D. Dimas, L. Giannopoulou, D.Panias, Polymerization in sodium silicate solutions: a fundamental process in geopolymerization technology, J Mater Sci, **44**, 3719–30 (2009).
6. Y. J. Zhang, Y. C Wang, D. L Xu, S. Li, Mechanical performance and hydration mechanism of geopolymer composite reinforced by resin, Materials Science and Engineering A, **527**, 6574–6580 (2010)
7. P. Duxson, A. Fernández-Jiménez J. L. Provis G. C. Lukey A. Palomo J. S. J. van Deventer. Geopolymer technology: the current state of the art, J Mater Sci, 42, 2917–33 (2007).
8. P. Duxson, John L. Provis, Grant C. Lukey, Jannie S.J. van Deventeret al, The role of inorganic polymer technology in the development of 'Green Concrete', Cement and Concrete Research, **37**, 1590–7 (2007).
9. A. Palomo, M.T. Blanco-Varelaa, M.L. Granizoa, F. Puertasa, T. Vazqueza, M.W. Grutzeckb,*. Chemical stability of cementitious materials based on métakaolin, Cem Concr Res, **29**, 997–1004 (1999).
10. A. Autef , E. Joussein , G. Gasgnier , S. Rossignol, Role of the silica source on the geopolymerization rate, Journal of Non-Crystalline Solids **358**, 2886–2893 (2012).
11. M. Tohoué Tognonvi, J. Soro, S. Rossignol, Durability of Tubular Geopolymer Reinforced with

Silica Sand, New Journal of Glass and Ceramics, **2**, 85-90 (2012).

12. N. Gouzouli, A. Samdi, R.Moussa,M. Gomina, Physico-chemical and technological properties of ceramic tiles: Role of clay minerals on as pressed and dried compacts properties, MATEC Web of Conferences, **5**, 04011 (2013).
13. H. Xu, J.S.J Van Deventer, The geopolymerisation of aluminosilicate Minerals, International Journal of Mineral Processing, **59**, 247–266 (2000).
14. A. Bourlon, Physical chemistry and rheology of fresh geopolymer for oil well cementing, PhD thesis, Pierre and Marie Curie University, France (2010).
15. H. Xu, Geopolymerisation of aluminosilicate minerals, PhD Thesis, University of Melbourne, Australia. (2001).