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Rheological behavior of a fresh geopolymer based on metakaolin: effect of the introduction of calcium carbonate

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ABSTRACT: Geopolymers can be considered as inorganic polymers presenting good physicochemical properties. The principal advantage of these materials is their elaboration without a lot of energy spending compared to conventional materials. The choice of raw materials and the control of preparation conditions, represent important parameters controlling the rheological properties in the fresh state and physicochemical properties of consolidated geopolymers. Calcium carbonate powder is incorporated in a geopolymer formulation based on metakaolin. The rheological tests elaborated in different conditions allowed us to model their rheological behavior and follow the effect of carbonate introduction. Two models are observed, the Bingham model and the Herschel-Bulkley model. The introduction of calcium carbonates seems to have no effect on the evolution of the viscosity, while this latter has a remarkable sensitivity to the geopolymerization temperature.

KEYWORDS: rheology, clay, kaolin, alkali-activation, metakaolin, $CaCO_3$, filler, geopolymerisation

1 INTRODUCTION

The alkali aluminosilicate commonly known as geopolymers by Davidovits [1], are very dense "gels" of amorphous silico-aluminates obtained by attacking a mineral containing alumina and silica (such as metakaolin or fly ash etc...) with an alkaline solution of silicate. More appropriate wide-term that describes these materials is inorganic polymers [2].

Kaolinite clay is widely used as a starting material for the synthesis of geopolymers [3-6]. Metakaolinite is derived after the calcination of kaolinite, it is considered as an artificial pouzzolanic material widely used in industry and more reactive than the kaolinite.

Building materials industry is regarded as a major consumer of energy and seeks to optimize its spending by heading more and more towards new materials whose production is less expensive and less polluting. In this context, geopolymers appear as a very promising alternative to traditional cementitious materials, thanks to their stability and their physicochemical properties .The manufacturing process of geopolymers reduces practically the emission of CO_2, thanks to their elaboration at temperatures very close to the ambient.

Introducing mineral fillers by replacing the clay will reduce energy costs by minimizing the dependence of geopolymers on the kaolin since that latter requires a thermal activation by calcination.

Few studies were interested on the rheology of geopolymers [7-9]. Due to this reason, in the present work, we plan to study the effect of two factors on the rheological properties of a geopolymer based on metakaolin. The first factor is related to the composition represented by the rate of introduction of calcium carbonate, and the second one is related to the operating conditions represented by the manipulation's temperature.

2 MATERIALS AND EXPERIMENTAL METHODS

2.1 STARTING MATERIALS

The geopolymer material is synthesized by the reaction of an alkaline solution on previously activated kaolin and calcium carbonate 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 a density of 1.54 .

The dry matter is composed of:

- A commercial kaolin powder from Sibelco CompanyUK
- A commercial calcium carbonate ($CaCO_3$) from Janssen Chimica Company, of purity 98.5%.

2.2 ELABORATION METHOD

The composition of the alkaline solution used for the synthesis is shown in Table 2. To elaborate the geopolymer, we prepared an equal quantity mixture of alkaline solution and dry powders (metakaolin and calcium carbonate). Mixtures previously underwent stirring for two minutes prior to be injected into the rheometer.

The introduction of the calcium carbonate is realized by replacing the metakaolin. The formulations are shown on table 3 (wt. %). It is generally accepted that the temperature has a strong influence on the geopolymerization and accelerates the sitting phenomena [5]. The choice of temperature measurement was limited to 25, 30 and 40°C.

Table 1. Composition of the alkaline solution in wt. %.

Constituent	**H_2O**	**KOH +NaOH**	**Sodium silicate**
Wt. %.	33.5	22.5	44

Table 2. Formulations of prepared geopolymers.

$CaCO_3$ (g)	0	6	12
Metakaolin (g)	50	46	38
Alkaline solution (g)	50	50	50

2.3 MEASUREMENT PROTOCOL

Tests were carried out on a Haak Rheostress type I rheometer, in the plane-plane configuration (PP60Ti). Rheological behavior of suspensions was identified by studying the shear stress evolution (τ) versus the shear rate ($\dot{\gamma}$) according to the following protocol as shown in Figure 4:

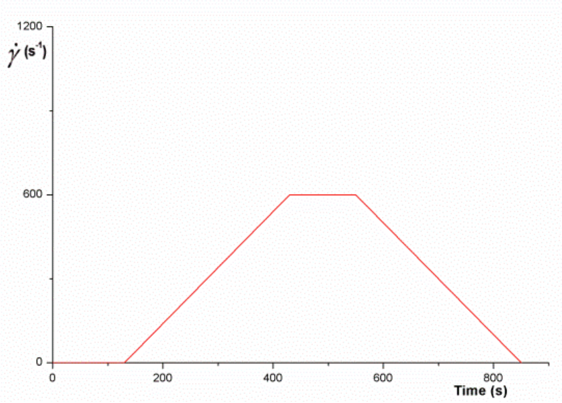


Fig. 1. Variation of shear rate with time.

- No shear during 130s in order to reach the temperature equilibrium.
- The shear rate increases from 0 s^{-1} to 600 s^{-1} during 300 s and maintain constant at 600 s^{-1} during 130 s. This operation is necessary to ensure a sufficient homogeneity of the medium.
- A decreasing ramp from 600 s^{-1} to 0 s^{-1} during 300 s where rheological analysis is performed.

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF STARTING MATERIALS

We determined the quantitative chemical composition of the kaolin by X-ray fluorescence (Magixpro, Panalytical) (Table I) and the mineralogical compositions of the kaolin and the calcium carbonate by X-ray diffraction (Panalytical X'Pert Pro) (Figure 1).

The XRD spectrum of the kaolin mainly presents the characteristic peaks of kaolinite and free quartz. Characterization results permit us to estimate that the kaolin is composed of 89.5 wt. % of kaolinite and 6 wt. % of free quartz. The XRD spectrum of the carbonate reveals its high purity, it shows only the characteristic peaks of $CaCO_3$. The synthesis of geopolymers requires the use of activated kaolin. Metakaolin is obtained by thermal treatment in order to amorphize clay particles, sources of aluminum by dehydroxylation [10].

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

Table 3. Quantitative chemical composition of the kaolin powder 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
47.54	35.49	0.89	0.18	0.43	0.33	0.09	2.15	0.02	0.05	0.01	12.61

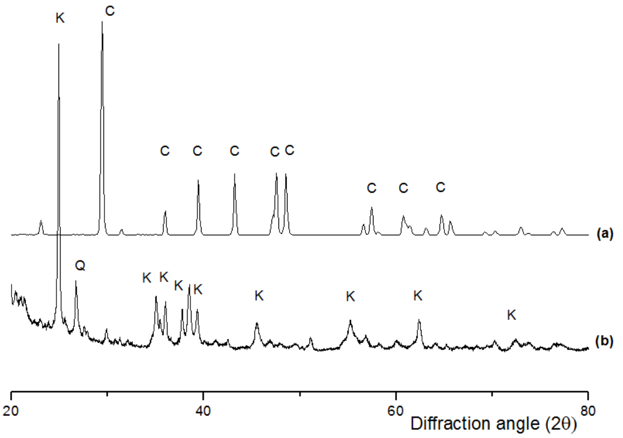


Fig. 2. X-ray diagram of the carbonate calcium powder (a) the carbonate calcium powder (a) and the kaolin powder (b). K: kaolinite, Q: quartz C: calcite.

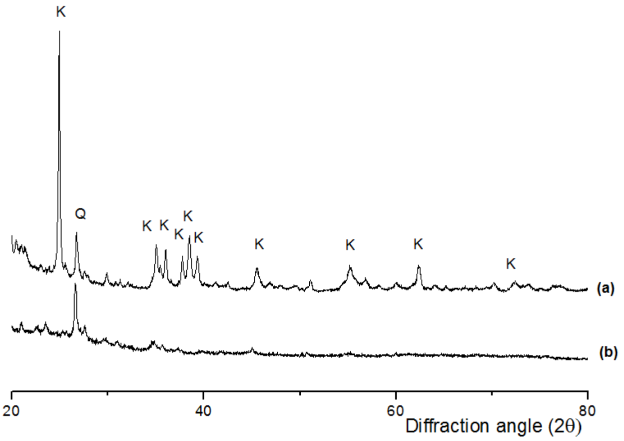


Fig. 3. XRD diffraction pattern of the kaolin before (a) and after heat treatment (b). K: kaolinite, Q: quartz.

We also conducted the particle size analysis of dry metakaolin and carbonate powders (laser particle size analyzer Coulter LS 230) (figure. 3). The results reveal very fine powders with average size of about 6-7 µm.

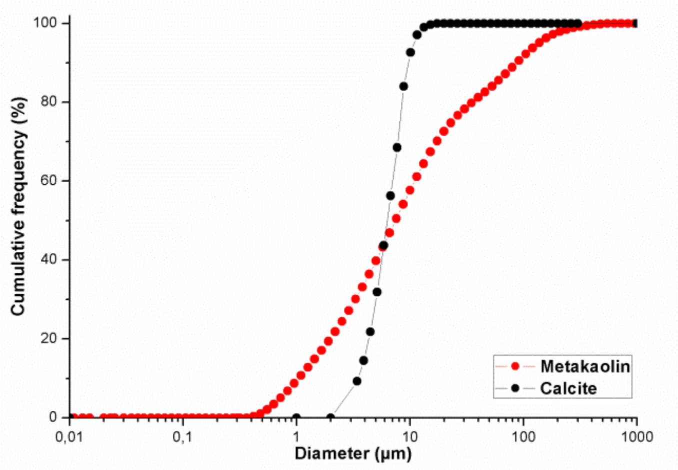


Fig. 4. Particle size distribution of powders.

3.2 RHEOLOGICAL BEHAVIOR MODELING

Numerous experimental studies have showed that the rheological behavior of the clay suspensions in water can be described by the Herschel-Bulkley model [11, 12].

$$\tau=\tau_0+k\gamma^n \quad (1)$$

τ: shear stress (Pa),
τ_0: yield point (Pa),
K: consistency index ($Pa \cdot s^n$),
γ : shear rate (s^{-1}),
n: flow behavior index.

The figure 5 presents the rheograms of the suspensions according to the two factors relating to this investigation. The flow curves present a yield stress. Parameters of observed models are presented in table 4.

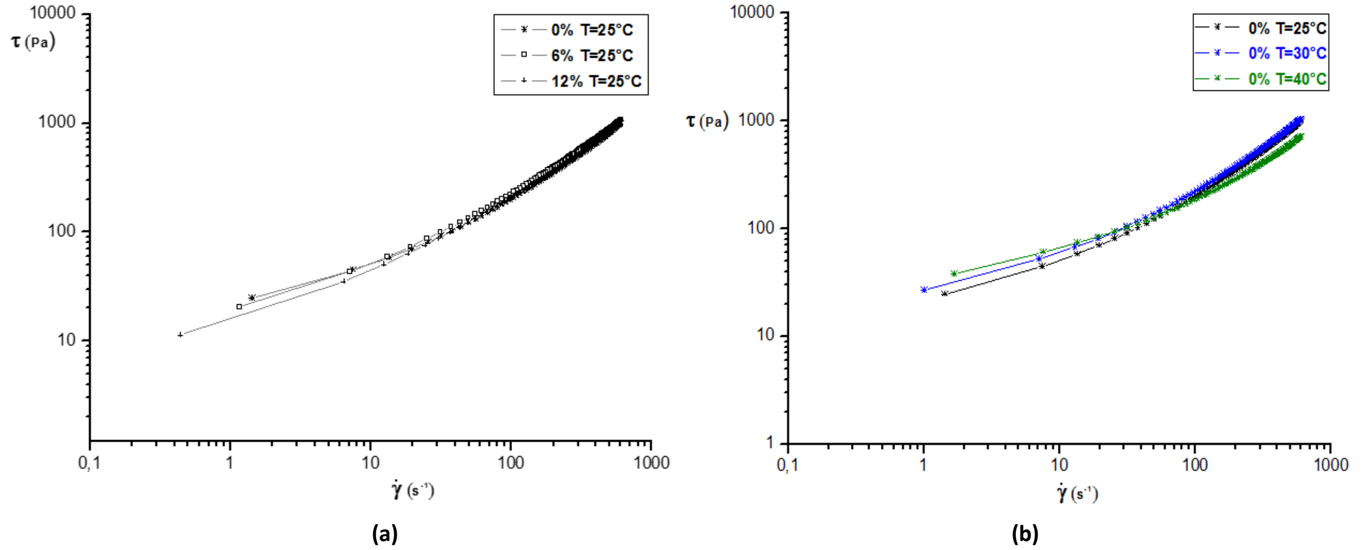


Fig. 5. Rheograms of fresh geopolymers at 25°C for different $CaCO_3$ content (a) and of fresh geopolymers of the composition with 0% of calcite at different temperatures (b).

One can notice that:

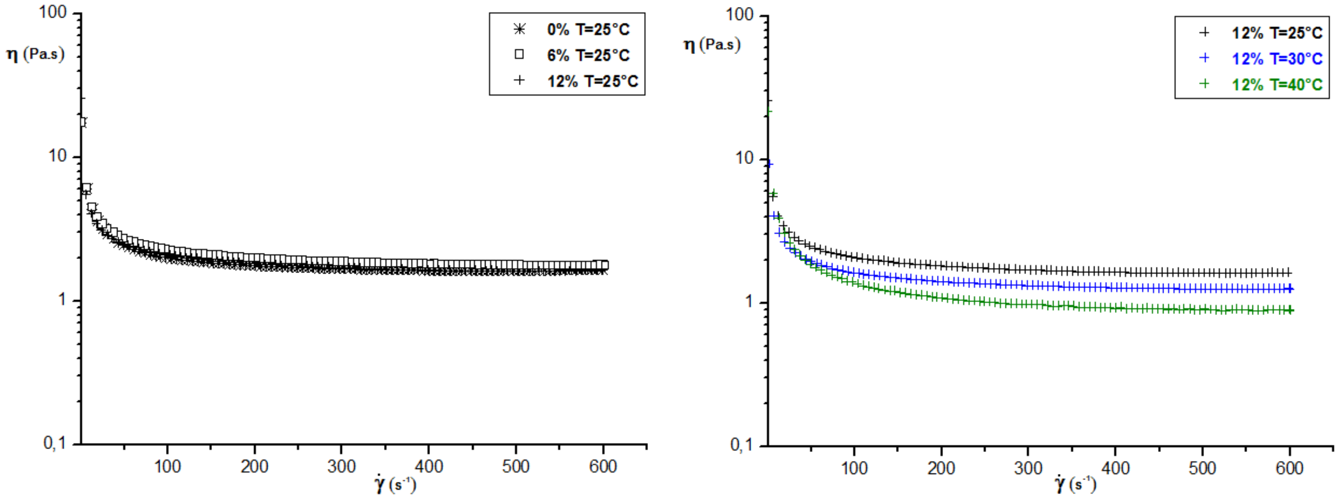
- The alkaline solution presents a Newtonian behavior.
- The suspensions tested at 25°C and 30°C which don't contain calcium carbonate are Bingham fluids, for which the yield stress $\tau 0$ and the plastic viscosity increase with increasing temperature.
- For the suspensions with 0% of $CaCO_3$ tested at 40°C and those containing 6% and 12% of $CaCO_3$, the fresh geopolymers are Herschel-Bulkley fluids which have a yield stress that decreases with the increase of $CaCO_3$ introduced. In contrast, the consistency index "k" increases slightly and the flow behavior index "n" does not show a noticeable variation.

Table 4. Viscosity Parameters of fresh geopolymers determined from the measurements of the figure 5

%	T (°C)	Shear (s^{-1})	Rheological model	Model's parameters		
				Plastic viscosity or consistency ηp / k (Pa.s)	yield stress τ_0 (Pa)	n
S	**25**	**--**	**Newton**	0.00957	--	1
0	**25**	**> 15**	**Bingham ($\tau=\tau_0+\eta p^{\gamma}$)**	1.55	40	1
	30	**>19**		1.62	53.62	1
	40	**>25**	**Herschel-Bulkley ($\tau=\tau_0+k\gamma^{n}$)**	1.76	63.62	0.95
6	**25**	**>19**		2.269	38.76	0.95
12	**25**	**>24**		2.126	34	0.94

3.3 EVOLUTION OF THE VISCOSITY VERSUS THE SHEAR

The figures 6 (a) and (b) represent the evolution of the apparent viscosity versus the shear rate. Curves follow the same allure for all studied temperatures and compositions. The viscosity decreases with the increase of the shear rate. This decrease is due, on the one hand, to the agglomerations that the suspensions present in the beginning of the mixing process, the flow accelerates when the clay is subjected to a stress and therefore the clay particles deagglomerate . On the other hand, it is also due to the strong alkaline pH conditions of the silicate solution which provoke the solubility of the clay particles.



(a) **(b)**

Fig. 6. Evolution of the viscosity of fresh geopolymers versus the incorporated $CaCO_3$ content (a) and versus the geopolymerization temperature (b)

The analysis of these curves shows that:

- The introduction of the calcium carbonate seems to have no effect on the evolution of the viscosity versus shear rate (figure 6-a).
- The viscosity presents a high sensibility to the geopolymerization temperature (figure 6-b). We note a weak decrease of viscosity with an average of few Pa.s when the temperature increases. It indicates that the behavior of the mixtures is dominated by the silicate solution whose water molecules mobility increases with the increase of the temperature and causes the decrease of the apparent viscosity.

3.4 EVOLUTION OF VISCOSITY VERSUS TIME

We present in figure 7 the evolution of the viscosity versus time at a shear rate held constant at $5s^{-1}$.

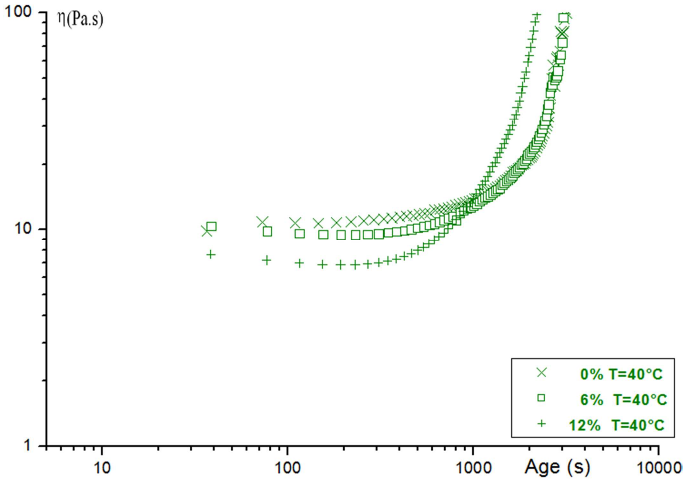


Fig. 7. Evolution of fresh geopolymers viscosity versus time under the effect of $CaCO_3$ content.

The curves (for all the studied temperatures and compositions) show the same allure and consist of two variation areas:

- A first stage where the viscosity decreases slightly with time, this phenomenon becomes more remarkable when the introduced quantity of $CaCO_3$ increases.
- A second stage where the viscosity increases strongly showing the appearance of a new process varying the consistency of the mixtures.

Under alkaline conditions (high pH), $CaCO_3$ is very slightly soluble and aluminosilicates are transformed to highly reactive materials. In the first moments of mixing, the dissolution process of clays is initiated by the presence of hydroxyl ions which facilitate the dissociation of different silicates and aluminates species promoting a later polymerization responsible of the increase of the viscosity until the hardening of the gel (second stage). When the age of suspensions increases, we note that the viscosity reaches its maximal value more rapidly when the $CaCO_3$ content is more significant.

4 CONCLUSION

The main objective of this work is to investigate rheological properties of a fresh geopolymer based on metakaolin where calcium carbonate was incorporated.

We have found models that are able to describe the rheological behavior of the selected compositions. The tests show that two models characterize these formulations: Bingham model and Herschel-Bukley model. The introduction of calcium carbonates doesn't seem to have any effect on the evolution of viscosity, while the latter presents a remarkable sensibility to geopolymerization temperature.

With these results, we hope to continue this study by developing a system that allows the optimization of the operating conditions from a rheological point of view in order to ensure the elaboration of finished materials with good physicochemical properties.

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