Journal of Materials Science and Engineering B 9 (1-2) (2019) 6-12
doi: 10.17265/2161-6221/2019.1-2.002

Effect of the Formulation of Sodium Activation Solutions on the Setting Time of Metakaolin Based Geopolymers

Lahlou Nouha[1], Ouazzani Touhami Mohamed[1], Moussa Redouane[2] and Hattaf Rabii[2]

1. Faculté des Sciences Aïnchock, Université HassanII, Laboratoire de Mécanique, Casablanca 20000, Maroc

2. Faculté des Sciences Aïnchock, Université HassanII, Laboratoire de Physico-Chimie des Matériaux Inorganiques, Casablanca 20000, Maroc

Abstract: Geopolymer materials today represent innovative products, used frequently as a substitute for cementitious traditional materials. They are obtained by the action of an alkaline activation solution (composed of mainly of silicon dioxide (SiO_2) and sodium hydroxide (NaOH) and water) on a powder natural or synthetic aluminosilicates. In this work, we seek to highlight the effect of the percentage of sodium dioxide firstly, on the evolution of the viscosity of the alkali-activated solution and secondly, on the evolution of the viscosity of geopolymeric solution. Another aspect of this work is the determination of the effect of this percentage on the kinetics that characterize the start of the percolation phenomenon (transition from the fresh state to the hardened state). At last result concerns the impact of temperature on this transition. This contribution consolidates the control protocols for the formulation of geopolymers and allows the optimization of the processes of their exploitation.

Key words: Sodium activation solutions, geopolymer, metakaolin, setting time, rheological behavior, polynomial regression.

1. Introduction

Geopolymer materials, which were considered in this study, are obtained by activating an aluminosilicate powder with a sodium solution [1]. The evolution of knowledge about these products has, in recent years, become particularly important from the moment they are considered as an alternative to traditional materials (cement, plastic, and ceramic) in view of their good hydrothermal stability, their resistance to acid attacks and their good endowment of mechanical properties [2-4]. Several factors govern the performance of these materials in the fresh state, including raw material, temperature, alkaline nature or the percentage of sodium oxide and directly impact their behavior in the hardened state [5]. In this context, we can mention the results already observed [6] concerning the effect of the formulation of the activation solution on the rheological behavior of the geopolymer considered. We can also mention the studies which concern the impact of physicochemical and rheological behavior in the fresh state on solid state mechanical behavior [7], or those which are about the analysis of the effect of the alkaline nature on the macroscopic properties of the finished product [8].

Our work is part of these approaches and is meant as an additional contribution for the control of the evolution of the flows of the geopolymers in the fresh state. This also makes it possible to consolidate the control protocols of the formulation of alkali-activated solutions and to optimize the processes of their use. In this context, an approach for converting the weighing of the components (sodium hydroxide pellets, silicates solution and distilled water) into molar ratios $R_1 = SiO_2/Na_2O$ and $R_2 = H_2O/Na_2O$ is introduced. An empirical law allowing a correlation between the viscosity of these solutions and the percentage of oxide sodium is proposed. A second result concerns the rheological behavior of geopolymeric solutions, which depend directly on this percentage. We are able

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Corresponding author: Lahlou Nouha, Ph.D. student, research fields: rheological behavior, materials science and fluid mechanics.

to further describe how, for the same ratio L/S (L = Quantity of SAA and S = Quantity of aluminosilicate powder), the setting time is directly affected by this structural parameter and by the temperature.

2. Materials and Experiments

We consider the following products:

- The sodium hydroxides of Cadilhac company, purity 98.5%.
- An alkaline solution of sodium silicate from Cadilhac company with 45% by weight of dry matter, an SiO_2/Na_2O molar ratio of 2 ± 0.1 (15% Na_2O, 30% SiO_2 and 55% H_2O).
- An artificial Pozzolan (Metakaolin) “ARGICAL-M 1000”, obtained by calcination and grinding of a kaolin clay from the Charentes. Its chemical composition is: SiO_2: 55%; Fe_2O_3: 1.4%; Al_2O_3: 40%; TiO_2: 1.5%; $K_2O + Na_2O$: 0.8%; CaO + MgO: 0.3%. It is a dehydroxylated alumina silicate of general composition: $Al_2O_3{\cdot}2SiO_2$. It is an amorphous material, not crystallized, whose particles have a lamellar form Fig. 1.

The sodium hydroxide (NaOH) pellets are dissolved in distilled water under magnetic stirring of 6 tr/s for one hour before adding the commercial solution. The mixture thus obtained is solicited by the same agitation for two hours in order to ensure the chemical equilibrium between the silicate species. After carrying out the necessary weighing of the solution and the powder, the two components are mixed using a kneader for 2 min. This leads to the formation of a homogeneous paste that evolves over time. The values retained in this work exceed those considered in the literature (Table 1).

For the rheological tests, we use the “Rheostress 1” rotary rheometer from “ThermoHaake” operating at imposed speed and controlled by Rheowin software. The rheological tests are carried out using the plane-plane cell called PP60 for which the lower plane is fixed and the upper plane is movable. This geometry presents for this study a double advantage; first, ease of handling and then a small amount of sample used.

The flow regime considered is quasi-stationary allowing the determination and the follow-up of the evolution of the viscosity as a function of the shear rate;

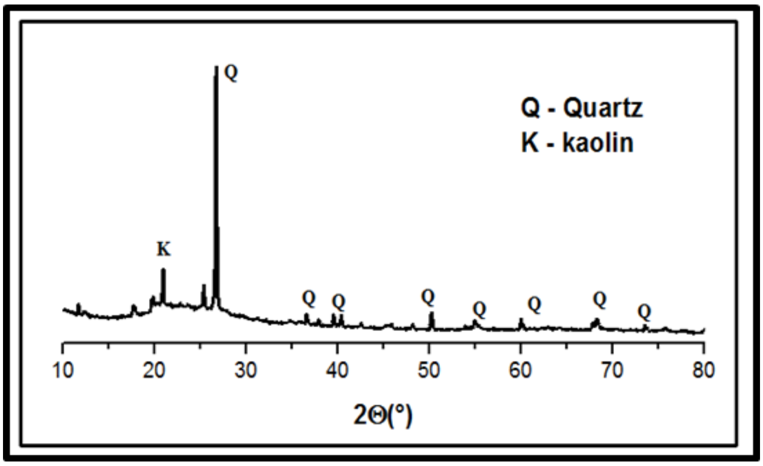

Fig. 1 Metakaolin DRX diagram.

Table 1 The experimental values of the structural parameters.

Q_1 (NaOH) (g)	Q_2 (Com Sol) (g)	$Q_3(H_2O)$ (g)	$\%Na_2O$	R_1	R_2
0	100	26.75	11.83	2	5.45
2.76	100	30.71	12.98	1.75	5
10.42	100	37.53	16.18	1.3	4.01
15.84	100	49.45	16.86	1.1	3.83

the sample in question is subjected to a triangular signal with an imposed speed ranging from 0 to 100 s^{-1} for a rise time of 300 s. For the determination of the setting time, the tests carried out are at a constant speed imposed of 5 s^{-1} for a duration of 3,600 s.

3. Results and discussions

At first we note that considering the equation $\%Na_2O = \frac{100}{R1+R2+1}$ (valuable for 100 g of the commercial solution), we are able to determine the values of R_1 and R_2 directly from the weighing (Q_1, Q_2 and Q_3) of the different constituents of the alkaline activation solution. This percentage of Na_2O affects directly the sum of the ratios $R_1 + R_2$, and allows integrating at least, on the theoretical level, a set of cases for which this sum remains constant. It should be noted that our contribution in the conversion of weighing to ratios verifies the results found by Bourlon and Steins [2, 3].

We carry in Fig. 2a the evolution of the viscosity of the alkali-activated solution as a function of this percentage. To do this, we conduct fifty tests corresponding to fifty different values of this percentage varying between 11% and 20%. Qualitatively, the behavior of these solutions remains Newtonian for all the different cases. In addition and in accordance with a logic of control, an empirical expression is proposed to describe the evolution of the viscosity according to the variations of this percentage. Exploitation of this relationship in a reverse manner would be, in our opinion, a considerable contribution to the prediction of $\%Na_2O$ values which act implicitly on the values of the R_1 and R_2 ratios for a given solution. This expression, obtained using a polynomial regression (Fig. 2b) with a coefficient of determination of $R^2 = 0.908$, is given by:

$$\eta = 9\times10^{-5}x^5 - 0.0071\,x^4 + 0.227\,x^3 - 3.5901\,x^2 + 28.112\,x - 87.144$$

where x represents a percentage of Na_2O.

Concerning the fresh state of the geopolymeric solutions, the rheological behavior is well described by the Herschel-Bulkley model (Fig. 3a) defined by the relation: $\tau = \tau_0 + k\,(\dot{\gamma})^n$, where τ_0 is the yield stress (Pa), k is the consistency (Pa. s^{-n}) and n is the flow index. This behavior remains shear thinning, for the cases considered in this work, with quasi-Newtonian steps for values of share rate greater than 10 s^{-1} (Fig. 3b).

Also and to highlight the effect of the alkaline solutions on the apparent viscosity, we represent in Fig. 4 the evolution of this physical characteristic for a different values of $\%Na_2O$. We note the existence of a

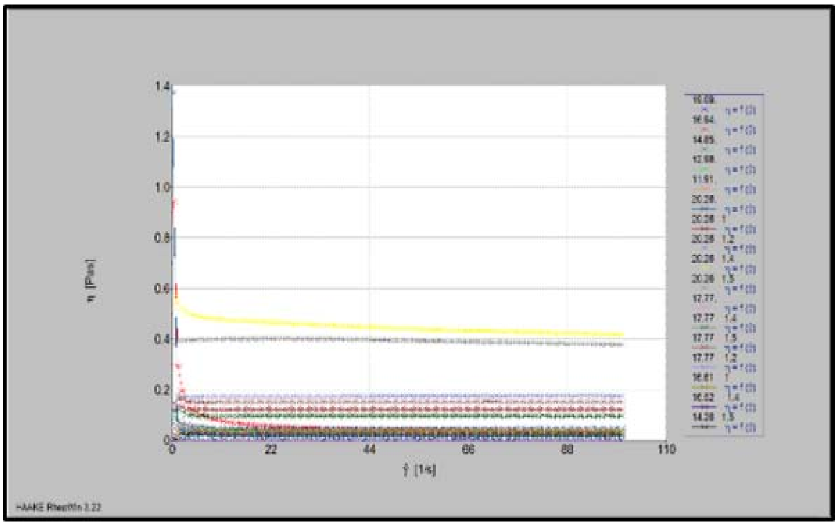

Fig. 2a The viscosity of the alkali.

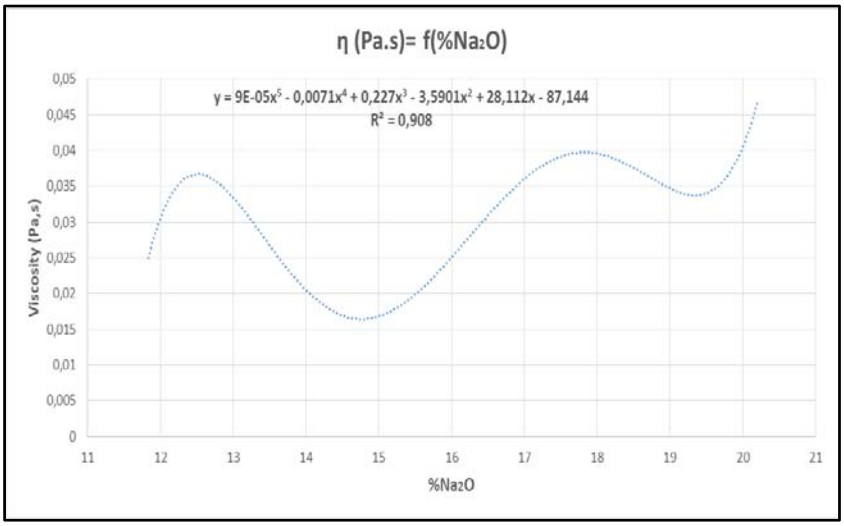

Fig. 2b **The graphical evolution of the proposed for activated solutions from Rheowin software empirical law.**

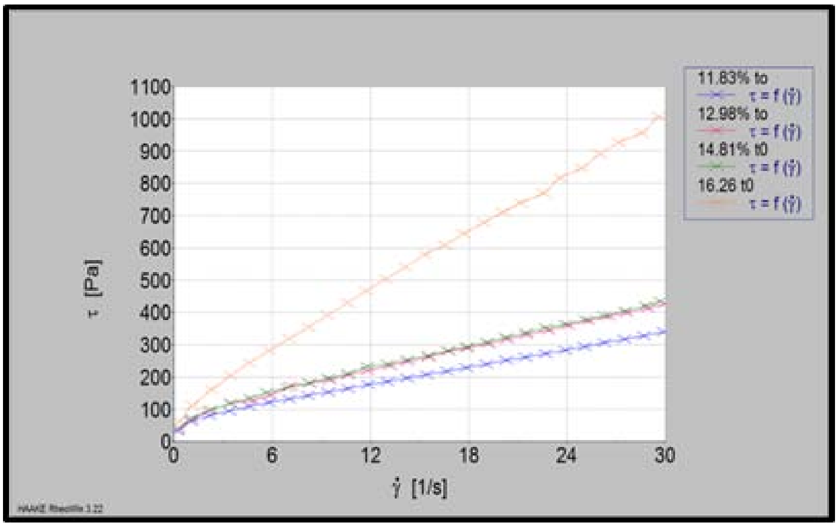

Fig. 3a **Rheograms for different %Na_2O.**

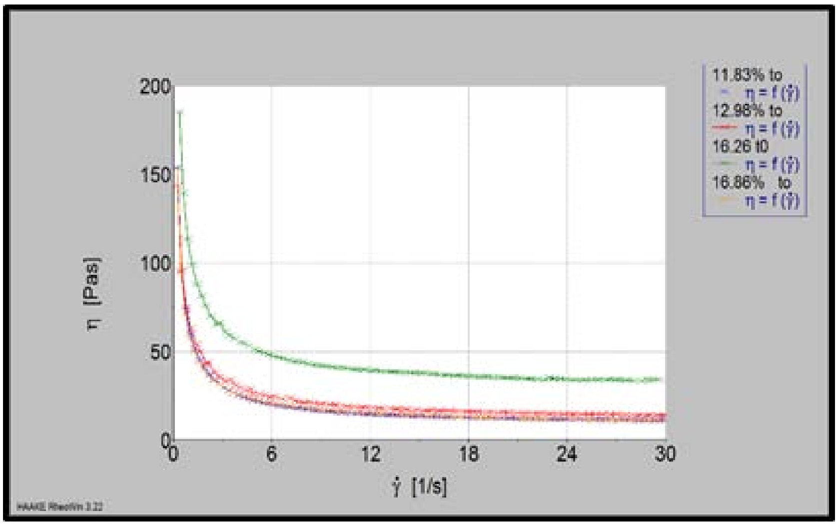

Fig. 3b **Evolution of the apparent viscosity.**

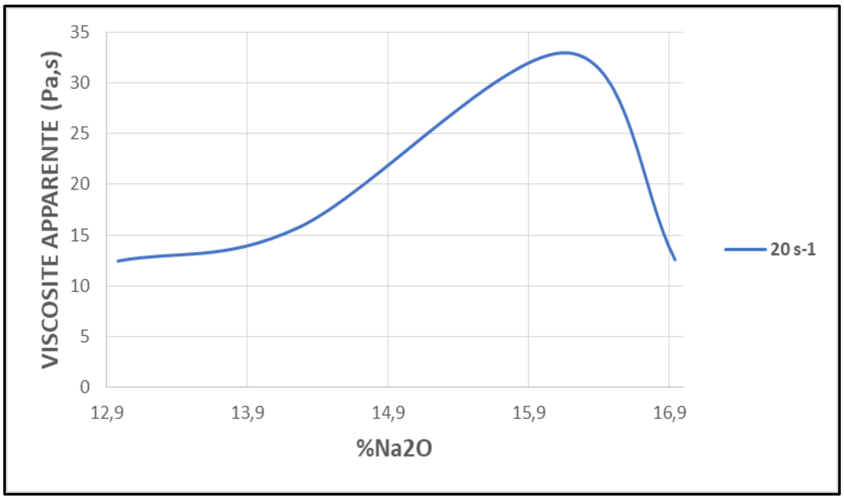

Fig. 4 **Evolution of the apparent viscosity for $\dot{\gamma} = 20\ s^{-1}$.**

Table 2 **Correlation between a setting time and SAA's viscosity.**

$\%Na_2O$	Viscosity (SAA) (Pa·s)	Setting time (s)
16.94	0.042	612.6
16.18	0.019	1340
14.26	0.022	539.9
12.98	0.033	903.5

viscosity peak for values between 16% and 17%. This remark may, in our opinion, have particular importance for the determination of an optimized formulation of geopolymer matrices.

The main result of this work is one which concerns the effect of this percentage on the kinetics setting. The evolution of the viscosity over time is divided into two parts, one presents the first times where the viscosity remains almost constant and the second where the viscosity follows an inflection and grows rapidly. This setting phenomenon, which characterizes the percolation path, is due to the bond between siliceous and aluminous oligomers. The determination of the exact setting time lies in the intersection of the two tangents representing the two parts.

In Fig. 5a where all the tests are conducted for a constant L/S ratio equal to 0.87, a direct impact of the percentage of $\%Na_2O$ on the setting time of the geopolymer is observed. For the considered values, we notice from Table 2 that the slowest setting time corresponds to a least viscous alkaline activation solution.

We can also report that the setting time depends on the L/S ratio, the increase of this parameter decelerates the percolation phenomenon (Fig. 5b).

On the other hand and to translate the effect of temperature on this setting time, we consider the case where $\%Na_2O = 16.18$ and L/S = 0.87, the evolution observed in Fig. 5c is in agreement with the results related in the literature [2-4]. Indeed, when the temperature increases, the setting phenomenon accelerates; the temperature which corresponds to the longest setting time flow is 40 °C.

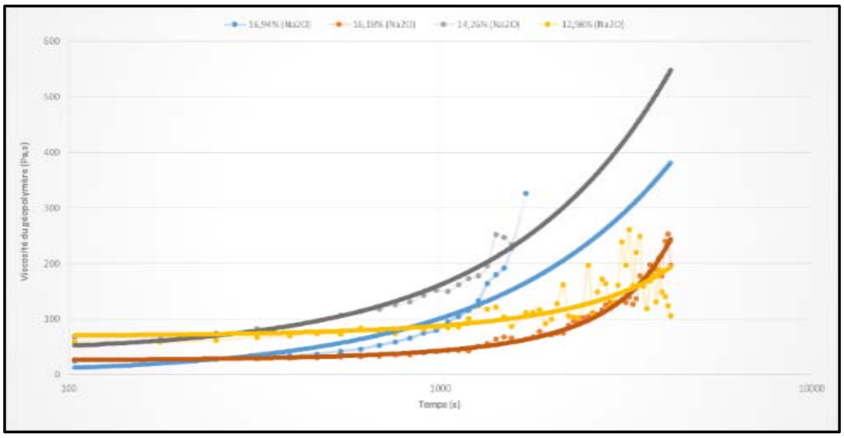

Fig. 5a **Kinetics setting of geopolymers for different percentage %Na_2O.**

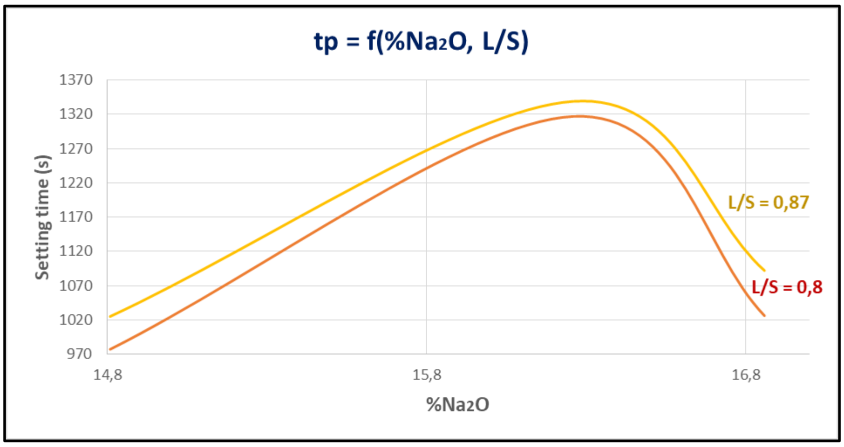

Fig. 5b **Evolution of the setting time for L/S = 0.8 and 0.87.**

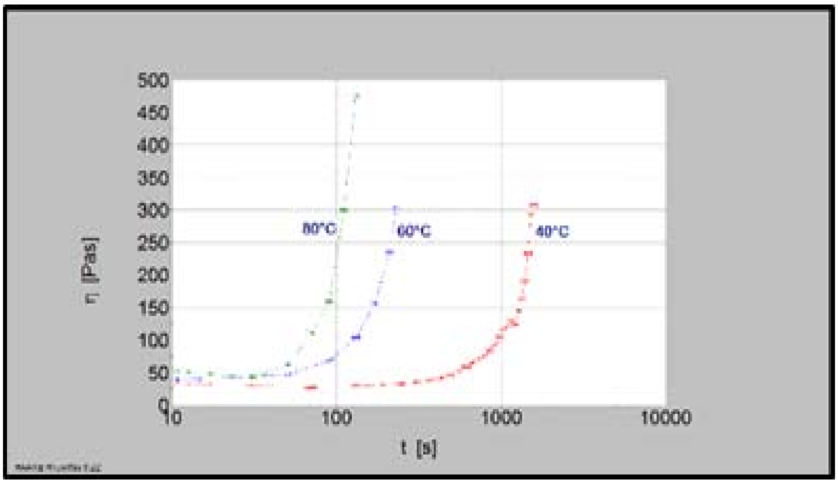

Fig. 5c **Kinetics setting in function of the temperature.**

4. Conclusions

This work is a contribution that focuses on the determination of the impact of the formulation of activation solutions on the development of geopolymer matrices and their transition from the fresh state to the hardened state. It concerns the particular case of sodium-based activation solutions and Metakaolin-based geopolymer matrices. It is part of the efforts made within the scientific and industrial community to better formulate these matrices in correlation with expectations expressed on both sides. This work comes through the production of some process that allows for more control in the different steps considered in the production of finished products.

Acknowledgements

The authors would like to acknowledge IGREX Engineering Service Ltd. for their support and help during this research work.

Appel à projetsautour des phosphates APPHOS sponsored by OCP (OCP Foundation, R&D OCP, Mohammed VI Polytechnic University, National Center of Scientific and technical Research CNRST, Ministry of Higher Education, Scientific Research and Professional Training of Morocco MESRSFC) under the project entitled “Matériaux de construction à base de matrices géopolymères et d’agrégats sous-produits de l’industrie des phosphates”, project ID: MAT-MOS-01/2017.

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