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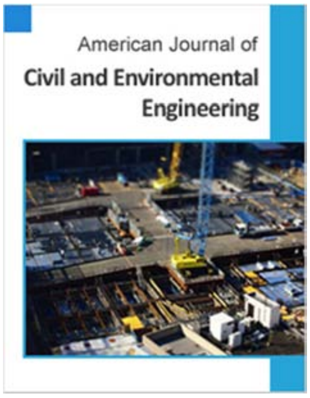

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Strength and Setting Times of Metakaolin-Cement-Based Geopolymer Pastes

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Abstract

The objective of this research is, in a first time, to synthesize geopolymer materials from two types of activator concentrated solutions prepared respectively with two different bases (NaOH and KOH). These solutions have been mixed thereafter with a kaolin previously heated under 550°C in order to obtain geopolymers samples, while optimizing the Si/Al ratio. Secondly, the influence of the partial substitution of metakaolin by a Portland cement has been studied in order to reduce the curing time of geo-polymer pastes. Thereafter, mechanical properties of the specimens at hardened state, notably the compressive strengths and the resistances on traction are investigated. The results showed that the use of the activator solution containing KOH during the preparation of the activator solution increases the solubility between KOH and silica gel. However, the solution based on sodium hydroxide (NaOH) promotes obtaining better mechanical resistances in the geopolymer materials. Otherwise, the partial substitution of metakaolin by Portland cement (PC) reduces the setting time of pastes and improves the mechanical resistances of hardened specimens but to a certain percentage before inverse effect appears. Finally, recommendations and perspectives are proposed in relation with the used raw materials and the mechanical performances of the geo-polymers materials found.

1. Introduction

Currently, concrete based on Portland cement (PC) is the most used construction material, given that it is more economical (compared to metals and other materials). One of the negative aspects of PC is that its fabrication generates CO_2 through calcination of raw materials and fuel consumption. It is calculated that one (1) ton of PC generates one (1) ton of CO_2 [1]. It is estimated that with demographic growth and industrialization, the pollution generated by cement production in a few years will represent 17% of worldwide CO_2 emissions (currently it is around 7%) [2].

With the threat of CO_2 emissions, the geopolymer materials are emerging as a clear alternative in many areas. Mutual organic polymers, but with the advantage of not burning, do not give off gases or toxic fumes, geopolymer could substitute tomorrow cement and plastics from petroleum.

Davidovits initially reported geopolymer in 1978 [3]. As a kind of inorganic material with ceramic-like properties, geopolymeric materials are attracting increasing interest as ecologically friend fireproof building materials [4]. Geopolymeric reaction was applied to reuse some waste products with pozzolanic properties, for example, fly ash [5]. Geopolymers were used to immobilize toxic metal [6, 7]. Due to its cage structure, geopolymer is even thought to be a valid approach to solidify radioactive element.

Due to the fact that aluminosilicates are the compounds most abundant in the earth's crust, there exist a large number of raw material sources rich in alumina and silicon with the potential for producing geopolymers. Among the materials with which have been used for procuring geopolymers predominates flying ash [8, 9] and include calcined clays [10], tailings [11, 12], kaolin [13], and puzzolans [14, 15]. These works have shown that geopolymerization with calcined materials promote quick dissolution and gelafication and at the same time develop high mechanical strength in short time [16]. These facts make geopolymers a serious consideration as a material of the future due to its low ecological impact and relatively high yield from raw materials.

They are used pure, filled or reinforced, the geopolymer find applications where traditional materials (metals, ceramics, organic polymers) do not provide a satisfactory solution. In the medical field, scientists are interested in the use of geopolymer associated with various phosphates as a potential biomaterial in orthopedic and maxillofacial surgery. The studies focus on geopolymer high silicon content (high ratio Si/Al) on the one hand finding the best compromise between porosity and mechanical properties, and also minimize the element aluminum can be toxic to the body.

However, the disadvantage of some geopolymer materials is their hardening that takes a lot of time under standard conditions, moreover, for their hardness, they must be put under a temperature of about 60°C.

The aim of this research is to synthesize geopolymer materials from two types of concentrated activator solutions prepared with two different bases (NaOH and KOH). These solutions were mixed after 24 hours with the previously calcined kaolin to obtain specimens of geopolymer. In addition, the influence of the partial substitution of métakaolin by a portland cement is studied in order to reduce the curing time of geopolymer paste. Therefore, the progression of structural and physico-mechanical properties, such as compressive strength and tensile splitting is deducted. Findings reported in this article would help to reveal the feasibility of using geopolymer materials as building material with higher mechanical strength than traditional cement product.

2. Experimental Procedure

Three raw materials were used in the experimental investigation: Kaolin, Portland cement (PC) and alkaline solutions.

2.1. Materials Used

2.1.1. Kaolin

The kaolin used in our study is that of Brittany area (France). X-ray diffraction (Figure 1) is formed on facing mineral powder in suspension in water. A Philips diffractometer PW 3710 is provided with a copper anticathode, and a Nickel filter, the wavelength is λ = 1.54Å. Registration ‘’stepper’’ is formed between 2 and 30° 2θ and this for a period of 1 hour and 30 minutes.

X-ray diffraction analysis was carried out: Untreated sample; sample treated with glycerol (under vacuum at 90°C) and sample heated to 550°C for one hour.

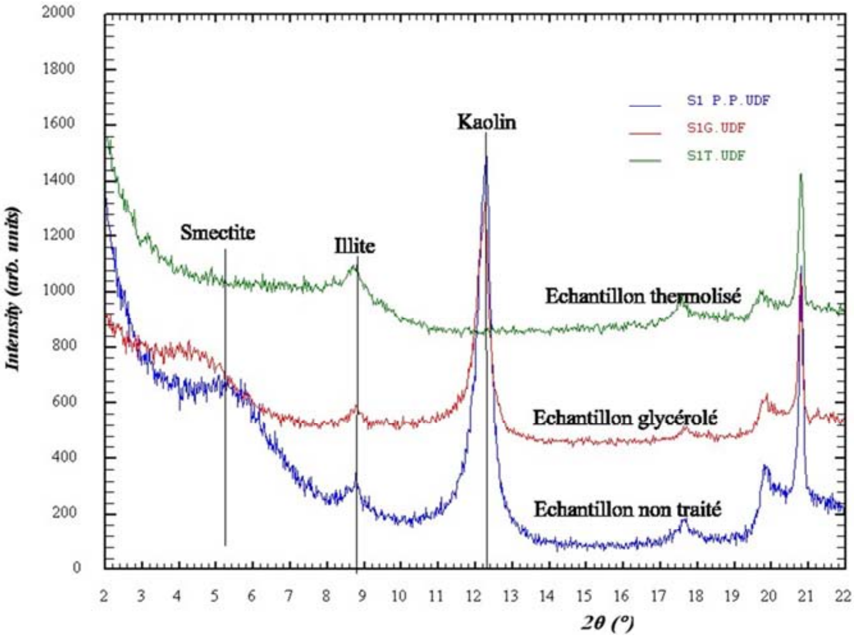

Figure 1. *X-ray diffraction of the kaolin.*

The analysis clearly emphasizes the following clay minerals:

Illite with diffraction at 8.7° 2θ under all treatments.

Kaolinat 12.2° 2θ in untreated sample remains unchanged under treatment with glycerol and disappears by heating.

Montmorillonite under 5.5° 2θ in untreated sample, decreased at 4.8° 2θ on glycerol sample and superimposed on the line of illite by heating.

The predominant clay is kaolin, illite in very small quantities. Montmorillonite, expansive in geological terms is clearly identified.

The micro analysis and EDS spectrum reported respectively in table 1 and Figure 2, carried out on kaolin powder shows clearly the nature and its composition which is mainly composed of alumina and silica with respectively anatomic percentage of 20% and 24%.

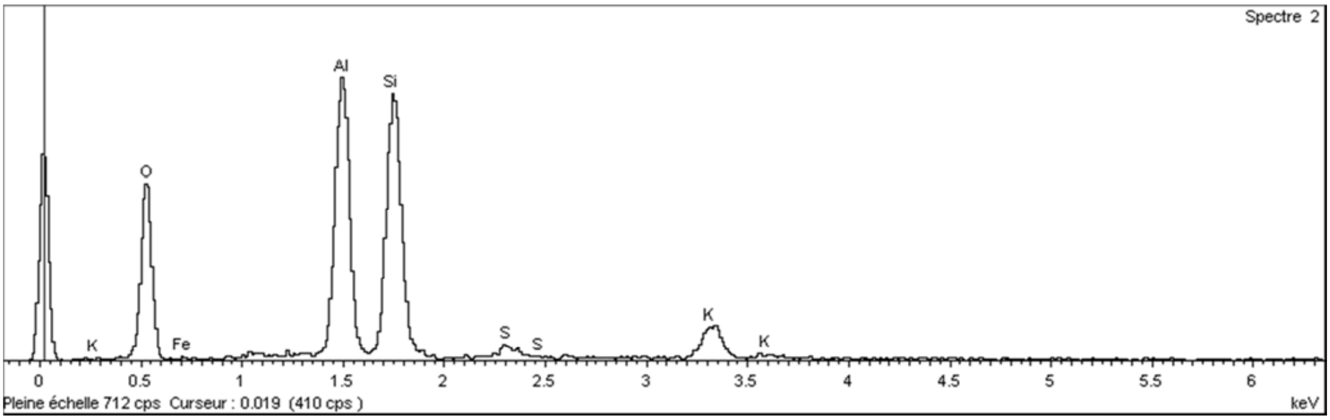

Figure 2. *EDS spectrum of the kaolin.*

Table 1. *Micro analysis of the kaolin.*

Element	Mass %	Atomic %
OK	48.13	62.57
Al K	20.08	15.47
Si K	24.55	18.17
S K	1.23	0.80
K K	4.69	2.49
Fe K	1.33	0.50
Totals	100	

2.1.2. Portland Cement (PC)

The mineralogical and chemical composition of the Portland cement (CEM I 52.5 N CE PM-ES-CP2 NF) used are respectively given in table 2 and table 3. This cement is produced by the plant TEIL (France).

Table 2. *Mineralogical composition of the Portland cement.*

Mineral	Content (%)
C_3S	65.3%,
C_3A	4.35%
C_2S	18.16%.
C_4AF	7.14%,

Table 3. *Chemical composition of the Portland cement.*

Oxyde	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CaO_L
%	22.40	2.96	2.33	66.60	0.95	0.15	0.10	2.13	0.50

2.2. Synthesis and Methods

The Kaolin was calcined at a temperature of 550°C for six (6) hours with a rate of 1°/min in order to obtain metakaolin ($Al_2O_3.SiO_2$). Two types of activator solutions were prepared, using NaOH and KOH bases at a concentration of 9M. The alkaline activator was prepared in the laboratory. In order to avoid the effect of unknown contaminants, distilled water was used to dissolve the sodium hydroxide and potassium hydroxide pellets. After 24 hours of their preparations, the two solutions are mixed and stirred for 5min (every kind) with a specific amount of metakaolin powder (MK) while optimizing a molar ratio Si/Al equal to 2. Thus the mixture was then cast into cylindrical mold and room temperature for about 3min to allow the fabrication of the molded samples (figure 3).

Figure 3. *Overall appearance of the geopolymer specimens.*

In order to investigate the influence of metakaolin partial substitution by a Portland cement (PC) on the setting time of pastes and its effects on mechanical properties, several specimens (variants) are developed with the following substitutions percentages:

a. Specimen with 100% Metakaolin (No substitution).
b. Specimen with 100% Portland cement. (Total substitution).
c. Specimen with 75% Metakaolin + 25% PC. (Partial substitution).
d. Specimen with ratio Metakaolin/PC=1. (Partial substitution). 50% PC and 50% MK.

The pastes prepared from these solutions were subjected to 28, and 90 day curing times. The temperature conditions used during setting and curing is ambient temperature. Final samples were used for the mechanical strength measurement.

3. Testing and Characterization

3.1. Geopolymer Pastes Setting Time

This test is performed using the Vicat apparatus which is provided with a needle diameter of 1.1 mm and a length of 50 mm. The results of the different tests taken are summarized in Table 4.

Table 4. *Test results of setting time (Initial and final).*

Sample type (variant)	Activator type	Setting time	
		Initial set	**Final set**
100%PC	NaOH	40 min	1h 40min
	KOH	20 min	1h 10min
75% MK + 25% PC	NaOH	90 min	3h 3min
	KOH	60 min	2h
50% MK + 50% PC	NaOH	80 min	2h 50min
	KOH	50 min	2h 20min
Normal cement Paste	H_2O	60 à 90 min	2h 30min
100% MK	NaOH	> 1 day	/
	KOH	> 1 day	/

PC: Portland cement
MK: Metakaolin.

It was noted that samples made with the activator solution containing NaOH have a high setting time and cure than those based on KOH.

In the first variant (100% PC), it was found that the setting time (initial and final set) are extremely fast and are faster than the time taken for normal cement paste with water-cement ratio equal to 0.5, this is due to the exothermic reactions between cement powder and activator solutions, the heat dissipation contributes to the rapid curing. The second variant (75% metakaolin, 25% PC), it was noted that the initial setting is the same as a normal cement paste but the final setting time is slow compared to the time taken for a normal cement paste.

In variant 3 where the MK/PC ratio is equal to 1, it was observed that the setting times are the same as the time taken for normal cement paste. However, for sample 4 with a content of 100% metakaolin, the dough does not harden itself under conditions of room temperature (25°C).

a. Initial set. Occurs when the paste begins to stiffen considerably.
b. Final set. Occurs when the paste has hardened to the point in which it can sustain some load.

3.2. Compressive Strength

Compressive strength tests were performed using INSTRON 4507 press, executed with a speed of 0.5 mm/min. The results showed respectively in table 5 and figure 4. A correction of the resistance was performed according to the ASTM C42-90. (For a report $L.D^{-1}$= 1.5, the coefficient of correction is 0.96) with ‘’L” is the length and ‘’D” is the diameter. It is worth noting that the value of the force is the average performed on three (3) specimens after 28 days.

Table 5. *Results of compressive strengths after 28 days.*

Specimen	Activator type	Diameter (D)(mm)	Maximum Loading (N)	Compressive strength corrected (N/mm^2)
100% MK	NaOH	33.3	16900	19.41
	KOH	33.1	15000	17.44
100% PC	NaOH	33.0	9670	11.31
	KOH	33.0	3210	3.75
75%MK	NaOH	33.0	17400	20.35
+25% PC	KOH	33.0	16600	19.41
50% MK	NaOH	33.0	15600	18.24
+ 50% PC	KOH	33.0	13800	16.14

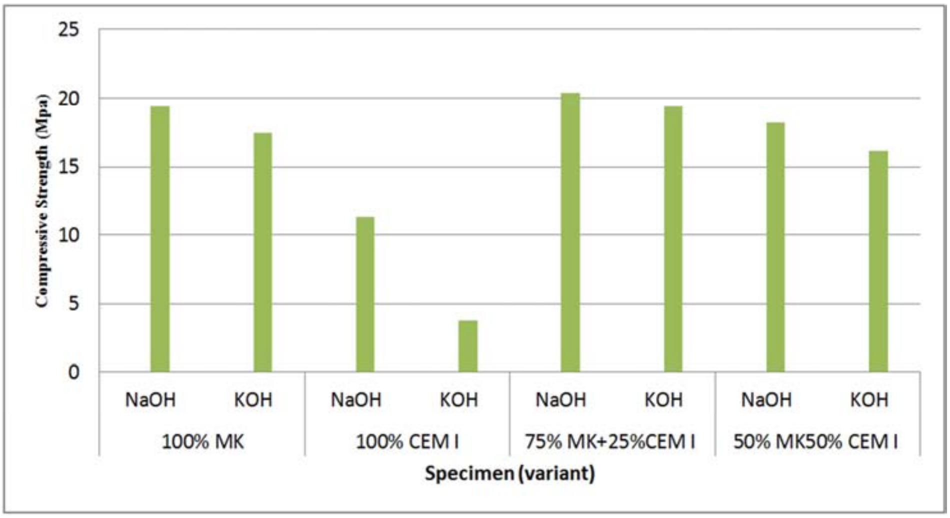

Figure 4. *Results of compressive strengths.*

It was noted that the resistances of specimens made with NaOH solution are better than those of KOH solution. Formation of the geopolymer framework is greatly dependent on the dissolution of the métakaolin particulates, which is directly affected by concentration of the basic solution. NaOH solution with higher concentration (9M) provides better dissolving ability to metakaolin particulates and produces more reactive bond for the monomer, which will increase inter-molecular bonding strength of the geopolymer material.

3.3. Splitting Tensile Strength

The indirect tensile strength test, called also “Brazilian test” consists to apply a centered compressive load between two generators. Induced stresses caused rupture along a diametrical plane of the specimen. This test is realized according to NF P 94-422 standard. Table 6 and figure 5 give the values found for each variant after 28 days.

Table 6. *Results of splitting tensile strengths after 28 days.*

Specimen	Activator type	Diameter(mm)	Length (mm)	Maximum laoding (N)	Tensile strength (N/mm^2)
100% MK	NaOH	33.0	39.2	3300	0.162
	KOH	33.0	35.0	3610	0.201
100% PC	NaOH	33.0	34.5	850	0.475
	KOH	33.0	34.9	612	0.338
75% MK+ 25% PC	NaOH	33.0	37.2	1660	0.861
	KOH	33.0	36.5	1210	0.639
50% MK+ 50% PC	NaOH	33.0	37.5	1380	0.710
	KOH	33.0	37.2	1400	0.726

We note that samples made with the activator solution containing NaOH have indirect tensile stresses better than those containing KOH. On the other hand, substitution partial of 25% of matakaolin by the Portland cement gives the best results.

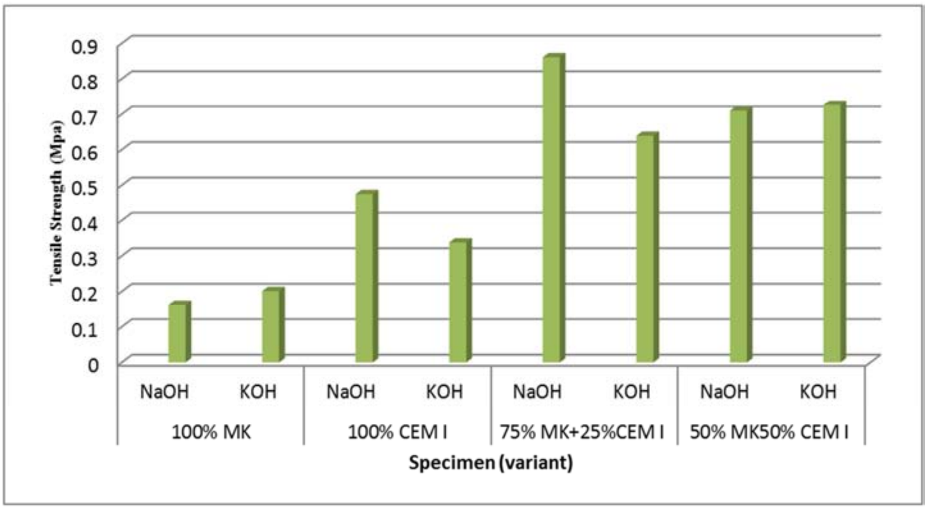

Figure 5. *Results of splitting tensile strengths.*

4. Results and Discussion of Mechanical Properties

For sample with 100% MK, in the compressive test, a very clean break is noted. In addition, due to "noise" during the break and the form of cracks, we deduce that we have a fragile material failure (when the force is maximum). For sample with Portland cement content of 100%, a formation of a multitude of cracks is seen during the compressive test; it means that a more fragile material that previous sample.

For sample where, the Portland cement content of 25% and 75% of metakaolin, it was see the appearance of some cracks before total failure. The break is slower, the material is less brittle. It was also note that within the samples is very dense and homogeneous. For sample (MK/PC = 1), it was observed a formation of a multitude of cracks during the compressive test and the material crumbles even more than the precedent. Samples disintegrate, probably due to the presence of too much content Portland cement.

Finally, the worst composition is that with 100% Portland cement. Indeed, there is certainly no compatibility between the binder (cement) and the activator solution causing therefore a faster and larger disentanglement with very poor compressive and splitting tensile strengths.

To sum up, the geopolymerization reaction process can be rationally expressed as follow. First, surface layer of metakaolin particulates are dissolved by NaOH or KOH solution, and soluble aluminosilicate unit are immediately polymerized in the presence of the self-polymerizing species (monomer, dimer and larger oligomer containing Si-O-Si chain) come from sodium silicate solution. Then the dissolved metakaolin particulates are linked by polymerization product network. Since NaOH or KOH solution of higher concentration has better ability to dissolve metakaolin particulates and forms a polymerized network having strengthened link with the dissolved metakaolin particulates, therefore it was practicable to prepare molded geopolymer samples with more compact and better mechanical strength using bases solutions with higher concentration (9M).

5. Conclusions

Geopolymers are materials with interesting chemical and physical properties with implementation and a fairly simple process.

Our practice study allowed us to synthesize a geopolymer material from metakaolin with two types of activator solutions, one containing NaOH and another KOH. Then study the influence of substitute part of metakaolin by Portland cement (PC) on the setting time and mechanical strengths.

From the results obtained, it was concluded:

The use of activators based solution of NaOH gives compressive strength and splitting tensile better than those based on KOH.

The partial substitution metakaolin by artificial Portland cement significantly improves the time and cure the geopolymer fresh and closer to those of ordinary cement which is a major advantage knowing that the pure geopolymer require temperature about 60° C for their setting time.

The best dosage that was finally chosen is composed of 75% metakaolin and 25% cement. Such proportions allow the material to have a sufficiently large quantity to metakaolin and cement particles without the brittle surface to make the tensile and compression. In addition, the mixture is homogeneous and compact which tends to increase its mechanical strength.

A characterization of the microstructure by SEM and EDS tests on geopolymer material prove necessary in order to interpret results more accurately and thus see the chemical changes recorded.

A study of mortars or concretes based geopolymer binder would be interesting to extend the results found in this experimental research.

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