***Algerian Journal of Environmental Science and Technology***
***September edition. Vol.7. Nº3. (2021)***
***ISSN : 2437-1114***
***www.aljest.org***

# Effect of sodium sulfate in a mortar incorporating metakaolin

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## ARTICLE INFO

***Article History:***

*Received* ***: 22/02/2020***
*Accepted* ***: 08/08/2020***

***Key Words*:**

*Metakaolin;*
*Chemical activation;*
*Mortar;*
*Compressive strength;*
*Sodium sulfate.*

## ABSTRACT/RESUME

***Abstract:*** *Metakaolin is a pozzolanic addition, it was developed as a partial substitution of cement to reduce cement consumption and improve the durability of concrete. However, the incorporation of metakaolin introduces, at early age, a lack of mechanical performance of concretes at room temperature.This work aims to chemically activate metakaolin in cement past in such a way that, the same early age performance can be achieved in concrete as achieved without metakaolin. The study was carried out at cement mortar to observe the influence of sodium sulfates on compressive strength. The increase in resistance at early age was observed with the activation of metakaolin. The metakaolin activation was confirmed in cement matrices by physio-chemical analyses. The increase in compressive strength at early age can be explained by a decrease of porosity and setting time, an increase in the amount of C-S-H and a decrease in the amount of CH.*

## I. Introduction

The incorporation of chemical activators into a cementitious matrix in the fresh state accelerates the hydration of the cement but also aims to improve the reactivity of the mineral additions.
The alkaline activation can accentuate the dissolution of the siliceous phases in slag (Si-Ca system), siliceous and aluminous in fly ash and metakaolins (Si-Al system) since this dissolution is largely accentuated with the increase of ph at above 12.5 [15]. The literature presents that sodium sulfate (NS) is effective activator for increasing the compressive strength of young slag cements while maturing [9] or even increase it to 28 days [16].Similar results are obtained in other systems like silico-aliminic fly ash / CEM I [8] [11] and perlite / CEM I [6]. The same results with system metakaolin (MK)/CEMI where the pozzolanic reaction is effectively accelerated in the presence of sodium sulfate [12].
The interest of the activation of metakaolin appears at early ages to keep the rates of casting / stripping and not in a long-term since it has been shown that the incorporation of metakaolin [13] in the cement matrix until a rate of 25 % substitution of cement leads to an improvement in mechanical strength at 28 and 90 days [1] [12][14].
The alkaline activation of metakaolin in the presence of lime considerably increases the consumption of portlandite during the first 14 days of hydration but portlandite may still exist at the 28 days exchange [4] [5] , suggesting that the metakaolin pozzalanic reaction is inhibited by the presence of activating agents. This work is therefore aimed at deepening the behavior of the CEMI / MK cement system activated by sodium sulfate .The effect of activation is observed on compressive strength. XRD and thermal analysis and water porosity confirm the results obtained on mechanical strength.

## II. Experimental procedure

### II.1. Materials

The cement OPC or CEM I was used. The metakaolin (MK) was obtained by flash calcination. The main properties of cements and metakaolin are gathered together in Table 1.
Standardized quartz sand complying with European Standard EN 196-1 was used for making mortar (particle size ranging from 0.08 mm to 2 mm; specific gravity = 2680 kg/m$^3$).
Sodium sulfates activator was employed.

### II.2. Methods

The Standardized mortars were made up according to EN 196-1. They were composed of one part by mass of binder (cement or cement + metakaolin), three parts of sand, and a half part of tap water. The mortars were cast in metal molds with dimensions 4 cm x 4 cm x 16 cm. The molds were sealed with plastic film and stored at 20°C ± 1°C. The specimens were demolded as soon as 0.67 day (16 hours) after casting and stored at 20°C ± 1°C in plastic bags preventing any water loss until the time of the compressive strength test.

The compressive strength was measured on prismatic specimens (4 cm x 4 cm x 16 cm) in accordance with EN 196-1 at 0.67, 1, 2, 7, and 28 days of age. Each result corresponded to the average of six individual tests.

The hydration of cement pastes was monitored using thermal analysis (thermogravimetric – TG).

The portlandite consumption was quantified by calculating the loss of water in the range 400–600 °C and a decarbonation of calcite $CaCO_3$ between 600 and 800 ° C, the other hydrates AFT and CSH are decomposed between 50 ° C and 400 ° C.

***Table 1.****Cement and Metakaolin properties*

| | C CEM I 52.5N | MK |
|---|---|---|
| **Specific gravity ($g/cm^3$)** | 3.14 | 2.54 |
| **Blaine fineness, $cm^2/g$** | 380* | 15 000** |
| **Loss of ignition, %** | 1.8 | 0.8 |
| **$SiO_2$, %** | 19.8 | 67.1 |
| **$Al_2O_3$, %** | 5.3 | 26.8 |
| **CaO, %** | 64.0 | 1.1 |
| **MgO, %** | 1.9 | 0.1 |
| **$SO_3$, %** | 3.0 | - |
| **$Na_2O$, %** | 0.2 | 0.0 |
| **$K_2O$, %** | 0.5 | 0.1 |
| **$Fe_2O_3$, %** | 2.4 | 2.6 |

* Blaine method; **BET method
– = not measured items.

## III. Results and discussion

### III.1. Compressive strength

Figure 1 presents the effect of sodium sulfate ($Na_2SO_4$) on the compressive strength of 25% MK-mortar at curing times between 16 hours and 28 days with a reference 100%C.

The compressive strength of a mortar (75% cement– 25% MK) without activation has the same resistance of the reference (100% cement) at 28 days. It can be seen that the beneficial effect of sodium sulfate was still present before 48 hours of curing. At 28 days, 25% MK-mortar with sodium sulfate did not reach the level of the reference composed of cement only. These results confirm the work of Erdogan and Saglik, who activated chemically 25% perlite with 4% NS in a cement matrix [6]. This type of behavior, a fast reaction followed by a strong decrease of the reaction rate, has sometimes been observed in chemically activated pozzolan matrices, but more often in thermally activated plain cements. The same kinetic of reaction observed also in chemically activated slag cement [9], and it looked like the classic one seen in thermal activation of hydration and highlighted by several authors. According to Verbeck and Helmuth [18], rapid hydration led to encapsulation of the reactive grains by a layer of product having low porosity, which retarded or prevented further hydration.

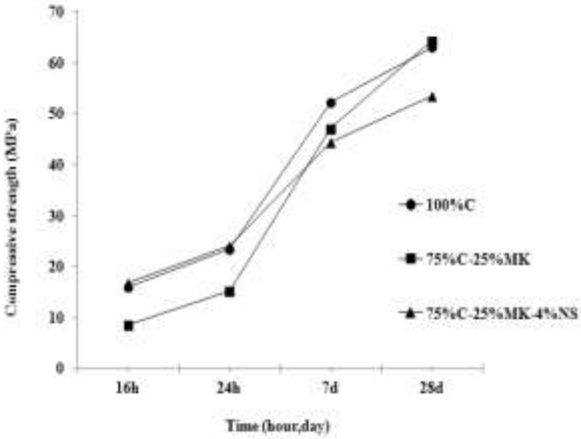


***Figure 1.*** *Compressive strength of mortars (75%C-25%MK) without and with activation by sodium sulfate and reference (100% cement) between 16 hours and 28 days.*

### III.2. Flowing time

Table 2 presents the results flowing time of reference, MK-mortars with and without sodium sulfate. It can be seen that a gain was obtained when the metakaolin mortar [3]. The sodium sulfate accelerates the setting of the cement / MK binder and the hardening of the corresponding mortar. There is therefore a correlation between the setting acceleration and the increase in short-term mechanical resistance.

*Algerian Journal of Environmental Science and Technology*
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***Table 2.*** *Flowing time of mortars (75%C-25%MK) with and without activation by sodium sulfate and reference (100% cement).*

| mortars | flowing time (Min) |
|---|---|
| **100% C** | 259 |
| **75%C-25%MK** | 218 |
| **75%C-25%MK-4% NS** | 176 |

### III.3. Relationship between mechanical strength and porosity

Figure 2 presents the compressive strengths according to the porosity of mortars at 28 days. There is a tendency for resistance to decrease as porosity increases.

It can be seen that:

• Porosity of mixtures with metakaolin is always higher than the reference, a same result has been observed by other authors Khatib and Clay [2].
• The porosity of the activated mixtures is higher than the non-activated mixtures, this increase can have consequences on the compressive strength; this could be due to the decrease in the number of hydrates at 28 days of the activated mixtures compared to the others; it is also possible that there is a link with the very rapid initial kinetics of hydration, leading rapidly to incomplete hydration in the long term.

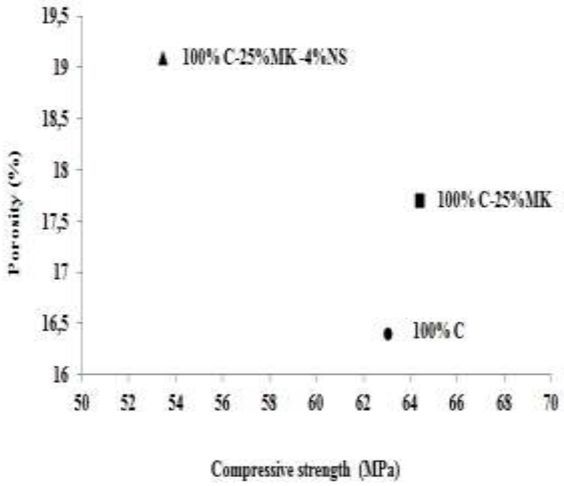


***Figure 2.*** *The compressive strengths according to the porosity of mortars (75%C-25%MK) with and without activation by sodium sulfate and reference (100% cement) at 28 days.*

### III.4. Qualitative analysis

The qualitative evolution of the reaction in MK-cement mixtures is shown on Figure 3 (XRD).

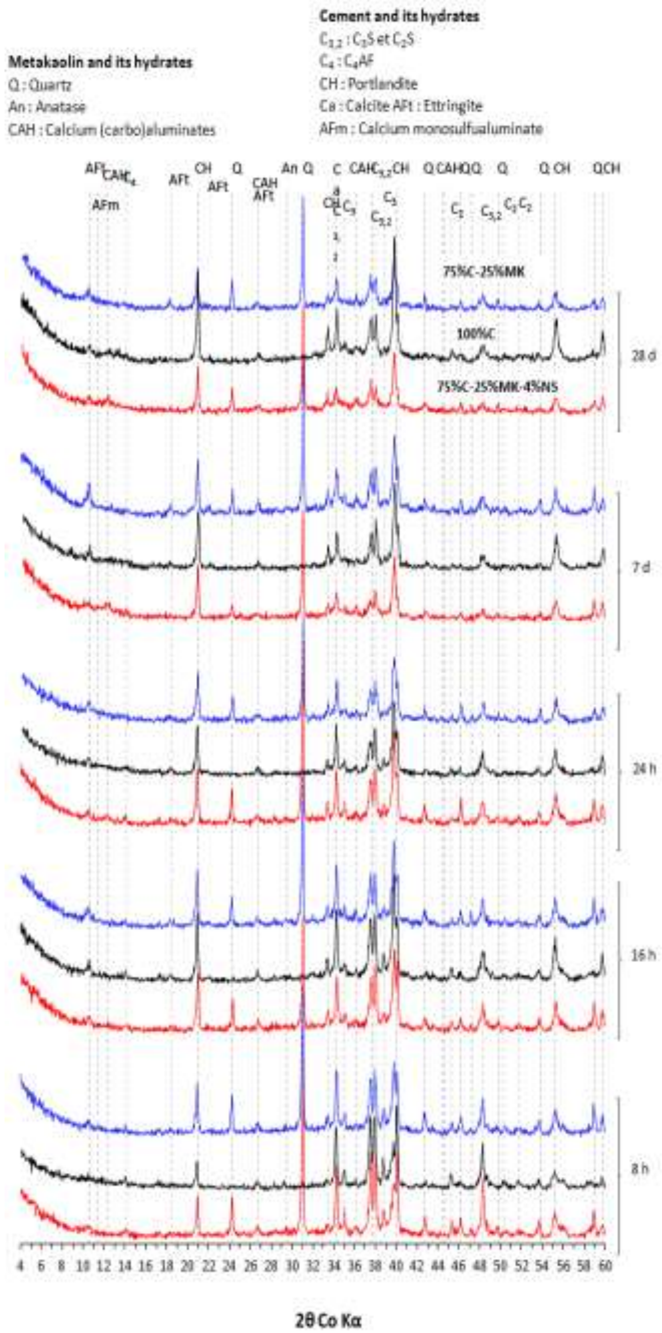


***Figure 3.*** *The XRD diagrams of mortars (75%C-25%MK) with and without activation by sodium sulfate and reference (100% cement) at 8h, 16h, 24h, 7 and28 days.*

It can be seen that:

- the presence of cement silicate, confirming that all of the cement has not yet reacted at 28 days, as well as the presence of quartz and traces of anatase from metakaolin.
- Portlandite produced by the hydration of $C_3S$ and $C_2S$ (XRD peak at 21° 2θ Co Kα – Figure. 3) disappeared over time as it was consumed by the MK [3].
- There was a clear difference in the reaction kinetics of MK between mortars with and without sodium sulfate.
- The reaction of MK was confirmed by the difference of kinetics in the formation of stratlingite ($C_2ASH_8$) or hydrated calcium aluminates type $C_4AH_{13}$, a typical hydrate formed in MK systems. This mineral, characterized by XRD peaks at 12.5, 6.27 and 4.18 Å (8.2°, 16.4° and 24.7° 2θ Co Kα, respectively). It should be noted that stratlingite can thermodynamically precipitate only when portlandite has been totally consumed. The simultaneous presence of both portlandite and stratlingite indicated some local inhomogeneity in the pastes [4] [5] [17].
- There is no trace of stratlingite ($C_2ASH_8$) at 8h, 16h, 24h, 7 and28 days because the main lines of this mineral are systematically absent from diffractograms.
- In the presence of sodium sulfate (NS), there is no production of $C_4AH_{13}$ between 8h and 28 days. This absence of $C_4AH_{13}$ has been linked to the presence of $SO_4^{-2}$ ions in the matrix [4] [7].

### III.5. Quantitative analysis

Figure 4 and Figure 5 present the evolution of the portlandite and other hydrates content in grams of cement between 16 hours and 28 days, for paste (75%C-25%MK) without and with activation by sodium sulfate and reference (100% cement).

Some notes can be removed:

<u>Mixtures without activation by 4% NS</u>

• After 8 hours of hydration, reference (100%Cement) and (75%C-25%MK) have a same quantity of portlandite and a same quantity of other hydrates (the MK plays a role of activator by physical effect).

• Between 16h and 24 h of hydration, the reference paste (100%Cement) produces more hydrates than pastes with metakaolin (75%C-25%MK), a continuous increase of the portlandite content in reference mortar was observed. The large difference in the content of portlandite (-30% compared to the reference) can be due to two phenomena:

1. The reference contains 100% cement; it has high reaction kinetics to produce more hydrates [3].
2. The presence of metakaolin, the pozzolanic reaction begins to consume a part of CH to form pozzolanic C-S-H [17].

• After 24 hours, the paste with metakaolin had much lower portlandite contents than the reference, which is a sign of the development of the pozzolanic reaction.

• At 7 days, the curves of hydrates intersect (as in the case of compressive strengths) and, at 28 days, the amount of C-S-H is more important for the mortar with metakaolin.

<u>Mixtures with activation by 4% NS</u>

• After 8 hours of hydration, the effect of activation of metakaolin by $Na_2SO_4$ is clearly visible at 8 hours, meaning that metakaolin was active in the short term. The paste with actived metakaolin contained more hydrates than reference and mixture with metakaolin non actived.

• The Hydrate (C-S-H) development kinetics was slowed after 16 hours; the mixture with activated MK has same hydrates as a reference at 7 days. This slowing of hydration of the activated mixture explains the results of compressive strength. Meaning that the rapid development of hydrates around the grains of cement and metakaolin blocks the dissolution of cement and metakaolin.

• The presence of $SO4^{-2}$ ions in mortar can lead to an absence of hydrated calcium aluminates of the $C_4AH_{13}$ type [4][7], its presence depends essentially on the MK / lime ratio in the matrix [10], [4], [5] or of the MK / cement ratio [7]. It is probably that the aluminum ions of the MK enter into AFt or CASH hydrates.

• All portlandite had been consumed for tow mixtures 75%C-25%MK-with and without activation by NS. Meaning that the sodium sulfate accelerates the dissolution of metakaolin to facilitate its pozzolanic reaction.

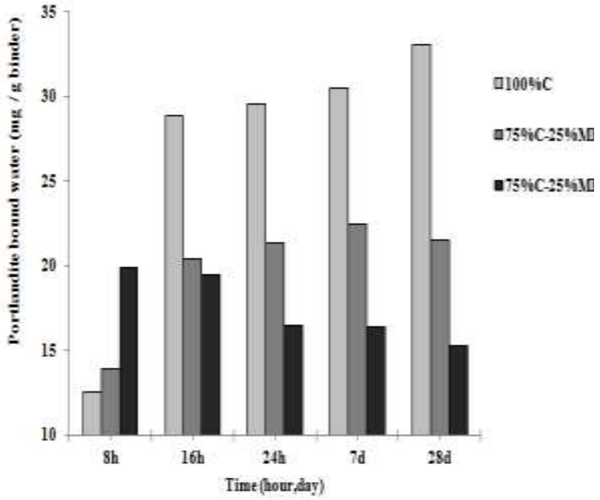


***Figure 4.*** *Evolution of portlandite content in mortar (75%C-25%MK) without and with activation by sodium sulfate and reference (100% cement).*

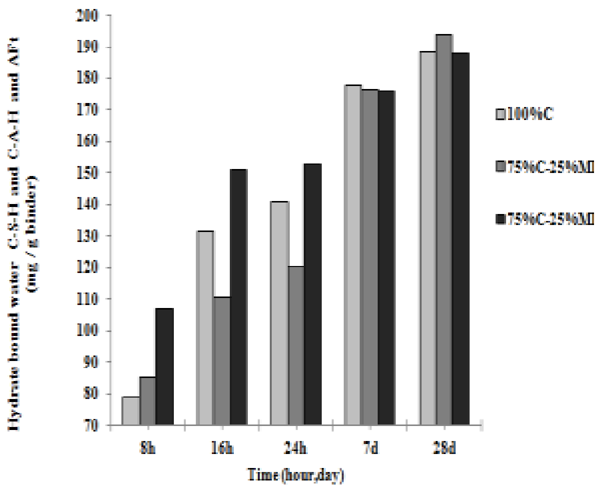


***Figure 5.*** *Evolution of other hydrates content in mortar (75%C-25%MK) without and with activation by sodium sulfate and reference (100% cement).*

**III.6. Relationship between mechanical strength and hydrates**

Figure 6 presents the relation between the quantity of hydrates produced and the mechanical strengths of metakaolin mortars with and without 4% NS.
It can be seen that:

- There is a clear correlation between resistance and hydrate production, the resistance depends on the amount of hydrates that will be produced.
- The quantity of bound water increased significantly with time, meaning that the quantity of hydrates produced also increased (C-S-H, ettringite, aluminates).
- The hydrate content in mortar with activated metakaolin was higher than in reference (cement only). Erdogan and Saglik affirme that the increase of compressive strength is due to the presence of alkaline sulfate and the production of excess ettringite [6].

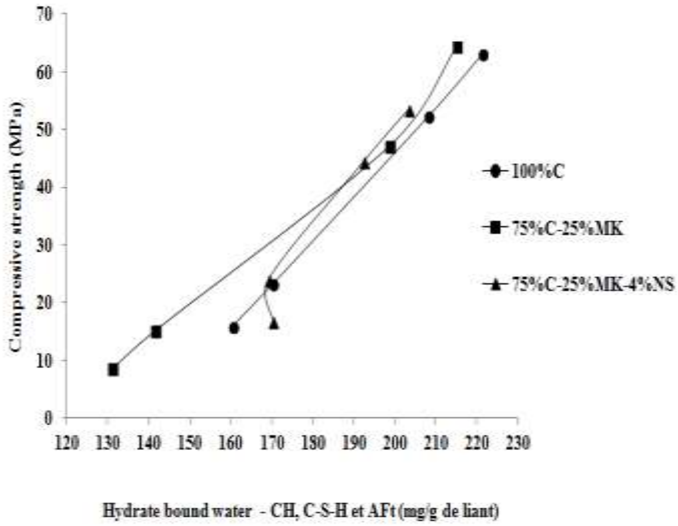


***Figure 6.*** *Compressive strength between 16 hours and 28 days of reference (100% cement) and pastes containing 25%MK with and without 4% NS, versus the quantity of bound water (in C-H, C-S-H, AFt, AFm, $C_2ASH_8$ and other aluminates).*

## IV. Conclusion

This work presents the chemical activation of a cement matrix incorporating 25% metakaolin by sodium sulfates (4% NS) to solve the problem of slow development of mechanical resistance by incorporating metakaolin. Chemical activation of metakaolin by sodium sulfates ($Na_2SO_4$) accelerates hydration in the short term which helps to augment of compressive strength. Early activation at early age alters the resistance of mortars at later age (28 days) by counteracting the pozzolanic action of metakaolin. The thermal analysis results clarified the development of compressive strengths in the presence of metakaolin (25% MK) with and without chemical activation by sodium sulfates (4% NS).

The qualitative analysis presented that in the presence of sodium sulfate, there is no trace of stratlingite ($C_2ASH_8$) and $C_4AH_{13}$ before 28 days.

The quantitative analysis presented that early activation slows the hydrate production in the later term. The increase of compressive strength was associated with a higher amount of hydrates from the age of 8 hours but not with a surplus of ettringite.The quantification of hydrates confirmed the activation of metakaolin in cement matrix since portlandite consumption is apparent at one day, and the metakaolin plays an activating role on the hydration of the cement.The lower C-S-H contents and the high porosity of the activated mixtures explain the alteration of the resistances.

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**Please cite this Article as:**
Saidat F., Cyr M., Mouret M., Idir R., Effect of sodium sulfate in a mortar incorporating metakaolin, ***Algerian J. Env. Sc. Technology***, ***7*****:3 (2021) 2072-2077**