Effect of fineness variation on the chemical reactivity of Metakaolin

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RESUME Metakaolin (MK) affects the cement matrix physically, due to its filler effect, and chemically through the generation of additional C-S-H compounds. These actions are closely linked to the fineness of the material. In the literature, the effect of MK fineness on the evolution of mechanical strength is widely studied. However, the effect of fineness variation on the pozzolanic reactivity of MK, measured by chemical tests, is not well discussed. The aim of this study is to contribute to the clarification of the relationship between the fineness of a MK and its pozzolanic reactivity evaluated by chemical tests of Frattini, modified Chapelle and saturated lime. To do this, two MKs (obtained by appropriate calcination of two kaolins from Algeria) were used. Both materials were ground to several Blaine finenesses, which vary between 4000 and 8000 cm^2/g, before their pozzolanicity was assessed. The results obtained showed that the reactivity of MKs increased absolutely with the increase in their fineness, regardless of the chemical test used. The fineness of MK favours its chemical reaction with Portlandite in the different chemical test systems despite their differences in temperature, time and MK-lime ratio. It was concluded that these tests are more sensitive to the variation in the fineness of the MK than the classic compressive strength test.

Mots-clefs Metakaolin, fineness, reactivity, pozzolanic reactions, Frattini test, modified Chapelle test, saturated lime test.

I. INTRODUCTION

Cement is one of the most used materials in the world civil engineering industry. It is well known that its manufacturing process produces huge quantities of carbon dioxide, reaching 0.99 ton per each ton of cement (Hasanbeigi et al. 2012). The release of carbon dioxide during cement manufacturing is linked to two causes : the combustion of fossil fuels necessary for the production of clinker and the decarbonation process which converts limestone into CaO and CO_2. Among the solutions proposed to reduce these greenhouse-gas emissions from cement production, it is commonly recommended to produce blended cement, in which the clinker is partially substituted by some specific materials (Mohammed S. 2017). These additions may be inert such as limestone or active like fly ash, silica fume and Metakaolin. The partial substitution of the clinker by active additions may significantly improve some characteristics of concretes and mortars as mechanical response, durability and transfer properties. Indeed, the enhancement of these properties is attributed to the pozzolanic reaction that occurs between Portlandite and the reactive compounds

of the addition, which generally results in the formation of supplementary cementitious materials SCM such as C-S-H, C-A-H and C-A-S-H (Gruber et al. 2001; Badogiannis and Tsivilis. 2009; Zhao and Khoshnazar. 2020).

Metakaolin (MK) is one of the most studied SCMs around the world, it has attracted the interest of many researchers in recent years. This artificial pozzolan is generally obtained after heat treatment, at temperatures varying between 500 and 900 °C, of kaolinitic clay (Bich et al. 2009). The kaolinitic clay is very abundant in many countries, including Algeria. The existing literature demonstrates that efficiency and pozzolanic reactivity of MK are primarily proportional, in addition to the kaolin content and purity level of the raw material, to the content of reactive silica and alumina, which in turn depends on the effectiveness of kaolin to MK conversion process (Boumediene et al. 2021). The transformation of kaolin into MK is a determining process, that considerably depends on the thermal treatment characteristics such as the temperature target and the holding time (Bich et al. 2009 ; Mohammed S. 2017). According to some standards, namely NF P18-513 and ASTM C-618, the highly reactive MK should satisfy some chemical and physical requirements (Table 1). The chemical ones are mainly concerned with the material's amorphousness and its chemical composition. It is believed that the higher content of reactive SiO_2 and Al_2O_3 is, the higher is the reactivity of MK (Mohammed and Boumedienne, 2022). While, physical requirements deal strongly with granulometry and fineness of the ground material (Lawrence et al. 2003 ; Cyr et al. 2006). In most cases, greater fineness and finer particle size distribution (PSD) allow obtaining a more reactive MK. These requirements allow MK, through its fine particles, to increase the compactness of the cement matrix, which is known as the physical effect or filler effect, and through its reactive SiO_2 and Al_2O_3, to react with Portlandite $Ca(OH)_2$ to produce additional C-S-H binding phases, which is commonly known by pozzolanic reactivity (Lawrence et al. 2003).

TABLE 1. Some physical and chemical requirements for artificial pozzolans according to ASTM C 618 and NF P18-513 standards

Requirements	Limit values	
	ASTM C 618	NF P18-513
$SiO_2 + Al_2O_3 + Fe_2O_3$: min (%)[1]	70	/
$SiO_2 + Al_2O_3$: min (%)[1]	/	90
Chloride (Cl^-): max (%)[1]		0.1
Sulfur trioxide SO_3: max (%)[1]	4	1.3
Moisture content: max (%)[1]	3	/
Free CaO: max (%)[1]	/	1
Loss on ignition: max (%)[1]	10	5
Amount retained when wet-sieved on 63 µm sieve: max (%)[1]	/	30
Amount retained when wet-sieved on 45 µm sieve: max (%)[1]	34	/
Strength activity index with OPC at 28 days: min (% of control)	75	85
Water requirement: max (% of control) [1]	115	115
Autoclave expansion or contraction: max	0.8 (%)	10 mm

[1] : % of dry mass.

In the literature, many papers have studied the effect of MK fineness on its reactivity (Vizcayno et al. 2010; Dong et al. 2011; Mitrovic and Zdujic, 2014; Liu et al. 2017;). These researchers used the evolution of mechanical response as an indirect indicator of the MK reactivity. It has been reported that the increase in the MK fineness, through the increase in the grinding time, leads to the increase in its reactivity and therefore the improvement of the mechanical response of the MK-based cementitious materials. On the other hand, the reactivity of MK can also be evaluated directly, by quantifying its consumption of lime or Portlandite. Chemical tests (Frattini, modified Chapelle and saturated lime), and physical methods (X-ray diffraction XRD and thermogravimetric TG analysis) are the main direct methods used for the evaluation of MK reactivity (Donatello et al. 2010 ; Mohammed S. 2017, Boumediene et al. 2021). However, the effect of MK fineness on its reactivity, evaluated by direct methods, notably chemical tests, has not been well clarified in the literature. Accordingly, the present study attempts to clarify the effect of varying the grinding time and therefore the fineness of MK on its physical and chemical reactivity, using both mechanical and chemical tests.

II. MATERIAL PROPERTIES

Two MKs were used in this study, MKT1 and MKT2, they were elaborated in laboratory from two kaolinitic clays KT1 (39% of kaolin) and KT2 (58% of kaolin). The raw kaolin clays were sourced from Tamazert in the north-east of Algeria, their chemical compositions, determined by X-ray fluorescence spectrometry (XRF), are presented in Table 2. First of all, KT1 and KT2 were ground, using a laboratory ball mill, for different periods (90, 120, 150 and 240 min). The effect of each grinding time on the particle size of the material was evaluated in terms of fineness and particle size. The Blaine finenesses, thus obtained, were determined according to NF EN 196-6 standard, while the particle size distributions of the materials were measured using a CILAS 1090 laser particle analyzer. Then, the ground samples were heat treated in an electric oven in order to convert kaolin into MK. The heat treatment consisted of a constant temperature rise rate (10 °C/min), a target temperature of 800 °C and a holding time of 5 h. These appropriate calcination parameters were the subject of a previous study (Boumediene et al. 2021). A local Portland cement CEM I 52.5 with a fineness of 3981 cm^2/g and an ordinary chemical composition (Table 2) was used for the Frattini test and the mortar mixtures.

TABLE 2. Chemical compositions (%) of the used materials.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI
KT1	70.91	17.15	1.67	0.32	0.36	0.09	4.06	0.32	5.68
KT2	56.63	26.15	3.7	0.33	0.66	0.07	3.51	0.4	9.26
MKT1-4000	68.22	22.54	1.55	0.28	0.34	0.07	4.01	0.28	1.03
MKT2-4000	53.3	36.5	3.95	0.29	0.62	0.07	3.92	0.24	1.1
CEM I	21.54	4.31	4.5	63.63	1.47	1.54	0.35	0.07	2.05

III. EXPERIMENTAL METHODS

The reactivity of MK samples, obtained after grinding to different finenesses then calcination of KT1 and KT2, was tested, in addition to the evolution of the mechanical response, by chemical

tests of Frattini, saturated lime and modified Chapelle. The samples of different fineness are denoted throughout this experimental study as: MKT1-4000, MKT1-6000, MKT1-7000, MKT1-8000, MKT2-4000, MKT2-6000, MKT2-7000 and MKT2-8000.

1. Mechanical test

The 28-day compressive strength was carried out on 4 × 4 × 16 cm^3 mortar specimens, prepared and tested according to NF EN 196-1. The control mortar was prepared by mixing 1350 g of standard sand, 450 g of cement and 225 ml of water. However, in the blended cement mortars 15% by mass of cement was replaced by each MK, as suggested by NF P-18 513. For each mixture, the retained compressive strength value was the average of six results. The strength activity index (SAI) presents the ratio of the 28-day compressive strength of the blended cement mortar to that of the control mortar.

2. Frattini test

According to NF EN 196-5, the Frattini test implies to determine the concentrations of Ca^{2+} and OH^-, dissolved in a solution containing cement and the tested MK. It consists of making into reacting 16 g of cement and 4 g of finely ground MK in 100 ml of deionized water. The mixtures were kept in a sealed plastic container at 40 °C. After 8 days, each solution was filtrated and the filtrate was analyzed for [OH^-] by titration against dilute HCl, while the [Ca^{2+}] was measured, after pH adjustment to 12.5, by titration with EDTA solution (0.03 mol/l) using murexide indicator. The tested sample is regarded as active pozzolan if the amounts of these ions are down the lime solubility curve.

3. Saturated lime test

Contrary to the previous test, in this one, MK is mixed with saturated $Ca(OH)_2$ solution, prepared by dissolving 2 g of hydrated lime in 1 L of deionized water. The saturated lime test, considered as a simplified and non-standardized version of the Frattini test, involves in reacting 75 ml of this solution with 1 g of the studied MK. Samples are kept in a sealed plastic bottles at 40 °C. The amount of lime, fixed by each sample (mmol/l), is obtained from the difference between the concentration in the control saturated lime solution, and the residual Ca^{2+} found in the solution containing this sample after 1, 3, 7 and 28 days.

4. Modified Chapelle test

In this test, standardized by NF P18-513 and considered as a shorter version of the saturated lime test, 1 g of each sample of MK is put into reaction with 2 g of CaO in the presence of 250 ml of distilled water, for 16 hours at 90 °C. The residual lime is determined by titration with HCl solution, in the presence of sucrose extraction. The final result, expressed in mg of CH fixed by g of MK, is determined using the following relation:

$$\text{Fixed lime} = 2 \times [(V1 - V2)/V1] \times (74/56) \times 1000 \quad (1)$$

Where V1 and V2 are the volume of HCl solution added for titration of the blank sample and the tested MK sample, respectively.

IV. RESULTS AND DISCUSSION

1. *Fineness and particle size characteristics*

Raw kaolins KT1 and KT2 were ground for 90, 120, 150 and 240 minutes before being calcined. Their Blaine finenesses (SSB) and their particle size indices d10, d50 and d90 are presented in Table 3. According to these results, it is clear that the SSB of kaolins increases with their grinding time while their indices d10, d50 and d90 decrease, except for the grinding time of 240 min where a slight increase is observed. It appears that prolonged grinding led to the agglomeration of particles as reported by Mitrovic and Zdujic (Mitrovic and Zdujic, 2014). After calcination at 800 °C for 5 h, SSBs of the resulting MKs do not seem to be affected, because they kept almost the same finenesses of the starting kaolins, while their particle size indices were remarkably increased. The increase in the particle size of kaolins following their calcination can be explained by the formation of new grains with a larger surface area, caused by the tendency for dehydroxylated particles to aggregate (Yanguatin et al. 2019). This shortcoming presents a potential disadvantage of this grinding-calcination process, so it is best to grind again after calcination.

TABLE 3. Finenesses and particle size characteristics of kaolins and derived MKs.

			SSB (cm^2/g)	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)
Grinding time (min)	90	KT1	4574	4.9	10.22	24.10
		MKT1	4380	5.7	21.14	38.45
		KT2	4340	4.5	9.11	21.53
		MKT2	4290	6.17	19,84	40.26
	120	KT1	6380	4.11	11.25	21.41
		MKT1	6320	5.42	16.88	30.10
		KT2	6110	3.98	9.06	19.65
		MKT2	6230	5.29	14.82	28.53
	150	KT1	7336	2.08	6.08	15.55
		MKT1	7290	2.45	9.42	30.61
		KT2	7040	1.49	6.22	16.95
		MKT2	7000	1.84	8.07	28.05
	240	KT1	8210	3.42	10,17	27.35
		MKT1	8330	5.18	14.33	65.66
		KT2	8090	2.85	8.81	25.49
		MKT2	8220	4.17	12.73	70.45

2. *Compressive strength results*

The 28-day compressive strength results of mortars made with or without different variants of kaolin and MK are presented in Figure 1. It can be seen that the replacement of 15% of cement with raw kaolin (KT1 or KT2) caused a drop in strength (more than 18%), which is certainly linked to the chemically inert state of the kaolins (Bich et al. 2009 ; Dong et al. 2011). However, the use of MKs, whatever their fineness, seems more beneficial and the mechanical response of the MK-based mortars appears to be favorably affected. The incorporation of MKT1 practically resulted in compressive strengths, similar to that of the control mortar (100% CEM I); a very slight improvement (of the order of 1.15%) was obtained for an SSB close to 7000 cm^2/g. Whereas, with

the same percentage of substitution, the use of MKT2 remains more beneficial because it has significantly improved the compressive strength of mortars. This improvement is more important when the SSB of MKT2 is large (+7.34% when SSB was in the range of 8000 cm^2/g). The results obtained for the MK-based mortars can be attributed exclusively to the chemical effect (pozzolanic activity) of these MKs, taking into account the results of kaolin-based mortars. It is well known that raw kaolins are inert materials incapable of reacting with Portlandite in the cementitious system (Liu et al. 2017). Therefore, the results obtained for the KT1 and KT2 mortar variants clearly reflect the physical effect of these kaolins which have practically the same fineness as MKT1-4000 and MKT2-4000 variants, which neglects any repercussions of the physical effect on the results obtained with MKs. It should be noted that although the grinding time of the raw kaolins increased from 90 min to 240 min, and the Blaine specific surface areas of the resulting MKs increased from 4290 to 8220 cm^2/g, the compressive strength seems slightly increased. The influence of the increase in fineness on the compressive strength is not obvious and can be neglected since the SAI increases very slightly for all MKs.

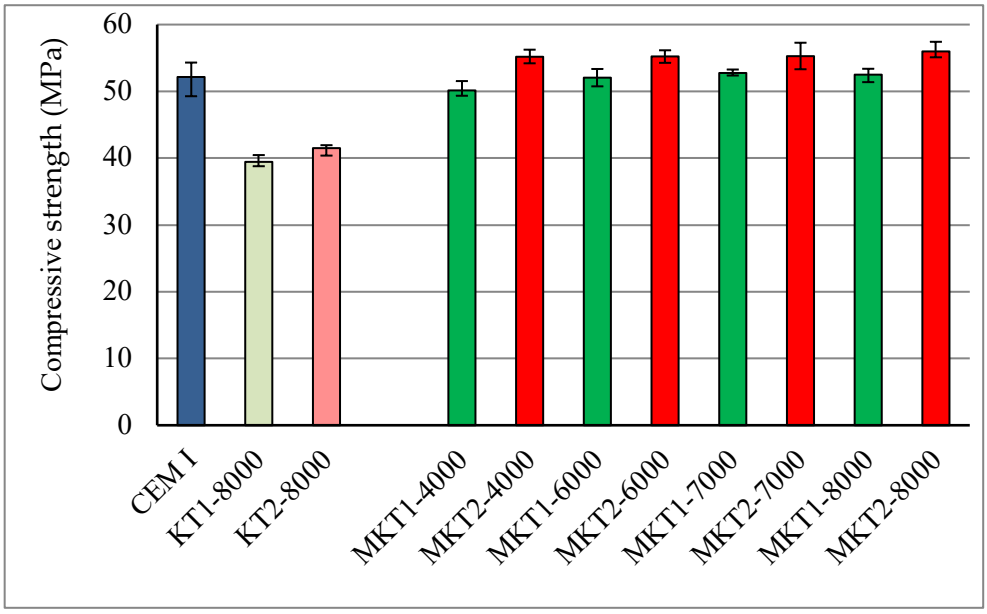

FIGURE 1. 28-day compressive strength results of mortars.

3. The 8-day Frattini test results

Figure 2 presents the 8 day results of Frattini tests, of different samples of MKT1 and MKT2 as well as the raw kaolins ground for 90 min. As can be seen, the location of [Ca^{2+}] and [OH-] for kaolins is above the lime solubility curve, meaning that KT1 and KT2 do not have any pozzolanic reactivity. However, the points ([Ca^{2+}], [OH-]) relative to all MK samples regardless of their SSB, are located below the lime solubility curve, indicating their pozzolanic potential. As the carbonate content of MKs is almost zero, we assume that all the Ca^{2+} cations present in the system come from the cement. It is generally believed that throughout this test, MK reacts chemically with the Portlandite issued from cement hydration, which reduces the content of residual Ca^{2+}. Therefore, it may be concluded that the lower the lime amount left in the system, the more reactive the MK.

However, the Frattini test, unlike other chemical tests, does not make it possible to determine exactly the quantity of this lime consumed (Donatello et al. 2010).

4. Saturated lime test results

Results of the saturated lime test are presented in Table 4, it can be seen that the lime fixation rate increased with time and SSB. The results show also that for all test periods, the raw kaolins KT1 and KT2, despite their high SBB, were only able to consume very little amount of lime compared to the corresponding MKs. However, for MK samples, the fixed lime percentage is more important, indicating a continuous MK-lime reaction over time. It increases from 61% after one day to 92% after 28 days when the SSB increases from 4000 to 7000 cm^2/g, in the case of MKT1 and from 53% after one day to 95% after 28 days when the grinding time increases from 90 to 240 min, in the case of MKT2. We can clearly see that the MKT2 samples always presented better results compared to those of MKT1, which is probably due to their higher kaolinite content (58% against 39%) (Boumediene et al. 2021). In terms of SSB, it seems that the finer MK reacts better with lime and therefore consumes more lime. In terms of time, the evolution of lime consumption over time means that the MK-lime reaction is continuous over time.

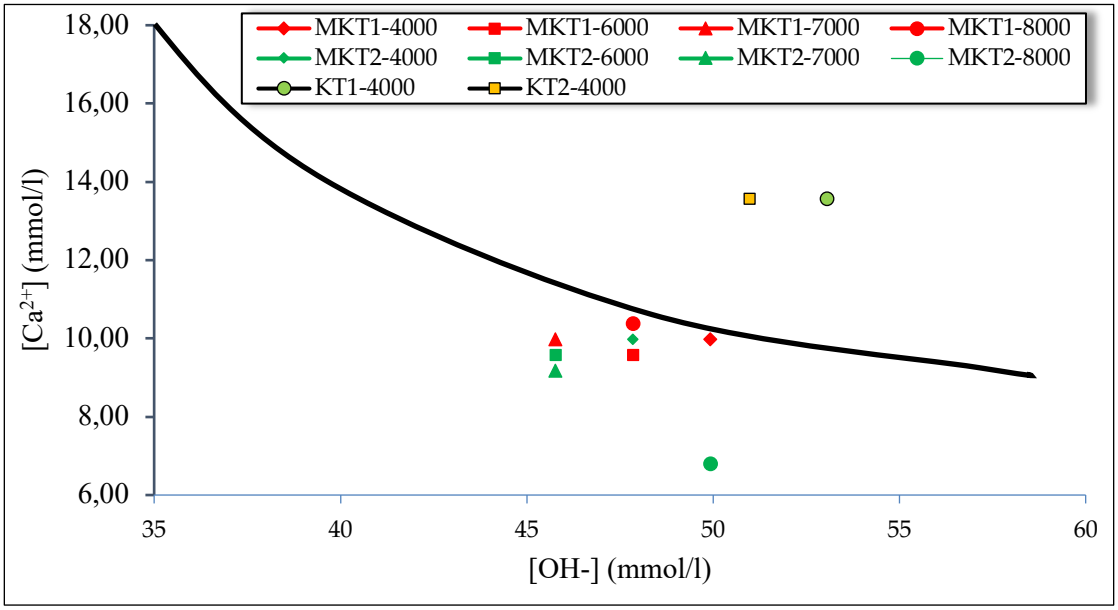

FIGURE 2. Eight days Frattini test results.

TABLE 4. Results of the saturated lime test, expressed as % de Ca^{2+} fixed at 1, 3, 7 and 28 days.

Time (days)	Kaolin		MK							
	KT1-7000	KT2-7000	MKT1-4000	MKT1-6000	MKT1-7000	MKT1-8000	MKT2-4000	MKT2-6000	MKT2-7000	MKT2-8000
1	30.13	35.63	61.33	62.19	65.8	73.14	53.12	56.5	62.13	63.63
3	35.73	42.5	68.5	70.63	80.15	83.25	62.25	65.63	71.63	75.13
7	37.83	46.2	77.65	83.44	91.65	87.88	77.87	84.25	93.75	94.12
28	45.2	51.38	83.1	86.38	92.36	90.4	82.5	88.11	94.37	95.63

5. Modified Chapelle test results

Figure 3 presents the quantity of lime (in mg) consumed by each MK sample, according to results of the modified Chapelle test. It can be clearly observed that the lime consumption increases with the increase in SSB of MK. Unlike KT1 and KT2, ground for 120 min, where the results did not reach the threshold of 300 mg, the lime consumption in the case of MKT1 increases from 712 to around 800 mg, and from 723 to almost 900 mg in the case of MKT2, when the SSB of the samples increases from 4000 to more than 8000 cm^2/g. These results indicate that increasing the fineness of MK improves its reactivity and therefore its lime consumption. It should be noted that the NF P18-513 standard assume that MK is considered reactive if it was able to fix at least 700 mg of lime by the Modified chapel test, which is the case in the present study for MKT1 and MKT2, regardless of their SSBs. Similar findings were reported in the literature for other MKs (Shafiq et al. 2015; Ferraz et al. 2015; Liu et al. 2017).

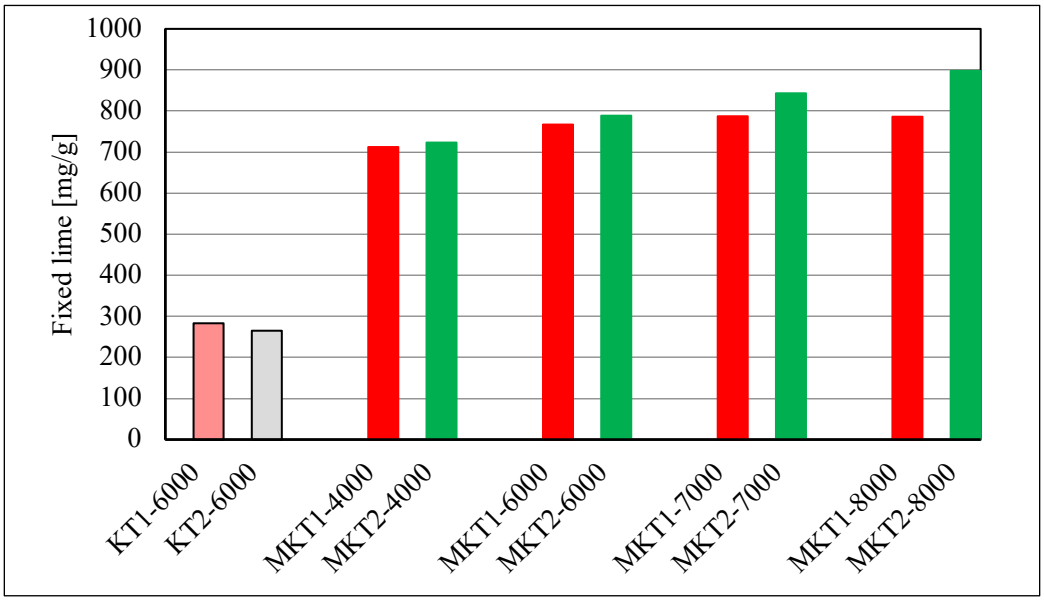

FIGURE 3. Modified Chapelle test results after 16 hours at 90 °C, expressed by mg of lime consumed per gram of kaolin or MK.

6. Discussion

On the bases of results of chemical test, it can be observed that reactivity of MK increases with its fineness. This means that fineness of MK is beneficial for its chemical reaction with lime in these systems, despite their differences in temperature, MK-lime ratio and time. However, the stagnation of compressive strength, despite the increase in SSB, means that the maximum chemical reactivity of MKs has been reached. This could be explained by the exhaustion of the reactive phases in the MKs, either because of the low MK content in the matrix (only 15%) or because of the low kaolinite content, particularly for KT1 (only 39%); in this case, increasing the fineness does not seem beneficial. Added to this is the undesirable effect of the aggregation of dehydroxylated particles and therefore the insufficiency of fine particles in the matrix, which is mainly due to the grinding-calcination process.

V. CONCLUSIONS

This research investigated the effect of increasing fineness on the reactivity of thermally treated Algerian kaolins KT1 and KT2. The following conclusions can be drawn based on this study:

- SSB of kaolins increases with the grinding time and consequently their particle size indices decrease.

- Calcination did not significantly change the fineness characteristics of the kaolins. SSB of the resulting MKs is almost unchanged, however, their particle size indices were remarkably increased due to the aggregation tendency of dehydroxylated particles.

- Lime consumption, measured by the Frattini, modified Chapelle and saturated lime chemical tests, increased with the increase in the SSB of MKs. It can be established that fineness favours the direct chemical reaction between MK and lime in all these systems, despite their differences in terms of temperature, time and MK-lime ratio.

- Whatever their SSB, the raw kaolins, KT1 and KT2, exhibited a little or no pozzolanic reactivity.

- The incorporation of 15% MK improves the compressive strength of mortars. However, increasing the finesse of the MKs does not seem beneficial, as the resistance remains unchanged.

- Chemical tests are more sensitive to the SSB of MK than the compressive strength test.

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