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Effect of mixture constituents on properties of slaked lime–metakaolin–sand mortars containing sodium hydroxide

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ABSTRACT

In the present study, percentage of slaked lime (20–30%) in binder with metakaolin, water–binder ratio (0.8–1.0), sand–binder ratio (1–3) and sodium hydroxide (NaOH)–binder ratio (0.02–0.04) were factors varied to investigate properties of fresh or hardened mortars. Sodium hydroxide was used as a chemical activator in the slaked lime–metakaolin binders. Properties studied after 7 or 28 days of curing mortars at 40 ± 1 °C were consistency, compressive strength and water absorption. The physical, chemical, mineralogical and pozzolanic characteristics of materials used in study were determined. It was concluded that water–binder and sand–binder ratios are the most influential factors for consistency and water absorption of mortars. Compressive strength is influenced by all mixture constituents but NaOH–binder ratios less than 0.03 are recommended for use in mortars.

1. Introduction

The use of burnt clays in mixture with lime and water for the fabrication of mortars dates back to the Neolithic era (700 years B.C.). With the discovery of Portland cement and its high promotion that followed, use of the burnt clay mixtures lessened over time [1,2]. The high porosity and low mechanical resistances of the hardened mortars affected the use of that material [3]. Nowadays, with the high consumption of energy by Portland cement industry, its release of high quantities of CO_2, the scarcity of Portland cement in some regions of the world, and its high cost compared to the incomes of some populations, researchers are developing alternative binders that can reduce Portland cement clinker consumption [4–7]. Lime–metakaolin binder could replace Portland cement for some building materials applications, such as concrete blocks for masonry, repair works and coating.

Metakaolin is the product obtained after kaolin is fired between 600 and 900 °C [8,9]. The optimization of the firing temperature of kaolin with the aim of obtaining a material of high reactivity was the subject of other studies [8,10,11]. Metakaolin with high reactivity is obtained between 700 and 800 °C. The heat treatment disorganizes the crystalline structure of kaolinite, the major mineral of kaolin, to an amorphous structure reactive to slaked lime in the presence of water through a pozzolanic reaction [7,12]. The side reaction of carbonation of lime by carbon dioxide from air is possible during the process [13]. New chemical components like Calcium Silicate Hydrate gels, hydrated silicates and aluminates of calcium such as C_2ASH_8, C_4AH_{13} and C_3AH_6, are formed during the reaction [10,12]. An increase in the curing temperature accelerates the reaction and influences the nature of the phases formed during the reaction [3,12]. Additives such as sodium hydroxide and sodium sulphate (NaOH, Na_2SO_4) or superplasticiser can be added when making mortars to improve their properties such as setting and consistency [3,8,13,14].

When making mortars with lime–metakaolin binder and sand, factors such as the proportion of lime in the binder, water–binder, sand–binder and additive–binder ratios are considered. Little knowledge exists in the literature on the effect of each factor on the properties of the fresh or hardened mortars. Fortes-Revilla et al. [14] determined the effect of dosage, curing conditions and use of a superplasticiser admixture on porosity, mechanical strength and composition of slaked lime–metakaolin mortars.

The objective of this investigation is to improve the porosity and mechanical strength of lime–metakaolin–sand mortars. Effects of the percentage of slaked lime in the binder, water–binder ratio, sand–binder ratio and sodium hydroxide (as chemical activator) – binder ratio on the consistency of fresh mortar, and the compressive strength and water absorption of hardened mortar, were evaluated. The study was based on a graeco-latin square type experimental design [15–17]. The chemical, mineralogical and pozzolanic characteristics of the raw materials were also determined.

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2. Materials and experimental procedure

2.1. Raw materials

Kaolin used for the production of metakaolin was extracted from Mayoum – Cameroon. This kaolin was previously studied (sample MY_3) by Njoya, [18] for use in ceramics. They reported that the kaolin consists of approximately 79% kaolinite.

The kaolin sample was fired in an electric furnace at 750 °C for 1 h with a heating rate of 3 °C/min. The sample was left to cool freely in the furnace. The fired product, metakaolin (MK), was finely crushed in a ball mill and sieved totally at 80 μm.

An industrial slaked lime (SL) of EN 459-1 CL 90-S type produced by the SB-Mercier company in France and laboratory grade (99.6%) sodium hydroxide from Prolabo was used.

MK and SL were chemically analysed by ICP–AES method and, for mineralogical analysis, X-ray diffractometry (XRD) using a Debye–Scherrer assembly equipped with a curved position detector (INEL CPS 120) was used. The X-ray source operates with 40 kV and 30 mA, producing a monochromatic radiation of wave length 1.540598 Å. MK was also tested using Differential Thermal and Gravimetric Analysis (DTA/TG) to supplement the evaluation of the state of amorphisation of the material. Absolute density using the pycnometer with helium and the B.E.T specific surface are other characteristics of MK and SL that were determined.

Sand used in the mortars was a siliceous sand consisting of grains that all passed through a 2 mm sieve. Water absorption of the sand was tested.

2.2. Experimental procedure

2.2.1. Pozzolanic properties of MK

Four types of mixtures made of 80%MK–20%SL, 70%MK–30%SL, (70%MK–30%SL)–2%NaOH and (70%MK–30%SL)–4%NaOH were formulated. The dry mixtures were homogenized in a ball mill containing few balls for 30 min. They were afterwards mixed with distilled water with or without the sodium hydroxide. The water–binder mass ratio was 0.8. The pastes were then introduced into plastic bowls and slightly vibrated. After 24 h, the pastes containing sodium hydroxide were demoulded and hermetically sealed in plastic bags in order to limit contact with the carbon dioxide of air. The samples not containing sodium hydroxide did not reach sufficient solidification that allowed them to be easily demoulded. They were sealed hermetically together with their moulds in plastic bags. All the samples were cured in a drying oven at 40 ± 1 °C for 28 days. After that, the hardened pastes were removed from the bowls, finely crushed and samples were prepared for DTA/TG analysis.

2.2.2. Study of the average effects of mixture constituents

A screening design indicated in Table 1 was used to evaluate the effect of the percentage of SL in the binder, water–binder, sand–binder and sodium hydroxide–binder ratios on the consistency of fresh mortar, compressive strength and water absorption of hardened mortar. This design used an orthogonal arrangement of experiments suggested by Fisher at the beginning of the 20th century [16,17]. Nine different types of mortar compositions were tested. The interval of variation of the effect of the percentage of SL in the binder and that of NaOH–binder ratio was chosen according to previous works [19–21]. The mortars were made by dry mixing suitable proportions of sand and binder in a mixer for 1 min. Then, distilled water containing sodium hydroxide was added to the mixture and all the components were mixed at a slow speed for 1 min, then at fast speed for 3 min. Thirty seconds break between the two speeds was observed to scrape the mortar, which became stuck to the interior body of the mixer tank. The mortar was then introduced in a miniature Abram's cone of 15 cm height following the NF-P-18–451 standard. When the cone was removed, the depression of the mortar (in cm) characterized its consistency. As soon as the consistency of the mortar was tested, it was quickly introduced and vibrated in $4 \times 4 \times 16$ cm metallic moulds, demoulded after 24 h and then sealed hermetically in plastic bags. To accelerate pozzolanic phenomena, the samples were cured at 40 ± 1 °C for 7 and 28 days. At each period, the hardened mortars were cut using a diamond mini-saw in the form of cubes of dimensions $2 \times 2 \times 2$ cm approximately and tested for compressive strength with a hydraulic press. The results obtained took into account the actual dimensions of every cube. For each type of mortar, the final strength was the average of three experimental values which did not deviate more than 10%. The average effect of a distinctive state or variation of a given factor was the arithmetic mean of experimental results in which that distinctive state intervened [16].

For the water absorption test, samples of hardened mortars were dried to 105 °C for 48 h, weighed and immersed in water for 24 h before being removed and reweighed. The relative difference (in percentage) in mass compared to the dry sample mass gave the percentage of water absorbed. Two tests were carried out for each type of samples.

Table 1
Design for the study of the average effects of mixture constituents.

No.	SL in the binder (%)	Water–binder ratio	Sand–binder ratio	NaOH–binder ratio
1	20	0.8	1	0.02
2	20	0.9	2	0.03
3	20	1.0	3	0.04
4	25	0.8	2	0.04
5	25	0.9	3	0.02
6	25	1.0	1	0.03
7	30	0.8	3	0.03
8	30	0.9	1	0.04
9	30	1.0	2	0.02

3. Results and discussions

3.1. Characteristics of raw materials

Table 2 gives major chemical elements and physical characteristics of MK and SL. MK and SL have similar specific surfaces. The chemical analysis shows that MK consists of SiO_2, Al_2O_3 and small quantities of Fe_2O_3, TiO_2 and K_2O. The sum $SiO_2 + Al_2O_3 + Fe_2O_3$ approximated to 85.5%, which is greater than the 70% recommended by the ASTM C 618 Standard for pozzolans [22]. SL contains CaO with small quantities of MgO and SiO_2, which could be in the form of insoluble quartz impurities. The mineralogical analyses of MK and its raw kaolin are shown in Fig. 1. The raw kaolin

Table 2
Major chemical components (wt.%) and physical characteristics of MK and SL.

Oxydes	MK	SL
SiO_2	48.74	1.05
Al_2O_3	34.85	0.85
Fe_2O_3	2.07	0.62
CaO	0.03	65.30
MgO	0.09	1.91
Na_2O	0.01	0.00
K_2O	1.29	0.00
TiO_2	4.26	0.00
L.O.I.	4.84	29.34
B.E.T. Specific surface (m^2/g)	17.94	19.12
Absolute density (g/cm^3)	2.63	2.26

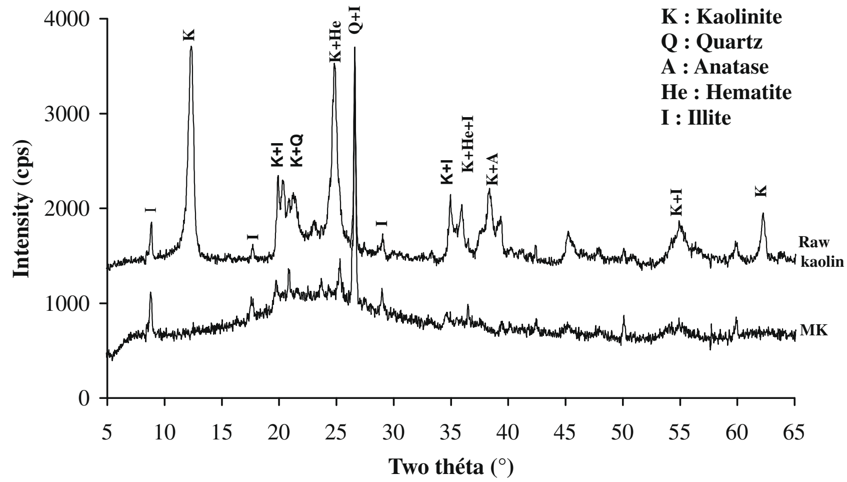

Fig. 1. XRD patterns of MK and its raw kaolin.

consists of kaolinite, illite and quartz as major minerals phases, whereas MK contains only illite and quartz. The heat treatment of the raw material at 750 °C causes the disappearance of the crystalline structure of kaolinite and the appearance of an amorphous structure (to X-rays) with the release of constitution water. The principal peak of kaolinite at around two theta = 12.29° disappeared. MK subjected to thermal analyses (Fig. 2) did not show any thermal change until approximately 900 °C. That was the indication that the amorphisation of material was completed and that the material contains a small proportion of quartz. The exothermic transformation that occurs in the material at about 900 °C is attributed to the reorganization of MK to other stable phases such as mullite [23]. The weak loss of mass observed on the thermo-gravimetric curve could be attributed to the presence of a little moisture in samples or the decomposition of some remaining components like carbonates.

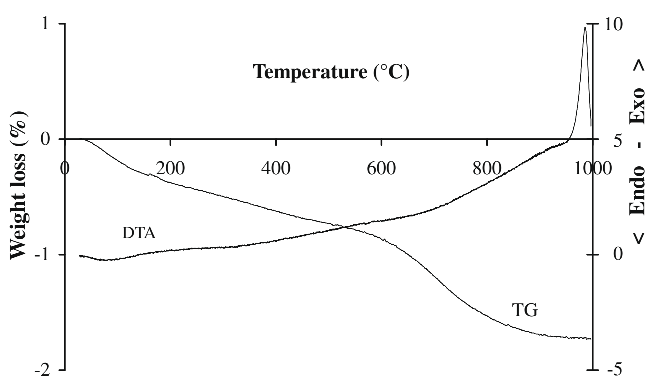

Fig. 2. DTA/TG thermograms of MK.

The XRD result of SL (Fig. 3) shows that it essentially consisted of calcium hydroxide ($Ca(OH)_2$).

The result of the granulometric analysis of the sand is shown in Fig. 4. The majority of the particles of that sand have diameters between 500 μm and 2 mm. Its average water absorption (4.4%) is low.

3.2. Pozzolanic properties of MK

Figs. 5 and 6 show the results of DTA/TG analysis of the reacted samples of pastes of MK–SL in the presence of water with or without sodium hydroxide. The presence of new phases in the mixtures shows that pozzolanic reactions took place. For the curing condition used, the nature of the phases that are formed depends on the percentage of lime in the MK–SL binder. When the binder

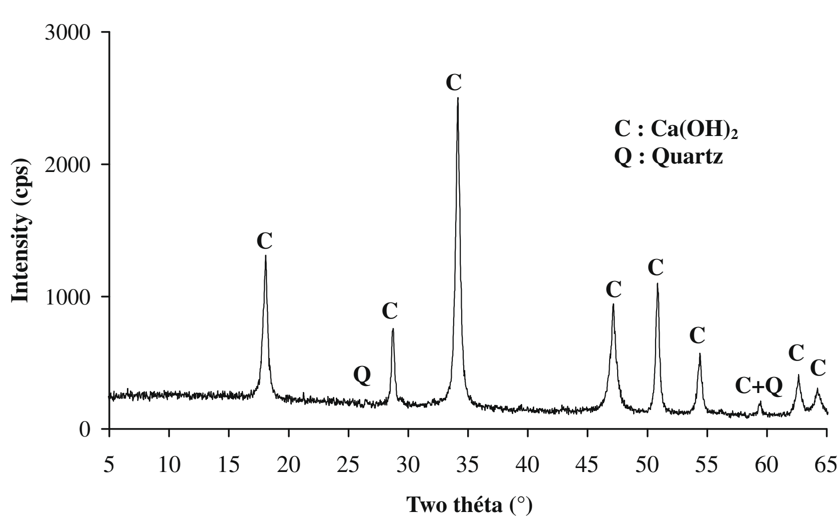

Fig. 3. XRD patterns of SL.

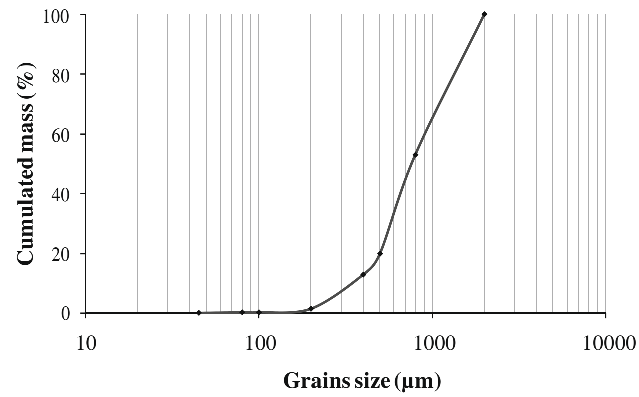

Fig. 4. Granulometry of the sand.

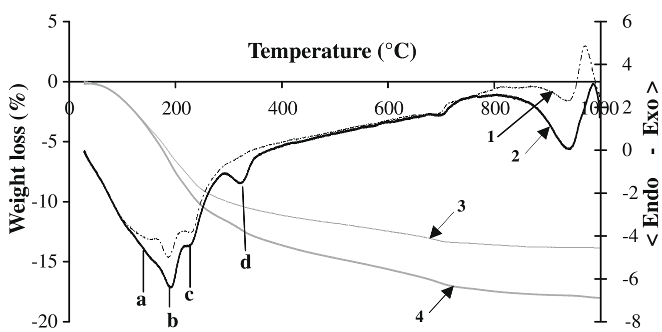

Fig. 5. DTA–TG thermograms of MK–SL pastes. 1: DTA 20%–80%MK; 2: DTA 30%SL–20%MK; 3: TG 20%SL–80%MK; 4: TG 30%SL–70%MK; a: CSH; b: C_2ASH_8; c: C_4AH_{13}; d: C_3AH_6.

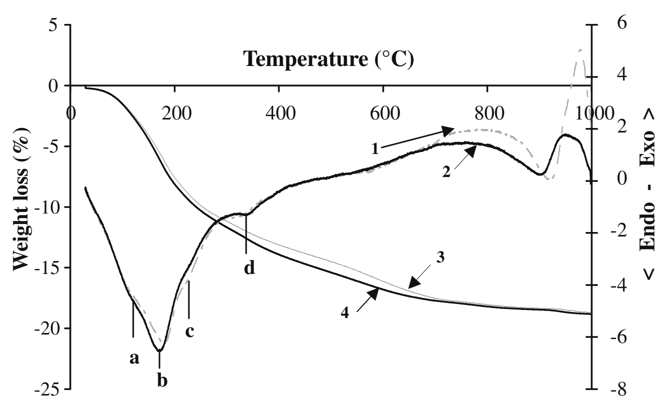

Fig. 6. DTA–TG thermograms of 70%MK-30%SL pastes containing sodium hydroxide. DTA 2% NaOH; 2: DTA 4% NaOH; 3: TG 2% NaOH; 4: TG 4% NaOH; a: CSH; b: C_2ASH_8; c: C_4AH_{13}; d: C_3AH_6.

contains 20% of SL, the phases present are CSH, C_2ASH_8 and C_4AH_{13}. When the percentage of SL increases to 30%, C_3AH_6 is formed in addition to the three previous phases. Little carbonation of the hardened material by the carbon dioxide of air occurred. That is indicated in the DTA curves by a small endothermic peak of decomposition of neoformed $CaCO_3$ around 700 °C accompanied by a loss of mass [24]. This side reaction probably happened during different stages of treatment of samples before testing. The presence of excessive $Ca(OH)_2$ was not detected in DTA curves. All SL reacted during the reaction.

When 2% and 4% in mass of NaOH of the binder is added on the mixture that contains 30% of SL, the curves shows the stability of CSH, C_2ASH_8 and C_4AH_{13} is affected. The occurrence of the C_4AH_{13} and C_3AH_6 was reduced in the curve. The results also show that, as the proportion of NaOH in samples increases, the degree of carbonation reduces. With a proportion of NaOH of 4%, the peak of decomposition of $CaCO_3$ disappeared.

3.3. Study of the average effects of mixture constituents

Fig. 7 presents the average effects of mixture constituents on the consistency of fresh mortars. The increase in the percentage of lime in the binder has a little effect on the consistency of the mortars at the mixing period used. For more than 25% of SL in MK, a slight decrease of the consistency of the mortar was observed. A great influence on the consistency of the mortar was observed for variations of the water–binder ratio and the sand–binder ratio with ranges of slump of 8.16 and 6.8 cm, respectively. The increase in the water–binder ratio thus decreases the consistency, whereas the increase in the sand–binder ratio rather increases the consistency because part of the water is absorbed by the sand. During the mixing period used, the increase in the NaOH–binder ratio had a little effect on the consistency.

Fig. 8a shows the result of the average effect of mixture constituents on compressive strength of the mortars. After 7 days of curing, the mortar containing 30% of SL in the binder shows a slight decrease on the compressive strength. At 28 days of curing, the compressive strength of the mortars increases with increase in the proportion of SL in the binder. On the other hand, the increase in the water–binder ratio causes a reduction in the compressive strength, as expected. The increase in the sand–binder ratio involves a reduction of the compressive strength due to a dilution effect, i.e., the reduction of the quantity of binder necessary to bind the sand grains. The result shows also that NaOH–binder ratios more than 0.03, especially at 28 days of curing, can decreases the compressive strength of the mortar. The presence of NaOH increases the appearance shrinkage cracks of hardened mortar. Globally, all the constituents studied have a great effect on the compressive strength.

Fig. 8b presents the average effect of constituents on water absorption of mortars. The increase in the percentage of SL in the binders does not have a notable effect on this property. However, the increase in the water–binder ratio increases water absorption due to the increase of open porosity. This porosity is responsible for the reduction of the compressive strength. For sand–binder ratio, the more it increases, the more the water absorption decreases. The presence of a significant quantity of sand improves the packing of the grains in the mixture and decreases the open porosity without contributing to mechanical strength. NaOH–binder ratio has a little effect on water absorption, but ratios greater than 0.03 can reduce water absorption. Water–binder and sand–binder ratios are the most influential factors on water absorption.

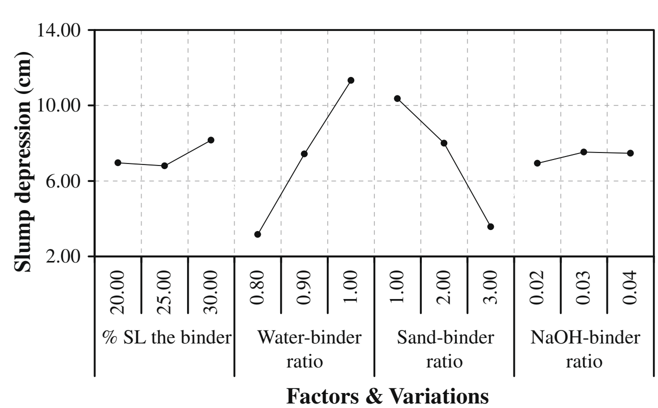

Fig. 7. Average effect of factors on the consistency of fresh mortars.

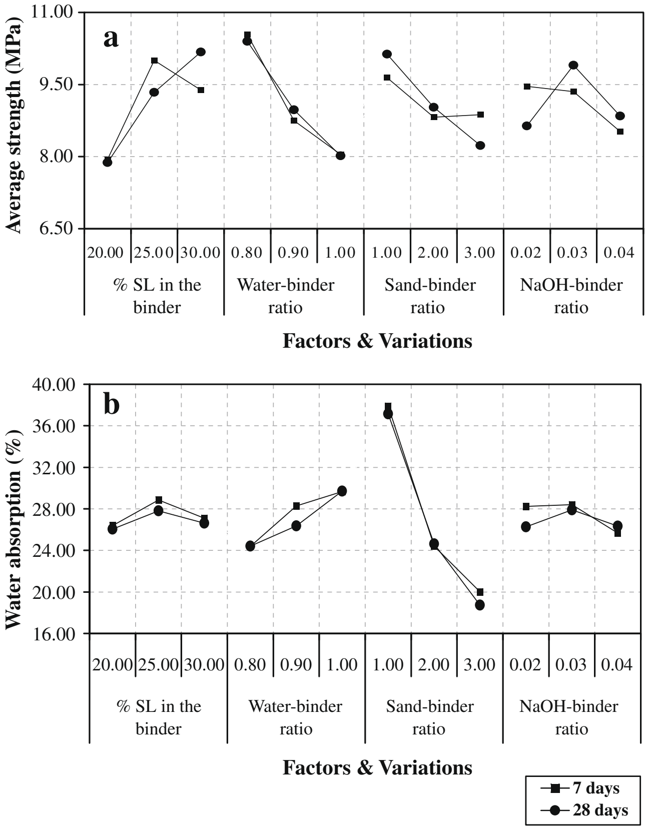

Fig. 8. Average effects of factors on the properties of mortars at 7 and 28 days: (a) compressive strength and (b) water absorption.

The average properties of the mortars at 7 and 28 days are similar. This behaviour of the mortars shows that the curing of samples at 40 °C accelerated strongly the pozzolanic reaction. At 7 days, the maximum of pozzolanic activity was almost achieved.

4. Conclusions

From the investigations carried out in this study, the following conclusions can be made concerning the effect of mixture constituents on properties of slaked lime–metakaolin–sand mortars containing sodium hydroxide:

- The percentage of hydrated lime and the NaOH–binder ratio do not have a great effect on the consistency of the fresh mortar which is mostly governed by water–binder and sand–binder ratios.
- Compressive strength of mortars is influenced by all mixture constituents. It increases with the increase of proportion of SL in the binder. It decreases when water–binder and sand–binder ratios increase.
- When using NaOH as chemical activator, NaOH–binder ratios less than 0.03 are recommended, since greater ratios can reduce compressive strength.
- Water absorption increases with the increase of water–binder ratio and decreases with the sand–binder ratio. It is believed that the increase in sand–binder ratio improves packing of particles in the mortar and reduces porosity.

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