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Characterization of Libyan metakaolin and its effects on the mechanical properties of mortar

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Abstract. Environmental concerns, stemming from high-energy demands and CO_2 emission associated with cement manufacture, have brought about pressures to reduce cement consumption through the use of supplementary cementitious materials (SCMs). Besides addressing environmental concerns, the incorporation of SCMs in cement bound materials and concrete can modify and improve specific concrete properties. Metakaolin (MK) in an important SCM which can enhance the performance of cementitious composites through its high pozzolanic reactivity. This study was carried out to characterize the materials and to assess the effect of Libyan metakaolin (LMK) on the mechanical properties including the compressive strength of cement mortar. LMK was produced by calcining kaolinite clay at 700°C for 2 h. X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Thermal Analysis / Thermo-Gravimetric analysis (DTA/TG) and Fourier Transform Infrared Spectroscopy (FTIR) s were performed on the raw and calcined kaolinite powders. Seven mixes were prepared with different LMK replacement percentages (0.0 to 30%), by weight of cement, and a constant water binder ratio (w/b) of 0.5. The specimens were cured for 3, 7, 28, 56 and 90 days. At the end of each curing period, the specimens were tested for compressive strength. The results confirm the transformation of kaolinite clay into metakaolin and the pozzolanic reactivity of the produced LMK and conforms to ASTM requirements in this respect. The study confirms that LMK could be effectively used in reducing cement content up to 30% by weight without compromising compressive strength of the cement mortar.

Keywords*:* Libyan clay, metakaolin, cement mortar

1. Introduction

The production of Portland cement is not only costly and energy intensive, but it also requires large quantities of natural raw materials and produces large amount of carbon emission. The production of one ton of Portland cement produces approximately one ton of CO_2 in the atmosphere [1]. Supplementary cementitious materials (SCMs) are often used to reduce cement content in concrete and to improve some desired property. The addition of SCMs in cement based materials effectively addresses environmental concerns associated with cement production but also leads to improved durability performance of Portland cement based materials, in particular when exposed to aggressive environments.

Alternative SCMs such as metakaolin, silica fume, and quarry dust are effectively used in concrete. Specific SCMs constitute silica or silica-alumina that react with portlandite released during cement hydration to produce additional CSH, enhancing the properties and pore structure of concrete or cement mortar.

There is a growing interest in utilizing calcined clays rather than industrial by-products as SCMs, as these materials are highly available all over the world and present more homogeneous physico-chemical properties compared with by-products, simplifying the process of quality control of the finished cement [2]. Many studies have been conducted regarding the characterization and the use of different types of SCMs, and different results have been introduced.

A. Tironia, et al. 2012 [3], studied the influence of different thermal treatments on the pozzolanic activity of raw kaolin with 98 % kaolinite and ordered structure. The results showed that for the production of metakaolin to be used as pozzolanic material, the calcination temperature and the residence time are variables to be considered. The used kaolin treated at 700 °C showed that its pozzolanic activity were directly proportional to the residence time. On the other hand, when it was treated at 800 °C the pozzolanic activity decreases when the residence time increases. The peak area of bands assigned to the amorphous phase in FTIR spectrum of kaolin calcined at 700 ºC during 30 min is higher than that obtained at 800 ºC. For 800 °C and 750 °C, a low residence time (10 minutes) reduces the structural rearrangement and increases the pozzolanic activity.

Biljana R. Ilic, et al. [4], investigated the ability of the metakaolin to be used as a supplementary cementitious material and they reported that the metakaolin can be produced by thermal treatment (calcination) of the starting high-quality kaolin clay from Serbia. They stated that the optimal calcination parameters, for which nearly complete dehydroxylation of the material was achieved, are: temperature 650 °C and heating time of 90 min. The conversion of the kaolinite to metakaolin was confirmed by XRD and IR analyses of the starting and thermally treated kaolin samples.

He et al. 1995 [5], measured compressive strength of mortars on mini-RILEM prisms cured in water at 40°C for 28 days. The mortars had a ratio of cement, clays and sand of 70, 30 and 300 by weight, respectively. Kaolin compared with other clays and Ordinary Portland Cement (OPC) increases the compressive strength the most, up to 113 % of pure OPC when calcined at 550°C. And it remains in this range during further calcination up to 950°C.

This study is based on Libyan metakaolin (LMK) as partial replacement of cement in cement based materials. The research reported in this paper is based on the material characterization and experimental investigation with respect to mechanical properties of the concrete. LMK was produced by calcining Libyan kaolinite clay at 700°C for 2 h. X-Ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis / thermo-gravimetric analysis (DTA/TG) and Fourier transform infrared spectroscopy (FTIR) techniques were implemented for material characterization. The Strength Activity Index (SAI) was also determined for the pozzolanic activity. All of the characterization tests confirmed the transformation of the Libyan kaolinite clay into metakaolin. Seven cement mortar mixes with different cement-metakaolin replacement levels (0.0 – 30 %) by weight were prepared, cured and tested for compressive strength at 3, 7, 28, 56 and 90 days. The results showed that up to 30% replacement level, the blended mixes had higher compressive strengths than the control mix, at all testing ages, but for the 3 days strength.

2. Materials

Metakaolin which was obtained by calcining Libyan kaolinite clay at a temperature of 700ºC for two hours was used. The metakaolin was used as a partial replacement of cement at 0 to 30%) by weight. Ordinary Portland cement CEM II/42.5 R and certified natural standard sand to ISO 679:2009 [6] were used in the study. Cement mortar strength was determined using EN 196-1:2005 [7].

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3. Experimental programme

3.1 Material characterization

Metakaolin was obtained by calcining Libyan natural kaolinite clay at temperatures of 700ºC for 2 hours. The material was collected from the village of Samnu located at the South part of Libya. The material preparation, calcination process and material characterization and testing were conducted in the University of Malta laboratories. The DTA/TGA analysis was carried out at University of Kaunas, Lithuania. The material was characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Thermal Analysis / Thermo-Gravimetric (DTA/TG) and Fourier Transform Infrared Spectroscopy (FTIR) techniques for raw clay and calcined materials.

The X-Ray Diffraction (XRD) results of raw and calcined materials are presented in figures 1 and 2 respectively. As indicated in the figures, the kaolinite peaks disappeared during the calcining process, indicating complete transformation of kaolinite to metakaolin. The XRD pattern revealed the presence of quartz, which could be distinguished from XRD pattern before and after calcinations (peak position and intensities). The characteristic peaks (2ϴ= 12.18º, 20.26º and 24.72º), which look to be in principle Smectite-Kaolinite disappeared while the peaks representing Quartz (2ϴ= 20.72º and 26.46º) remained after calcination. Figures 1 and 2 also show SEM images of raw (crystalline plates) and calcined (amorphous) materials respectively.

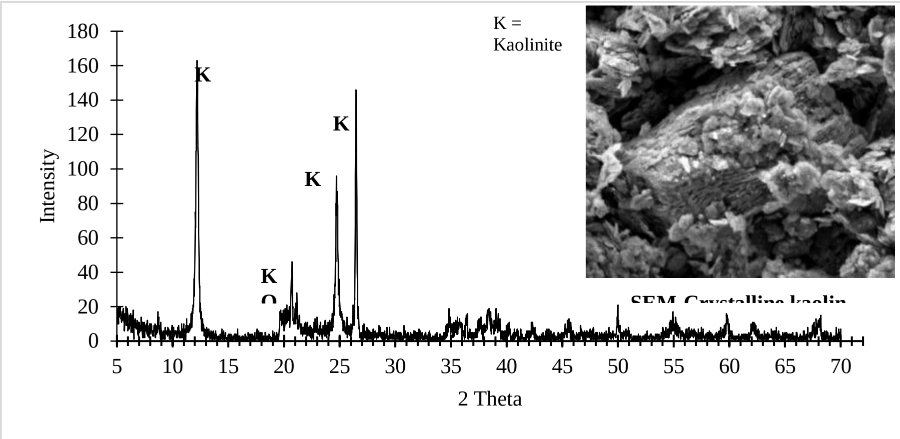

Figure 1. XRD pattern and SEM image of the raw kaolin

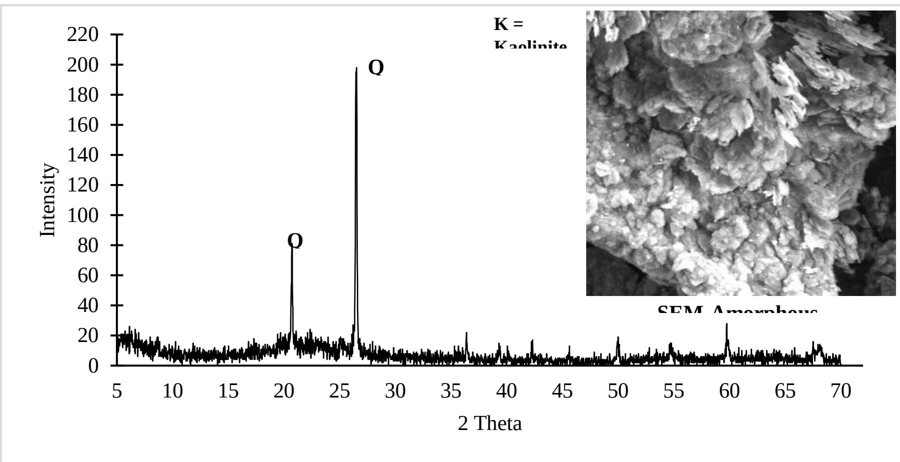

Figure 2. XRD pattern and SEM image of the metakaolin

Figure 3 represents Differential Thermal Analysis / Thermo-Gravimetric analysis DTA/TG test results obtained. It shows that the sample exhibits a total loss of 10.87 % of weight. The curve shows peaks between 38-179°C, 250-283°C and 460-582°C normally associated with loss of surface and absorbed water, pre-dehydroxylation and dehydroxylation processes of the clay material respectively. Pure kaolinite has a theoretical total loss of (±14 %) [9&10]. The difference noted between experimental result and those reported in literature confirm that this clay is associated with microcline and quartz.

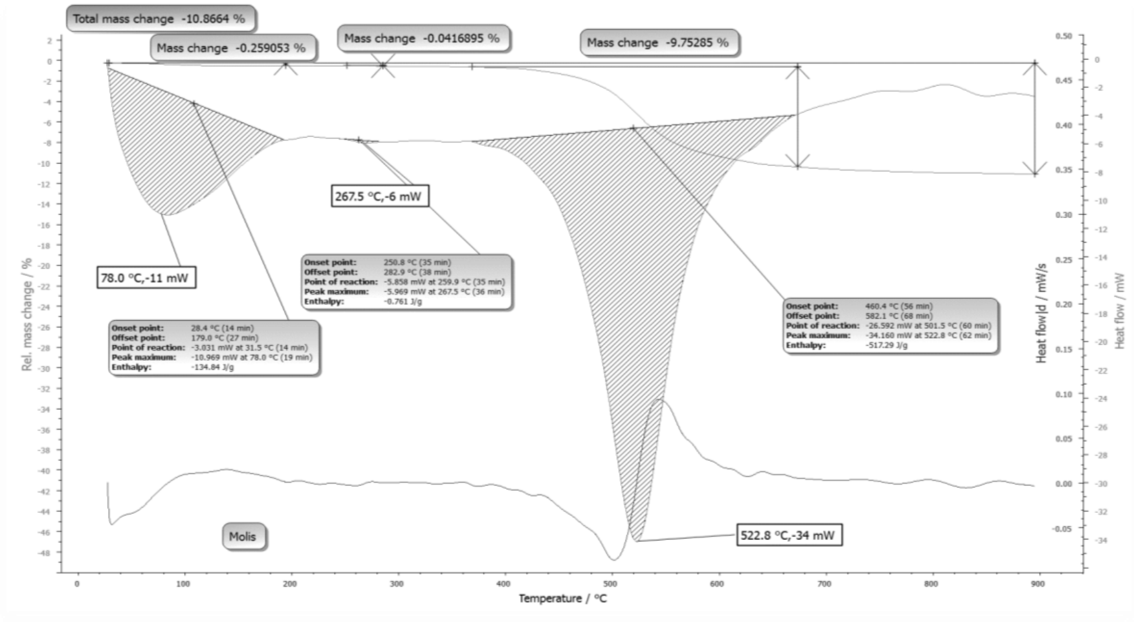

Figure 3. DTA/TG for the Libyan kaolin clay

The Fourier Transform Infrared Spectroscopy (FTIR) technique was used to distinguish between different types of clay minerals and to derive information concerning their structure, composition and structural changes upon chemical modification. A KBr pressed disk technique was used for the material characterization. Figures 4 and 5 show the FTIR spectrum of raw and calcined clay respectively.

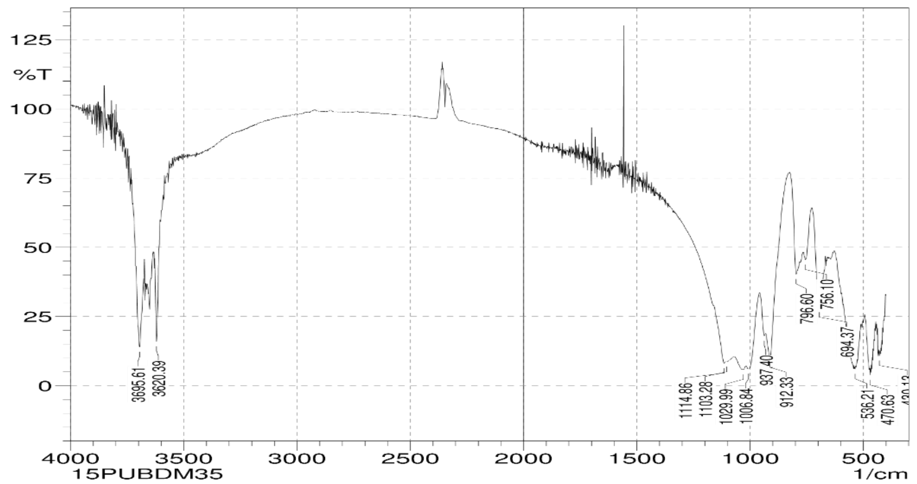

Figure 4. FTIR for the raw kaolin clay

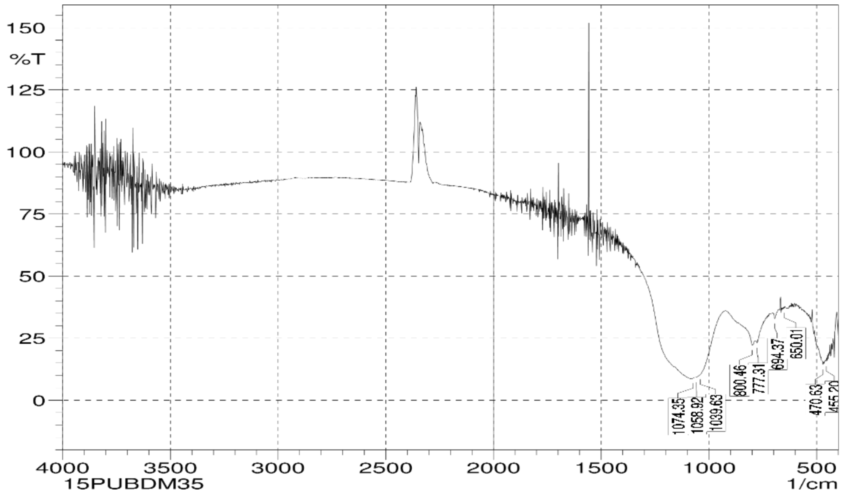

Figure 5. FTIR for the calcined kaolin clay (LMK)

The absorption band at 3695 cm-1 represents free OH stretching (hydroxyl sheet) which is very close to the 3699 cm^{-1} value obtained by Yleana [12], while the 3620 cm^{-1} frequency band represents the inner layer OH (Al-O…H) which falls at 3626 and 3622cm^{-1} obtained by Davarcioglu et al [13] and Yleana [12] respectively. The absorption band at 1114cm^{-1} is assigned to Si-O normal to the plane stretching which is very close to the band at 1120cm^{-1} obtained by Aroke et al [11]. The bands placed at 1029cm^{-1} and 1006cm^{-1} correspond to Si-O planar stretching which agree closely with 1027 and 1009cm^{-1} obtained by Davarcioglu et al [13]. The peaks at 937cm-1 and 912cm^{-1} correspond to inner-surface Al-OH deformation which agree to 940cm-1 and 913cm-1 obtained by Aroke et al [11] and Ilic et al [14] respectively. After calcinations, the absorption bands in the 3695 cm^{-1} and 3620.39cm-1 region as well as 1114 cm^{-1} disappeared or merged into a broad profile. The appearance of a new band at 800.46 cm^{-1} as obtained by Ilic et al [14].

3.2 Compressive strength

3.2.1 Strength activity index (SAI). The pozzolanic activity of the Libyan kaolinite clay before and after calcination was determined through the strength activity index test (SAI). Three sets of test specimens were prepared with respect to the standard mix design: one with 100 % Cement (control), and the other two were prepared with part of the Cement replaced by a corresponding mass (20%) of the materials to be tested. After curing, the specimens were tested for compressive strength. The effect of the pozzolanic material is expressed as strength activity index SAI = stress (tested mix) / stress (control). ASTM C618 [15] requires a SAI greater than 0.75 after 7 and 28 days for fly ash (FA) and natural pozzolans at a cement replacement of 20% [8]. Table 1 shows the result of SAI for the raw and calcined (metakaolin) Libyan clay. The test results showed that the calcined clay was active and could be considered as a pozzolanic material, while the raw clay was not active.

Table 1, Result of SAI for the raw and calcined Libyan clay.

Material	7 day Stress (MPa)	28 day Stress (MPa)	SAI	
			7 d	28 d
OPC	33	39		
Raw clay	18	22.3	0.55	0.57
Calcined clay (LMK)	32	44	0.97	1.13

3.2.2 Compressive strength of LMK mortar. After confirming the pozzolanic activity of LMK, specimens were cast for the determination of compressive strength, using mortar containing one part by mass of cement and three parts by mass of standard sand with a water/cement ratio of 0,50. The cement was partially replaced with LMK at different levels (0 - 30%) of the cement weight. The mortar was mixed mechanically n a mortar mixer, cast in 50 mm cube moulds and then compacted with the aid of a vibrating table. The specimens in the moulds were stored for 24 hours under laboratory conditions before demoulding. All samples were cured in a water bath until the time of testing (3, 7, 28, 56 and 90 days). The compressive strength test was conducted based on the EN 196-1:2005.

4. Results and Discussion

Results of the compressive strength test for mortar containing LMK at different replacement levels (0.0 – 30%) by weight of cement and at various curing ages (3, 7, 28, 56 and 90 days) are presented in figure 6. It can be seen that the incorporation of LMK improves the compressive strengths at early and later stages and for all replacement levels. The exception was for 3 days curing age where the control mix showed better compressive strength with respect to the higher replacement values. It is worth mentioning that mixes with LMK replacement level of 15% and higher were less workable than the mixes with lower replacement values. To overcome the workability issue, a separate set of additional mixes for those replacement levels were prepared with the use of superplasticizer (sp) type Master Glenium SKY 698, at a dosages of 1%, 1.25%, 1.5% and 1.5% of the total powder for 15%, 20%, 25% and 30% LMK replacement levels, respectively. The specimens were cast, cured and tested as indicated above. Figure 7 presents the results of 28 days compressive strength of the specimens with and without sp. Slightly higher compressive strength is reported for the specimens with sp when compared to specimen without sp. This can be attributed to the, improved workability and compaction achieved for samples with sp. The superior performance of specimens containing metakaolin could be due to both the pozzolanic reaction and micro-filler effect of metakaolin.

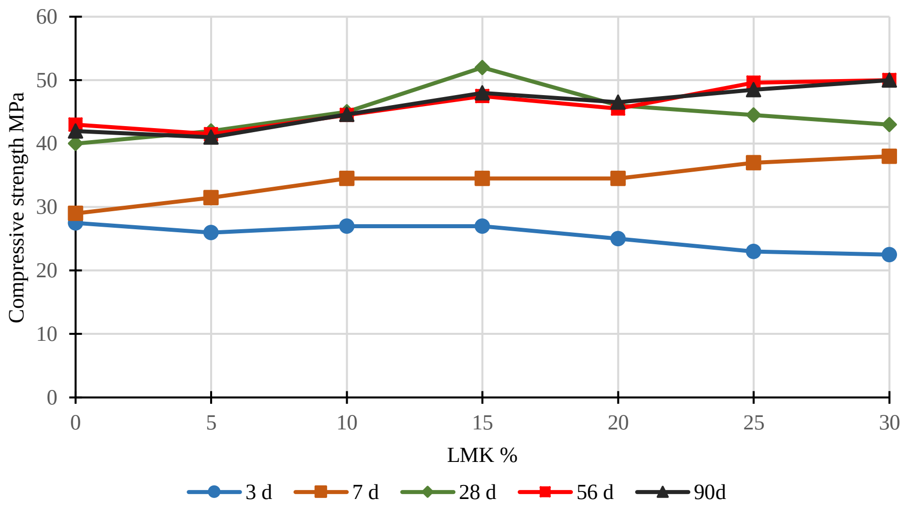

Figure 6. Compressive strength with different LMK levels and different ages

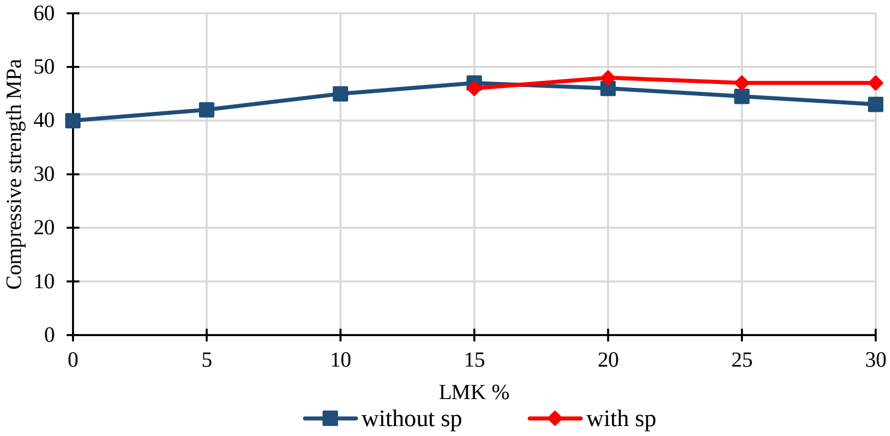

Figure 7. 28 day compressive strength of cement mortar with and without superplasticizer

5. Conclusions

From the study of the Libyan kaolinite clay and its effect on the strength of cement mortar, the following conclusions are drawn:

1. The utilization of different characterization techniques allows one to distinguish between different clay minerals and to provide fundamental information on their chemical composition and structural changes that occur as a consequence of their chemical modifications.
2. The two main components of the tested clay are kaolinite and quartz.
3. The Libyan kaolinite clay can be effectively transformed into an active metakaolin.
4. The compressive strengths of blended mortar specimens containing up to 30% replacement of LMK by weight of cement were superior to the control, both fort early age and also longer term.
5. LMK can be effectively used as a cement replacement, resulting in sufficiently high strength and a reduction in the consumption of cement.
6. The incorporation of higher quantities of LMK in concrete leads to a reduction in workability, Therefore, the use of chemical admixtures is necessary for higher cement replacement levels.

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