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Production of Green Cement from Slag Enhanced by Egyptian Metakaolin Materials

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Abstract. New geopolymer-based materials offer excellent perspectives for the future; they should not be regarded as competitive materials for Portland cement, which has been the reference construction material for so long, but as alternative materials with a series of important advantages to be considered. Metakaolin (MK) produced from firing kaolin material up to 750 ºC for 2 h with a heating rate of 5ºC/min; leads to an enhancement in mechanical and microstructural properties of alkali activated geopolymer of water cooled slag material using (6:6, wt%) of sodium hydroxide and sodium silicate. In the present work the ratios of MK which will be added are less than 20% of the total mass, because of the used MK was very fine with average pore structure less than 30 mμ, which hinders the geopolymerization reaction if used as high ratio. Curing was performed under 100% relative humidity at a temperature of 38ºC and ages of 7, 14, 28 & 90 days. The properties of geopolymer specimens have been studied through measurement of XRD, SEM imaging, FTIR, compressive strength and water absorption. Results showed that the mixes of metakaolin up to 15% results in an enhancement in the mechanical properties as compared with slag control mix up to 90 days.

Key words: Geopolymer, kaolin, metakaolin, slag, alkali activation.

1. Introduction

Geopolymers can be thought as a new generation binder that can substitute for the calcium silicate hydrate which are essential components of Portland cement, where they have a lower impact on global warming than OPC but on the other side they have a higher environmental impact regarding other impact categories (Davidovits, 1999).

During the last decade, considerable research efforts have been directed towards the development of inorganic geopolymers, due to the wide range of potential applications for these materials. Many reports can be found in the previous works on the synthesis, properties and applications of geopolymers (Steveson & Sagoe-Crentsil, 2005). It is found that fly ash, one of the most abundant sources for making geopolymer binders and used it till date is very limited (Hardjito et al., 2004). The wide variety of applications of geopolymer includes: fire resistant materials, low energy ceramic tiles, refractory items, cements and concretes (Davidovits, 2008). MK is a thermally treated product from kaolin, which is one of the naturally occurring abundant minerals in the earth's crust. Kaolin refers to a family of kaolinitic clays that consist of a 1:1-type clay mineral with one tetrahedral sheet and one octahedral sheet depending on the geological and weathering conditions.

In geopolymer cement, Al plays an important role because of its availability of aluminum controls to a large degree of the geopolymer properties (Duxson et al., 2007; Fernández-Jiménez, 2006). The absolute amount of available aluminum and the rate of its release throughout reaction not only affect final strength, but other properties in the wet and hardened states including setting characteristics, flexural strength, acid resistance, microstructure, and strength development profile. Generally, there are about 10% aluminum oxide in slag and 40% in metakaolin. According to the differences in the hydration products and, obviously, the role of Al in these two systems is different. Alonso and Palomo (2001-a,b) found that with the highly alkaline activation of metakaolin in the presence of calcium hydroxide led to the formation of an amorphous sodium aluminosilicate, which has the same properties of geopolymeric gel. This geopolymeric gel formed was found to be similar to that obtained when metakaolin was activated in the absence of calcium hydroxide. CSH gel was also formed as a secondary product when metakaolin was activated in the presence of calcium hydroxide. The high water demand of the reacting mixes and the high surface area and particle shape of MK due to calcination (Provis et al., 2010), affect the mechanical strength development and stability of these materials, which does not always compare well with the performance of other alkali activated binders based on industrial by-products, such as granulated blast furnace slag (GBFS) or with lower cost and higher potential for large-scale industrial applications than MK. Other than the lower aspect ratio of the particles, the main difference between these precursors is the presence of calcium in the GBFS which leads to the development of a microstructure enriched with stable and high density phases such as C-S-H gels, which promotes high compressive strengths (Lecomte et al., 2006; Lloyd, 2009).

The main purpose of this work is to study the preparation of geopolymer materials by alkaline activation of amorphous water cooled slag and different ratios of MK materials. However, MK is not commonly used in most construction cases due to the relatively large specific surface area, which may demand high water/binder ratio to achieve satisfying workability. This means that such a family of abundant resource is not utilized in large volume in geopolymer concrete. So, in the present work the ratios of MK which will be added are less than 20% of the total mass, because of the used metakaolin was very fine with average pore structure less than 30 mμ, which hinders the geopolymerization reaction if used as high ratio.

The effect of addition of different ratios of MK on alkali activated slag will be investigated as well as the impacts on mechanical and microstructural characteristics. X-ray florescence, X-ray diffraction, FTIR and SEM were used to identify the chemical, mineralogical and micro-structure of geopolymer composites. The compressive strength measurement was executed to evaluate the mechanical performance of the geopolymer specimens.

2. Experimental procedures

2.1 Materials

Materials used in this work were metakaolin prepared from kaolin collected from Sinai, West of Gebel Gunna, Egypt; water cooled slag also called ground granulate blast furnace slag (GGBFS) sourced from Iron and Steel Factory- Helwan, Egypt. Sodium hydroxide (NaOH) with purity 98 % in the form of pellets and sodium silicate (Na_2SiO_3) are used as alkali activators. MK was prepared by firing kaolin at 750 ºC for 2 h with heating rate of 5ºC /min. The chemical composition of the starting raw materials is tabulated in Table (1).

Table 1. Chemical composition of the starting raw materials (Mass, %)

Materials	Water cooled slag (GGBFS)	Metakaolin
SiO_2	35.63	56.00
Al_2O_3	12.69	38.11
Fe_2O_3	0.48	0.48
CaO	31.72	0.21
MgO	5.08	0.37
SO_3	2.35	0.18
Na_2O	1.23	0.00
K_2O	1.52	0.02
TiO_2	0.55	1.14
P_2O_5	0.031	0.26
MnO	4.72	0.00
Cl	0.24	0.00
Loss	0.03	3.13
TOTAL	99.89	99.89
Note	BaO=3.63	

The major components of GGBFS are SiO_2, CaO, Al_2O_3 and MgO. While in metakaolin, the two major components are $SiO_2$and Al_2O_3. Table 2 summarizes the major chemical composition of GGBFS and metakaolin (Buchwald et al., 2007; Li & Ding, 2003; Cheng & Chiu, 2003). From the chemical composition, we can consider that GGBFS is (Si+Ca) system and (Si+Al) is suitable for MK. Generally, GGBFS contains massive glass phase, while some crystalline phases may exist in minor level, such as gehlenite and akermanite. On the other hand, MK is ideally synthesized by dehydroxylation of phase pure kaolin while most commercial MK contains levels of impurities, primarily muscovite and titanium dioxide.

Laser particle size distribution of Mk reflected its very fine pore structure. This mean most particle size lower than 30 mμ as indicated in Fig. 1.

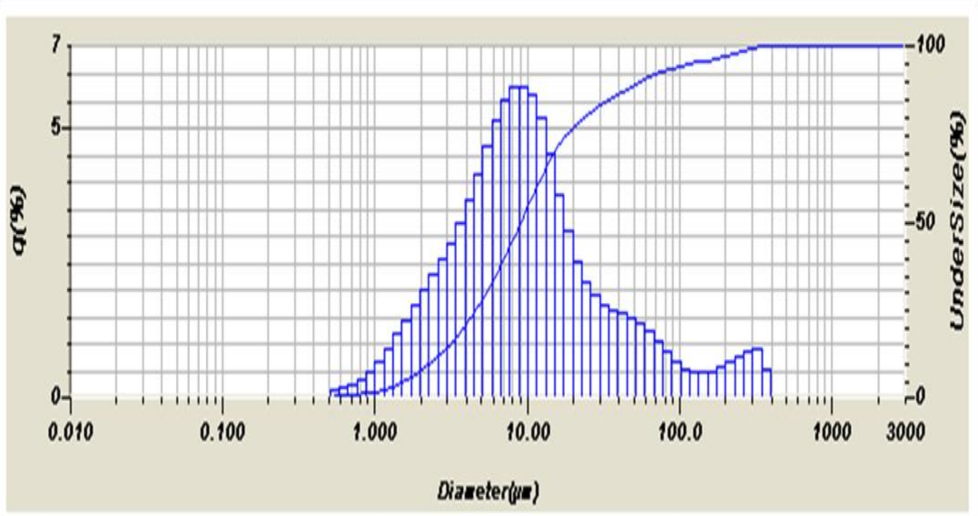

Fig. 1. Laser particle size distribution of Mk.

Mineralogical characterization of the raw materials was done using X-ray diffraction analysis in powder form as represented in Fig. 2.

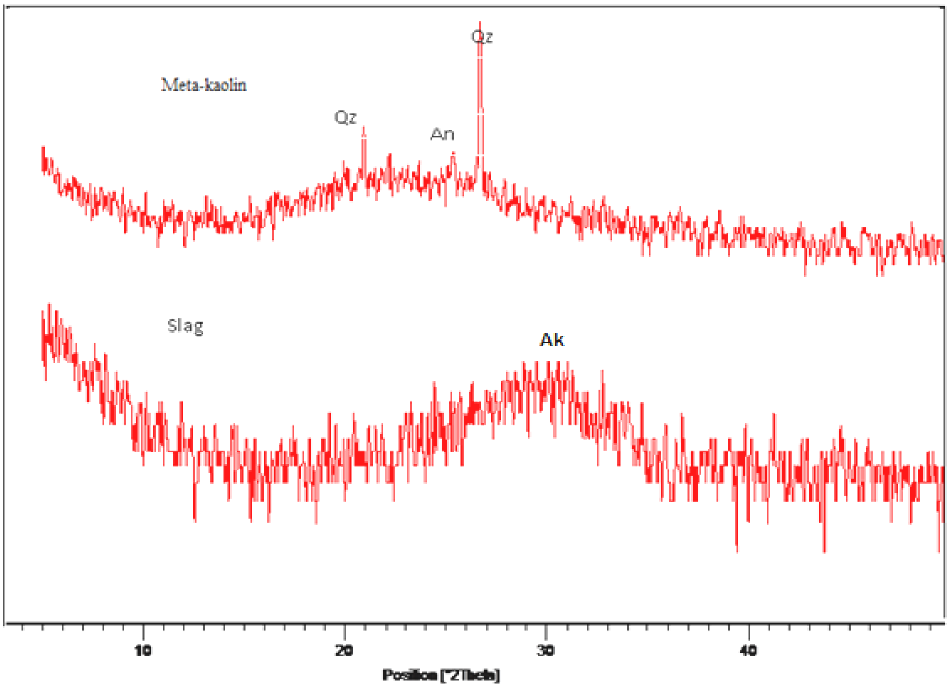

Fig. 2. X-ray differaction pattern for the starting raw materials. [Qz: Quartz An: Anataze Ak:Akermanite]

The patterns show that GGBFS composed mainly of glassy phases and few crystalline material of akermanite (Ca2MgSi2O7), while MK material is composed of quartz and anataze minerals

2.2 Geopolymerization and curing

Geopolymer was made by hand-mixing raw materials of each mixture with the alkaline solution for 5 min and a further 5 min in a mixer. MK was mixed with the GGBFS in ratios as illustrated in Table (2). The water binder material ratio (w/c) was different from 0.28 to 0.38% by mass, the other part of water was mixed with the 6% (NaOH) + 6% (Na_2SiO_3) alkali activators. Paste mixture were cast into 25×25×25 mm cubic shaped moulds, vibrated for compaction and sealed with a lid to minimize any loss of evaporable water.

All mixes were left to cure at ambient temperature for 24 h, and then subjected to curing temperature of 38 °C and 100% relative humidity. The crushed specimens which obtained from compressive strength test were subjected to stopping of the hydration process by drying at 105ºC for 24 h (Bakharev, 2006) and then preserved in a well tight container until the time of testing.

Table 2. Mix design of MK and GGBFS materials.

Mix	Meta-Kaolin, %	Slag, %	NaOH, %	Na2SiO3, %	W/C, %
A	0	100	6	6	0.34
B	5	95	6	6	0.34
C	10	90	6	6	0.36
D	15	85	6	6	0.38
E	20	80	6	6	0.38

These hardened materials were characterized using XRF, XRD, FTIR, and SEM. The instrumental conditions used are shown below:

Chemical analysis was carried out using Axios, WD-XRF Sequential Spectrometer (Panalytical, Netherland, 2009). XRD analysis was carried out using a Philips PW3050/60 Diffractometer. The data were identified according to the XRD software. Perkin Elmer FTIR Spectrum RX1 Spectrometer was used to evaluate the functional groups in the sample. Small amount of potassium bromide (KBr) and geopolymer powder were put into a mould with KBr pellets and pressed at 295 MPa for 2 min to produce specimen for examination, The wave number was ranged from 400 to 4000 cm^{-1} (Panias et al., 2007; Bakharev, 2006).

Compressive strength tests were carried out using five tones German Brüf pressing machine with a loading rate of 100kg/min determined according to ASTM-C109-07 (2007). The microstructure of the hardened specimens was studied using SEM Inspect S (FEI Company, Netherland). The removal free water was accomplished by drying at 105ºC for 24 h (Bakharev, 2006).

3. Results and discussion

3.1. Mineralogical investigation

XRD patterns of 90 days of alkali-activated slag specimens incorporating various ratios of MK activated by sodium hydroxide and sodium silicate in the ratios illustrated previously in table (2).The XRD patterns of alkali activated slag pastes with 0%, 5%, 10%, 15 and 20% MK replacement are shown in Fig. 3.

The main reaction products of all mixes are amorphous phases except small amount of crystalline phases that obtained from the raw materials such as quartz. Also, CAH was detected as a result phase of slag geopolymerization. The amorphous phases with humps ranging from 25° to 35° 2θcan be regarded as a result of glassy phase of slag geopolymerization progress.

On the other hand, the agglomerated MK results in an increased porosity as well as increased carbonation within the matrix as indicated in calcite peak at 29.35° 2θ, more clear in specimens 15% and 20% MK. As the slag content continues to decrease, the intensity peaks at around 30°2θ decrease, which represents the formation of C-S-H type gel from alkali activated slag. The intensity peaks that represent C-S-H gel were more significant in control specimen with higher slag content.

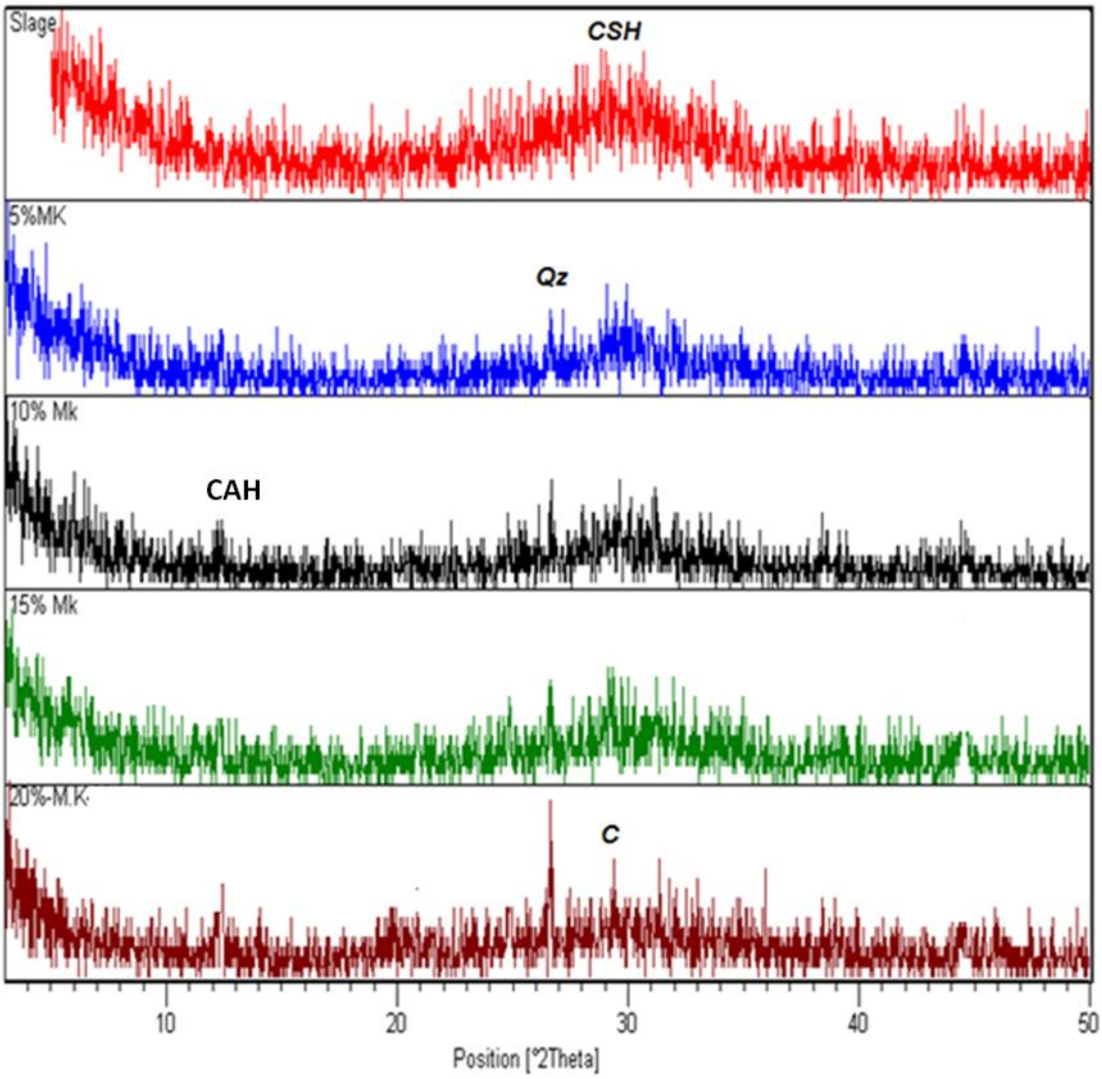

Fig. 3. The XRD patterns of slag-MK blends cured at 90 days. [Qz: Quartz, CAH: Calcium aluminate hydrate CSH: Calcium silicate hydrate, C: Calcite]

3.2. Scanning electron microscopy (SEM)

The scanning electron micrograph of 90 days geopolymer specimens having various MK ratios are shown in Fig. 4. Its noticed that the microstructure of 10% MK displayed compaction of matrix with the presence of geopolymer gel which filled the pores of the matrix specimens, as compared to the less dense structure 5and 20% of MK percentages of dry mixes. Substitution of slag by10% MK leads to the enhancement in the morphological structure of the resulting geopolymer chains.

The added MK resulted in exceeds of amorphous alumino-silicate structure that enrich the morphological shape and leads to the enhancement in mechanical properties as revealed previously in the compressive strength results.

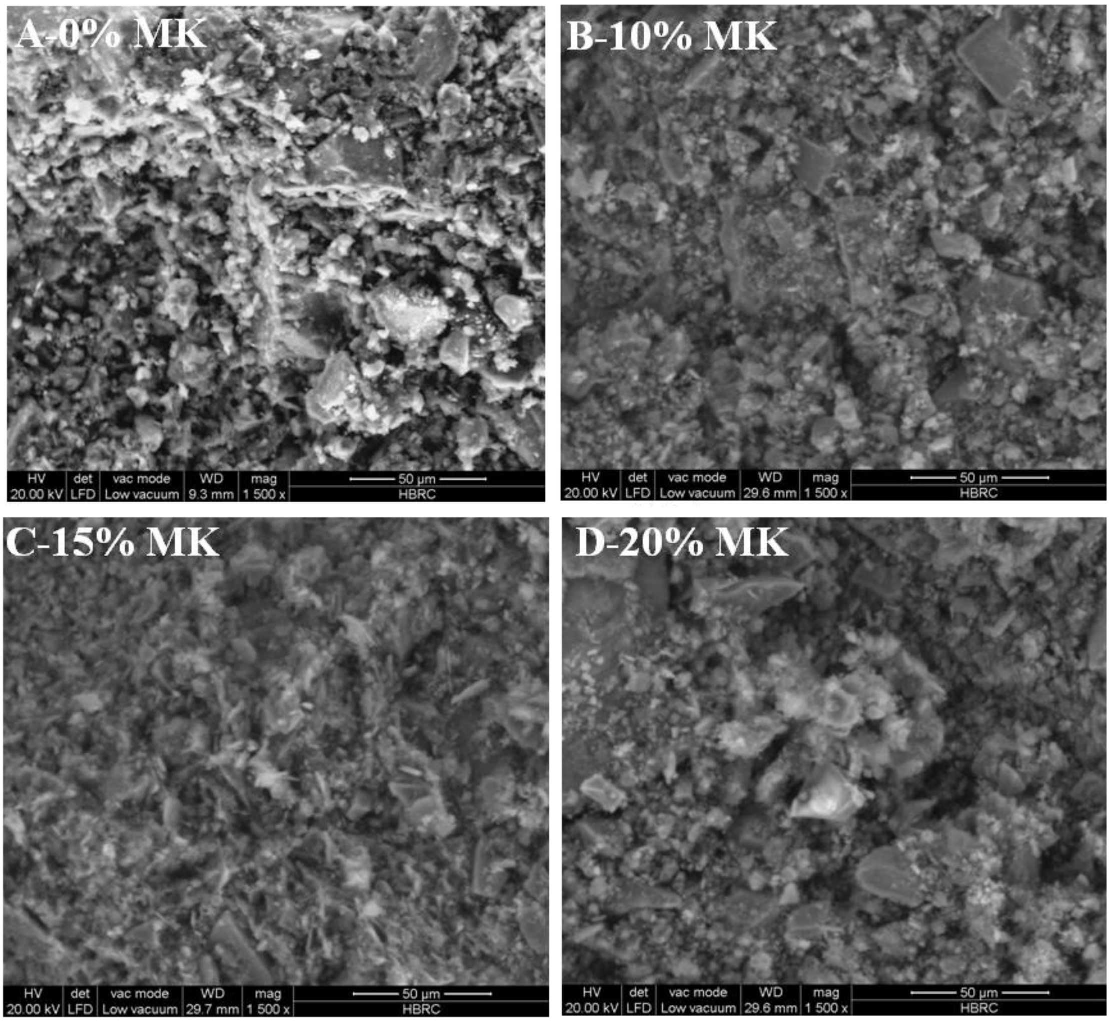

Fig. 4. The scanning electron micrograph of geopolymer specimens of slag and MK materials cured at 90 days.

The alkaline activation of MK is believed to be a surface reaction, with silicate and aluminate species dissociated from the surface of MK (Yunsheng et al., 2010). This phase was found to have no regular shape or morphology and the particles in (Fig. 4, B) appear broken than a platy shape.

The large surface area of MK and their abundance because of their small size can facilitate the chemical reactions necessary to produce a dense cement matrix with more calcium silicate hydrate (C-S-H) and less calcium hydroxide. On the other hand adding 20% MK lead to the formation of agglomerate which hinders the intact between the reacting materials as shown in (Fig. 4, D).

3.3. Fourier Transform Infrared FTIR spectroscopy

FTIR spectra of 90 days cured geopolymer specimens having metakaolin content as a partial replacement of slag are shown in Fig. (5). The characteristics bands for the present geopolymer structure are: hydration groups and combined water allocated for stretching vibration of O-H bond at about 3500 cm^{-1} and bending vibration for HO-H at about 1650 cm^{-1}, stretching vibration of CO_2located at about1440-1450 cm^{-1}, asymmetric stretching vibration (Si–O–Si) at about 1050 cm^{-1} for non-solublized silica, asymmetric stretching vibration (Ti–O–Si) at about

970-1000 cm^{-1} where T=Si or Al, symmetric stretching vibration (Al –O–Si)between740-770 cm^{-1} and bending vibration (Si–O–Si and O–Si–O) in the region 440-450 cm^{-1}.

Also the main asymmetric band around 1000 cm^{-1} turned to be wider with the increase of the added slag up to 90% reflecting the increase of the geopolymerization reaction.

CASH at 685 cm^{-1} for the hydration phases resulted from amorphous slag especially in 10% MK specimen and decrease up to 20% MK. Also, it is noticed that non-solublized silica decreased in 10% MK specimen but obviously appears when GGBFS replaced by 15% and 20% MK. The weak band observed around 840 cm−1 on 5%, 15% and 20% MK specimens is assigned to the bending vibration of Si OH. The presence of Si OH in the geopolymer products will lead to decrease the degree of polycondensation reaction, thus a reduction in mechanical strength (Yunsheng et al., 2010).

The main asymmetric band for T-O-Si shifted to higher wave number with increasing MK more than 10% because of adding MK with its fine pore structure hinder propagation of geopolymer chain.

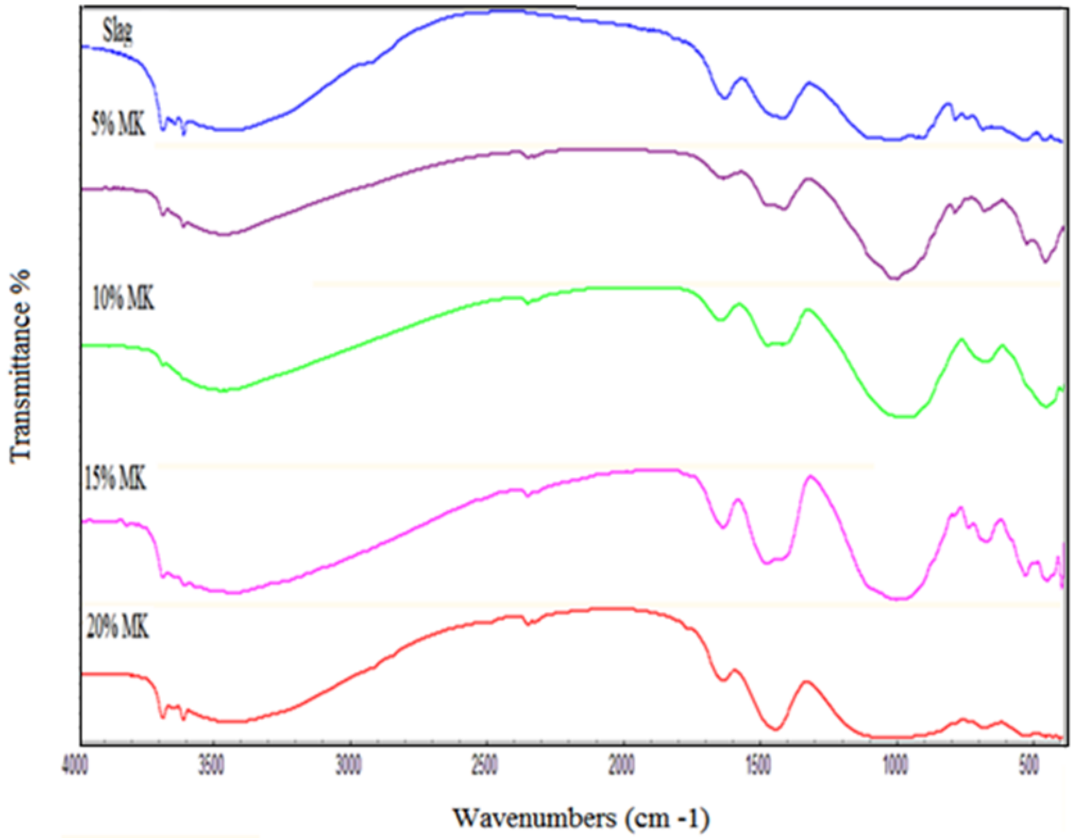

Fig. 5. FTIR spectra of geopolymer specimens of water cooled slag having various Mk percentages cured at 90 days.

3.4. Compressive Strength

Results of the compressive strength for geopolymer mixes along with cured at 100% relative humidity and at 38° C up to 90 days are shown in (Fig. 6).The results show the increase of strength in all mixes along with hydration age up to 90 days.

From Fig. 5, it can be seen that when the replacement percentage is 10% meta-kaolin, maximum strength is obtained. In other word, as the amount of MK increases up to 20% the compressive strength is accordingly decreases, because of increasing dose of MK with its fine pore structure leads to the formation of agglomerate which increased porosity and hinders the intact between the reacting materials.

Replacing glassy slag by amorphous MK results in the formation of more homogeneous matrix, also there is coexistence of geopolymer chains along with CSH binding gel that acts as seeding agent for geopolymer accumulation and so results in a more compact and dense structure, this effect will decrease with increasing MK.

The geopolymer manufactured only from 100% slag as a control mix was found to have the highest early strength while that from slag and MK was found to has the highest lately strength and better than 100% of slag control sample especially which has 10% and 15% MK.

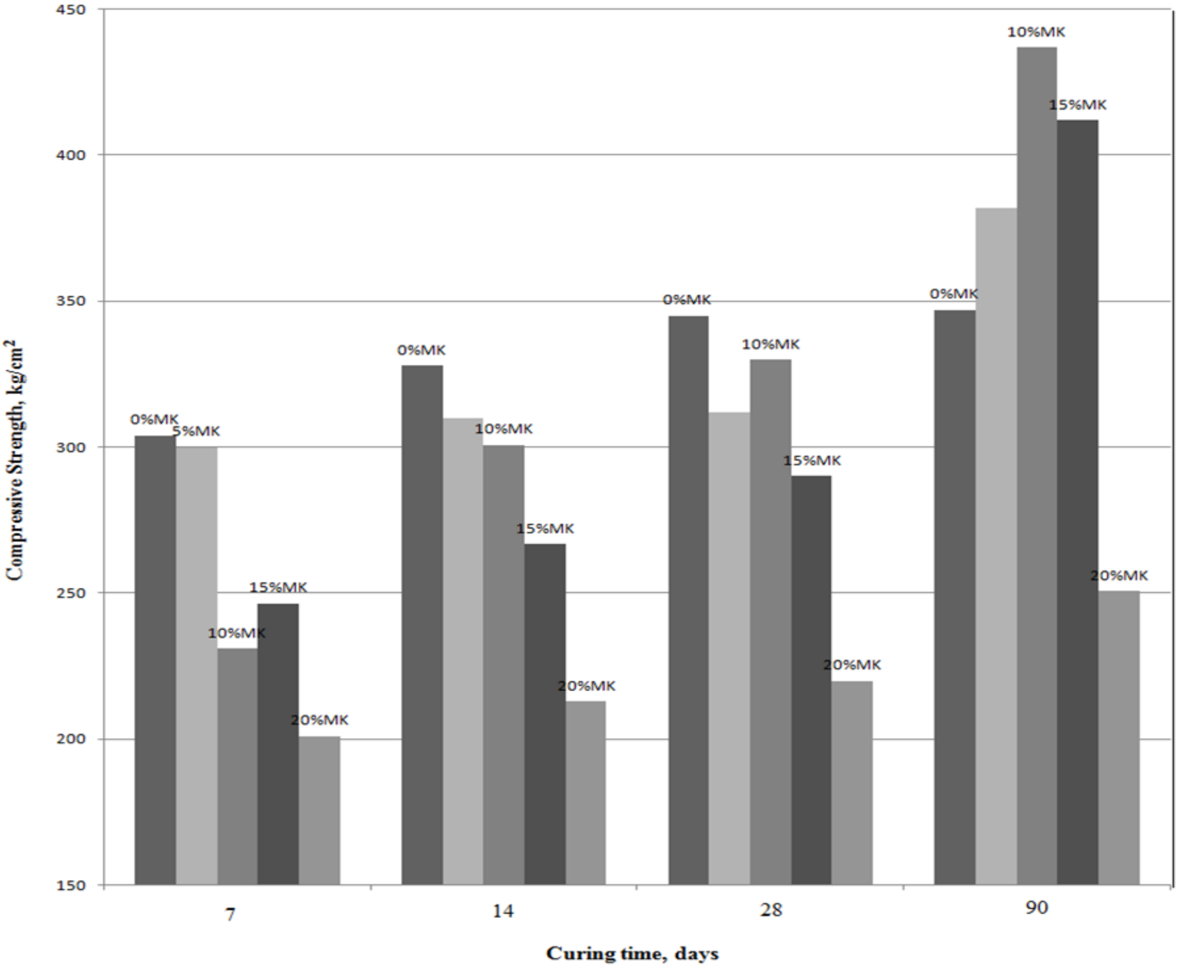

Fig. 6. Compressive strength of geopolymer specimens of water cooled slag having various Mk percentages cured at 90 days.

Generally, mechanical strength improvement with the inclusion of calcium has been reported, the main binding phases in the microstructure are alkali alumino-silicate gel and Al-substituted calcium silicate hydrate (C-S-H) gel. For MK/GGBFS blends, it has been identified that the mechanism of activation is highly dependent on both the alkalinity of the alkali activator and the ratio between MK and GGBFS, which act together to control the rate of Ca^{2+} dissolution and availability during the reaction (Xu & Van Deventer, 2000).

3.5. Water Absorption

The water absorption of all samples (Fig. 7) decreases with increase of curing time, in opposing to compressive strength. Also, the water absorption decreases up to 10% MK up to 90 days of curing in all of the mixes. The geopolymer gel formed at 10%MK results in a decrease in the porosity of the matrix and as well as water absorption, while on using 20%, the fine structure and high surface area of added metakaolin, requires higher amount of water and thus cause increase in the porosity of resultant geopolymer

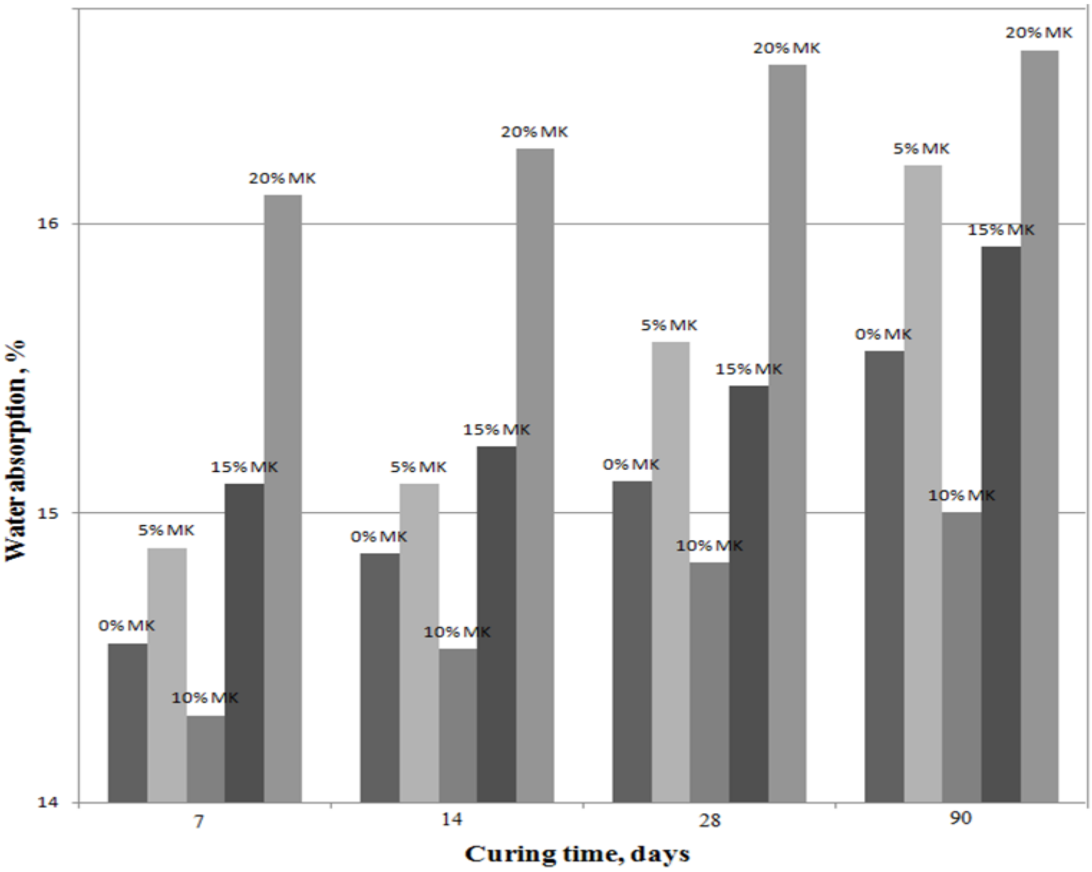

Fig. 7. Water absorption of geopolymer specimens of water cooled slag having various Mk percentages cured at 90 days.

4. Conclusion

Addition of different percentages of meta-kaolin improves mechanical and microstructural properties, where:

1. Addition of metakaolin provided an enhancement in geopolymer microstructure and results in the formation of well compacted dense structure.
2. FTIR spectra confirm the intense amorphous geopolymer structure up on using 10% metakaolin, while the increased crystalline phases are predominant with further metakaolin increase.
3. The compressive strength increase with increasing percentages of metakaolin up to 10%, increasing dose of metakaolin leads to the formation of agglomerate which hinders the intact between the reacting materials
4. The geopolymer manufactured only from 100% slag as a control mix was found to has the highest early strength while that formed from slag and metakaolin was found to has the highest lately strength and better than 100% of slag control sample especially which has 10% and 15% metakaolin.
5. In order to obtain good and low cost alkali activated geopolymer slag-metakaolin binding materials, metakaolin should be added in percent lesser than 20% of the total mass.

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