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# Assessment of the Pozzolanic Activity of Some Available Local Mineral Concrete Admixtures

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*This current paper aims to evaluate the pozzolanic activity of some available local mineral admixtures in order to use them in improving the engineering properties of structural concrete that's because, there is no standard specification on Egyptian Standard Specification (ESS) to be used for evaluation of the pozzolanic activity and suitability of the local mineral admixtures as a pozzolanic supplementary cementing materials. For this purpose, seven physico-chemical-mechanical methods have been used to enable of evaluating of pozzolanic activity and makes a comparison between different tested admixtures. Where, Particle size and fineness were evaluated via visual assessment and by nitrogen adsorption method. The chemical analysis of these local admixtures was determined by XRF test. As well as, in order to check the disappearance of the characteristic peaks of these admixtures, XRD testes were carried out. SEM was used to investigate the microstructure. To quantify the potential contribution of mineral admixtures on the mechanical behavior, SAI and HPF were conducted on mortar mixes containing these admixtures. The local tested admixtures are three types of (MK24, MK33 and NMK), CBC, GBB and BFS. On the other hand, commercially FA was also used and tested as a reference admixture for comparison. The results of this study concluded that, the studied assessment methods might be effectively on assistance for evaluation of pozzolanic activity of concrete admixtures which, can be used to improve concrete performance.*

## 1. Introduction

In recent years, researchers have been focusing on developing more sustainable cementitious systems in order to curb the negative environmental impacts and disintegration of concrete structures associated with ordinary Portland cement (OPC). Several attempts have been made to develop sustainable binders through the use of pozzolans such as slag, fly ash (FA), palm oil fuel ash (POFA), metakaolin (MK), silica fume (SF), rice husk ash (RHA) etc. with a relatively larger amount of replacement of OPC. A certain level of cement replacement with those pozzolans is highly advantageous in terms of cost, energy efficiency, ecological and environmental benefits as well as durability properties [1].

Pozzolans are a broad class of siliceous and aluminous materials which, in themselves, possess little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide (Ca (OH)2) at ordinary temperature to form compounds possessing cementitious properties [2]. The quantification of the capacity of a pozzolan to react with calcium hydroxide and water is given by measuring its pozzolanic activity [3].

In accordance with ASTM C595[4], a pozzolan is defined as " a siliceous or siliceous and aluminous materials which in itself possesses little or no cementitious value but in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.

Supplementary cementing materials (SCMs) contribute to the hydration of Portland cement by physical phenomena (e.g. nucleation effect) or by chemical reactions (e.g. pozzolanic activity). The partial substitution of Portland cement with SCMs can significantly reduce the CO2 emission during the production of concrete and, therefore, can make concrete a more sustainable and environmental-friendly material [5]. Technical literature provides experimental evidence for a long time that (SCMs) contribute to the hydration of Portland cement by physical phenomena (e.g. nucleation effect) or by chemical reactions (e.g. pozzolanic activity) [6–12].

By reviewing of literature on the pozzolanic activity evaluation of SCMs reveals that, firstly, many of the standard specifications emphasize compressive strength as the primary means for assessing the pozzolanic activity [13]. Determination of the pozzolanic activity with certainty is a complex problem [14,15]. Many techniques have been developed to investigate lime-pozzolan reactions at early ages of hydration. These include isothermal conduction calorimatery and conductivity or resistivity measurements [16,17]. It also concluded that, pozzolanic activity assessment was performed by using chemical or physical tests [18].

X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material [19]. In addition, X-ray fluorescence (XRF) spectrometers are a non-destructive analyzer, either handheld or benchtop, used to provide chemical, elemental and trace element analysis. XRF can typically analyze elements from sodium (11) to uranium (92) in concentrations ranging from parts per million (ppm) to high percent in solids, liquids and powders. Compared to other analytical techniques XRF requires no or very little sample preparation, and it's low-cost [20]. It is well known that blended cement strength is more strongly

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dependent on the type, microstructure, and pore size distribution of the hydration products than on the extent of the pozzolan chemical reaction [21]. But these factors are affected by mix design and curing conditions and thus, can be controlled. Therefore, the extent of pozzolan reaction is a primary factor in assessing the suitability of the different nano-materials as pozzolans [22].

Recently, Khashayar Jafari [23] conducted an extensive study to identify, characterize, improve, and facilitate the use of impure calcined clays (CC) as viable SCMs in Portland cement concrete and as a precursor in geopolymer concrete. the chemical and mineralogical compositions of all tested CC samples were determined via (XRF) and (XRD) and (SEM) was used to obtain 2D (polished surface) images of tested powders. In addition, in this research, the R3 test is applied to three calcined clays as well as other eight SCMs and the results are compared with other measures of the pozzolanic reactivity including SAI, degree of reaction measured by selective acid dissolution, and measuring the residual portlandite content via thermogravimetric analysis (TGA). The pozzolanic reactivity of CC and pure CC were measured using three methods: the strength activity index (SAI according to ASTM C311-17), the mortar strength at constant w/cm, and the pozzolanicity/R3 test (according to ASTMC1897-20). It was concluded that, the pozzolanic reactivity of PCC was significantly improved as measured by the SAI, compressive strength of mortar and concrete, and the R3 bound water test. PCC also showed improved performance against ASR, chloride penetration, and drying shrinkage.

It is worth mentioning here that there is no standard specification on Egyptian Standard Specification (ESS) to be used for estimating the pozzolanic activity and suitability of available mineral admixtures as a pozzolanic supplementary cementing materials. Moreover, locally very few experimental data exist on this subject. Therefore, an attempt by series of measurements which have been performed for assessment the pozzolanic activity of some available local admixtures.

## 2. EXPERIMENTAL WORK

### *2.1. materials*

On this study, three different types of raw Egyptian kaolins clay (K24, K33 and NK (were used to experimentally produce three of metakaolins (MK24, MK33, NMK) after an adequate thermal treatment (calcination) by a Lab electric oven. An attempt to consider calcined ball-clay as metakaolin, raw local ball-clay (BC) was thermal treated to produce calcined ball-clay (CBC). The optimum calcination conditions to produce two types of metakaolins (MK24 and MK33) was at 800º C for 3 h, while for nano metakaolin (NMK) was at 700º C for 2 h and, at 800º C for 4 h burning period to obtain CBC. the chemical composition of K24, K33, NK and BC are carried out and given in Table 1.

Unlike of the examined metakaolins and CBC as manufactured admixtures, ground broken bricks (GBB) and blast furnace slag (BFS) are as by-product or waste pozzolanic materials were studied. BFS was a by-product of pig iron and steel industry. It is produced by rapid cooling of molten slag at the exit of the furnace. BFS were obtained from Egyptian iron and steel company, Helwan, Egypt. Waste sample of broken bricks from a local brick factory was collected. The samples of broken bricks and BFS were grounded by employing a laboratory rotary mill. On the other hand, commercially imported Class F fly ash (FA) conforming to ASTM C618 [23] was also used for comparison.

A local Ordinary Portland Cement OPC (CEM I 42.5 N) compiling with Egyptian Standard Specifications (ESS 1-4756/2007) and having specific gravity of 3.12 and Blaine fineness of 3470 cm2/gm was employed in all concrete and mortar mixtures. Chemical composition of the cement is shown also in Table 2. Fine aggregate was clean natural siliceous sand was chosen with maximum aggregate size of 4.75 mm. Whereas coarse aggregate used in this research was natural gravel with maximum aggregate size of 40 mm. The coarse aggregates have a specific gravity, crushing value and water absorption of 2.5, 11.75 and 0.58%, respectively, and the fine aggregate has water absorption of 0.73%, fineness modulus of 2.42 and a specific gravity of 2.55. Aggregates were obtained from local sources. Grading of the aggregate mixture was kept constant at sand/gravel (S/G) 0.60 for all concretes. Sulphonated naphthalene formaldehyde based high range water-reducing admixture with specific gravity of 1.19 was employed to achieve a slump of 10± 2 cm for the ease of handling, placing, and consolidation in all concrete mixtures. The superplasticizer was adjusted at the time of mixing to achieve the specified slump.

### *2.2. Pozzolanic Activity of Available Local Admixtures Test Methods*

In order to determine and evaluate the pozzolanic activity of selected available local admixtures (MK24, MK33 and NMK), (CBC), (BFS), (GBB) and (FA), eight measurements / approaches were used to compare between them in terms of its physical, chemical, microstructure and mechanical properties. These approaches are illustrated in Figure 1.

#### *2.2.1. Visual Assessment*

To illustrate a visual comparison in term of' color and volume for available local admixtures, 50 gm sample was taken from each admixture. The samples of these admixtures were placed together on a disk and one photo was taken for them. The samples color and volume can be significantly seen as a physical method of assessment. Moreover, the specific gravities of these admixtures were determined.

#### *2.2.2. X-ray diffraction analysis (XRD)*

The mineralogical analyses of these admixtures were performed by X-ray diffraction (XRD) test. XRD is one important method to identify the main minerals, and crystalline or amorphous states of the materials. The results from an XRD analysis are a diffractogram exhibiting the intensity as function of the diffraction angles. As well as, in order to check the disappearance of the characteristic peaks of these admixtures, XRD testes were carried out by X-ray diffraction apparatus as shown in Figure 2. This apparatus is existing in Faculty of Science, Assiut, Egypt. Quantitative and qualitative analyses

have been computed and the patterns characterizes were obtained for these admixtures.

*2.2.3. X-ray fluorescence analysis (XRF)*

The chemical analysis (oxide compositions) of these local admixtures were determined by X-ray fluorescence (XRF) tests. The XRF is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays ("a fingerprint") that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition. To clarify the chemical characteristics of these admixtures, the chemical analyses are conducted by XRF apparatus in central lap in Qena university, Egypt as shown in Figure 3.

*2.2.4. The Hydraulic Pozzolanic Factor (HPF)*

According to Arabic Standard Specifications ASS 2-2 (2010) [24], the hydraulic pozzolanic factor (HPF) is important technique that were conducted to assess the pozzolanic activity for the mineral pozzolanic materials. Arabic Standard Specifications ASS 2-2 (2010) have been developed by Saudi Organization for Standardization, Metrology and Quality under supervision of Arab Organization for Industrial Development and Mining.

HPF is computing by using the following equation in conformity with the Arabic Standard Specifications ASS 2-2 (2010).

$$HPF = [(F1-F3) / (F2-F3)] \times 100 \quad (1)$$

Where,

*Fl*: is the compressive strength of standard cement mortar cubes incorporating pozzolanic material as a 30% partial replacement of cement after 28 days of age.

*F2*: is the compressive strength of reference cement mortar cubes (without any pozzolanic materials) after 28 days of age.

*F3*: is the compressive strength of cement mortar cubes incorporating a 30% quartz powder as a partial replacement of cement after 28 days of age.

The required conditions for the correct use of this equation are that, the specific surface area of cement or blended cement must be more than 3000 cm2/gm also, the used sand must be standard sand. The material is considered a pozzolanic active material if HPF is more than 30%. The standard mortar mix contains the binder and standard sand by ratio of 1:3 according to ESS (2421 - 2013) and the water/binder ratio (w/b) was 0.4. ADDICRETE B-V-F superplasticizer is used by 1.5 % of the weight of the binder. The specimens were cured in water till the age of 28 days and then tested.

*2-2-5. Strength Activity Index (SAI)*

The pozzolanic activity (strength activity index) is considered as the most appropriate to quantify the potential contribution of mineral admixtures on the mechanical behavior. Strength activity index (SAI) in accordance with ASTM C311 [13] "American Society for Testing and Materials, Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete". SAI is defined as the ratio between the compressive strength of two specimens, the mortar with 20% admixture (mass substitution) and the reference mortar (without admixture). Such compressive strength is obtained at age of 28 days of curing. SAI is calculating by using the following equation:

$$SAI = (Fcu\ d/Fcu\ c) *100 \quad (2)$$

Where:

*Fcu d* = compressive strength of mortar mix with 20% pozzolanic material as a partial replacement of cement after 28 days of age.

*Fcu c* = compressive strength of control mortar mix after 28 days of age.

The SAI was evaluated as a preliminary characterization of these admixtures. The mortar mixes were prepared according to the ASTM C311, [13] where the proportions (binder: sand) was 1:3, water/binder (w/b) ratio was around at 0.484, superplasticiser (SP) was added by 1.5 % of the weight of the binder in order to obtain a constant workability.

The SAI is a measure for the degree of reaction over time or the reaction rate between a pozzolan and Ca2+ or calcium hydroxide (Ca(OH)2) in the presence of water. The rate of the pozzolanic reaction is dependent on the intrinsic characteristics of the pozzolan such as the specific surface area, the chemical composition and the active phase content.

The pozzolanic reaction is the chemical reaction that occurs in Portland cement upon the addition of pozzolans. It is the main reaction involved in the Roman concrete invented in Ancient Rome and used to build, for example, the Pantheon. The pozzolanic reaction converts a silica-rich precursor with no cementing properties, to a calcium silicate, with good cementing properties.

*2.2.5.* Nitrogen adsorption method

The Measurement of the particle size and fineness of these local mineral admixtures by using nitrogen adsorption method according to (ASTM D3037) [25] " Standard Test Methods for Carbon Black—Surface Area by Nitrogen Adsorption" (Withdrawn 1999). Nitrogen adsorption was performed by NOVA touch 4LX instrument in Surface Area Lap in National Research Centre- central laboratories network (CLN) y as shown in Figure 4. This technique needs approximately 0.3 g of powdered starting material. Also involves dosing the sample with a known amount of nitrogen and measuring the volume of adsorbate gas retained by the sample. This volume is determined based on the residual pressure in the sample chamber formed by the molecules that do not adsorb. The process is repeated at the same temperature and at incremental pressures to form an isotherm data set.

Surface area was measured on the adsorption isotherm according to the BET (Brunauer, Emmett, Teller) [26] theory.

The BET surface area is calculated from a multilayer adsorption theory that assumes the first layer of molecules adsorbed involves adsorbate-adsorbent energies and subsequent layers are governed by the energy of vaporization of this adsorbate-adsorbent interaction. BET specific surface area is measured on the adsorption isotherm in the relative pressure range of 0.050 to 0.300.

*2.2.6. The scanning electron microscope (SEM)*

The scanning electron microscope (SEM) was used to investigate the microstructure of these local mineral admixtures. A SEM is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the intensity of the detected signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector (Everhart-Thornley detector). The number of secondary electrons that can be detected, and thus the signal intensity, depends, among other things, on specimen topography. Some SEMs can achieve resolutions better than 1 nanometer. Specimens are observed in high vacuum in a conventional SEM, or in low vacuum or wet conditions in a variable pressure or environmental SEM, and at a wide range of cryogenic or elevated temperatures with specialized instruments. The SEM tests were carried out on samples weighing 5 g from each of these admixtures by the SEM device which existed on the electron microscope unit at Assiut University in as shown in Figure 5.

*2.2.7. Compressive Strength Test*

The activity of the concrete mixes containing the tested local admixtures as partial replacement of cement weight at various replacement levels were also checked by compressive strength after 28 days of water curing. Concrete specimens of size 15*15*15 cm3 were used for compressive strength measurement. Specimens were cast in steel moulds and kept in a moist of the lap for 24 h. Demolding took place after that and specimens were placed in water tank for curing period. Compressive strength results are the average of three specimens.

Local admixtures concrete mixes were designed at constant 0.4 water/binder (w/b) ratio and having a constant total binder (cement + admixtures) content of 400 kg/m3. In this paper, the examined replacement levels of (MK24, MK33, CBC and GBB) are 10%, 15% and 20% by weight of cement, while, of NMK are 5%, 7% and 10% while, 20%, 30%, 35% and 40% of BFS. On the other hand, for comprehension three replacement levels (15%, 20%, and 30%) of FA were used. As well as one plain mix without any admixture was produced as bench mark. Details of the mixtures are presented in Table 3. Slumps were kept constant at 10 ± 2 cm. Superplasticizer was used at very low percentages according to the results obtained for the slumps.

## 3. Results and Discussion

*3.1. Results of Visual Observation*

The Figure 6 clearly shows the visual comparison between the different seven samples of tested local mineral admixtures in terms of color and volume. The colors and specific gravities are given in Table 4. It can be noticed from fig, 6 that, although, the weights of tested samples have been constant in this comparison (50 gm), but its volumes were not equal, that's because the different fineness and the variable specific gravities of tested admixtures.

The results of this comparison indicates that the admixtures colors depend on the source of its raw materials and method of manufacturing. That is clearly evident in the color of three types of metakaolins MK24, MK33 and NMK samples. Where the color of MK24 and MK33 was creamy and reddish-pinkish while it was pure white for NMK. This is demonstrated that, the color was depended on impurities and the degree of burning the Kaolin (the raw material of metakaolins). As for volume of each admixture, generally whenever the larger size of the sample, this indicates that the softness is higher. This is a significantly appeared in volume of the NMK sample which has the largest volume compared to other samples because of its super-fineness as shown in Figure 6.

*3.2. X-ray Diffraction Analysis (XRD) Results*

X-ray Diffraction Analysis test is one of the most commonly used tests to clarify mineral contents types and proportions of compounds, as well as the material states; amorphous or crystalline. The obtained X-ray diffractograms of tested local admixtures (MK24, MK33, NMK, FA, CBC, GBB and BFS) are presented in Figures (7- 13) respectively.

It can be seen from Figures 7 and 8 that, two metakaolins MK24 and MK33 are a crystalline material. Another observation, there is no difference between XRD diffractograms of both two metakaolins only except the intensity count of maximum main beak of MK33 was 4438 compared with that for MK24 which was recorded 2950 that's may be attributed to the raw material of MK33 had higher purity than MK24.

Figures 9 and 10 indicate that, the BFS and NMK are as amorphous materials that's clearly shown from its XRD patterns. These results may be due to the thermal treatment of raw nano-kaolinite and manufacturing heat of BFS resulted in the disappearance of its crystalline structure and the formation of an X-ray amorphous phase structure.

From Figure 11 it can be noticed that, XRD diffractogram of CBC almost similar to MK24 and MK33 diffractograms with a difference in the main beak intensity value, which was decreased and reached 2362. This observation clearly demonstrated that, the mineral origin of the composition of these materials is actually similar, which was kaolinite clay.

Figure 12 shows the XRD diffractogram phase of GBB structure. Clearly notes GBB has the highest sharp peaks 4736 which, indicated that, GBB was highly crystalline material. The XRD pattern of used FA in this investigation is shown in Fig. 13.

It consists of a minor amount of glassy phase with major amount of crystalline inclusions of mullite, hematite, and quartz.

### *3.3. X-ray Fluorescence Analysis (XRF) Results*

In order to clarify the oxide compositions of tested local admixtures, samples of these admixtures were analyzed by XRF tests. The results of chemical analysis of examined admixtures are summarized in Table 5. In general, by comparing the chemical analysis of tested admixtures with that of OPC which, was mentioned before in Table 1. It can be concluded that, the oxides that make up these admixtures are almost similar to that of OPC but with a difference on its percentages. Therefor. It is worth mentioning that these local admixtures can considered as supplementary cementing materials without harmful affecting on the properties of cement concrete or mortar mixtures.

### *3.4. Hydraulic Pozzolanic Factor (HPF) Results*

To determine the (HPF) according to Arabic Standard Specifications ASS 2-1 (2010) [24], the equation (l) as mentioned before was applied in order to assess the activity of tested local admixtures. The results of Fl, F2 and F3 were obtained from the compressive strength of the mortar mixes specimens. Where, the values of F3 and F2 are constant F2 = 432 kg/cm2 (control mortar mix without any pozzolanic materials after 28 days of age) and F3 = 205 kg/cm2 (mortar mixes incorporating a 30% quartz powder as a partial replacement of cement after 28 days of age). While F1 for each admixture specimen is given in Table 6. HPF of all tested admixtures were computed by using equation (l) and presented in Table 6. In addition to, according to Arabic Standard Specifications ASS 2-1 requirement, the admixture state is pozzolanic if its HPF value is equal or more than 30 %. Based on the obtained HPF results, all examined local admixtures have pozzolanic activity state expect GBB only has unpozzolanic state.

### *3.5. Strength Activity Index (SAI) Results*

In conformity with ASTM C311[13], The Strength Activity Index (SAI) test is the most common technique to evaluate the degree of pozzolanic activity of the mineral pozzolanic materials. The equation (2) as mentioned before was applied in order to determine the SAI value of each tested local admixtures. To consider any material as a pozzolanic active material, the SAI% value should be more than 75%, that's the minimum requirement of ASTM C 618 standard specification [27] for pozzolanic materials. The obtained results of SAI test are plotted in Fig. 14. This figure indicates clearly that, all tested local admixtures are considered as pozzolanic materials expect the sample of GBB only has unpozzolanic state. It is worth mentioning that This result is largely consistent with the results of HPF, but on SAI test GBB recorded SAI% value near the pozzolanic materials limits. Another observation also can be seen NMK sample has very high pozzolanic activity.

### *3.6. Nitrogen Adsorption Method Results*

Because of Blaine device was specially designed to measure the fineness of cement only. Therefore, in this paper, the nitrogen adsorption technique was used to measure BET (Brunauer, Emmett, Teller) specific surface area of tested local admixtures to estimate its finesses. The test results of BET specific surface area, are given in Table 7.

From the results shown in Table 7, in general for all examined samples, the measured specific surface area by the nitrogen adsorption method is much higher than what is often measured by the Blaine method. This result may be due to difference in technology and the mechanism that were relied on measuring, analyzing and producing of the output result. It is clearly evident that, the BET specific surface area of examined samples of MK24, MK33, NMK, FA and CBC exhibited a higher surface area than cement one. Another observation that can be also notice the BET specific surface area of examined samples of GBB and BFS are smaller than that of other tested admixtures that's was expected because both of GBB and BFS were grounded in available laboratory mills. Based on these results, it can be concluded that, the nitrogen adsorption method is the best in measuring the surface area because their technique depends on the shape of the sample grains as well as, the volume of the voids takes into account. Another important benefit from applying nitrogen adsorption method is their results does not affect whether there is moisture in the tested sample or not.

### *3.7. The scanning electron microscope (SEM) results*

The SEM micrographs of studied local admixtures shown in Figures (15-20) displayed the comparison between the particle size and shape of different samples. Figures 15 and 16 show SEM micrographs of two types of local metakaolins. They have the same grains shape, which appears to be almost polygonal slices in three-dimensional. The CBC TEM micrograph shown in Figure 17 indicated that, it has a shape that is very almost similar to the shape both of the metakaolins but, with a slightly larger of slices thickness. As usually known, the shape of FA particles is spherical shape. It is so significant noticed from FA SEM micrograph that's in Figure 18. As can be seen in Figure 19, the GBB sample has an almost hexagonal shape with the largest particles size. The SEM image shown in Figure 20 displays the morphology of BFS which having triangular shape in three-dimensional. Figure 21 shows the SEM image of NMK. It is characterized by mineral platelet large length to thickness aspect ratio. Its particle plates look less dark, have very uniform shape, smallest particles size and polygon edges more clearly. It ensures that, these results compatible with the results of the BET specific surface area of examined samples.

### *3.8. Concrete Compressive Strength Result*

The compressive strength results of hardened cubes (15x15x15 cm) of concrete mixes modified with tested local

admixtures at various ratios of cement replacement after 28 days are listed in Table 8. The most important observation can be concluded from Table 8. that, all cement substitution ratios of local admixtures achieved enhancing in compressive strength expect only the mix containing 20% of GBB which, decreased the compressive strength than the control by 10.8 %. It is clearly evident that, the optimum modified concrete mixes are FA20, 15MK24, 15MK33, CBC10, NMK7, GBB10 and BFS35 that had the highest rate of increasing in compressive strength over control one by 41.1, 28.1, 30.5, 28.1, 53.5, 14 and 25.9, respectively. From these results, it should be argued that, incorporating these studied local admixtures into concrete industry is beneficial and effective in enhancing the compressive strength of concrete.

By comparing the obtained results of the three studied mechanical methods, hydraulic pozzolanic factor (HPF), strength activity index (SAI) and concrete compressive strength, it was found that, the results of these tests are consistent with each other for all the studied admixtures except for GBB. Another important absorption although, the incorporation of GBB in concrete as cement partial replacement could improve the concrete compressive strength but, it didn't achieve the HPF and SAI test limits for the pozzolanic materials. Therefore, it is interesting to suggest that, decreasing the minimum requirement of SAI% value for pozzolanic materials to 70%. In addition to, the used dosage 30% of admixtures as partial replacement of cement should be modified, in order not to affect the strength of concrete mixtures.

## 4. Conclusions

From the results obtained in this paper, the following conclusions can be drawn out.

- The studied local admixtures have an effective pozzolanic influence similar to that of commercial FA in improving the mechanical properties of mortar and concrete mixtures.
- Nitrogen adsorption technique exhibited as efficient and most suitable method to measuring the surface area because it depends on the shape of the sample grains as well as, the volume of the voids takes into account during the measurements. Another important benefit from applying nitrogen adsorption method, their results does not affect whether there is a moisture in the tested sample or not.
- The partial substitution of OPC by GBB could improve the concrete compressive strength nevertheless, it didn't achieve the HPF and SAI test limits for the pozzolanic materials. Therefore, it is interesting here to suggest that, decreasing the minimum requirement of SAI% value for pozzolanic materials to 70%. In addition to, the used dosage 30% of admixtures as partial replacement of cement should be modified, in order not to affect the characteristics of concrete mixture.
- From XRD test results, the CBC diffractogram is almost similar to that of MK24 and MK33. This clearly confirms that, the mineral origin of the composition of these materials is actually similar, which was kaolinite clay.
- After comparing the XRD test results with concrete compressive strengths, it can be argued that there is no effect of the admixture state, whether it is crystalline or amorphous phase, does not affect the contribution on improving the cement concrete mechanical properties.
- The XRF tests illustrate that, these local admixtures contain oxides almost similar to that of OPC but with a difference on its percentages. Therefore, it is worth mentioning that these local admixtures can considered as supplementary cementing materials without harmful affecting on the characteristics of cement concrete or mortar mixtures.
- The studied assessment methods might be effectively assisted for evaluating the pozzolanic activity of local concrete admixtures which, can be used to improve concrete performance.

## 5. Tables and Figures

**Table 1: The chemical analysis of raw two kaolins (K24&K33), nano kaolin (NK) and raw ball- clay (BC).**

| Chemical compositions | Percentage by weight (%) | | | |
|---|---|---|---|---|
| | K24 | K33 | NK | BC |
| Silica ($SiO_2$) | 56.94 | 52.26 | 51.60 | 53.6 |
| Alumina ($Al_2O_3$) | 24.11 | 33.22 | 35.43 | 23.2 |
| Iron Oxide ($Fe_2O_3$) | 3.58 | 1,43 | 0.07 | 8.2 |
| Calcium Oxide (CaO) | 1.98 | 1.61 | 0.1 | 0.78 |
| Magnesium Oxide (MgO) | 0.72 | 0.40 | 0.02 | 0.15 |
| Titanium Oxide ($TIO_2$) | 1.84 | 1.31 | 0.42 | 2.2 |
| Potassium Oxide ($K_2O$) | 0.07 | 0.08 | -- | 0.3 |
| Sodium Oxide ($Na_2O$) | 0.3 | 0.3 | -- | 0.54 |
| Total Sulphur ($SO_3$) | 0.04 | 0.03 | -- | 0.03 |
| Loss on ignition | 10.4 | 9.8 | 12.36 | 11 |

**Table 2: Chemical composition and Physical properties of used cement**

| Type Of Cem-ent | Chemical analysis (%) | | | | | | | | | Physical properties | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $TiO_2$ | $K_2O$ | $Na_2O$ | $SO_3$ | Spec-ific gravi-ty | Blaine ($cm^2/gm$) | App-ear-ance |
| OPC | 22.3 | 3.82 | 3.50 | 62.6 | 1.40 | -- | 0.24 | 0.4 | 2.54 | 3.15 | 3732 | Gray |

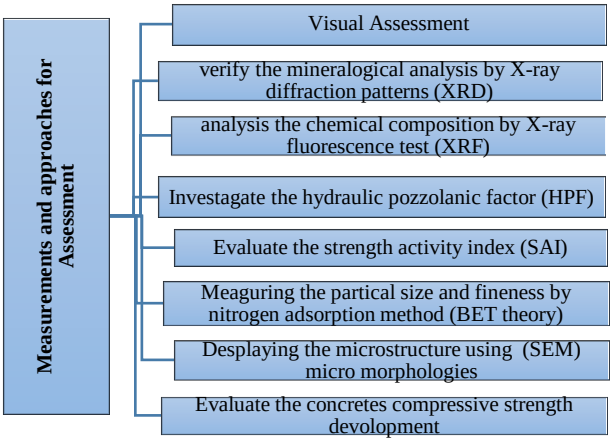


**Figure 1: Measurements and approaches for assessment of the pozzolanic activity**

**Table: 3. Mix proportions of tested concrete mixtures.**

| Mix code | O.P.C Kg/m$^3$ | W/b | Water Kg/m$^3$ | Rep, Level, % | NMK Kg/m$^3$ | FA Kg/m$^3$ | *CBC/ MK24/ MK33/ GBB Kg/m$^3$ | BFS Kg/m$^3$ | Gravel Kg/m$^3$ | sand Kg/m$^3$ | Slump cm | Super-plast L/m$^3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PC | 400 | 0.40 | 160 | -- | -- | -- | -- | -- | 1114 | 668 | 9 | 2.63 |
| NMK5 | 380 | 0.40 | 160 | 5 | 20 | -- | -- | -- | 1110 | 666 | 8 | 3.29 |
| NMK7 | 372 | 0.40 | 160 | 7 | | -- | -- | -- | 1108 | 665 | 9 | 6.58 |
| NMK10 | 360 | 0.40 | 160 | 10 | 40 | -- | -- | -- | 1106 | 664 | 11 | 8.16 |
| FA15 | 340 | 0.40 | 160 | 15 | -- | 60 | -- | -- | 1101 | 661 | 11 | 4.45 |
| FA20 | 320 | 0.40 | 160 | 20 | -- | 80 | -- | -- | 1097 | 658 | 9 | 5.10 |
| FA30 | 280 | 0.40 | 160 | 30 | -- | 120 | -- | -- | 1089 | 653 | 10 | 7.28 |
| CBC10 | 360 | 0.40 | 160 | 10 | -- | -- | 40 | -- | 1108 | 665 | 10 | 4.47 |
| 10MK24 | | | | | | | | | | | 9 | 4.47 |
| 10MK33 | | | | | | | | | | | 10 | 4.47 |
| GBB10 | | | | | | | | | | | 11 | 3.16 |
| CBC15 | 340 | 0.40 | 160 | 15 | -- | -- | 60 | -- | 1105 | 663 | 12 | 5.78 |
| 15MK24 | | | | | | | | | | | 10 | 5.78 |
| 15MK33 | | | | | | | | | | | 8 | 5.78 |
| GBB15 | | | | | | | | | | | 12 | 4.29 |
| CBC20 | 320 | 0.40 | 160 | 20 | -- | -- | 80 | -- | 1101 | 660 | 8 | 7.37 |
| 20MK24 | | | | | | | | | | | 9 | 6.58 |
| 20MK33 | | | | | | | | | | | 8 | 6.84 |
| GBB20 | | | | | | | | | | | 11 | 4.73 |
| BFS20 | 320 | 0.40 | 160 | 20 | -- | -- | -- | 80 | 1110 | 666 | 12 | 4.47 |
| BFS30 | 280 | 0.40 | 160 | 30 | -- | -- | -- | 120 | 1109 | 665.5 | 10 | 5.26 |
| BFS35 | 260 | 0.40 | 160 | 35 | -- | -- | -- | 140 | 1108 | 664.8 | 9 | 5.52 |
| BFS40 | 240 | 0.40 | 160 | 40 | -- | -- | -- | 160 | 1107 | 664.2 | 9 | 6.06 |

| Physical properties | Description | | | | | | |
|---|---|---|---|---|---|---|---|
| | MK24 | MK33 | NMK | FA | CBC | GBB | BFS |
| colure | Creamy, slightly reddish | Creamy, pinkish | pure white | Light Grey | yellowish white | Bricks red | yellowish gray |
| Specific Gravity | 2.4 | 2.4 | 2.3 | 2.4 | 2.4 | 2.4 | 2.9 |

**Figure 2: X-ray diffraction (XRD) diffractometer**


**Figure 3: X-ray fluorescence analysis (XRF) test apparatus**

**Figure 4: NOVA touch 4LX instrument**

**Table 4: Physical properties of the local mineral admixtures.**

**Figure 5: The scanning electron microscope (SEM) device**

**Figure 6: Visual comparison between the local mineral admixtures samples**

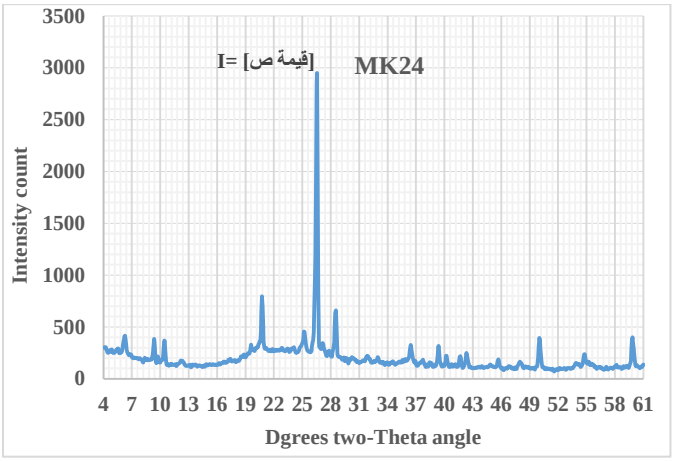


**Figure 7: XRD pattern of MK24 sample**

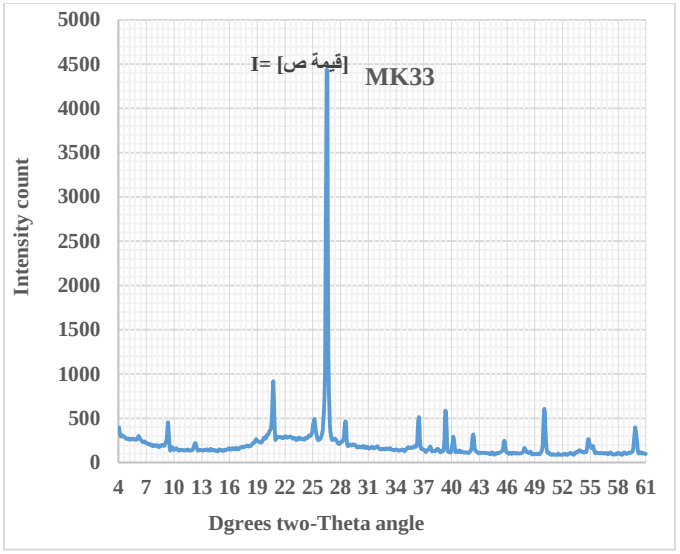


**Figure 8: XRD pattern of MK33 sample.**

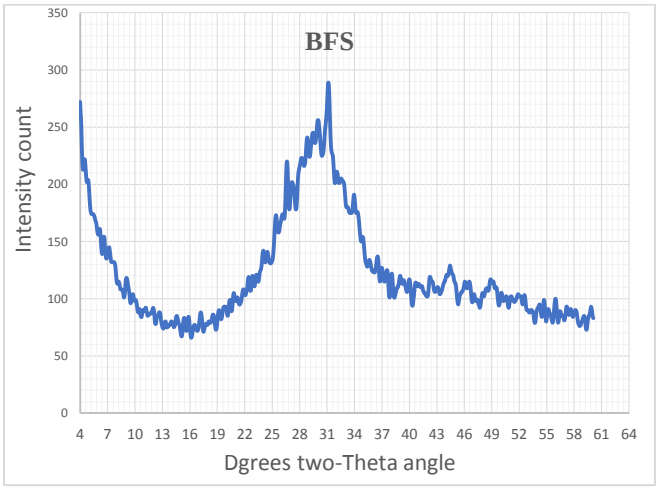


**Figure 9: XRD pattern of BFS sample**

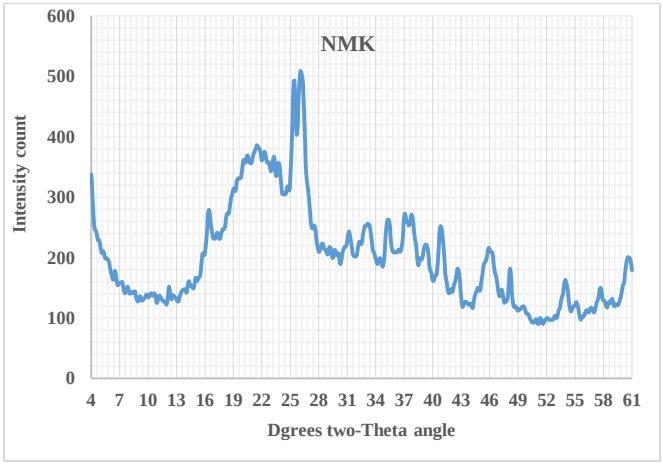

Figure 10: XRD pattern of BFS sample

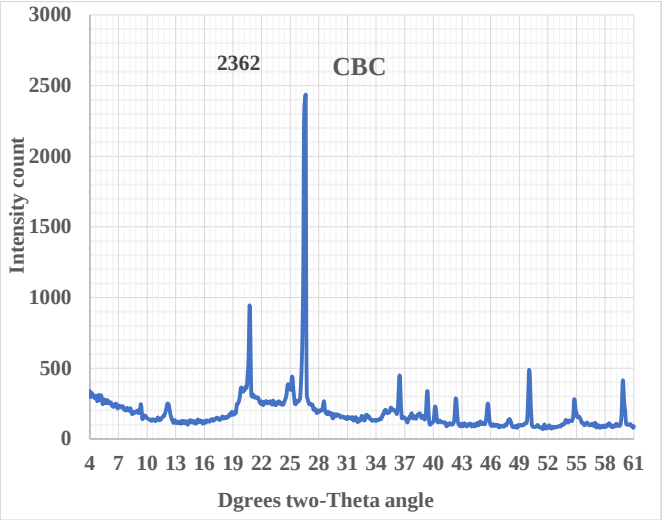


Figure 11: XRD pattern of CBC sample

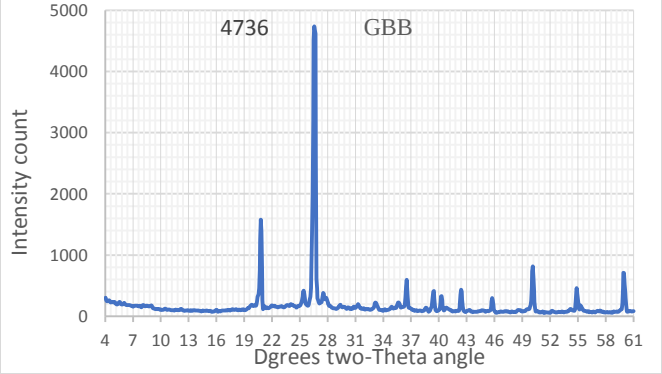


Figure 12: XRD pattern of GBB sample

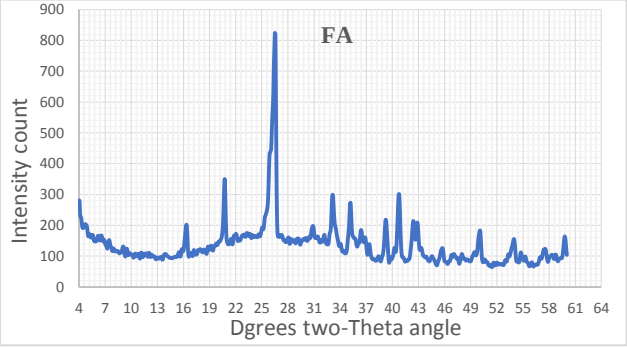


Figure 13: XRD pattern of FA sample

Table 5: The chemical analysis results of examined local admixtures

| Chemical compositions | Percentage by weight (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | MK24 | MK33 | NMK | CBC | GBB | FA | BFS |
| Silica ($SiO_2$) | 59.94 | 57.46 | 58.10 | 57.6 | 66.63 | 44.1 | 36.95 |
| Alumina ($Al_2O_3$) | 24.42 | 33.42 | 39.13 | 24.34 | 14.43 | 26.30 | 10.02 |
| Iron Oxide ($Fe_2O_3$) | 3.84 | 2,25 | 0.07 | 10.2 | 7.28 | 7.90 | 1.47 |
| Calcium Oxide (CaO) | 4.98 | 1.61 | 0.1 | 0.98 | 5.68 | 9.60 | 33.08 |
| Magnesium Oxide (MgO) | 0.72 | 0.40 | 0.02 | 0.16 | 1.96 | 2.77 | 6.42 |
| Titanium Oxide ($TIO_2$) | 2.34 | 2.31 | 0.42 | 2.87 | 0.87 | 1.78 | 0.52 |
| Potassium Oxide ($K_2O$) | 0.07 | 0.08 | -- | 0.46 | 1.76 | 0.92 | 0.77 |
| Sodium Oxide ($Na_2O$) | 0.3 | 0.3 | -- | 0.09 | 0.66 | 0.53 | 1.39 |
| Total Sulphur ($SO_3$) | 0.04 | 0.03 | -- | 0.2 | 0.73 | 1.41 | 3.44 |
| Loss on ignition | 3.4 | 2.54 | 2.16 | 3.1 | 0.0 | 3.21 | 0.00 |

Table 6: The HPF percent values of examined local admixtures

| | Examined local admixtures | | | | | | |
|---|---|---|---|---|---|---|---|
| | MK24 | MK33 | NMK | FA | CBC | GBB | BFS |
| $F_1$ (kg/cm$^2$) | 299 | 291 | 433 | 306 | 326 | 227 | 287 |
| HPF | 41.4% | 38% | 100.4 % | 37.3 % | 44.8% | 9.7% | 32% |
| admixture state | pozzolanic | Pozzolanic | Pozzolanic | Pozz,lanic | Pozzolanic | Unpozzolanic | Pozzolanic |

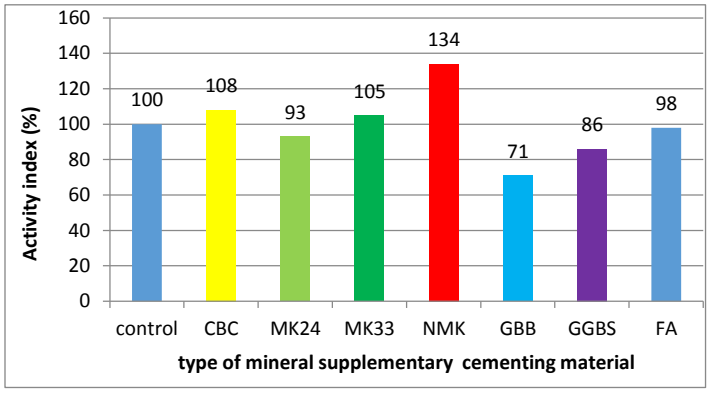


Figure 14: Strength Activity Index (SAI%) of different types of tested local admixtures

Table 7: The Nitrogen adsorption BET specific surface area of tested local admixtures.

| | Examined local admixtures |
|---|---|

| | cement | MK24 | MK33 | NMK | FA | CBC | GBB | BFS |
|---|---|---|---|---|---|---|---|---|
| **BET specific surface area($m^2$/g)** | 1.02 | 21.33 | 21.54 | 250.8 | 13.70 | 21.78 | 2.50 | 8.19 |

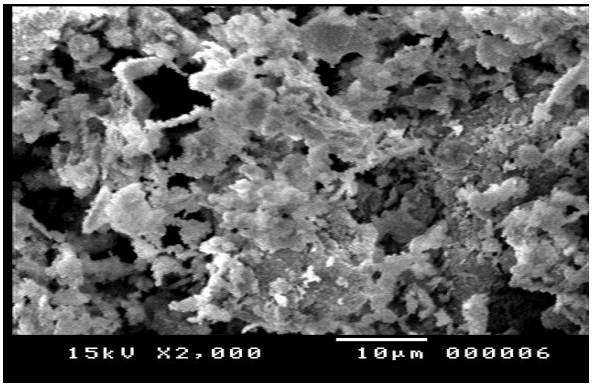


**Figure 15: SEM micrograph of MK24 sample**

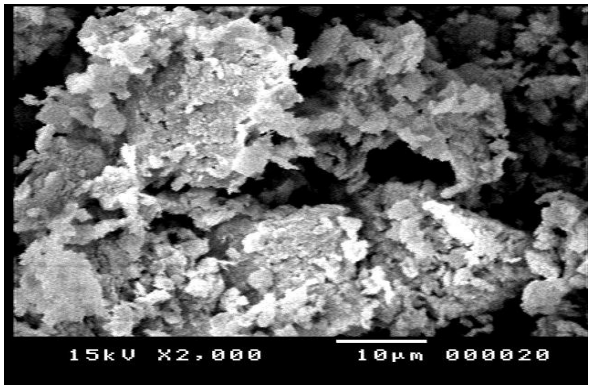


**Figure 16: SEM micrograph of MK33 sample**

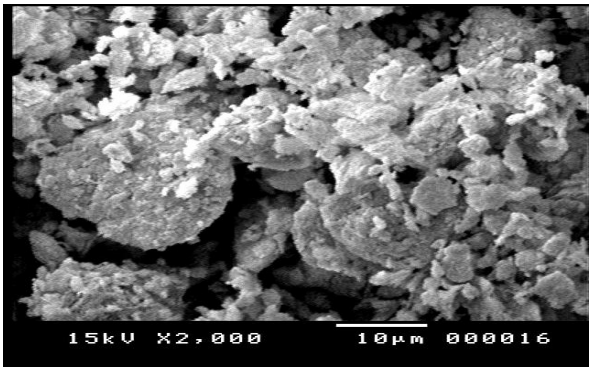


**Figure 17: SEM micrograph of CBC sample**

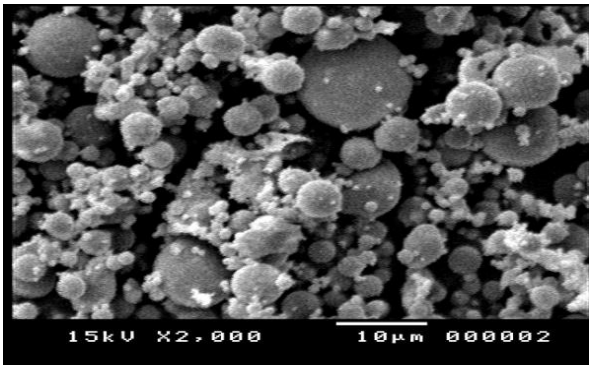


**Figure 18: SEM micrograph of FA sample**

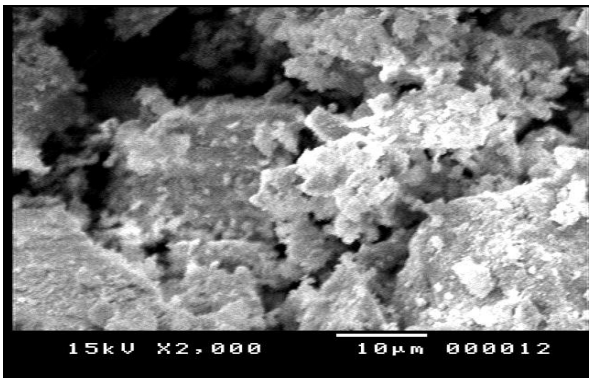


**Figure 19: SEM micrograph of GBB sample**

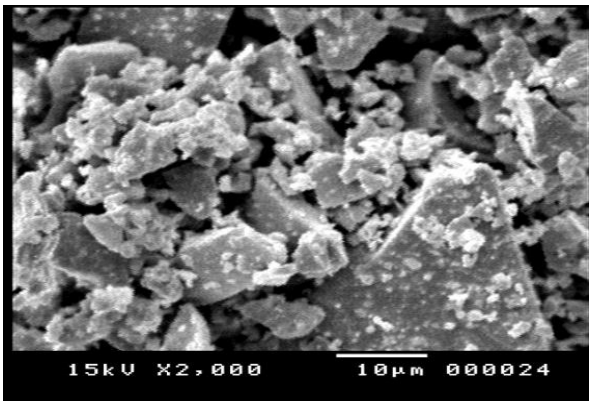


**Figure 20: SEM micrograph of BFS sample**

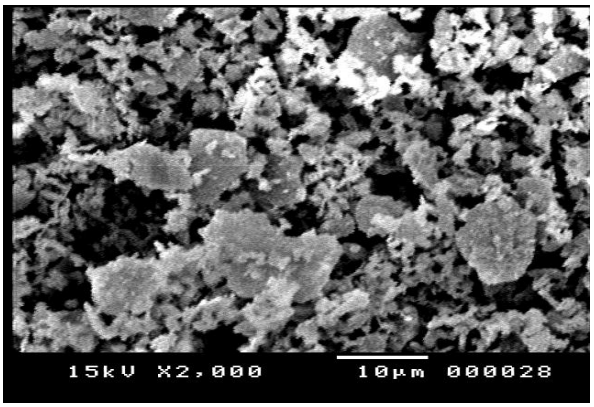


**Figure 21: SEM micrograph of NMK sample**

**Table 8: Effect of tested local admixtures addition on concrete compressive strength**

| Mix code | $F_{cu28}$ (kg/cm$^2$) | Increasing % over control | Mix discretion |
|---|---|---|---|
| PC | 370 | control | Control mix |
| FA15 | 484 | + 30.8 | Mix with 15% FA replacement |
| FA20 | 522 | + 41.1 | Mix with 20% FA replacement |
| FA30 | 449 | + 21.3 | Mix with 30% FA replacement |
| 10MK24 | 412 | + 11.3 | Mix with 10% MK24 replacement |
| 15MK24 | 474 | + 28.1 | Mix with 15% MK24 replacement |
| 20MK24 | 380 | + 2.7 | Mix with 20% MK24 replacement |
| 10MK33 | 375 | + 1.3 | Mix with 10% MK33 replacement |
| 15MK33 | 483 | + 30.5 | Mix with 15% MK33 replacement |
| 20MK33 | 411 | + 11.1 | Mix with 20% MK33 replacement |
| CBC10 | 474 | + 28.1 | Mix with 10% CBC replacement |
| CBC15 | 420 | + 13.5 | Mix with 15% CBC replacement |
| CBC20 | 390 | + 5.4 | Mix with 20% CBC replacement |
| NMK5 | 436 | + 17.8 | Mix with 5% NMK replacement |
| NMK7 | 568 | + 53.5 | Mix with 7% NMK replacement |
| NMK10 | 505 | + 36.5 | Mix with 10% NMK replacement |
| GBB10 | 422 | + 14 | Mix with 10% GBB replacement |
| GBB15 | 390 | + 5.4 | Mix with 15% GBB replacement |
| GBB20 | 330 | - 10.8 | Mix with 20% GBB replacement |
| BFS20 | 387 | + 4.6 | Mix with 20% BFS replacement |
| BFS30 | 430 | + 8.1 | Mix with 30% BFS replacement |
| BFS35 | 466 | + 25.9 | Mix with 35% BFS replacement |
| BFS40 | 390 | + 5.4 | Mix with 40% BFS replacement |

## Acknowledgment

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## Abbreviation and symbols

| | |
|---|---|
| **XRF** | **X-ray fluorescence test** |
| **XRD** | **X-ray diffraction testes** |
| **SAI** | **Strength activity index** |
| **HPF** | **Hydraulic Pozzolanic Factor** |
| **MK24, MK33 and NMK** | **Three types of local metakaolin** |
| **CBC** | **Calcined ball-clay** |
| **GBB** | **Ground broken bricks** |
| **BFS** | **Blast furnace slag** |
| **FA** | **Fly ash** |
| **K24, K33 and NK** | **Raw Egyptian kaolins clay** |
| **BC** | **Raw local ball-clay** |
| **OPC** | **Ordinary Portland Cement** |
| **S/G** | **Sand/gravel** |
| **BET** | **(Brunauer, Emmett, Teller) theory** |
| **w/b** | **Water/binder** |