Effect of $MgSO_4$ Solution on the Physicochemical and Mechanical Properties of OPC-Metakaolin and OPC-Metakaolin-Limestone Blends

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Abstract: This study aims to investigate the effect of $MgSO_4$ solution on the durability of the pastes made of ordinary Portland cement (OPC) blended with 10, 20 and 30 wt.% metakaolin (MK) and the pastes made by partial substitution of metakaolin in the mix containing 30% metakaolin by 5 and 10 wt.% limestone (LS). All pastes were prepared using the suitable amount of water for standard consistency. The pastes cured in tab water for 28 days then divided into two sets; the first one continued for hydration in tab water up to two years. The second set was immersed in 5% $MgSO_4$ solution for the same period of hydration. Compressive strength, chemically combined water content and free lime content of the two sets of the hardened cement pastes were determined and compared to each other. Also, mass change of the set samples immersed in sulphate solution was investigated. In addition, phase composition and microstructure of some selected samples in the two solutions were examined by using XRD and SEM techniques respectively. It was found that the paste made of (70% OPC + 20% MK + 10% LS) represent the most durable against sulphate attack.

Keywords: Hydration characteristics, sulphate attack, metakaolin, limestone, durability.

1. INTRODUCTION

Improvement of sulfate resistance of Portland cement concrete still attracting the attention of a lot of researchers.

Many authors [1-5] studied the sulphate attack on the hardened ordinary Portland cement as well as, metakaolin, limestone, ground granulated blast furnace slag, silica fume blended cement pastes. The mechanism of sulfate attack on Portland cements (OPC) containing limestone filler was investigated. Microstructure was studied using quantitative X-ray diffraction (XRD). Results showed that sulfate attack in mortars containing limestone filler is characterized by an inward movement of the reaction front leading first to the formation of ettringite, later to gypsum deposition, and finally to thaumasite formation when the decalcification of mortar leads to the breakdown of C-S-H [4].

Hekal *et al*. [6] described the sulphate resistance of some hardened blended Portland cement pastes. The effects of immersion in 10% $MgSO_4$ on the compressive strength of the various hardened blended cement pastes were studied. It was found that the slag and $CaCO_3$ improve the sulphate resistance of ordinary Portland cement (OPC) paste.

Al-Akhras [7] investigated the effect of metakaolin (MK) replacement of cement on the durability of concrete to sulphate attack. The study showed that MK replacement of cement increased the sulphate resistance of concrete. The magnesium sulphate resistance of mortar and paste specimens incorporating 0%, 5%, 10% and 15% metakaolin (MK) was studied [8]. Results confirmed that mortar specimens with a high replacement level of metakaolin showed lower resistance to a higher sulphate concentration of magnesium solution.

In this study the durability of cement pastes containing 10, 20 and 30 wt. % of MK and the pastes made by partial substitution of metakaolin in the mix contains 30% MK by 5 and 10 wt.% limestone (LS) immersed in 5% $Mg(SO)_4$ solution up to two years was studied.

2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1. Materials

The materials used in this investigation were Ordinary Portland Cement (OPC) provided from Egyptian Tourah_Portland Cement Company and Kaolinite Clay was obtained from The Egyptian Shabba Company, The clay was fired at 800°C for 3 hours to obtain Metakaolin (MK). In addition, commercial grade of Limestone (LS) was used. The chemical oxide composition of the OPC and metakaolin are given in Table **1**.

2.2. Experimental Techniques

Table **2** shows the mix composition of the different mixes and their designations. Different blended

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Table 1: Chemical Oxide Composition of OPC and MK, wt %

Oxide (wt %)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Loss on Ignition
OPC	20.89	4.68	3.43	63.33	2.18	2.95	0.44	0.25	-	-	-	1.85
MK	49.55	35.22	1.05	0.2	0.36	0.59	0.01	0.19	1.56	0.01	-	11.23

Table 2: Mix Proportions, Optimum Water of Consistency and Setting Times of the Investigated Pastes

Mixes	W/S (%)	Initial Setting Time (min)	Final Setting Time (min)	Mix Proportion, wt%		
				OPC	MK	LS
Mix I (blank)	29	77	105	100	-	-
Mix IIA	30.3	74	100	90	10	-
Mix IIB	31.3	53	93	80	20	-
Mix IIC	32.5	50	80	70	30	-
Mix IIIA	31.4	59	90	70	25	5
Mix IIIB	30.9	48	78	70	20	10

cements were prepared by using various ratios of OPC, metakaolin and limestone. Each dry blend was mechanically mixed in a porcelain ball mill using three balls for one hour to ascertain complete homogeneity of the mix. The water of consistency and setting times for each mix were determined according to ASTM specifications [9, 10]. The various cement pastes were prepared by mixing the dry solid mixture with the required amount of water (suitable for standard consistency) and molded in one-inch cubic molds. The moulds containing the pastes were then cured at about 100% relative humidity for the first 24 hours in order to attain the final setting of the specimens, then demoulded and cured under water at room temperature (23-25°C) for different time intervals of 3, 7, 28, 90, 180, 360, 540 and 720 days.

After 28 days of curing under tab water, half of the rest of cement pastes were removed and immersed in 5% magnesium sulphate ($MgSO_4$) solution at room temperature to continue hydration at the remaining time intervals (90, 180, 360, 540 and 720 days). The mass change of each hardened cement paste immersed in $MgSO_4$ solution was determined up to two years with respect to the weights of samples at the beginning of the immersion in sulphate solution (28 days) [6]. At each time interval, the compressive strength tests were performed on the hardened pozzolanic cement pastes using three cubic specimens at each hydration time and the average value was recorded as kg/cm_2. This was performed using a Tonindustrie machine (West Germany) for maximum load of 60 tons. The resulting crushed specimens of the hardened cement pastes were ground and the hydration reaction was stopped using the method described in an earlier publication [11]. The samples were then dried at 90°C for three hours in CO_2-free atmosphere and maintained in a desiccator containing soda lime and $CaCl_2$ until the time of testing.

The kinetics of hydration reaction was studied by the determination of chemically combined water and free lime contents at the different ages of hydration using the ground dried samples. The chemically combined water content, Wn (%), was determined by the ignition loss test at 1000°C for 1 hour. Duplicate measurements were carried out for each sample and the mean value was recorded.

$$Wn\ (\%) = [(W_o - W_i) / W_i] * 100 \qquad (1)$$

Where: W_o = dried sample mass and W_i = ignited sample mass.

The free lime content, CaO (%), was determined by using the glycerol/ethanol extraction method and the mean value of the two independent determinations was recorded [12].

The phase composition of the formed hydrates was investigated by means of X-ray diffraction (XRD). XRD was studied using cobalt target (λ = 0.17889nm) and nickel filter under working conditions of 40kV and 40mA. The morphology and microstructure of hydrated phases were identified using JSM-5410 scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

3.1. Water of Consistency and Setting Times

The required water of standard consistency as well as setting times for OPC and blended cement pastes were measured by using Vicat apparatus and shown in Table **2**. It is obvious that the water of consistency of all blended cement pastes is higher than that of blank Mix. This is attributed to the high fineness of metakaolin as compared to that of OPC, this high fineness of MK needs high water demand to attain the same consistency. This result is in agreement to that of the earlier publication [7]. Also the replacement of metakaolin (MK) in mix IIC by 5 and 10 wt.% LS corresponding to Mixes IIIA and IIIB decreases the water demand required for standard consistency as compared to that of mix IIC made of 70% OPC + 30% MK. This is attributed to the less hydraulic character and less absorption of limestone compared to that of MK. On the other hand all OPC-MK blended pastes made of mixes (IIA, IIB and IIC) possess lower setting times (initial and final) compared to mix I (100% OPC), also as the MK percentage increases the setting time decreases. This may be attributed to the relatively high reactivity of MK leading to fast rate of hydration at early ages, consequently short setting times. On the other hand mix IIIA (70% OPC + 25% MK + 5% LS) possesses higher setting times (initial and final) compared to those of Mix IIC (70% OPC + 30% MK). It can be explained as a result of replacement fraction of MK of higher reactivity by LS of non hydraulic character, a reason which may elongate the setting times. On contrary replacement of MK in Mix IIC by 10 wt.% LS (Mix IIIB) leads to a decrease in setting times (initial and final). It can be explained as a result of the formation of relatively large amount of calcium carboaluminate hydrates.

3.2. Compressive Strength

The results of compressive strength for the OPC and the various hardened blended cement pastes containing metakaolin and/or limestone as a function of the curing time in tap water are represented in Figures **1** and **2**. All mixes showed a continuous and gradual increase in the compressive strength. The continuous increase in the compressive strength can be attributed to the formation and accumulation of hydration products, mainly calcium silicate hydrates (CSH) and/or calcium aluminate hydrates. The slight decrease in compressive strength for mixes IIB and IIC at later ages of hydration may be attributed to the stabilization of the hydration products *via* crystallization; the crystalline hydration products possess lower hydraulic character than the amorphous ones.

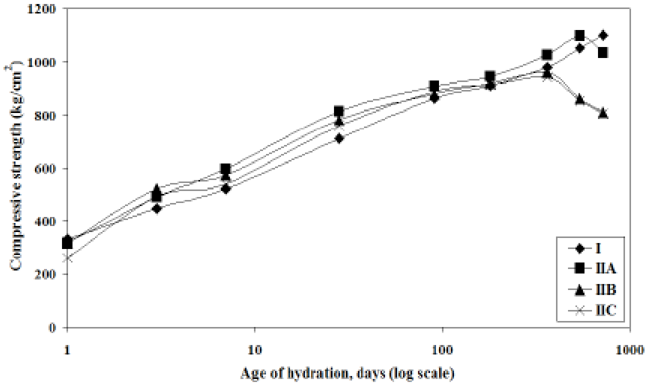

Figure 1: Compressive strength as a function of curing time for hardened cement pastes in tap water.

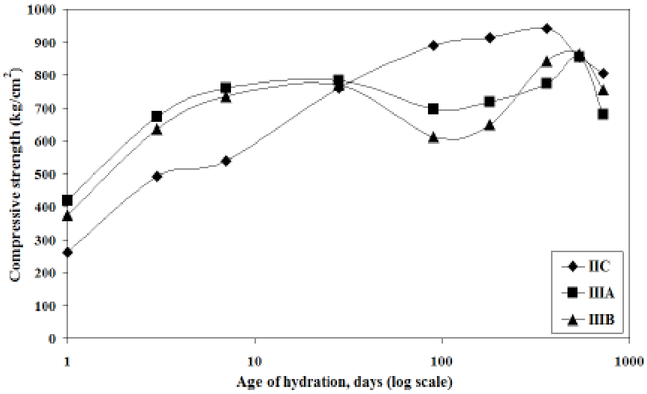

Figure 2: Compressive strength as a function of curing time for hardened cement pastes in tap water.

On the other hand the hardened blended cement paste made of mix IIA (90% OPC + 10% MK) possess the highest compressive strength compared to the other mixes. The high values of compressive strength of mix IIA can be attributed to the pozzolanic effect of MK. MK reacts with some of the liberated lime from OPC hydration to form additional calcium silicate hydrates which are the main binding agent. These results agree to the results published elsewhere (13, 14, 15**)** reported that, metakaolin (as an artificial pozzolana) can be used up to 10% as a replacement to ordinary Portland cement in the pozzolanic OPC-MK blends without any reduction in strength. On contrary, the Portland cement mixes blended with 20 and 30 wt.% MK made of mixes IIB and IIC, respectively possess lower compressive strength values compared to those of the blank mix and mix IIA. This can be attributed to high replacement of more hydration component (OPC) by less hydraulic one (MK).

The results of compressive strength for the various OPC-MK-LS blends as a function of the curing time in tap water are represented in Figure **2**. It is clear from the results of Figure **2** that the compressive strength increases for all OPC-MK-LS blends during stages of hydration except at 28 days a drop occurs which follow by the increase in compressive strength up to 18 months. A second drop in the compressive strength occurs at the final age of hydration (24 months). The increase in the compressive strength can be attributed to the formation and accumulation of hydration products, mainly calcium silicate hydrates (CSH), which act as the main binding centers between the remaining unhydrated parts of cement grains. On contrary, the notable decrease in the compressive strength for Mixes IIIA and IIIB may be attributed to phase transformation and/or the stabilization of the hydration products *via* crystallization.

It is clear also from Figure **2**, that all OPC-MK-LS blends made of Mixes IIIA and IIIB possess higher compressive strength values compared to Mix IIC made of 70% OPC + 30% MK up to 28 days of hydration. This higher values upon replacement of MK in Mix IIC by 5 and 10 wt.% LS may be attributed to the accelerating effect of limestone which act as neucleating agent, in addition to its filling effect. On the other hand Mixes IIIA and IIIB possess lower compressive strength values compared to Mix IIC from 28 days up to 2 years of hydration. It can be explained as a result of less fraction of MK and/or transformation of the hydration products from stronger to weaker hydraulic character as a result of the stabilization of the hydration products *via* crystallization.

The compressive strength of Portland cement blended with 0, 10, 20 and 30 wt.% MK made of mixes I* (blank) IIA*, IIB* and IIC*, respectively and cured in 5% $MgSO_4$ solution are represented as a function of immersing time in Figure **3**. Mix I made of 100% OPC (blank) show a significant increase in the compressive strength after curing in sulphate solution during the first 2 months of immersing in sulphate solution (~ 3 months of hydration). This was followed by a notable decrease in strength during the period from 3 to 6 months of hydration. After 6 and up to 12 months of hydration; a slight increase was observed. In the period from 12 up to 24 months the blank mix show no great change in compressive strength. The increase of compressive strength during the early months can be attributed to the formation and precipitation of both gypsum and ettringite inside the pores and voids of the hydrated matrix [16]. On the other hand, all other blended mixes containing different fractions of MK show a continuous decrease in the compressive strength values up to 23 months of immersing in sulphate solution (24 months of hydration). It can be attributed to the fact that CSH and calcium hydroxide are attacked deeply by aggressive ions, and therefore the deterioration accelerates with age [17]. As a result of this acceleration to sulphate attack, ettringite formation increases which characterized by its large volume. The precipitation of ettringite inside the pores causes an internal stress [18]. This internal stress forms micro-cracks which, by its role, decrease the compressive strength.

In addition, magnesium sulphate reacts with the formed $Ca(OH)_2$, forming gypsum and $Mg(OH)_2$, which has low solubility and precipitates as a gel. At later ages, it attacks C-S-H to form $Ca(OH)_2$ and magnesium silicate hydrates, which have no binding properties [19, 20].

Generally, deterioration of hardened cement pastes, as a result of sulphate attack, may be originated from three factors: 1) the expansion due to ettringite formation which causes an internal stress and subsequent micro-cracks in the paste; 2) the expansion due to gypsum formation and 3) MSH formation which may accelerate the deterioration of the hardened pastes. All these factors may combine together to enhance the deterioration of pastes under sulphate attack.

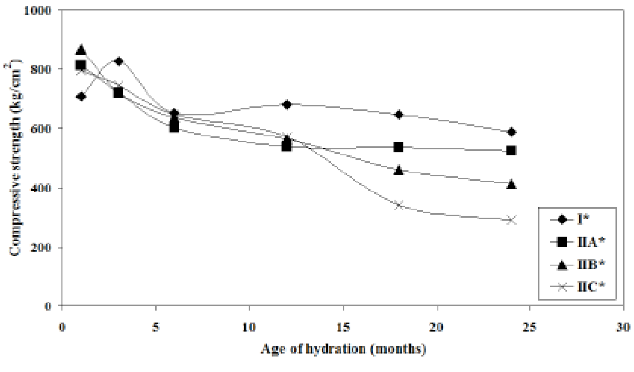

Figure 3: Compressive strength as a function of immersing time for hardened cement pastes in sulphate solution.

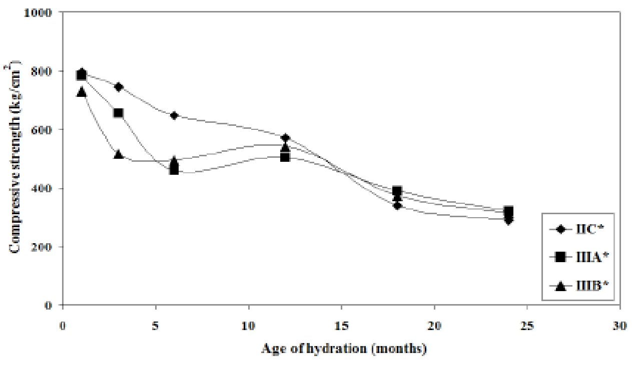

Figure 4: Compressive strength as a function of immersing time for hardened cement pastes in sulphate solution.

The compressive strength of OPC-MK-LS blends and cured in 5% $MgSO_4$ solution are represented as a function of immersing time in Figure **4**. The trend of Mix IIC* was discussed previously. The most important note in this curve is the positive effect and the improvement in the compressive strength values for Mixes IIIA* and IIIB* as a result of replacement of MK by 5 and 10 wt.% LS, respectively against sulphate attack at the later ages of immersing in sulphate solution (after 12 and up to 24 months of immersing). This result can be attributed to the filler effect of limestone (LS) as well as the formation of calcium carboaluminate which improve the microstructure and hence retard the diffusion of the aggressive ions inward consequently the resistance of the pastes towards sulphate attack is slightly improved.

3.3. Hydration Kinetics

Kinetics of hydration was studied by the determination of chemically combined water and free lime contents at the different ages of hydration.

3.4. Chemically Combined Water Content (Wn, %)

Chemically combined (non-evaporable) water contents of the various hardened blank and blended cement pastes cured in tap water were determined to study the progress of the hydration reaction of the different cement pastes. The results of chemically combined water contents (Wn, %) of the various hardened cement pastes cured in tap water are graphically represented in Figure **5** and **6**.

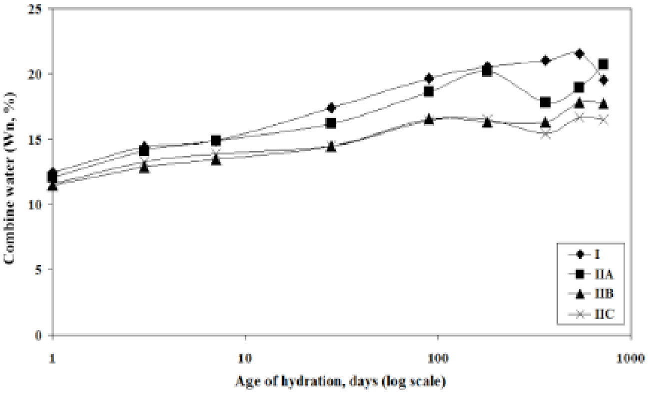

Figure 5: Combined water content in relation with curing time for hardened cement pastes in tap water.

The results of Figure **5** indicate that combined water content of the blank cement paste increases gradually with the hydration time (from 1 day up to 18 months of hydration) indicating a progress of the hydration reaction. The results of chemically combined water content (Wn, %) indicate that a fast hydration reaction takes place during the first 24 hours. After that the initially formed hydration products shield the cement grains leading to a slow and continuous rate of hydration reaction up to the final ages (540 days). The slightly decrease in the chemically combined water contents at later ages can be explained as a result of crystallization of the hydration products and/or the transformation of high water content CSH to low water content.

It is clear also from the results of Figure **5** that the hardened blended cement pastes containing 10, 20 and 30% of MK (Mixes IIA, IIB and IIC, respectively) give nearly similar trend of chemically combined water contents as that of blank Mix up to 6 months of hydration. During the period from 6 to 12 months, a noticeable decrease in combined water contents can be observed. This may be attributed to the crystallization of hydration products and/or the transformation of CSH of high water contents to CSH of low water contents. After 12 months a notable increase in the combined water contents can be observed for all blended mixes as a result of further hydration of the unhydrated parts.

The results of Figure **6** indicate that the OPC-MKLS blends Mixes IIIA and IIIB corresponding to 5 and 10 wt.% LS replacement, respectively possess higher chemically combined water content (Wn, %) up to the final age of hydration compared to that of Mix IIC (70% OPC + 30% MK). The increase of combined water content as a result of the addition of limestone may be due to the formation of rims of CSH surrounding C_3S particles which increases the rate of hydration of C_3S [22] as well as the formation of calcium carboaluminate.

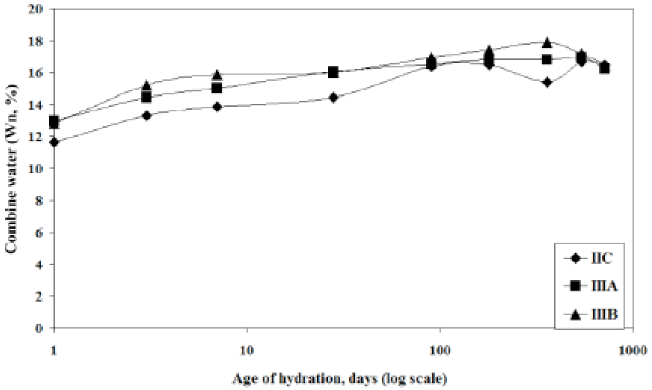

Figure 6: Combined water content in relation with curing time for hardened cement pastes in tap water.

The results of chemically combined water contents of the blank and blended Mixes (mixes I*, IIA*, IIB* and IIC*) immersed in 5% $MgSO_4$ solution are represented

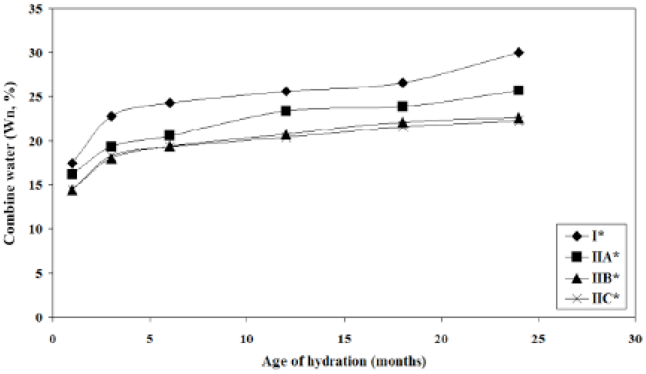

Figure 7: Combined water content as a function of immersing time for hardened cement pastes in sulphate solution.

in Figure **7**. All mixes show a continuous increase in the combined water content (Wn, %) with the curing time up to the final ages of immersing (24 months). The results of Figure **7** show that combined water content increases sharply during the initial period of immersing up to 3 months of hydration indicating a fast rate of hydration for blank as well as blended mixes during this period. After 3 months the combined water increases gradually for all mixes without and with MK up to the final age of immersing in 5% $MgSO_4$ (24 months). Obviously, the increase in the chemically combined water with the curing time can be attributed to the progress of the hydration reaction, as well as, the formation of tricalcium aluminate trisulphate hydrate (ettringite) which has high water content.

On the other hand, the blended mixes (mixes IIA*, IIB* and IIC*) give chemically combined water contents lower than that of blank mix (mix I*). In addition; increasing the ratio of MK replacement from 10% (Mix IIA*) up to 30% (Mix IIC*) leads to a decrease in the values of combined water contents at all curing times. The lower values of chemically combined water recorded for the mixes containing MK indicate that the amount of the formed ettringite (of high water content) is less compared to the blank mix as a result of the lower amounts of C_3A in the blended mixes. Actually, C_3A phase is responsible for the formation of monosulphate and ettringite phases. The lower ettringite content in case of MK-blended pastes, appears to contradict the conclusion that replacement of OPC with MK does not improve the sulphate resistance, discussed in the previous section. But if we take in consideration the compressive strength results which clarify that gypsum, not ettringite, has a significant relation with the considerable expansion and a subsequent deterioration of the pastes and/or the formation of MSH, especially in pastes with a high replacement level of MK [20]. In this case the results of combined water contents are in convenient to the results of compressive strength.

The results of Figure **8** indicate that the OPC-MKLS blends made of Mixes IIIA and IIIB corresponding to 5 and 10 wt.% LS replacement, respectively possess higher chemically combined water content (Wn, %) up to the final age of hydration compared to that of Mix IIC (70% OPC + 30% MK). The increase of combined water content as a result of the addition of limestone again, may be due to the formation of rims of CSH surrounding C_3S particles which increases the rate of hydration of C_3S [21], as well as the formation of calcium carboaluminate.

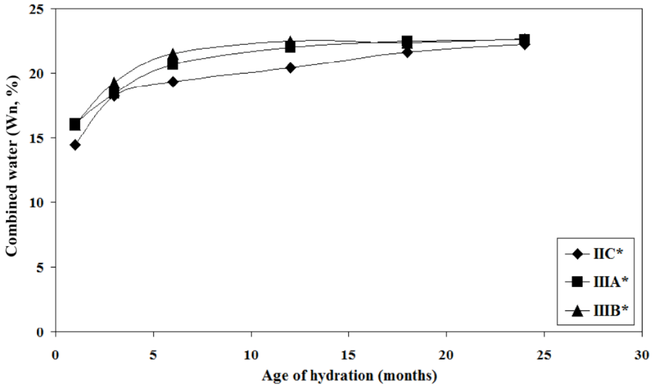

Figure 8: Combined water content as a function of immersing time for hardened cement pastes in sulphate solution.

3.5. Free Lime Content (CaO, %)

Figure **9** shows the variation of free lime contents (CaO, %) with hydration ages for pastes hydrated in water. The free lime of blank mix increases gradually and continuously with the hydration age up to 360 days. This can be attributed to the progress of hydration reaction and thus formation of more $Ca(OH)_2$ as a result of the continuous hydration of silicate

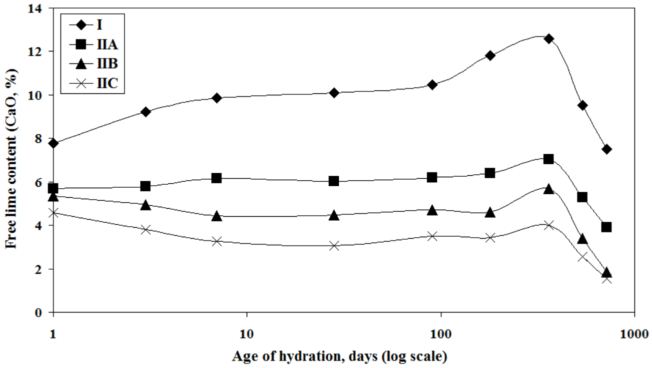

Figure 9: Free lime content as a function of curing time for hardened cement pastes cured in water.

phases. The decrease of free lime contents of blank cement pastes after 360 days up to 720 days may be due to the carbonation and leaching of lime in water. The free lime contents (CaO, %) for all OPC-MK blended cement pastes are lower than that of OPC (blank) and as the percentage of MK replacement increases the free lime content decreases. This is due to the consumption of free CH by the pozzolanic reaction with MK also as a result of the decrease of the OPC portion. Obviously the blended cement paste having the highest MK content (Mix IIC) has the lowest free lime contents at all ages of hydration; this is due to the marked consumption of free lime by MK as a result of the pozzolanic reaction. These results are in agreement with the results reported in earlier publications [14].

The variation of the free lime content (CaO, %) versus age of hydration for all OPC-MK-LS blended pastes hydrated in tap water are represented in Figure **10**. As shown from the data of Figure **10**, the blended pastes containing 5 and 10 wt. % LS replacement and made of Mixes IIIA and IIIB, respectively possess higher free lime contents compared to that of Mix IIC. It can be attributed to that the decreasing of the metakaolin (MK) fraction.

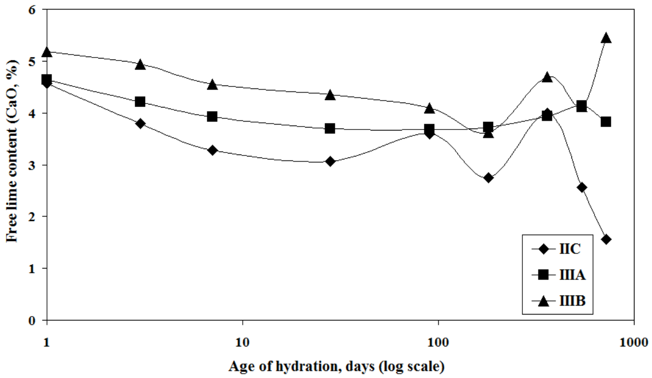

Figure 10: Free lime content as a function of curing time for hardened cement pastes cured in water.

The variation of the free lime contents of blank and blended mixes cured in 5% $MgSO_4$ solution with immersion time is represented in Figure **11**. In general, there is no considerable change in free lime contents for all mixes during the first year of curing in sulphate solution. This was followed by a marked decrease in free lime contents at the later ages of curing. During the first year of curing, there is a reaction of $MgSO_4$ with CH forming gypsum and $Mg(OH)_2$. On the other hand, there is liberation of more CH due to the progress of hydration of OPC as well as due to the decalcification of CSH. This explains the less variation of free lime contents when compared with those cured in water. The significant decrease in CH contents at the later ages is due to the reaction with $MgSO_4$ as well as MK with no more liberation of CH as a result of the reaction of most Portland cement.

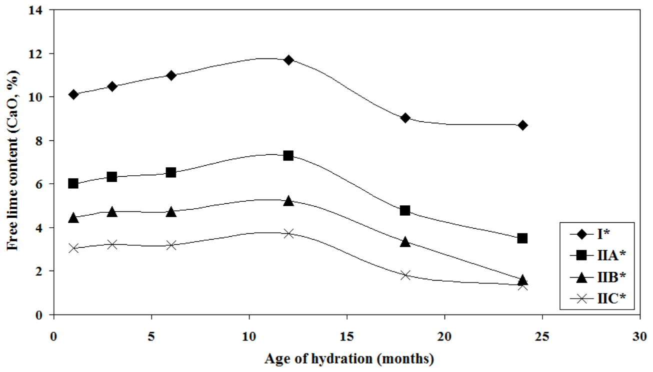

Figure 11: Free lime content with immersed time for hardened cement pastes in sulphate solution.

The variation of the free lime contents of OPC-MK and OPC-MK-LS blended mixes made of mixes (IIC*, 70% OPC + 30% MK; IIIA*, 70% OPC + 25% MK + 5% LS and IIIB*, 70% OPC + 20% MK + 10% LS) and cured in 5% $MgSO_4$ solution with immersion time is represented in Figure **12**. In general, there is a considerable higher free lime contents for the multiblended pastes. Again, these high values of free lime content can be attributed either to the decrease of the MK content, which reacts with liberated lime from OPC hydration, or to the leaching of calcium ions from limestone.

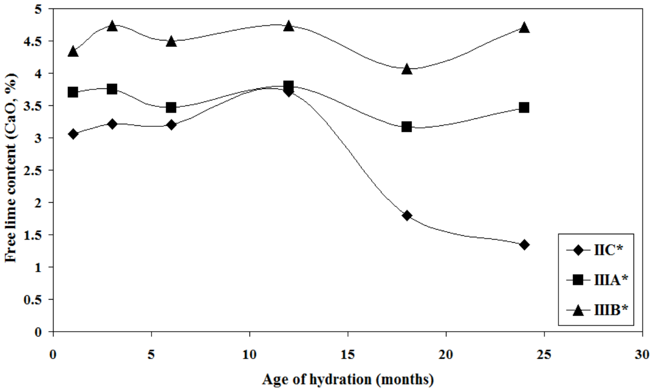

Figure 12: Free lime content with immersed time for hardened cement pastes in sulphate solution.

3.6. Mass Change

Mass change was measured for all hardened cement pastes cured in magnesium sulphate solution

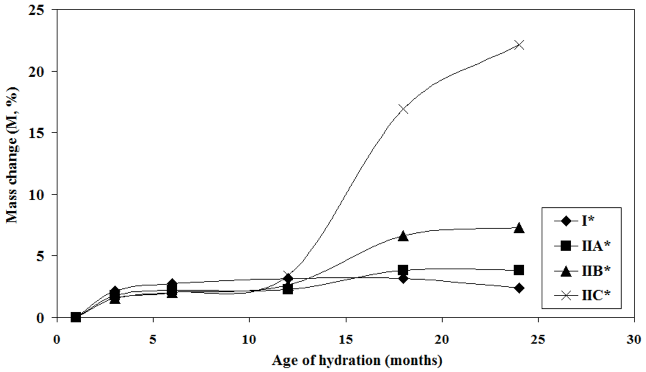

Figure 13: Mass change with immersed time for hardened cement pastes in sulphate solution.

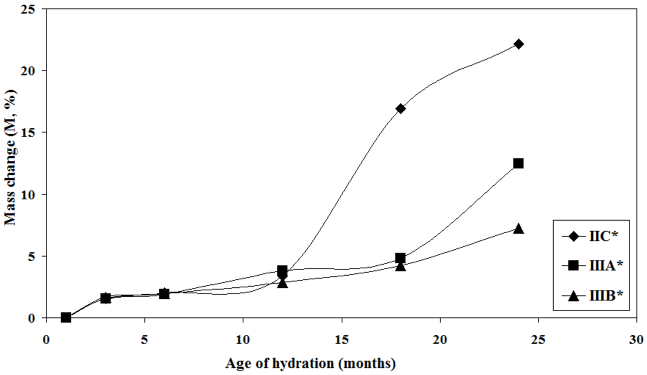

Figure 14: Mass change with immersed time for hardened cement pastes in sulphate solution.

at the investigated ages of hydration to determine the extent of sulphate attack. The results of mass change with curing ages are shown in Figures **13** and **14**. The results indicate that mass change increase for hardened cement pastes blended with 0, 10, 20 and 30% MK mixes I, IIA, IIB and IIC, respectively up to the final age of immersing see Figure **13**. This increase is attributes to the formation of more sulphoaluminate hydrates as ettringite or monosulphate and/or gypsum. Also The results indicate that all hardened blended cement pastes (Mixes IIA*, IIB* and IIC*) possess comparable (or slightly lower) values of mass change as compared to those of blank mix at the first period of immersing (up to 1 year of immersing) and higher values at the later ages of curing (from 1 up to 2 years of immersing). It is concluded that MK cannot be used to improve the sulphate resistance of the cement pastes. This may be attributed to its higher alumina content. These results are in consistence with the results of compressive strength measurements.

Mass change for OPC-MK-LS blends with curing ages are represented in Figure **14**. The results indicate that the mass change increases for all OPC-MK-LS hardened cement pastes mixes IIIA and IIIB, up to the final age of immersion. This increase is attributed to the formation of more sulphoaluminate hydrates as ettringite or monosulphate and/or gypsum, as discussed previously. The lower mass change of the pastes containing limestone is an indication for the good sulphate resistance of these pastes compared to the paste without limestone. In conclusion, mass change can be considered as an indicative test to measure the sulphate resistance of the cement pastes.

3.7. X-ray Diffraction (XRD) Analysis

The X-ray diffractograms of the hardened cement pastes made of (100% OPC) and Mix IIA (90% OPC + 10% MK) after 3, 90 and 360 days of hydration in water are shown in Figures **15** and **16**, respectively. The results of Figure **15** indicate that the main hydration products of the hardened OPC paste are the nearly

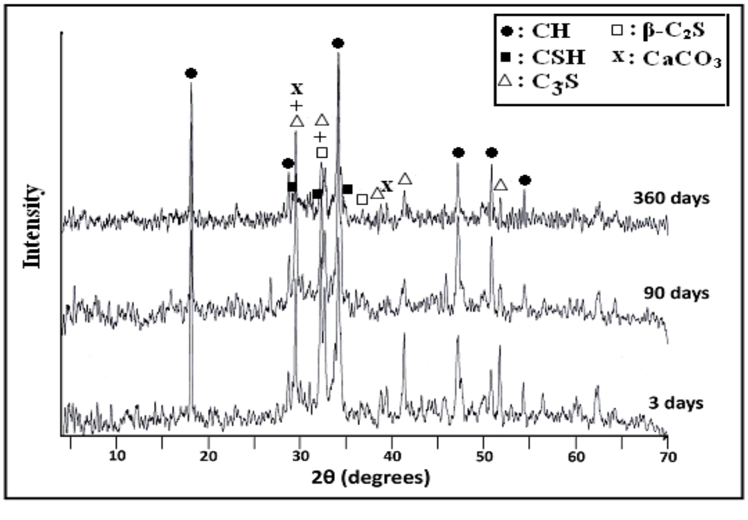

Figure 15: XRD patterns for hardened neat Portland cement pastes after various ages of curing in water.

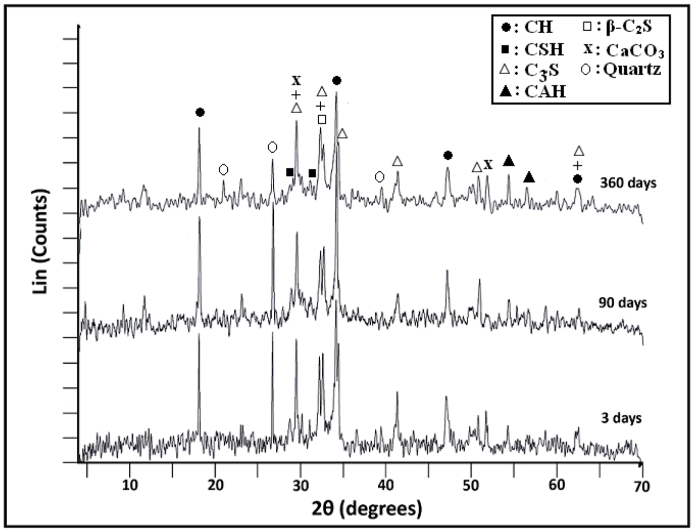

Figure 16: XRD patterns for hardened blended cement paste containing 30% MK (mix IIA) after various ages of curing in water.

amorphous and microcrystalline calcium silicate hydrates (CSH) as well as the well crystallized calcium hydroxide (CH). Obviously, the intensities of the peaks characterizing C_3S, β-C_2S and C_3A decrease with age of hydration; meanwhile, the intensities of the peaks characterizing the hydration products, namely calcium silicate hydrates (CSH) and calcium hydroxide (CH) increase with the time of hydration indicating the progress of the hydration reaction. The peak of $CaCO_3$ was overlapped with that of CSH.

The X-ray diffractograms of the hardened cement pastes made of mix IIA (90% OPC + 10% MK) after 3, 90 and 360 days of hydration in water are shown in (Figure **16**), and compared with the X-ray diffrractograms of the hardened cement paste made of mix I (Figure **15**). The results of Figure **16** indicate that the intensity of the peaks characteristics to CH is lower compared to those of the blank. This is a result the pozzolanic reaction of MK with CaO hydration.

Figures **17** and **18** Show the XRD patterns for blank mix (mixI*) and mix IIC*, respectively after 3 and 12 months of curing in 5% $MgSO_4$ solution. The peaks characterized of the nearly amorphous and microcrystalline CSH and portlandite (CH) as the main hydration products can be observed. It can be noticed that the peaks characteristic to calcium hydroxide (CH) for the pastes exposed to sulphate solutions have low intensities as compared to those cured in water. This can be attributed to the reaction of CH with magnesium sulphate to form gypsum and magnesium hydroxide; these data are in agreement with those data obtained from free lime determination. In addition the peaks characterized to ettringite and gypsum, although with low intensities, are also distinguished as a result of sulphate attack. The lower intensities of the peaks characteristic to ettringite confirm the conclusion that the main reason of deterioration of the hardened cement pastes cured in 5% $MgSO_4$ is not only the

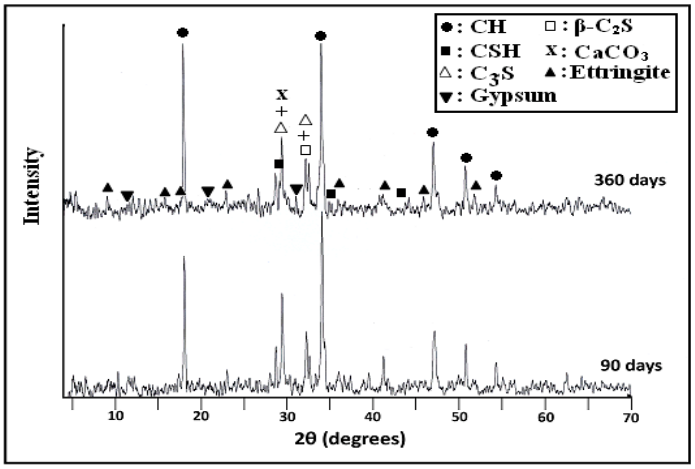

Figure 17: XRD patterns for hardened neat Portland cement pastes after various ages of curing in sulphate solution.

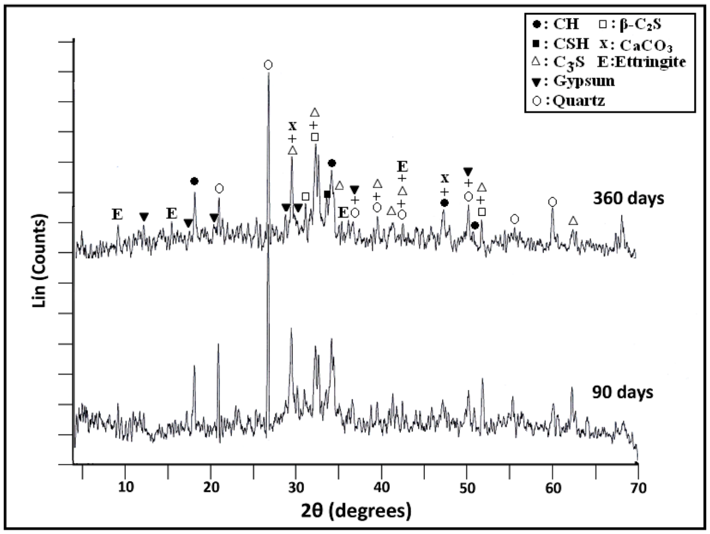

Figure 18: XRD patterns for hardened blended cement paste containing 30% MK (mix IIC*) after various ages of curing in sulphate solution.

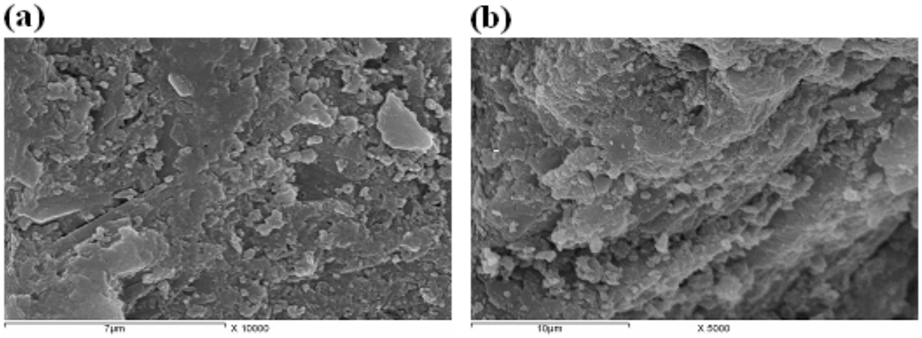

Figure 19: SEM micrographs for neat hardened Portland cement (mix I) after a) 90 and b) 360 days of curing in water.

formation of ettringite but there are another two main reasons. The first one is the formation and precipitation of gypsum inside the pore system. The second reason is the formation of magnesium silicate hydrate (MSH), with non-cementing properties, as the result of the reaction between $Mg(OH)_2$ and calcium silicate hydrate (CSH).

3.8. Morphology and Microstructure

Figures **19** and **20** show the Scanning electron microscope examination (SEM) for neat Portland cement paste (mix I) and Portland cement blended with 30% metakaolin (mix IIC) hydrated for 90 and 360 days in water.

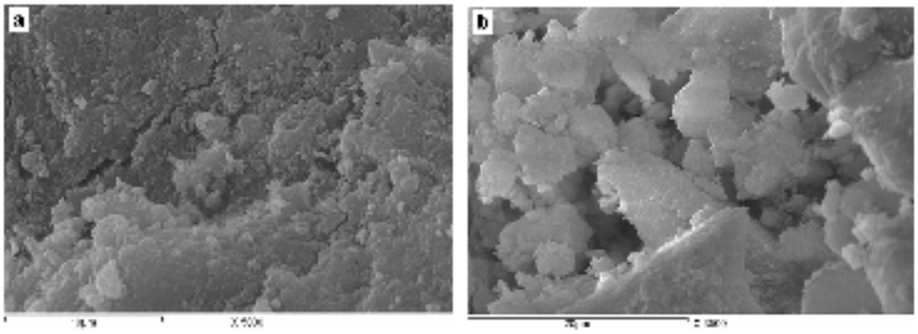

Figure 20: SEM micrographs for hardened blended cement paste containing 30% MK (mix IIC) after a) 90 and b) 360 days of curing in water.

SEM micrographs of blank mix after 90 and 360 days (Figure **19a** and **b**) show a massive structure composed mainly of nearly amorphous calcium silicate hydrates which cover the unhydrated cement grains. In addition, a platy crystals of $Ca(OH)_2$ can be identified after 360 days, the gel character of CSH decreases due to its crystallization.

Figure **20** show the Scanning electron microscope examination (SEM) for Portland cement paste blended with 30% MK (mix IIC) hydrated for 90 and 360 days in water. Obviously it can be noticed, that it is composed mainly of a massive structure of nearly amorphous calcium silicate hydrates. In addition, thin platelets of calcium monosulphate aluminates hydrates. The lack of the hexagonal crystals of $Ca(OH)_2$ in the SEM micrographs for mix IIC, especially after 360 days of hydration, is attributed to the pozzolanic action of MK which consumes the lime liberated from OPC hydration. These results are in agreement with results of free lime.

The micrographs of mixes I* and IIC* immersed for 90 and 360 days in 5% $MgSO_4$ solution are shown in Figures **21** and **22**. SEM micrographs of blank mix show the same needle like crystals of ettringite phase, in addition to well crystallized CH and CSH phases. The formation of ettringite which characterized by its large volume can cause an internal stress inside pores. This internal stress leads to the formation of microcracks, hence compressive strength decreases.

The micrographs of mix IIC* immersed for 90 and 360 days in 5% $MgSO_4$ solution are shown in Figure **22**. Figure **22-a** shows the SEM micrograph of mix IIC* after 90 days of immersing which indicate the presence of well crystallized ettringite in the form of rode-like crystals. Also, hexagonal plates of aluminate hydrates and gypsum crystals can be identified. An open structure with the formation of microcracks as well as large caracks can be seen as a result of the formation of gypsum and/or few needles of ettringite. These effects are responsible for the drop of the compressive strength as well as the deterioration of the paste.

3.9. Physical Appearance

The external appearance of the various mixes after 2 years of curing in water and in 5% $MgSO_4$ solution

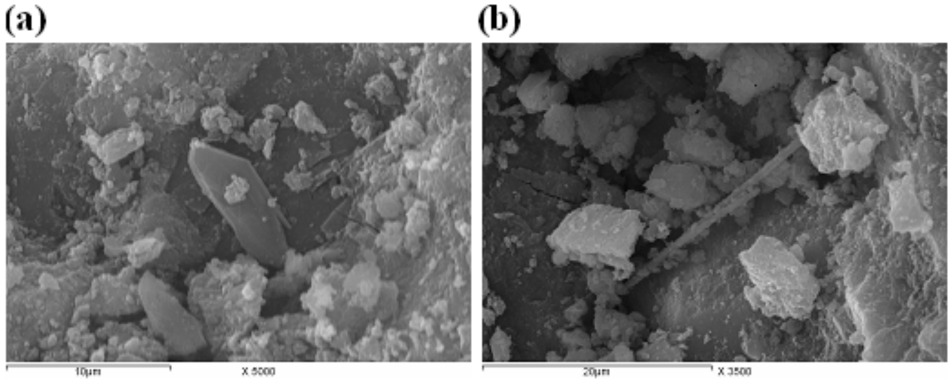

Figure 21: SEM micrographs for neat hardened Portland cement (mix I) after a) 90 and b) 360 days of curing in sulphate solution.

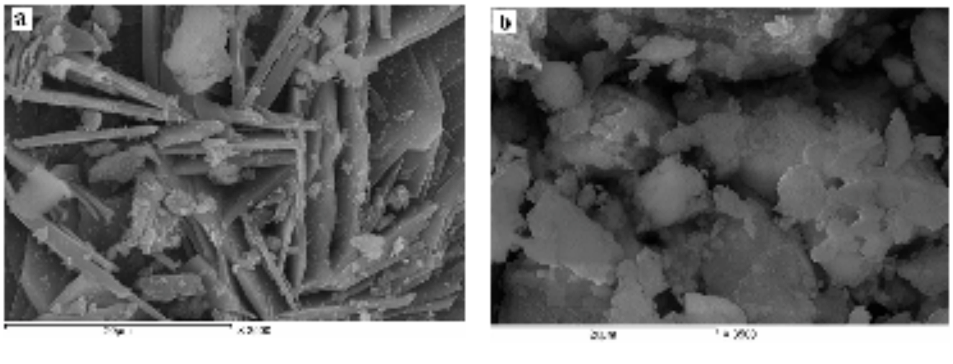

Figure 22: SEM micrographs for hardened blended cement paste containing 30% MK (mix IIC*) after a) 90 and b) 360 days of curing in sulphate solution.

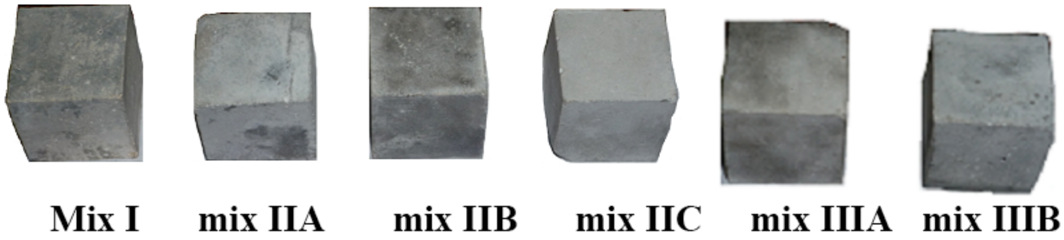

Figure 23: External physical appearance of the hardened cement pastes cured in tab water for 2 years.

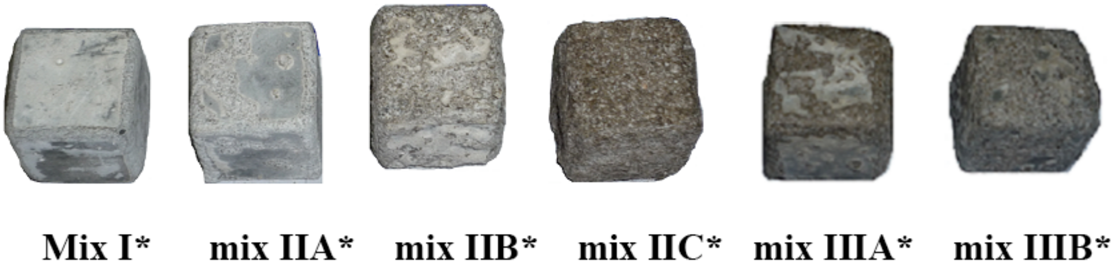

Figure 24: External physical appearance of the hardened cement pastes cured in sulphate solution for 2 years.

are shown in Figures **23** and **24** respectively. It can be noticed that increasing the ratio of metakaolin leads to a more surface corrosion especially at edges and corners. Obviously, partial replacement of metakaolin in mix IIC by limestone mixes (IIIA*, IIIB*) decrease the corrosion of the surface and thus improves the external appearance. This can lead to increasing sulphate resistance. Such observations are correlated well with the results of compressive strength and mass change.

CONCLUSIONS

On the basis of this investigation, the following conclusions may be derived;

- The setting time for blended cement pastes with metakaolin is lower than that of the blank Mix (100% OPC).
- The results of chemically combined water of multi-blended mixes were higher than those of PC-MK blend at most of hydration ages (cured in water or sulphate solution).
- All mixes blended with metakaolin showed less sulphate resistance than the neat Portland cement paste.
- Partial substitution of metakaolin by 5 or 10% limestone in mix IIC improves the sulphate resistance especially at later ages.
- Mixes blended with metakaolin showed considerable increase in mass compared with blank. This indicates that these mixes have less resistance to sulphate attack.
- The increase in mass for the multi-blended mixes was less than that for PC-MK blend.

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