Long Term Durability Properties of Concrete Modified with Metakaolin and Polymer Admixture

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ABSTRACT

Previous studies show that both metakaolin (MK) and polymer can respectively improve certain mechanical and durability properties of concrete. Also, recent studies show that a combination of MK and polymer further enhances the mechanical properties by complement of each other. However, the knowledge of the effect on durability, a critical governing factor of concrete for the applications in extreme environments such as sewage, off-shore and bridge structures, has not been well established yet. This paper reports on a comprehensive study of the effect of metakaolin as a supplementary cementitious material together with polymer as admixture on the durability of concrete at relatively old ages. The results confirm that replacing Portland cement with 15% metakaolin and an additional 5% polymer (by weight) provide the optimum improvement for Portland cement concrete on both mechanical properties and durability.

Keywords: Metakaolin; Polymer; High Performance Concrete; Durability

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1. INTRODUCTION

Using mineral supplementary cementitious materials (SCM), such as fly ash (FA), silica fume (SF) and thermally activated kaolin (also known as metakaolin (MK)), as additives has already been proved effective to improve properties of concrete (Kamseu et al., 2014). MK requires less energy to produce compared to cement (Rashad, 2013; Souri et al., 2015), which, in recent years, has attracted more and more interest in the use for the SCM (Aiswarya et al., 2013; Srinivasu et al., 2014) because of the environmental concern and the decreasing supply capacity of fly ash and silica fume(Souri et al., 2015). The MK product has predominant alumina (Al_2O_3) and silica (SiO_2) composition, which have an active pozzolanic nature (Ambroise et al., 1994). The pozzolanic reaction of MK with portlandite ($Ca(OH)_2$) will result in significant compositional changes of calcium silicate hydrate (CSH) gel to give high Al uptake and low Ca content in a new gel formation known as CASH, which has a low Ca/(Al + Si) ratio but a high Al/Ca ratio (Souri et al., 2015).

Previous research showed that a 20% replacement of cement using MK resulted in a substantial 50% increase of the compressive strength of mortar (Khatib et al., 2012), and the concrete using MK additive displayed a lower water sorptivity compared to that using silica fume (Guneyisi et al., 2012). Recently, Pouhet and Cyr (2016) studied the pore solution carbonation of MK-based geopolymer and found that the pH decreased rapidly in the first few days when the normal concrete was exposed to natural CO_2 conditions. Moreover, a high CO_2 content or a relatively high environmental temperature led to durability issues when the pH was lower than 10. However, the pozzolanic nature of MK increased the pH and kept it above 12 even after one year, indicating a minimum carbonation inside the concrete. Another study (Kannan and Ganesan, 2014) showed that self-compacting concrete (SCC) with a high MK content (up to 30%) exhibited a significant resistance to chloride ion penetration. For acid attack resistance, the same SCC with 5 and 10% of MK showed the lowest weight loss after 12 weeks immersed in 5% HCl and 5% H_2SO_4 solutions, respectively. Contrary to these advantages, it was also found, however, that the MK significantly reduces the workability of concrete and thus more water is required to improve the workability (Ambroise et al., 1994). However, the additional water to improve the workability would lead to durability issues, causing aggregate segregation, excess voids and increased porosity of the concrete.

Polymers, such as styrene-butadiene rubber (SBR) latex and polyvinyl acetate (PVA) emulsion have been commonly used as admixtures in concrete practice (Atkins et al., 1991; Konar et al., 2011). Polymer admixtures are known to not only increase the workability but also modify the physical properties of cement pastes by reducing macro voids and improving the bond strength of the polymer cement mortars to aggregates. For example, the mortar of SBR showed improvement in chloride penetration resistance along with general ionic permeability. SBR also slightly reduced portlandite content and mitigated the carbonation process (Yang et al., 2009).

The nature of the interactions between the polymers and the Portland and aluminous cements is significantly different. For Portland cement both SBR and PVA were found to retard the hydration rate to some extent, but SBR appeared to have very little chemical interaction with ordinary Portland cement (OPC) while PVA is fully hydrolysed (Atkins et al., 1991). A recent study on polymer-modified pervious concrete also found that both SBR and PVA polymers retarded the hydration reactions of cement particles and thus improved mechanical resistance and durability at prolonged curing time, for which PVA showed a better performance, but SBR showed no increase of the concrete stiffness (Giustozzi, 2016). For aluminous cement, SBR showed very little effect on the rate of hydration, but PVA was partially hydrolysed. PVA, when added to aluminous cements, produces a so-called macro-defect-free (MDF) matrix of superior strength and fracture toughness (Atkins et al., 1991).

A literature study shows that the MK and polymer complement each other in order to improve the mechanical and durability properties. A study on Portland cement concrete using polymer, MK and FA showed a significant effect on the compressive strength, the flexural strength and the modulus of elasticity (Kou and Poon, 2013). However, it is noted that the knowledge of the durability properties of concrete modified with polymer and MK have not been well established yet (Ahmed, 2011). To meet the high-performance requirement for sewage and off-shore applications, where the durability of concrete governs the use of concrete, a series of investigations have been conducted on the combined effect of the use of MK and a polymer mixture together on the mechanical properties and durability of the modified concrete. A previous publication has reported a study of the conventional mechanical properties (Al Menhosh et al., 2016). This paper at first gives a brief review on the major findings in the previous work. After then, it reports a followed on experimental investigation on the long term durability properties of the optimum mixture identified in the previous study on mechanical properties. The durability of the optimum mix has been compared with other three benchmarks to understand the effects of the MK, polymer and their combination.

2. MIXTURES

2.1 Raw Materials

Portland limestone cement, CEM II/A-LL (BS EN 197-1:2011), supplied by Lafarge cement UK LTD under the trade name of Mastercrete, and a premium metakaolin, produced by IMERYS group under the trade name of MetaStar 501, were used in the study. The material compositions are referenced in Table 1.

Table 1: Typical composition of cement and metakaolin

	CEM II/A-LL Cement (BS EN 197-1:2011)		Metakaolin (Ambroise et al., 1994)
Component	Values %	Standard	Values %
Al_2O_3	4.19	3 – 5%	40.18
Fe_2O_3	2.75	2.0 – 3.5%	1.23
CaO	65.00	60 – 70%	2.0
SO_3	3.19	Less than 3.5%	0.0
MgO	0.86	0.5 – 1.5%	0.12
Na_2O	0.14	Less than 0.75%	0.08
K_2O	0.51	-	0.53
SiO_2	16.19	15 – 25%	51.52
TiO_2	-	-	2.27
Loss on ignition (L.O.I)	-	-	2.01

The polymer additive was styrene butadiene rubber (SBR) latex, poly vinyl acetate (PVA) emulsion and their mixtures. Normal sands were used for the fine aggregates while crushed limestone gravels were used for the coarse aggregates with a maximum size of 10 mm. The particle size distributions of the aggregates (Menhosh et al. 2016) follow the requirements in BS 882:1992.

2.2 Mixture Design

Various combinations of the MK and polymers as listed in Table 2 were tested in a previous study on conventional mechanical properties (Menhosh et al. 2016). An optimum proportion was derived based on the mechanical properties of the modified concrete. To establish a baseline, a mass ratio of 1:1.5:3 for cement:sand:gravel was considered as a control mix.

Table 2: The mixtures designed (Al Menhosh et al., 2016)

Concrete Mixtures

<table>
<tr><th colspan="3">MK/Cementitious Binder (MK/C) %*</th><th colspan="3">Polymer/Cementitious Binder (P/C) %</th><th colspan="2">Water/Cementitious Binder ratio W/C</th></tr>
<tr><td colspan="3">0</td><td colspan="3" rowspan="6">0/2.5/5/7.5</td><td colspan="2" rowspan="6">0.35/0.38/0.40/0.45/0.50</td></tr>
<tr><td colspan="3">10</td></tr>
<tr><td colspan="3">15</td></tr>
<tr><td colspan="3">20</td></tr>
<tr><td colspan="3">30</td></tr>
<tr><td colspan="3">40</td></tr>
<tr><td colspan="8">Composition of Polymer Admixture</td></tr>
<tr><td>Component</td><td colspan="7">Percentage %</td></tr>
<tr><td>SBR</td><td>0</td><td>20</td><td>40</td><td>50</td><td>60</td><td>80</td><td>100</td></tr>
<tr><td>PVA</td><td>100</td><td>80</td><td>60</td><td>50</td><td>40</td><td>20</td><td>0</td></tr>
</table>

* % by weight, cementitious binder = cement +MK

3. CONVENTIONAL MECHANICAL PROPERTIES AND THE OPTIMUM MIX

All the mixes in the Table 2 were tested for their workability and the mechanical properties at the ages of 7 and 28 days. Figure 1 shows that MK significantly reduces the workability of the modified mixes. The mix of 10% MK/C ratio has a slump value much lower than the targeted range of 75 mm to 100 mm even at a high W/C ratio of 0.5. Figure 2 shows the cubic compressive strengths of the MK modified concretes at the age of 7 and 28 days for the W/C of 0.45. It shows that the MK/C ratio in the range of 15~20% presents the maximum compressive strength at the two ages.

Figures 3~5 show the effect of two polymers and their mixtures on their modified concretes. It can be seen that when the polymer to cementitious binder ratio (P/C) is more than 5%, the strength of the modified concrete starts to deteriorate considerably. Meanwhile, when W/C ratio is more than 0.45, the deterioration on concrete strength accelerates using polymer. Figure 5 shows that the polymer mixture of 80% SBR and 20% PVA at the 5% P/C and 0.45 W/C presents the highest improvement on concrete strength. Figure 6 shows that the polymer mixture of 80% SBR and 20% PVA gives the modified mixture a slump value of about 82 mm at 0.45 W/C.

Figure 7 compares the 28 days compressive strength of mixtures using the optimum polymer mixture at 5% P/C and MK at 15% MK/C separately and both together. Figure 8 shows the effect of three different curing methods on the compressive strength of the mixtures using 15% MK/C and varied P/C ratios. All the results have suggested that using 15% MK/C, 5% P/C of a polymer mixture of 80% SBR and 20% PVA, 0.45 W/C and moist curing gives the modified concrete an optimum mechanical properties.

4. LONG-TERM PROPERTIES OF THE OPTIMUM CONCRETE

This paper focuses on the long-term durability properties of the optimum mixture identified in section 3, and compares it with three other representative benchmark mixtures. All the four mixtures are listed in Table 3. For each data point, three samples were tested and their average value is presented as the result.

Table 3: Mixtures studied in this paper

Mixtures	MK/C %*	P/C %*	Water to cement ratio W/C
1 (Control)	0	0	0.45
2	15	0	0.45
3	15	5	0.45
4	0	5	0.45

* % by the weight of cementitious binder (cement + MK)

4.1 Mechanical Properties

- **Compressive Strength**

Long-term compressive strengths of concrete cubes (BS EN 12390-3: 2009) of these four mixtures up to 545 days are shown in Figure 9. It can be seen that mixtures 2 and 3 present a significant improvement on the control mix 1 in the long term with about 16% increase of the compressive strength at the age of 545 days. The results indicate that MK has a considerable effect on strength increase, but the polymer at 5% P/C has little influence on this property.

- **Splitting and Flexural Tensile Strength**

Figure 10 shows the splitting and flexural strengths at four ages up to 180 days. The tests were conducted according to BS EN 12390- 6:(2009) and BS EN 12390- 5:(2009), respectively. The results show that both the splitting and flexural strengths developed with age. Either using polymer (5% P/C) or MK (15% M/C) increases the tensile strength. The combination of 15% MK/C and 5% P/C resulted in the highest splitting and flexural strengths at almost all ages.

- **Young's Modulus**

Figure 11 shows the modulus of elasticity at the age of 28 days. The cast concrete cylinders (150 mm in diameter and 300 mm in height) were at first moist cured for 28 days according to BS 1881 Part -121: (1983). It can be seen that using MK has increased the Young's modulus of elasticity while polymer shows the opposite effect. The mix of 5% P/C and 15% MK/C shows a similar result as that of 5% P/C only. This suggests that the influence of MK on modulus in the presence of polymer has been minimised.

4.2. Durability

- **Drying Shrinkage**

Drying shrinkage is an important characteristic of concrete (Guneyisi et al., 2008), which affects the long-term mechanical properties and durability properties of structures (BS ISO 1920-8:2009; Hossain et al., 2016). Concrete prisms (100×100 ×400 mm) were cast and moist cured for 7 days. Thereafter they were stored in open atmosphere and their dimensional changes along the length of the prisms were monitored and recorded up to 365 days. Figure 12 shows that both MK and polymer respectively reduce the drying shrinkage. However, the optimum mix using both of them shows the lowest drying shrinkage at all ages.

- **Rate of Water Absorption**

Measurement of the rate of absorption of water was made according to ASTM C1585-04. This test method determines the rate of absorption of water by measuring the increase in the mass of a specimen due to water absorption when only one surface of the specimen is exposed to water, as shown in Figure 13. Concrete cylinders (100 mm diameter and 50 mm height) of all the mixes were cast and moist cured for 28 days. ASTM C1585-04 recommends conducting the investigation at the age of 28 days. However, reaction of MK with hydrated cement product continues over time and changes the internal microstructure (Aiswarya et al., 2013; Justice et al., 2005). In order to understand the long-term reaction of MK and changes in the microstructure, which influences the rate of water absorption, half of the specimens were dry cured for a further 28 days. After the curing, the specimens were treated for 3 days at a temperature of 50 degrees Celsius and relative humidity of 80%. One circular surface was immersed in water to a depth of 1 to 3 mm only, such that water ingress of unsaturated concrete was dominated by capillary suction during initial contact with water. The rate of water absorption I in the unit of mm is defined by Eq. (1) (ASTM C1585-04):

$$I = \frac{m_t}{A \times D} \tag{1}$$

where m_t is the change of weight with time (t), A is the cross-sectional area of the cylinder and D is the density of water. For the purpose of this test, the temperature dependence of the density of water is neglected and a value of 0.001 g/mm^3 is used. Figure 14 (a) and (b) show the water absorption test results for the concrete specimens cured for 28 days and the comparison of control and combined MK and polymer samples between 28 and 56 days, respectively. It can be seen that the combination of MK and polymer significantly reduces the water absorption in along run, which can be attributed to a significant reduction in the capillary pores because of the pozzolanic reaction of MK with the cement hydrated products and the hydrophobic effect of polymer.

- **Carbonation Test**

Concrete cylinders (100 mm in diameter and 200 mm in height) were made and moist cured for 7 days. After then having the two end surfaces coated using epoxy resin, they were stored openly exposed to atmosphere. At the ages of 21, 28, 56, 90, 120 and 180 days, the cylinders were split in half along the diameter to examine the depth of carbonation in the radial direction using 1% phenolphthalein (BS 1881-210, 2013; Papadakis, 2000; Chang and Chen, 2006). The carbonation depths were measured at six different locations in the direction of the height of the specimens (Otieno et al., 2014). Figure 15 shows the average values of carbonation depth. It can be seen that both MK and polymer helped to decrease the carbonation rate. The optimum mixture of 5% P/C and 15% MK/C shows the lowest carbonation rate, at approximately half of that of the control mixture at 180 days.

- **Chloride Penetration**

Similar cylindrical specimens as those used for the carbonation test were prepared and moist cured for 28 days. Thereafter, they were immersed in a 3% NaCl solution in order to simulate a chloride environment. The chloride penetration depth was monitored up to 180 days following a similar method as that used in the carbonation test. Chloride penetration depth was identified using a solution containing 0.1% sodium fluorescein and 0.1 N silver nitrate solution sprayed on the two surfaces exposed by splitting through the specimens along the diameter (Andrade at al., 1999; Meck and Sirivivatnanon, 2003). The penetration depth was measured in the same way as that for carbonation. Figure 16 shows a similar trend as that of the carbonation test. Both polymer and MK decreased the chloride penetration rate considerably. The optimum mixture of 5% P/C and 15% MK/C demonstrated the best resistance to chloride penetration.

- **Corrosion Weight Loss**

Reinforced concrete cubes (100×100×100 mm) were cast with a 60 mm long carbon steel rebar of diameter 16 mm positioned in each cube and parallel to a surface at a depth of 25 mm from that surface. Before casting, the carbon steel rebar was thoroughly cleaned and weighed to confirm its initial weight as that described by Parande et al. (2008). These cast reinforced specimens were moist cured for 28 days (Parande et al., 2008). To simulate the real world situation where concrete is subjected to various service conditions from normal atmosphere to submerged under saline environments over time, the samples were divided into three groups and each group was exposed to different conditions. One group was exposed to an open atmospheric environment, another group was immersed in a 20% NaCl solution, and the last group was alternately put in these two environmental conditions for 7 days each and up to 38 cycles in 365 days. On the time after 180, 270 and 365 days, the concrete specimens were split open using compressive machine and subjected to visual observation at first. Thereafter the steel reinforcements were pulled out from the concrete and their surfaces were carefully cleaned thoroughly using steel wire brush to get rid of all the concrete remains and the rusts of corrosion. Later the cleaned steel rebars were weighed again to work out their weight loss due to corrosion (Chung, 2000; Parande et al., 2008). Figure 17 shows that the weight losses of all samples under all three conditions are obvious, particularly, for the samples of the control mix of 0% P/C and MK/C. However, the samples of the optimum mix of 5% P/C and 15% MK/C has the lowest weight loss. It can be also noticed that the weight loss became significant after 270 days. Particularly, the alternated exposure to atmospheric condition and immersion in 20 % NaCl demonstrates a critical influence. It can be concluded that an alternating environmental condition accelerate the corrosion rate in concrete.

- **Chemical Resistance**

The chemical resistance was inspected by immersing cubic specimens (100×100×100 mm), after 28 days moist curing, in four different chemical solutions for 180 days. These solutions were 20% sodium hydroxide (NaOH), 5% sodium chloride (NaCl), 5% sulphuric acid (H_2SO_4) and 5% hydrochloric acid (HCl). They were selected to simulate various environmental conditions (Beulah and Prahallada, 2012). In practice, special cements (for example sulphur resistance cement), which are very expensive, have been used for the application in severe environments. This experimental investigation aims to help understand how effective using ordinary MK and polymer modified Portland cement to replace the special cements to meet these special requirements.

Figure 18 shows the appearance of the samples modified with 5% P/C and 15% MK/C after 90 days exposed to HCl and H_2SO_4, and all the samples after 180 days immersed in the acidic solutions. The weight changes of the specimens were recorded at 7, 14, 28, 56, 90 and 180 days. Figure 19 show that the mixtures using either MK or polymer had less weight increase when exposed to the alkaline and salty solutions, and less weight loss when exposed to acidic solutions, compared to the control mix with no modification using MK and polymer. It can be noticed, however, that when exposed to alkaline and salty solutions all mixtures had a steep weight increase in the first 56 days, which indicates that the cured concrete underwent further chemical reactions with infiltrated salt and alkali ions in an early stage. The MK modified mixtures have a significantly reduced weight change in all the tests. It effectively confirms the pozzolanic reactions between MK and cement hydration products, which result more hydration gel products with a formation of CASH and NASH (Kannan and Ganesan, 2014) to help the resistance to chemical attack. The optimum mixture of 5% P/C and 15% MK/C presents the least weight change in all the cases. It also can be seen that all these curves present a flatting trend after 90 days, indicating a long-term durability, in which the optimum mixture shows the best.

- **Water Flow Rate of Concrete**

In this study, both mortar and concrete specimens, of the dimension of 2.54 cm in diameter and 2.54 cm in length, were tested. The specimens were moist cured for 28 days and tested at ages 28, 56 and 90 days. The PERL-200 permeameter, provided by Core Lab Instruments, was used for the test. Similar to the test apparatus used by Kameche et al. (2014) and Li et al. (2016), incorporating a digital pressure transducer and a calibrated visual flow (measurement) cell, it uses the valves to control a flow system to enable the determination of flow rate of water through a one-inch diameter core sample plug. The water flow rate through the sample is determined by measuring the time required for the water (10 cm^3) to pass between the calibrations marks. Figure 20 shows the schematic diagram of the experimental setup. The permeability of the sample can be determined in terms of the Darcy's Law:

$$\boldsymbol{Q} = \frac{\boldsymbol{k} \times \boldsymbol{A}\,(\boldsymbol{P_1} - \boldsymbol{P_2})}{\mu \times \boldsymbol{L}} \qquad (2)$$

where, Q is flow rate (cc/sec), k is the permeability, L is the length of flow (cm), μ is the viscosity, A is the cross-sectional area of flow (cm^2), P_1 is the upstream pressure, and P_2 is the downstream pressure. All the concrete and mortar samples were tested using this apparatus. Figures 21 (a) and (b) illustrate the results obtained from concrete and mortar, respectively. Clear evidence can be seen that the water flow rate significantly reduced for concrete modified by MK and polymer. The mortar sample of the optimum mix of 5% P/C and 15% MK/C shows the lowest the permeability.

- **Depth of Penetration of Water under Pressure**

The water penetration test (BS EN-12390-8, 2009), the most commonly used test to evaluate the permeability of concrete, was conducted as well. In this test, water was applied on one face of the 150×150×150 mm concrete cube specimens under a pressure of 0.5 MPa (5 bars), as shown in Figure 22. This pressure was maintained constant for a period of 72 hrs. After the completion of the test, the specimens were taken out and split open into two halves. The water penetration front profile in concrete was then marked (Figure 23(a)) and the maximum depth of water penetration front in specimens was recorded and considered as an indicator of the water penetration (Dinakar et al., 2013). This test was conducted at 28, 56 and 90 days after moist curing for 28 days. As can be seen in Figures 23(b), the depth of penetration of water significantly reduced in the specimen of the optimum mix of 4% P/C and 15% MK/C compared with the rest of the samples. Furthermore, there is a development in water permeability of the modified concrete with increased age of the specimens compared with the control sample. This can be attributed to the continuous reaction of MK with the hydrated cement product, producing a less permeable matrix with time.

- **Gas Penetration of Concrete under Pressure**

In this test, the similar experimental setup and samples were used as in the test for depth of penetration of water under pressure. However, the CO_2 was applied from the top instead from the bottom with a pressure of 0.4 MPa (4 bars) for 8 hours. These arrangements were implemented to maintain the constant pressure in order to simulate the concrete under sewerage conditions. After the test, the specimens were taken out and split open into two halves. The penetration of carbonation was determined by treating a freshly broken surface with 1% phenolphthalein. The region of $Ca(OH)_2$ is coloured pink while the carbonated areas is uncoloured. The gas penetration profile on the concrete surface was then marked and the maximum depth of gas penetration in specimens was recorded and considered as an indicator of the gas penetration. Figure 24 compares the gas penetration depths of the four mixtures. It can be seen that using MK and polymer respectively have exhibited reductions in the gas penetration. The optimum mix of 5% P/C and 15% MK/C shows the best result for the gas penetration resistance.

5. CONCLUSIONS

This paper has reported an experimental study on long-term durability properties of concrete modified with MK and polymer. Various long-term durability tests were carried out to understand the behaviour of modified concrete subjected to an extremely harsh environment. The following conclusions can be drawn based on the experimental results:

- Metakaolin will accelerate the setting time of cement pastes but reduce the workability of concrete. However, polymer has an inverse influence on the two properties.
- The bi-polymer of composition 80% SBR and 20% PVA shows an optimised result when it works together with MK.
- The addition of 5% optimised bi-polymer and 15% cement replacement by metakaolin generates an optimised concrete mixture for long-term mechanical properties.
- All the long-term durability experimental investigations suggest that both MK and polymer improve the properties. Their combination presents a complement to each other. The optimum mix base on mechanical properties also demonstrates a great enhance on durability properties compared to using MK or polymer only.

Acknowledgments

This work was funded by the Iraqi Ministry of Higher Education and Scientific Research Scholarship Program.

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