

SUSTAINABLE HIGH-PERFORMANCE CONCRETE USING METAKAOLIN ADDITIVE AND POLYMER ADMIXTURE: MECHANICAL PROPERTIES, DURABILITY AND MICROSTRUCTURE

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ABSTRACT

In recent years, there has been a growing interest in the use of supplementary cementitious materials and polymers to produce high-performance concrete. This paper shows the results of a study on the effect of metakaolin and polymer admixture on mechanical behaviour and durability properties such as permeability, carbonation and chloride penetration, chemical attack, rate of water absorption and the corrosion rate of the steel reinforcement in the concrete. The results indicated that replacing Portland limestone cement with 15% of metakaolin and additional 4% of styrene-butadiene rubber and 1% of polyvinyl acetate polymer by weight of cement improve the properties of concrete. In addition, microscopic structure and chemical composition analyses were performed to confirm the underlying mechanisms and the improvement of material properties for this mix design. This study is aiming to preserve the environment by reducing CO₂ emissions in addition to the improvement of the sustainable high-performance concrete properties.

Keywords: Metakaolin, Polymer, SEM, XRD, microstructure

1. INTRODUCTION

Using mineral supplementary cementitious materials (SCMs), such as fly ash, silica fume and metakaolin (MK), as additives has already been proved effective to improve properties of concrete (Kamseu et al., 2014). With an increase of the environmental concern, in recent years, the use of MK as SCM has raised more and more interests (Aiswarya et al., 2013; Srinivasu et al., 2014) as the decreased supplying capacity of fly ash and silica fume (Souri et al., 2015). MK is normally produced by a thermal calcination of the kaolinite at a temperature ranging between 600°to~800°C (Rashad, 2013). MK is mainly composed of alumina (Al₂O₃) and silica (SiO₂), which determine an active pozzolanic behaviour (Ambroise et al., 1994). The pozzolanic reaction of MK, which consumes portlandite Ca(OH)₂, changes the hydration products of cement. Meanwhile, it made significant compositional changes of calcium silicate hydrate (CSH) gel, giving high Al uptake and low Ca content in the CSH phase (Souri et al., 2015). Previous studies showed that a 20% replacement of cement using MK had resulted in a substantial 50% increase of the compressive strength of mortar (Khatib et al., 2012); in addition,

concrete using MK additive displayed a less lower water absorption compared to that using silica fume (Guneyisi et al., 2012).

Polymers, such as styrene-butadiene rubber (SBR) latex and polyvinyl acetate (PVA) emulsion have been commonly used as admixtures in concrete (Atkins et al., 1991). Polymer admixtures are known to 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 SBR mortar showed an improvement in the chloride penetration resistance along with the general ionic permeability. 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 longer curing time, for which PVA showed to have a better performance, however SBR showed no increase of the concrete stiffness (Giustozzi, 2016). It was found that SBR promoted the reaction of calcium aluminate with gypsum and thus enhanced the formation of ettringite. As a result, it can effectively restrain the formation of the unstable C_4AH_{13} at early stage (Wang et al., 2006). A study on the Portland cement concrete using polymer, MK also proved a significant effect on the compressive and flexural strengths and the modulus of elasticity. Moreover, the addition of MK gave good chemical resistance for carbonation and sea water (Kou and Poon, 2013).

In summary, extensive researches, so far, have been conducted for cement and concrete materials using MK for the SCM and polymer for the admixture, and the effective results have been proved on that MK can improve that mechanical properties and durability because of its pozzolanic nature, and polymer has significant effects on the improvement for durability, and concrete workability. This paper aims to investigate the combined effect using MK and a polymer mixture for a high performance concrete development. The concrete is a quaternary binder system containing a Portland limestone cement, MK and a binary polymer mixture and aggregates (sand and coarse limestone). The optimum cementitious mixture is was assessed on the improvements in mechanical properties (compressive, split and flexural strengths) and durability tests (water absorption, carbonation and chloride penetration, corrosion weight loss and chemical resistance). The analysis of the composition and microstructure (using scanning electron microscopy, energy dispersive x-ray and computed tomography scan technology) of the hydrate products helps to understand how these components work together.

2. EXPERIMENTS

2.1 Raw Materials

The materials used were same as those used by [Menhosh et al. 2016]. A Portland limestone cement CEM II/A-LL, 32.5R, conforming with the criteria in British Standard EN 197-1:2011 was used for this study. The cement properties are shown in Tables 1 and 2. Fine aggregate used was with a maximum size of 4.75 mm with relative density of 2.47. The course aggregates used were crushed limestone coarse with a maximum size 14 mm and 2.21 specific gravity. The properties were tested according to BS 882: 1992. The metakaolin was supplied by IMERYS Performance Mineral. Table 3 shows the MK properties. Styrene butadiene rubber (SBR) is was the commercial Ceementone SBR which was supplied by Bostik Limited, a

synthetic organic chemical compound produced by Evo-Stik under the name Waterproof PVA, was supplied by Bostik Limited.

Table 1: Physical properties of the cement used (BS EN: 197-1: 2011)

Particulars	Unit	Compressive strength	Standard
2 days	(N/mm ²)	19	> 10
7 days	(N/mm ²)	29	27 - 37
28 days	(N/mm ²)	35	32.5 – 52.5

Table 2: Chemical composition of the cement (BS 12:1996)

Component	Values %	Standard
Al ₂ O ₃	4.19	3 - 5%
Fe ₂ O ₃	2.75	2.0 - 3.5%
CaO	65.00	60 - 70%
SO ₃	3.19	Less than 3.5%
MgO	0.86	0.5 - 1.5%
Na ₂ O	0.14	Less than 0.75%
SiO ₂	16.19	15 – 25%

Table 3: Properties of metakaolin

Particulars	Values
Colour	White
Specific gravity	2.5
ISO Brightness	>82.5
- 2 μm (mass %)	>60
+ 325 mesh (mass %)	<0.03
Moisture (mass %)	<1.0
Surface area (m ² /g)	14
Pozzolanas reactivity (mg Ca(OH) ₂ /g)	>950

2.2 Mixtures

Various combination of MK and polymer were tested by (Menhosh et al. 2016) to find the optimum weight ratio between the Portland limestone cement and the additives. The optimum mass ratios were derived based on the mechanical properties of concrete at 28 days of curing (compressive, splitting and flexural strengths). To establish a baseline, a mass ratio of 1:1.5:3 for cement:sand:gravel was considered as a control mix. Optimum performance occurred when using 15% MK to replace the cement and adding 4% SBR and 1% PVA as admixture. Optimum water/cement ratio occurred at 0.45. The concrete mixtures in this study are listed in Table 4

Table 4. Binder mixtures used in this study

Mixes	Cement (%)	MK (%)	Polymer/(Cement+MK) %	Water/Cement
Mix1	100	0	0	0.45
Mix2	85	15	0	
Mix3	85	15	5	
Mix4	100	0	5	

RESULTS AND DISCUSSION

3.1 MECHANICAL PROPERTIES

It was shown that the use of 15% MK and 5% polymer significantly increases the compressive strength of concrete at 7 and 28 days of curing [Menhosh et al. 2016]. However, Figure 1 shows the effect of water to cementitious material ratio on compressive strength at 28 and 90 days of curing, which shows that 0.45 gave the optimum result for a 15% MK and 5% Polymer mixture.

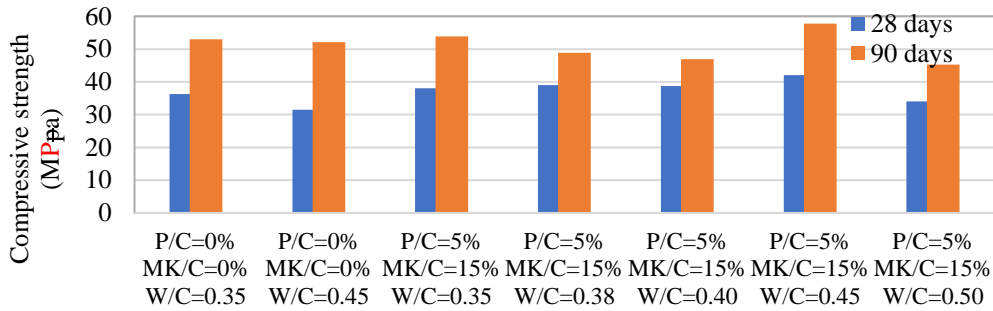


Figure 1. Effect of W/C ratio on compressive strength (results at 28 and 90 days of curing by Menhosh et al. 2016)

The sample with 15% of MK obtained a stable strength in about 60 days. The addition of polymer in control mixture decreased the strength for long term. The mixture of 15% MK and 5% polymer had a delayed time in strength development, but in long term it reached a close value to that using 15% MK only as shown in Figure 2.

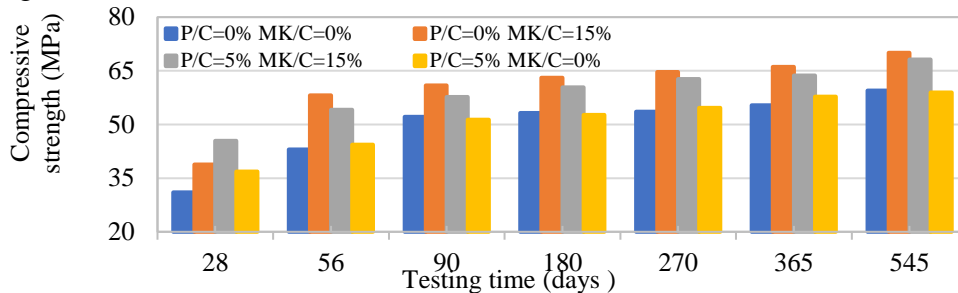


Figure 2. Compressive strength vs period of curing of the concretes

Tensile strength of concrete is an important property which significantly influences its behavior. Therefore, split cylinder and flexural strength tests were conducted according to BS EN 12390 (2009) part 5 and 6 specification, respectively and the results up to 180 days are shown in Figure 3-A/B. There are no significant changes in splitting tensile strength between mixes for certain age of concrete. However, sample with 15% MK and 5% polymer shows slightly higher flexural strength than sample with 15% of MK. This is resulted in the presence of polymer which increases the tensile properties in contrast with compressive strength according to Figure 3-B.

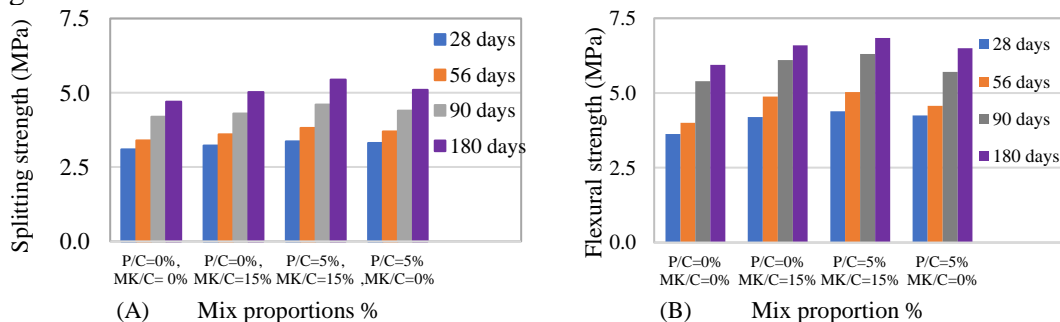


Figure 3. Splitting (A) and flexural (B) tensile strengths at age up to 180 days of curing

3.2. DURABILITY

WATER ABSORPTION TEST

Water absorption test (on concrete cube of 100x100x100 mm) suggested by BS 188-part 122-2011 Eq.1

$$m = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

where, m is the water mass adsorption in percentage, W_1 (g) is the average cube weight of three dry specimens, W_2 (g) is the average cube weight of three dry specimens after being immersed in water for 30 min. The results have showed that the mixture of 5% polymer and 15% MK had the lowest water mass adsorption of a test up to 56 days as shown in Figure 4.

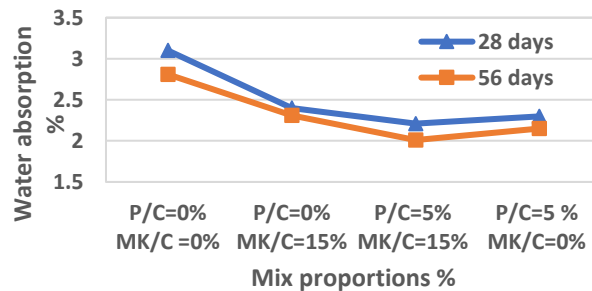


Figure 4. Water absorption %

CARBONATION AND CHLORIDE PENETRATION TESTS

Concrete cylinders (100 mm diameter and 200 mm height) were casted, and moist cured for 7 days, and then stored in air until testing was carried out to measure carbonation depth at ages up to 180 days and tested according to BS 1881-210. Top and bottom surface of the concrete cylinders were coated using epoxy resin and stored openly in atmosphere. Only the side surfaces of the specimens were exposed to the natural atmospheric condition. The carbonation depth was monitored and recorded by cutting the specimens in half along the diameter and measuring the carbonation depth of the two separated inner surfaces in diameter direction by treating a freshly broken surface with 1% phenolphthalein (Papadakis, 2000). It can be seen in Figure 5A that, either MK or polymer helped to decrease the carbonation rate. The optimum mixture of 5% polymer and 15% MK shows the lowest carbonation rate. Similar cylindrical specimens as those used for the carbonation test were prepared and moistly cured for 28 days for the chloride test (Ahmed, 2011). Thereafter, they were immersed in a 3% NaCl solution. The chloride penetration depth was monitored and recorded up to 180 days following a similar method used for carbonation test. Chloride penetration depth was identified using a solution containing 0.1% sodium fluorescein and 0.1 N silver nitrate, which was sprayed on the two surfaces cutting through the specimens in the direction of diameter (Meck and Sirivivatnanon, 2003). The penetration depths were measured at six different locations in the direction of the height of specimens (Otieno et al., 2014). Figure 5 B shows their average penetration depth after the specimens being exposed for different times in the 3% NaCl solution. Either polymer or MK decreased the chloride penetration rate considerably. The concrete mixture of 5% polymer and 15% MK demonstrated the best effect on the reduction of chloride

penetration, for which chloride penetration became extremely slow after 28 days exposure-when reached the depth of about 6mm.

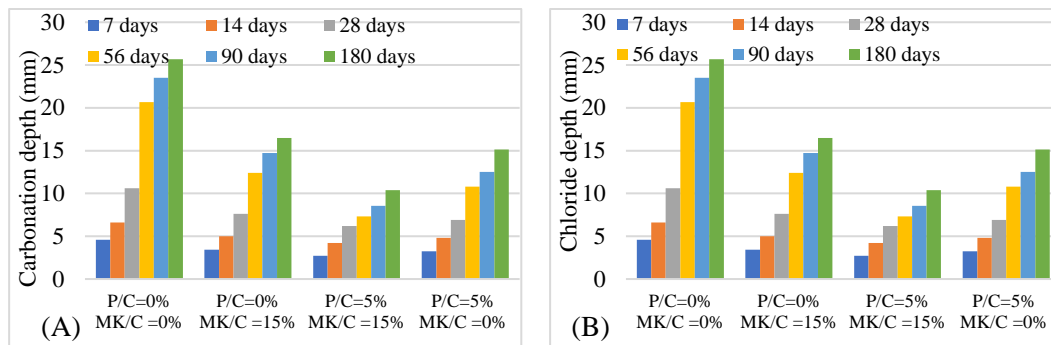


Figure 5. Carbonation (A) and Chloride penetration depth (B)

CORROSION WEIGHT LOSS

To quantify the corrosion rate in the steel reinforcement, reinforced concrete cubes of the size 100mm×100mm×100mm were casted. Carbon steel rod of a diameter of 16mm with 60 mm long was embedded in each cube, which was parallel to a surface and at a depth of 25mm from that surface. Before casting, the carbon steel rebar was thoroughly cleaned and weighed for its initial weight. The casted reinforced specimens were moistly cured for 28 days. The corrosion rate is calculated using the following equation (2):

$$\text{Corrosion rate} = \frac{87.6 \times W}{D \times A \times T} \quad (2)$$

where, W is the weight loss in g ($W = W_1 - W_0$), W_0 is the weight of sample before curing, W_1 is the weight of the sample after curing, D is the density of the material used, A is the area of the specimen (cm^2), T is time in h. (Parande et al., 2008). Thereafter, the specimens were divided into three groups, which were exposed to three different conditions. One group of the specimens was exposed to the open atmospheric environment for 365 days (curing 1). The second group was immersed into a 20% NaCl solution for 365 days (curing 2). The third group was alternately put in the two environmental conditions for 7 days each and up to 52 cycles for 365 days (curing 3). All the reinforcements were taken out by splitting the concrete cube and cleaned to measure the weight loss caused by corrosion (Chung, 2000). It has been found that the reinforcements in the third group showed a highest weight loss and the modified concrete by 15% metakaolin and 5% polymers showed the lower weight loss and corrosion rate of steel reinforcement compared with the conventional concrete mix as shown in Figure 6.

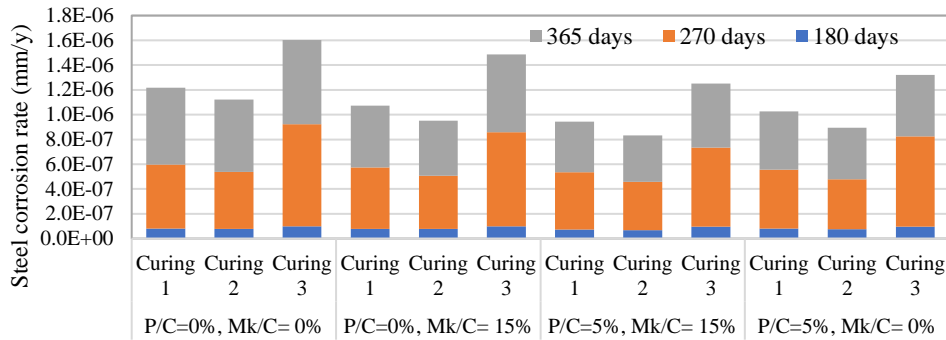


Figure 6. Steel corrosion rate of three curing condition (Curing 1, open atmospheric condition; Curing 2, immersed in to 20% NaCl; Curing 3, alternated between Curing 1 and 2 for 7days)

CHEMICAL RESISTANCE

The results of chemical resistance are shown in Figures 7 and 8. The chemical resistance was inspected by immersing a 100mm×100mm×100mm cube of each concrete mix in four different chemical reagents, after 28 days of moist curing, for up to 180 days. The solutions contained 20% sodium hydroxide (NaOH), 5% sodium chloride (NaCl), 5% Sulphuric acid (H₂SO₄) and 5% Hydrochloric acid (HCL). The change of the weight of the specimens were recorded and calculated using Eq. (1) (Beulah and Prahallada, 2012). From the Figure 7 (a) and (b) both the mixtures using MK and polymer had less weight increase compared with the control mixture when exposed to the 5% NaOH and 5% NaCl salt. Particularly, that using MK had much less weight change than that using polymer. The optimum mixture (5% polymer and 15% MK) presented the least weight change. The result demonstrates that cured concrete may take further chemical reactions with infiltrated salt and alkali ions in an early stage. Figure 8(a) and (b) shows that the weight loss of modified concrete immersed in sulfuric and hydrochloric acid increased with increasing immersion period, this might be due to the reactions between Ca(OH)₂ and calcium illuminate hydrate with the acid solution. So, these reactions lead to expansion and disruption of concrete. Also, the results show that the modified concrete (5% polymer and 15% MK) observed the lower weight loss compared with the conventional concrete, this might be due decreasing the permeability of modified concrete compared with the conventional concrete by filling of the most of pores system in concrete with the polymer film in addition to, the pozzolanic action with cement hydration products.

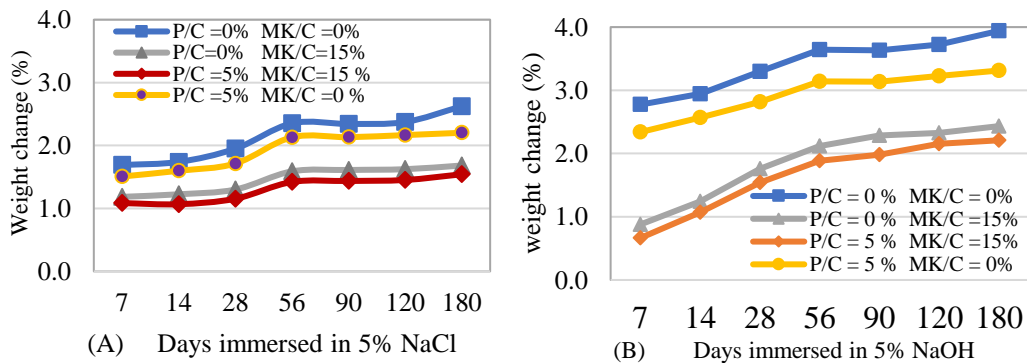


Figure 7. (a) Concrete weight change after exposed to 5 % NaCl, (b) Concrete weight change after exposed to 5 % NaOH

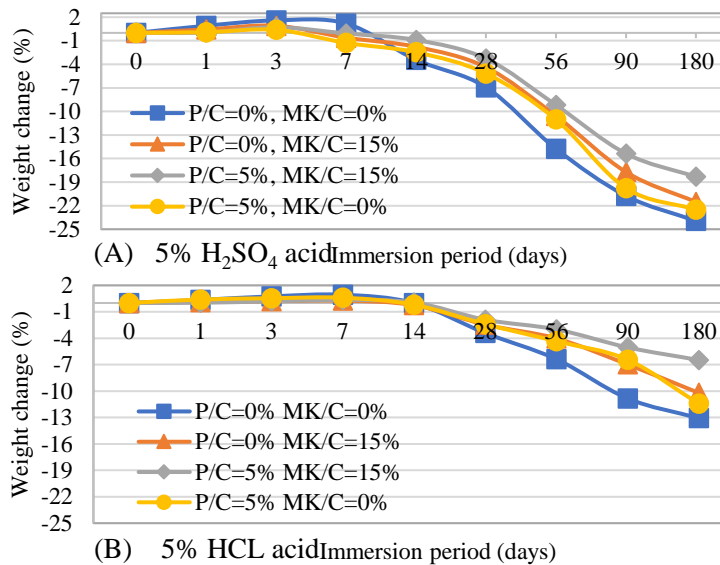


Figure 8. Concrete weight change after exposed to H₂SO₄ (A) and HCL (B) solutions

3.3 MICROSTRUCTURE PROPERTIES

SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAYS (EDX)

SEM images obtained using system magnifications of 5000x on concrete samples at the age of 7, 28, 56 and 270 days are shown in Table 4. In addition to SEM, all the samples were examined using EDX in order to identify the chemical elements contained in the sample.

COMPUTED TOMOGRAPHY SCAN TECHNOLOGY (CT scan)

The image segmentation technique was used to determine the volume, surface area and sphericity of voids of the hardened concrete from computed tomography scans (C.T.). Cube specimens (100 × 100 × 100 mm) were used to investigate the microscopic structure and pore size distribution for the modified concretes and to compare with those of conventional concrete cured 56 days. A general electric Phoenix V/Tome/X device with a voltage setting of 120 kV and a tube current of 200 μA was used for C.T. scans. The void defects were then detected using VG Studio Max 2.2 software. This test analysed the connection of the specimen components and displayed the pore size distribution in 2D and 3D connection with each other into a network. Also, pore percentage was analysed by examining the percentage of the voids volume compared with the total solid cubic volumes.

Figures 9 and 10 observed that the amount of CSH gel is increased and the Ca(OH)₂ content in the Mix 2 and Mix 3 is reduced as shown in the EDX analyse compared with the Mix 4 and (control concrete) Mix 1. The results show that increase of the amount of Si and Al in Mix 3. Also, the results show that the voids in concrete with 15% metakaolin and 5% polymers are seeming to be more circular than irregular shape as shown in the control mix leading to reduce the surface area and reduce the opportunity to be more interconnected with each other, that leads to reduction in

the porosity of the concrete. Figures 11 and 12 show that the modified concrete Mix3 has the lower porosity of the void volume has size larger than 75 mm³ compared with the control mixes. Also, it can be clearly seen that the number of voids larger than 75mm³ is lower in Mix 3. This improvement in the concrete microstructure provides the enhancement in mechanical and durability properties of concrete. SEM and CT scanner results show that the approach can be effectively applied in concrete related studies and provide further evidence on mechanical and durability properties.

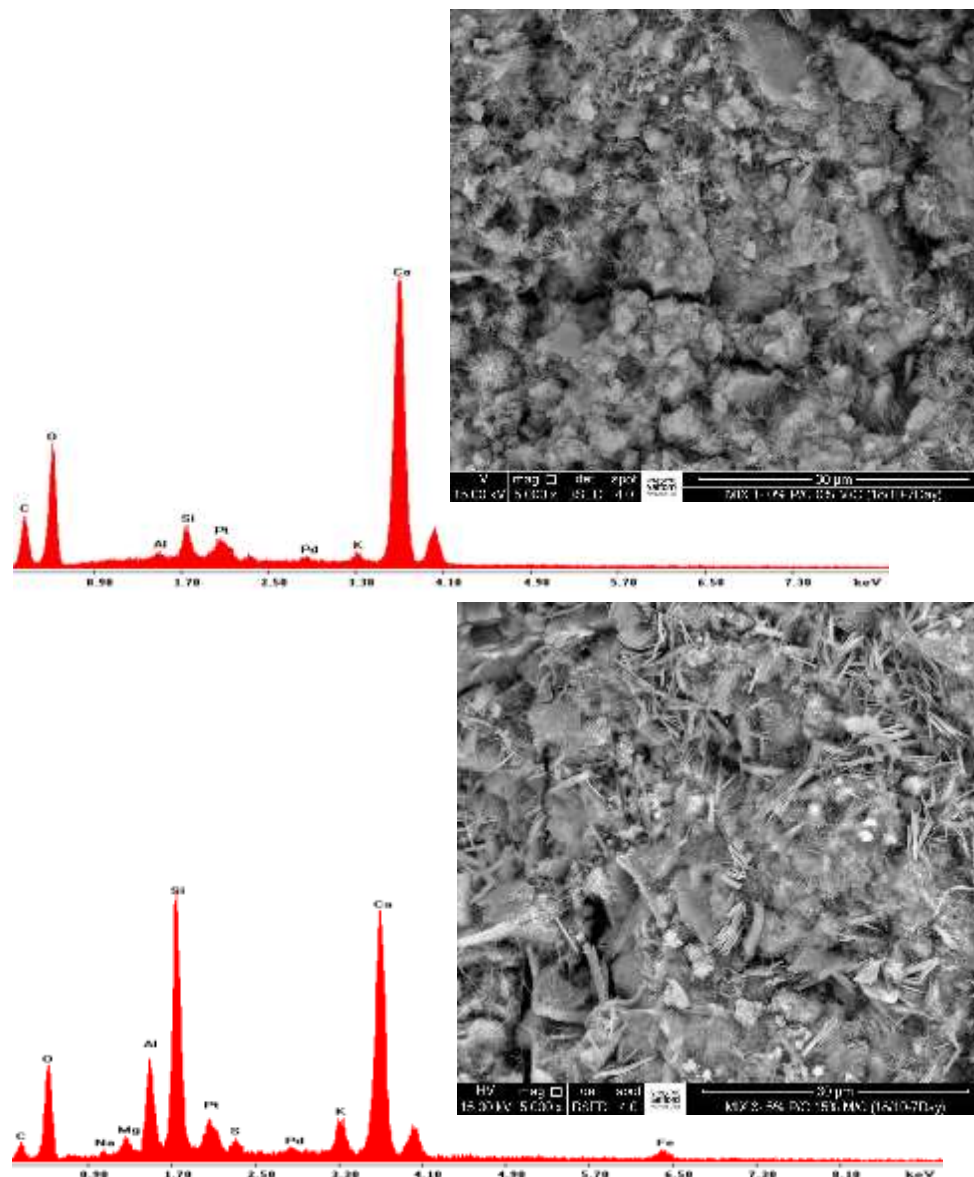


Figure 9: EDX results for the Mx1 (up) and Mix 3 (low) at age 7days, area at 5000x magnification

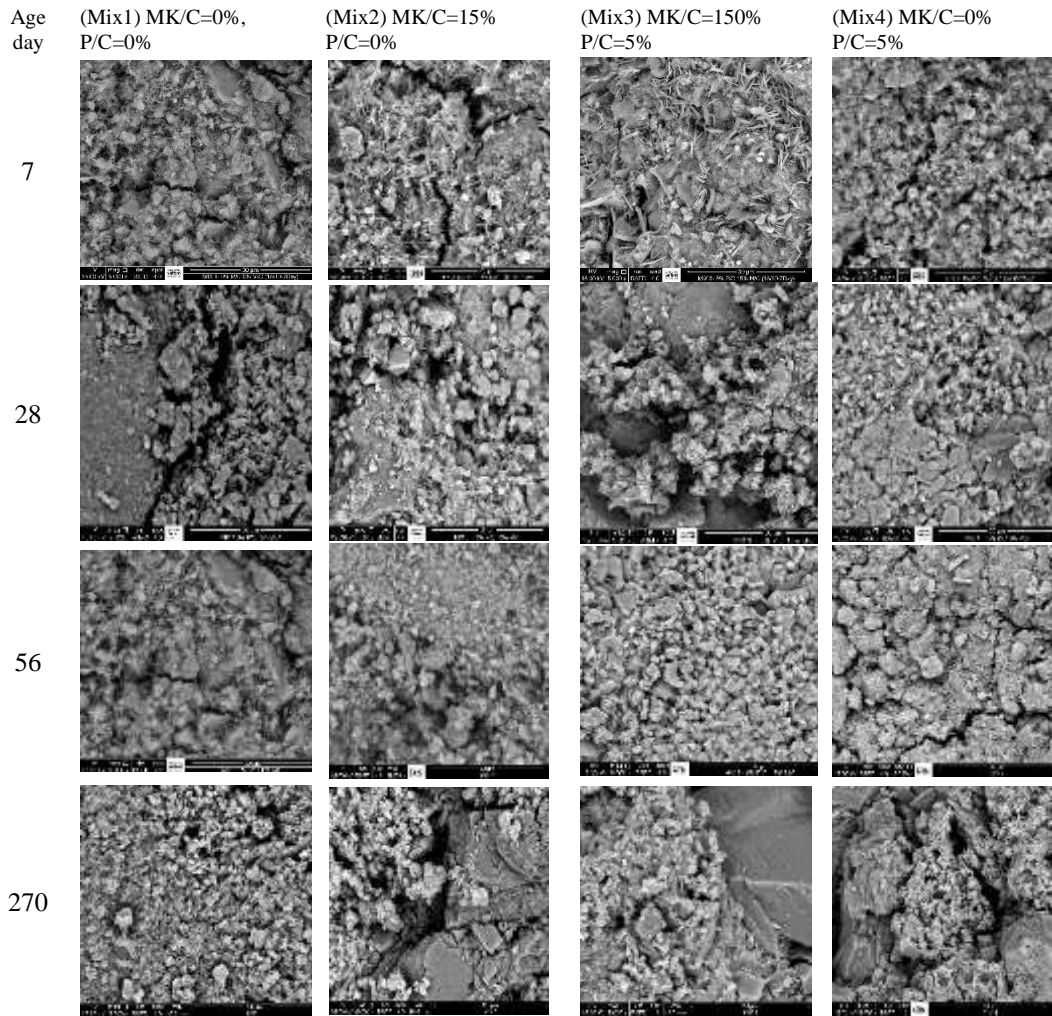


Figure 10: SEM for Mix1, Mix2, Mix3 and Mix4 at ages 7, 28, 56 and 270 days 5000x magnifications

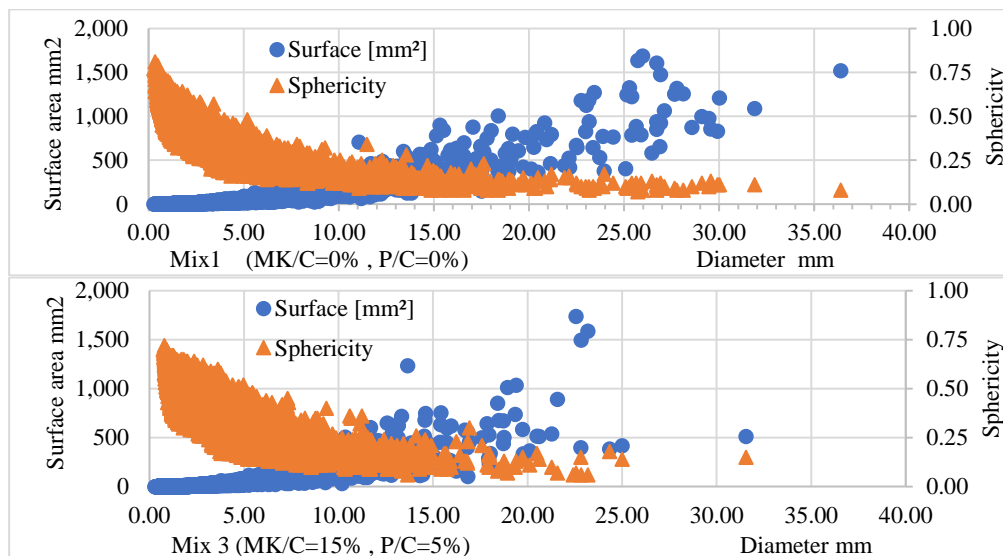


Figure 11: Voids surface area, diameter and sphericity at age 56 day

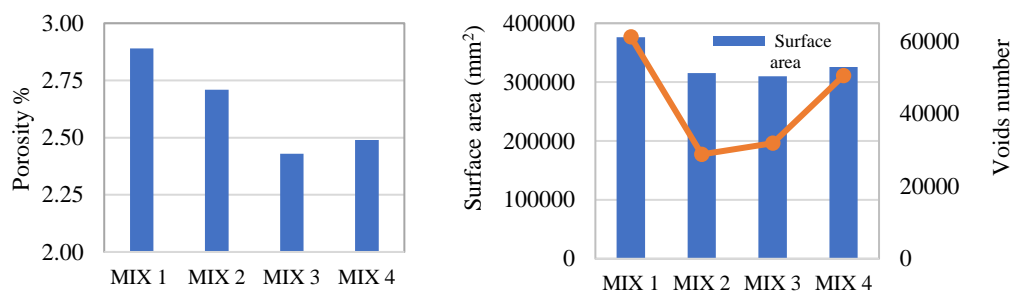


Figure 12: Concrete porosity, total voids surface area and total voids number

CONCLUSIONS

Partial replacement of cement by 15% metakaolin and adding of 5% polymers into concrete observed significant improvement in the mechanical and durability properties compared with the control concrete. SEM and CT scan technologies provides qualitative and quantitative description of the concrete properties. The visually analysis of presented SEM. Image and 3D analyses of CT scan prove that the concrete modified by both of metakaolin and two types of polymers have a significant change in the pores structure of concrete compared with other mixes. This modified concrete mixture has gained significant importance because of the requirements of environmental protection and sustainable construction in the future.

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