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Fracture behavior and pore structure of concrete with metakaolin

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Abstract. Metakaolin, a dehydroxylated product of the mineral kaolinite, is one of the most valuable admixtures for high-performance concrete applications, including constructing reinforced concrete bridges and impact- and fire-resistant structures. Concretes produced using metakaolin become more homogeneous and denser compared to normal-strength concrete. Yet, these changes cause a change of volume throughout hardening, and increase the brittleness of hardened concrete significantly. In order to examine how the use of metakaolin affects the fracture and mechanical behavior of high-performance concrete we produced concretes using a range of water to binder ratio (0.42, 0.35 and 0.28) at three different weight fractions of metakaolin replacement (8%, 16% and 24%). The results showed that the rigidity of concretes increased with using 8% and 16% metakaolin, while it decreased in all series with 24% of metakaolin replacement. Similar effect has also been observed for other mechanical properties. While the peak loads in load-displacement curves of concretes decreased significantly with increasing water to binder ratio, this effect have been found to be diminished by using metakaolin. Pore structure analysis through mercury intrusion porosimetry test showed that the addition of metakaolin decreased the critical pore size of paste phases of concrete, and increasing the amount of metakaolin reduced the total porosity for the specimens with low water to binder ratios in particular. To determine the optimal values of water to binder ratio and metakaolin content in producing high-strength and high-performance concrete we applied a multi-objective optimization, where several responses were simultaneously assessed to find the best solution for each parameter.

Keywords: Metakaolin; brittleness; fracture energy; pore structure; mechanical strength; optimization

1. Introduction

As part of the recent developments in concrete engineering, some industrial by-products are used used as important additives in partial replacement with cement. Among these, silica fume, ground granulated blast furnace slag and fly ash are the most widely used ones in producing high-strength and high-performance concrete, mostly because they have favorable engineering performances. As one of the relatively new admixtures, metakaolin is not produced as an industrial by-product, nor is is it entirely natural. Hence, unlike many other additives, metakaolin can be formed for specific conditions in appropriate size, mineral composition and color (Brooks *et al*. 2000). Dehydroxylation

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Dehydroxylation of kaolinite through thermal treatment in the temperature range 600–900℃ causes partial or complete breakdown of the crystal structure, resulting in the formation of highly reactive transition phases. At lower temperatures (500-600℃), on the other hand, calcination of kaolin-rich clay ($Al_2Si_2O_5(OH)_4$) results in the formation of metakaolin ($Al_2O_3.2SiO_2$ or AS_2). In the existence of water, the reaction between metakaolin and calcium hydroxide (CH) will produce calcium-silica-hydrate gel, calcium aluminate hydrate and alumina- silica hydrate crystalline products such as C_2ASH_8-stratlingite, C_4AH_{13} and rarely C_3ASH_6-hydrogarnet. The formation of crystalline phases depends on reaction temperature and AS_2/CH ratio (Murat 1983; Khatib *et al.* 1996). In addition, carbo-aluminates may also form if there is free carbonate. Based on XRD examination Frias and Cabrera (2001) showed that in Portland cement-metakaolin mixtures there was a rapid formation of C_2ASH_8 and C_4AH_{13}, while only C_2ASH_8 crystalline phase formed in lime-metakaolin mixtures. They observed no C_4AH_{13} formation and concluded that C_4AH_{13} is crystallized in much less abundance than C_2ASH_8 (Frias and Cabrera 2001). Hydration reaction and concrete properties depend on the reactivity of metakaolin in addition to the calcination conditions and purity of clay. The degree of reactivity is determined using Chapelle test and defined as consumption ratio of 1 g of CH. CH content in hardened concrete can be assessed through thermo-gravimetric and differential thermal analysis. Asbridge *et al*. (1994) calculated this ratio for metakaolin as 1050 mg CH/g, while it is 875 and 427 mg CH/g for silica fume and fly ash, respectively (Asbridge *et al*. 1994). In addition, pozzolanic reactivity of metakaolin can be estimated by comparing the hydration heat of pozzolan-PC mortar mixtures which can be used for other pozzolans (Frias *et al*. 2000).

The effect of metakaolin addition on fresh and hardened properties of normal and self-compacting concrete has been detailed in a number of studies (Brooks *et al*. 2001; Ding and Li 2002; Badogiannis *et al*. 2004; Badogiannis *et al*. 2005; Guneyisi *et al*. 2008; Siddique and Klaus 2009; Cassagnabère *et al*. 2010; Ramezanianpour *et al*. 2012; Guneyisi *et al*. 2014; Sfikas *et al*. 2014; Akcay and Tasdemir 2015). It has been postulated that increasing the amount of metakaolin in concrete enhances the compressive and splitting tensile strength (Qian and Li 2001; Ding and Li 2002; Badogiannis *et al*. 2004; Badogiannis *et al*. 2005; Poon *et al*. 2006; Guneyisi *et al*. 2008; Siddique and Klaus 2009; Cassagnabère *et al*. 2010; Hassan *et al*. 2012; Madandoust *et al*. 2012; Ramezanianpour *et al*. 2012; Guneyisi *et al*. 2014; Sfikas *et al*. 2014). It is now known that replacement of cement in part by metakaolin increases the strength of concrete, but it is not yet clear whether metakaolin is more effective than silica fume in increasing the strength. It is obvious that the use of metakaolin will have broad application areas in producing high performance concrete, if its effect in enhancing the concrete strength in a wider range is demonstrated (Abdul Razak and Wong 2005; Duan *et al*. 2013). Caldarone *et al*. (1994) produced concretes with silica fume or metakaolin at water/binder ratio of 0.40 and found that mixtures including 5 and 10% of metakaolin had 10% more compressive strength than that with the same amount of silica fume. The mixture with 5% of metakaolin had the highest compressive strength (78.3 MPa) at the end of a year, which decreased gradually with using 10% of metakaolin, 10% of silica fume and finally 5% of silica fume (63.5 MPa). Curcio *et al*. (1998) conducted a study on mortars with 0.33 water to binder (w/b) ratio in which 5% of cement was replaced by metakaolin or silica fume to observe the variations in compressive strength. The rate of strength at early ages was unexpectedly much quicker in mortars with metakaolin than those with silica fume. The authors explained the early high reactivity of metakaolin to be a result of two different Al_2O_3 contents as Al_{IV} and Al_V and stated that the formation of alumina phases (especially C_2ASH_8) increased the early strength of mortars.

Qian and Li (2001) found that tensile and bending strength increased with the amount of metakaolin in concretes containing 5, 10 and 15% metakaolin. Concrete in which 15% cement was replaced by metakaolin had 28% more tensile strength than the reference concrete which contains metakaolin. On the other hand, Courard *et al*. (2003) produced mortars with metakaolin using a replacement range of 5-20% and showed that mortars with metakaolin had lower flexural strength than the reference samples at 3 days, while they all gave the same results at 7 days. Moreover they found that metakaolin included mortars had higher tensile strength at 14 and 28 days. Guneyisi *et* (2008) stated that splitting tensile strength of concretes with 0.35 and 0.55 water/binder ratios increases with increasing metakaolin content.

On the other hand, there are limited studies regarding the possible effects of using metakaolin fracture properties of concrete (Moukwa *et al*. 1993; Dubey and Banthia 1998; Vejmelková *et al*. 2010). The concrete phases in most of these studies were reinforced using fibers, and this made it difficult to determine the effects of metakaolin accurately. Dubey and Banthia (1998) tested high strength concrete with metakaolin or silica fume under bending and found that concrete with pozzolans had 15% higher fracture modulus than the plain concrete. They stated that addition of steel fiber was necessary to reach this value of fracture modulus. They also showed that steel fiber reinforced concrete with metakaolin exhibit the best performance after peak load on stress-strain curve, while that with silica fume demonstrated more brittle behavior and less energy dissipation performance.

In this work, we investigated how the use of metakaolin as partially replaced material with cement affects the mechanical and fracture characteristics and the pore structure of concrete. For these purposes, we tested such possible effects on concrete samples with different weight fractions of metakaolin replacement (8%, 16% and 24%) and a range of w/b ratio (0.42, 0.35 and 0.28).

2. Experimental studies

2.1 Materials

For experimental investigations CEM I 42.5R cement was used in all concrete mixtures. Compressive strength of standard RILEM Cembureau of mortars was found as 48.1 and 60.5 MPa at 7 and 28 days, respectively. Some of the chemical and physical characteristics of the cement that we used are listed in Table 1.

The metakaolin powder used in mixtures was a kaolinite mineral formed by the combination of

Table 1 Physical and chemical characteristics of cement

<table>
<tr><td colspan="4">Specific gravity</td><td>3140 kg/m^3</td><td colspan="2" rowspan="2">Time of setting (Vicat Test)</td><td>initial set</td><td colspan="2">183 minutes</td></tr>
<tr><td colspan="4">Blaine specific surface</td><td>3490 cm^2/g</td><td>final set</td><td colspan="2">217 minutes</td></tr>
<tr><td colspan="4">Volume Stability (Le Chatelier)</td><td>1 mm</td><td colspan="5"></td></tr>
<tr><td colspan="2" rowspan="2">Compound composition (%)</td><td colspan="2">C_3S</td><td colspan="2">C_2S</td><td colspan="2">C_3A</td><td colspan="2">C_4AF</td></tr>
<tr><td colspan="2">62.82</td><td colspan="2">10.15</td><td colspan="2">6.08</td><td colspan="2">10.47</td></tr>
<tr><td colspan="10">Chemical composition (%)</td></tr>
<tr><td>SiO_2</td><td>Al_2O_3</td><td>Fe_2O_3</td><td>CaO</td><td>MgO</td><td>SO_3</td><td>Insoluble residue</td><td>Loss on ignition</td><td>Free lime</td><td>Total alkalis</td></tr>
<tr><td>20.07</td><td>4.49</td><td>3.44</td><td>64.66</td><td>1.23</td><td>2.76</td><td>0.58</td><td>2.61</td><td>1.21</td><td>0.53</td></tr>
</table>

Table 2 Grading of aggregates used in the mixtures

Sieve size (mm)	Percentage passing		
	Crushed stone	Crushed sand	Natural sand
16	100	100	100
8	57	100	100
4	2	85	95
2	1	46	71
1	1	21	49
0.50	1	8	32
0.25	0	3	17
0.120	0	1	9

tetrahedral sheet of silica and octahedral sheet of alumina with 7.2 Å inter-laminar distance. Embedded water with a proportion of 1:2 between SiO_2 and Al_2O_3 lamina evaporated during calcinations to form metakaolin. The chemical composition of metakaolin used is as follows: SiO_2=53.0; Al_2O_3=48.8; Fe_2O_3=0.43; CaO=0.02; MgO=0.03; TiO_2=1.70; K_2O=0.19; Na_2O=0.23. Its specific gravity and specific surface area are 2.50 g/cm^3 and 13m^2/g, respectively (Particle size distribution: d_{50}~1.3 μm and 66% passed 2 μm sieve). It is seen that this metakaolin can be identified as N type mineral additive according to ASTM C349.

Crushed limestone, crushed sand and natural sand were used as aggregates. Specific gravities of these three materials were 2720, 2610, and 2600 kg/m^3, respectively, while effective water absorptions were calculated as 1.1% , 1.2% and 2.1%, respectively using ASTM C127-C128 1994. The grading of used aggregates is given in Table 2. In order to regulate the slump of fresh concrete close to that of self-compacting concrete we used a polycarboxylic ether-based superplasticizer.

2.2 Mixture proportions

We produced concretes using three different w/b ratios (0.42, 0.35 and 0.28) and four different replacement ratios of cement by metakaolin (0, 8, 16 and 24%). Mixture proportions and some of the fresh state characteristics of all casted concrete are presented in Table 3. The numbers used with the letters C and MK in the description code represent w/b ratio and replacement ratio of metakaolin, respectively. Exception, however, are the control concretes which contain no metakaolin and are coded with only w/b ratios.

For sample preparation, we first blended the cement and metakaolin in dry condition, and then added the aggregates to mix them together. Care was taken to provide homogeneity in the mixture by adding the superplasticizer and water into the mixture gradually. The samples were cast in steel moulds after finishing the fresh state examinations. They were demoulded after 24 h and then saturated further with lime at 20^{o}C in a water tank until the testing day.

2.3 Experimental test details

We performed the tests to determine the fracture energy (G_F) following the recommendation by RILEM 50-FMC Technical Committee (1985). The three-point bending test setup is shown in Fig.

Table 3 Compositional and some fresh state properties of the mixtures (1 m^3)

	C42	C42MK8	C42MK16	C42MK24	C35	C35MK8	C35MK16	C35MK24	C28	C28MK8	C28MK16	C28MK24
Cement (kg)	415	382	343	310	547	508	460	412	589	530	488	442
Water (kg)	174	174	172	171	190	192	190	188	165	161	163	163
MK (kg)	0	33	66	98	0	44	88	130	0	46	93	140
Natural sand (kg)	343	343	338	337	315	319	316	313	319	312	315	316
Crushed sand (kg)	650	650	640	639	598	604	599	593	605	592	598	598
Crushed stone (kg)	868	868	855	853	798	806	800	792	808	790	798	799
Superplasticizer, (kg)	7.17	8.25	7.58	11.2	5.86	6.51	7.10	8.33	6.61	8.68	11.8	15
Air (%)	0.7	1.2	0.7	1.1	0.6	0.6	0.7	0.8	1.6	1.2	0.8	0.5
Flow radius (cm)	65	62	62	61	65	63	63	60	58	56	57	56
Unit weight (kg/m3)	2454	2459	2420	2420	2453	2479	2459	2436	2493	2451	2466	2470

1 as schematic representation and photograph. A linear variable displacement transducer was used to measure the deflection. We used a closed-loop testing machine (Instron 5500R) with a maximum capacity of 100 kN to apply the load. The tests to define the fracture energy were applied on beams that are 500 mm in length and 100 × 100 mm in cross section with a notch to depth ratios of 0.40. In order for large aggregates to be included in large quantities, the effective cross section was decreased to 100 × 60 mm, with a support span of 400 mm in length. To keep the tests stable we used crack mouth opening displacement (CMOD) as a feedback control variable. Hence, we obtained the load vs. CMOD and load vs. displacement at mid-span curves simultaneously for each sample. A constant loading rate of 0.02 mm/minute (for LVDT) was used for all the beams. The fracture energy was evaluated using the area under the load vs. deflection at mid-span curve (W_0). The fracture energy was calculated using the following expression (Rilem TC 50-FMC 1985)

$$G_F = \frac{W_0 + mg\frac{S}{L}\delta_s}{B(D-a)} \tag{1}$$

where, B, D, a, S, L, m, δ_s, and g are the width, depth, notch depth, span, length, mass, specified deflection of the beam and gravitational acceleration, respectively. The characteristic length (l_{ch}), which can be used to measure the brittleness, is calculated using the following expression (Hillerborg 1976)

$$l_{ch} = \frac{EG_F}{(\acute{f_t})^2} \tag{2}$$

where f'_t is the direct tensile strength of concrete, but in our case we used the splitting tensile strength (f_{st}) instead. For high strength concrete prepared using normal aggregate, increasing the compressive strength reduces the characteristic length, which may indicate an increase in

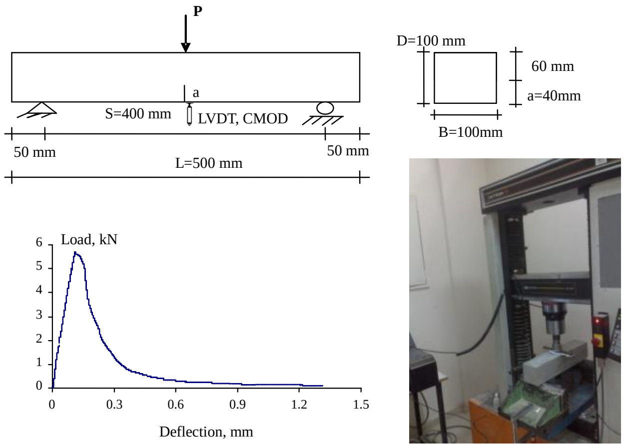

Fig. 1 Schematic representation and photograph of the three-point bending test setup and the graphical evaluation of fracture energy

brittleness. Net bending strength of concrete was determined using beam specimens, while cylindrical specimens (Ø100 mm×200 mm) were used to find the modulus of elasticity and compressive strength. Splitting tensile strength test was also applied on the broken parts of the beam from the bending tests. Since the samples contained pozzolan, all the mechanical tests were conducted after 50 days from the production.

In addition to the mechanical tests, Mercury Intrusion Porosimetry (MIP) tests were applied to paste specimens of different ages to show the variations in critical pore diameter (the pore width corresponding to the highest rate of mercury intrusion per change in pressure). By this way, it is also possible to show the alteration in pore structure with addition of metakaolin. For this purpose, first paste phases of each concrete series were produced and cylindrical samples with 8 mm diameter and 15 mm height were prepared. The plastic laboratory tubes were filled with paste and then sealed with paraffin. At the test age the vials were broken.

All the specimens for MIP test were treated by propanol for ceasing the hydration and dried at 70℃ for 4 hours before testing. The tests were done on a Quantachrome-33 in the Biomaterials Research & Characterization Laboratory at Istanbul Technical University. The maximum intrusion pressure used in the experiment was 220 MPa, the contact angle of mercury on the solid was 130° and the surface tension of mercury was 48.5 N/m^2. MIP test is based on introducing mercury (as a non-wetting fluid) with a pressure into a pore. It is assumed that the structure consists of interconnected, entirely open cylindrical pores. Washburn equation ($r=-(2\gamma\cos\theta)/p$; where r is radius, γ is surface tension, θ is contact angle and p is intrusion pressure) is usually applied assuming that the pores are equally accessible to the mercury.

3. Experimental results and discussion

3.1 Mechanical and fracture properties

The mechanical properties and some of the fracture parameters of the tested concrete are listed in Table 4. In all series, compressive strength of concretes enhanced with increasing metakaolin

Table 4 Mechanical properties and fracture parameters of concrete produced

	f_c, MPa	E, GPa	W_0, Nmm	G_F, N/m	δ_0, mm	f_{flex}, MPa	f_{st}, MPa	l_{ch}, mm
C42	83.7	32.7	467	83.4	0.41	5.2	6.1	59.8
C42MK8	87.5	39.9	440	77.8	0.39	5.6	6.1	64.0
C42MK16	90.1	37.5	319	57.9	0.28	5.9	5.7	50.6
C42MK24	92.9	40.8	316	57.6	0.30	5.9	5.9	51.2
C35	88.1	36.4	466	83.6	0.39	6.1	7.0	49.0
C35MK8	88.9	39.1	345	61.3	0.27	6.8	6.9	39.2
C35MK16	90.9	41.4	366	65.7	0.32	5.9	6.8	45.0
C35MK24	96.3	39.0	382	65.1	0.33	5.5	6.5	46.8
C28	98.6	40.8	410	73.9	0.33	7.4	7.1	46.0
C28MK8	110.0	44.6	364	62.6	0.26	7.4	6.9	44.9
C28MK16	117.4	48.4	340	58.0	0.25	6.6	7.1	42.2
C28MK24	114.6	43.6	349	59.7	0.27	6.0	6.6	47.7

f_c: compressive strength; E: modulus of elasticity; G_F: fracture energy; δ_0: final crack mouth opening displacement; f_{flex}: bending strength; f_{st}: splitting tensile strength; l_{ch}: characteristic length.

content and this effect is more significant in the samples with high w/b ratio. The compressive strength of other reference concrete series with w/b ratios of 0.35 and 0.28 were found as 88.1 and 98.6 MPa, respectively. While the average compressive strength of reference concrete with 0.42 w/b ratio was 83.7 MPa, replacement of 24% cement by metakaolin resulted in 12% increase in compressive strength. Since we aimed to produce self-compacting concrete with fresh state behavior, it was necessary to use high amount of superplasticizer, which in turn, decreased the amount of the large pores, resulting in higher compressive strength in all concretes. Also, moduli of elasticity of concretes increased with increasing the metakaolin content in all series, with the exception of 24% replacement ratio at which a relative decrease in modulus of elasticity values was observed. For example, modulus of elasticity for the C28 concrete increased from 40.8 to 48.4 GPa with 16% of metakaolin replacement, and then decreased to 43.6 GPa with 24% replacement. A similar effect is also seen on all other mechanical properties.

In series with low w/b ratios the bending strength of concretes decreased with using metakaolin, while no significant change was observed in their splitting tensile strength. The loading speed in the bending test was slower than that in the splitting test, which increased the possibility for the cracks in matrix phase to initiate and propagate towards the nearby defects. Thus, it has been observed that the mechanical improvement in compressive strength by using metakaolin may have different reflections on micro-structural properties. On the other hand, for the concretes with 0.42 w/b ratios there was a significant increase in bending strength. The bending strength of reference concrete of this series has been found 5.2 MPa, while it increased to 5.6, 5.9 and 5.9 MPa for 8, 16 and 24% of metakaolin addition, respectively. Consequently, it can be said that with increasing amount of metakaolin it is possible to gain increases in bending and splitting tensile strength, as well as compressive strength.

The effect of metakaolin addition on the load-CMOD curves is shown in Fig. 2, where a representative sample for each series has been plotted. It can be seen that peak load decreases with increasing w/b ratio in the reference sample without metakaolin, while this effect is diminished

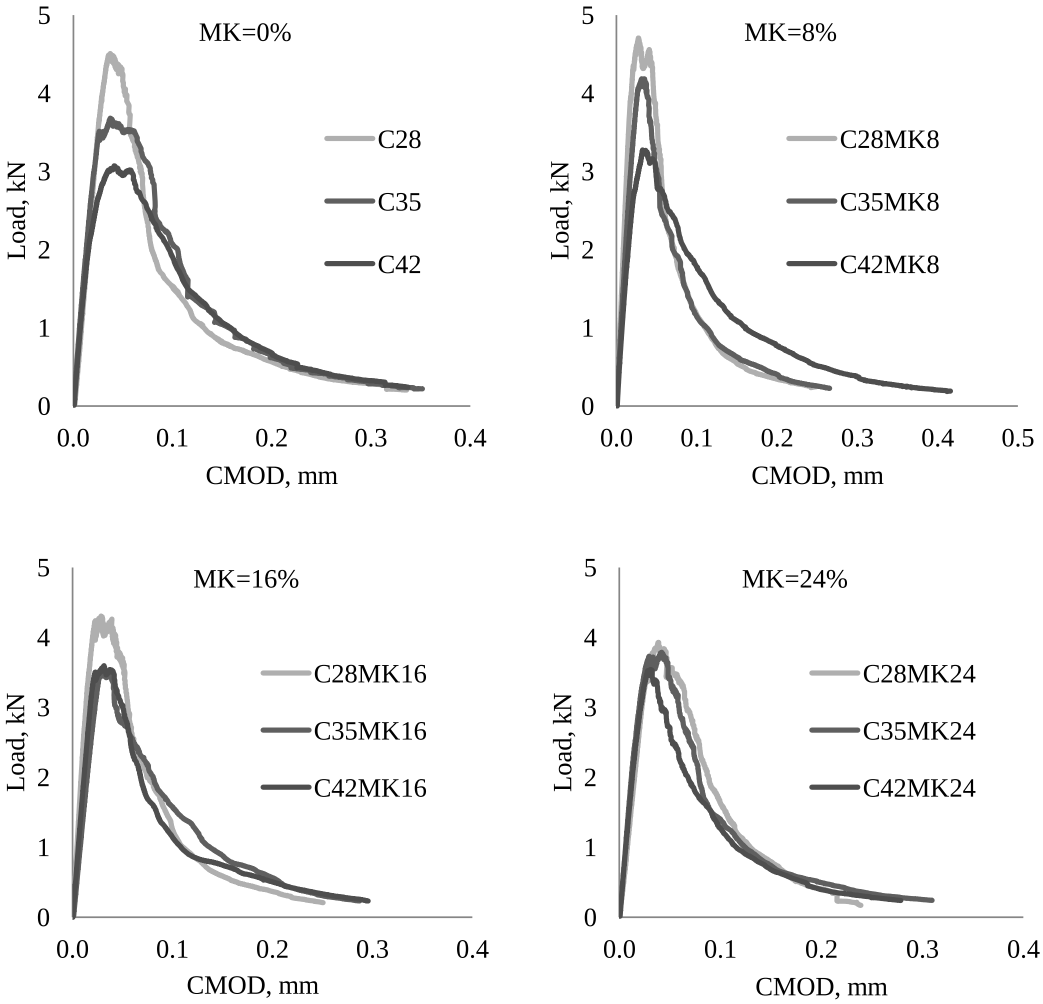

Fig. 2 The representative load-CMOD curves of concrete series

with increasing amount of metakaolin. This indicates that the fracture behavior of concrete with low amount of metakaolin was primarily controlled by w/b ratio, while with increasing amount of metakaolin concrete behavior began to be governed by metakaolin products. If higher amount of metakaolin is used to produce concretes the difference between load-displacement curves will be expected to be subsided. On the other hand, decrease in w/b ratio, which would increase the concrete strength, reduced the value of final displacement as well as deflection of midpoint of beam span, indicating that the concrete was getting less tough.

Similarly, the representative curve for each series is shown in Fig. 3 to reveal the effect of metakaolin content at a constant w/b ratio. The increase in the amount of metakaolin had some effects on the pre-peak part of the curve mainly because of the formation and localization of micro-cracks before the pre-peak load that occurred at small CMOD. On the other hand, the use of higher amount of metakaolin reduced the density of toughening mechanisms that are operational at the descending branch of the curve after peak load.

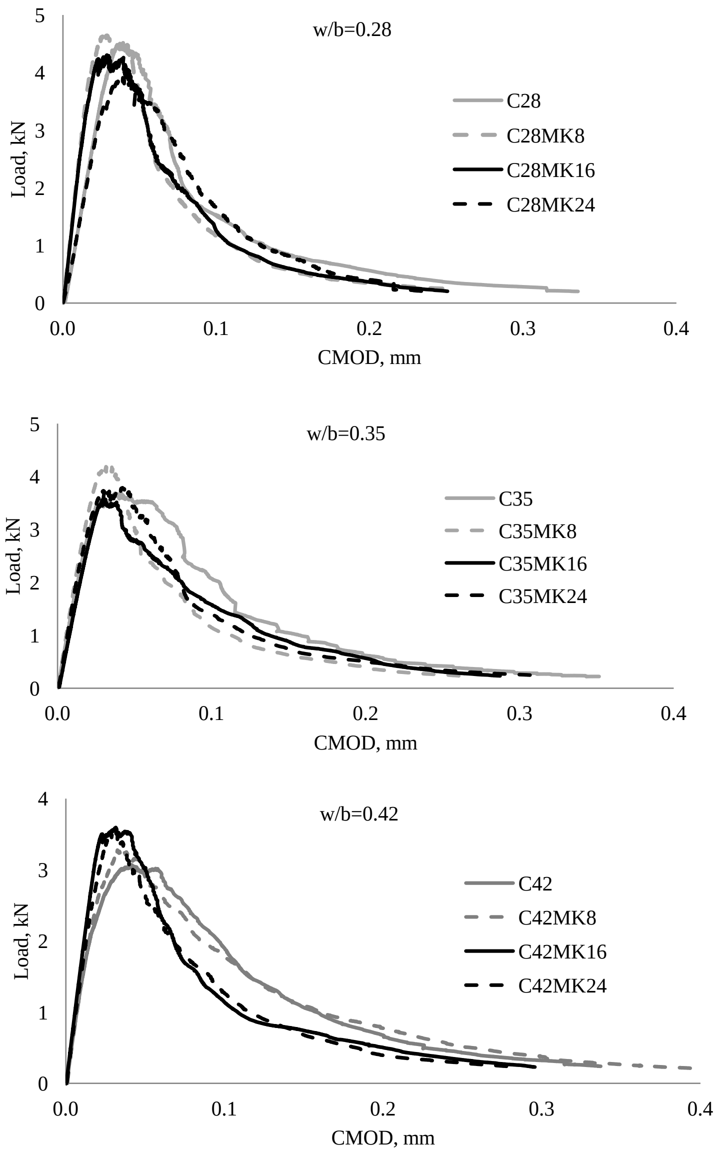

Fig. 3 The effect of adding metakaolin on load-CMOD curves of concretes with a constant w/b ratio

The results of fracture energy calculated from the area under the curve is shown in Fig. 4, where it can be seen that even in relatively small quantities (8%) of metakaolin addition has an effect of decreasing the fracture energy in comparison with the reference sample. However, no significant difference in the fracture energy values has been found between the concretes with 16 and 24% of metakaolin replacement. The results obtained are comparable with the findings of Vejmelková *et al*. (2010) who produced reference concrete with 0.30 w/b ratios and concrete with 10% metakaolin and found that effective fracture toughness was less in concrete with metakaolin (63 N/m) than that of the reference concrete (85 N/m) at 28th day, while it was contrarily higher at 90th day (74 and 58 N/m).

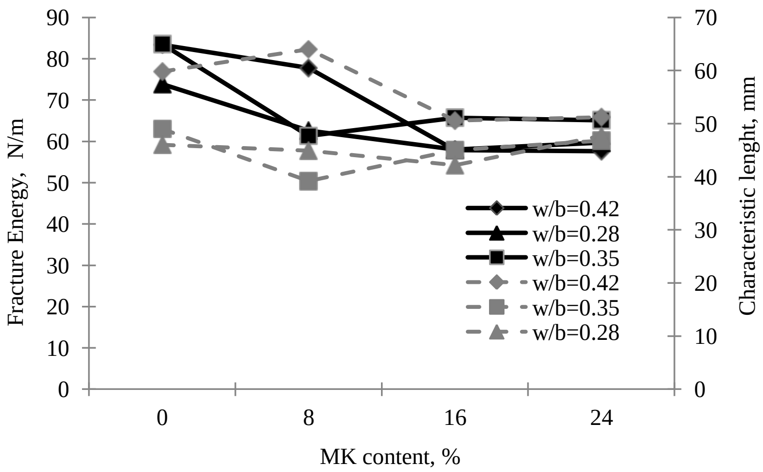

Fig. 4 Variation of fracture energy (solid lines) and characteristic length (dashed lines) of concretes with w/b ratio

As seen in Fig. 4, the amount of metakaolin used has an effect on the brittleness of material because of the alteration in microstructures. It is shown that 8% of metakaolin addition increased the characteristic length of concrete (at 0.42 w/b ratio), meaning that material became less brittle. Its fracture energy, on the other hand, decreased relative to that of the reference concrete. This is because the use of metakaolin decreased the critical pore diameter, which changed the micro cracking characteristics and led to the formation of a denser and more rigid matrix phase.

At the same w/b ratio, characteristic length of concrete decreased with increasing amount of metakaolin, due possibly to the rapid localization of micro-cracks as the material becomes more brittle, which led to an increase in both width and amount of cracks, hence decreasing CMOD or the ability of making deflection. On the other hand, for the concrete with 0.35 w/b ratio this effect is observed immediately at 8% of metakaolin replacement, which caused a decrease in characteristic length compared to the reference concrete of C35. For the concrete with 0.28 w/b ratios, although the fracture energies decreased with adding metakaolin in more abundance, there was no significant effect on brittleness.

3.2 Pore structure

As previously mentioned, for cementitious materials it is important to identify the possible effects of using metakaolin on the pore structure. MIP test results obtained from the paste specimens for 2 and 28 days are given in Fig. 5 with the calculated porosities given in Table 5. The critical pore diameter of the paste specimen seems to have decreased with increasing metakaolin content, particularly at 28th day. We determined the total porosity as the volume ratio of intruded mercury to the sample. We observed that the total porosity enlarged with increasing the metakaolin content by up to 24 percent replacement. The reason for this is that there was an insufficient amount of CH to react with metakaolin at 2-days in particular. In addition, since metakaolin is composed of fine particles, it has a dense microstructure. For the samples with high w/b ratios (0.42), the critical pore diameter, an important parameter for durability, was observed to have been decreased with the use of metakaolin even at early ages (2-days). In the samples with lower w/b

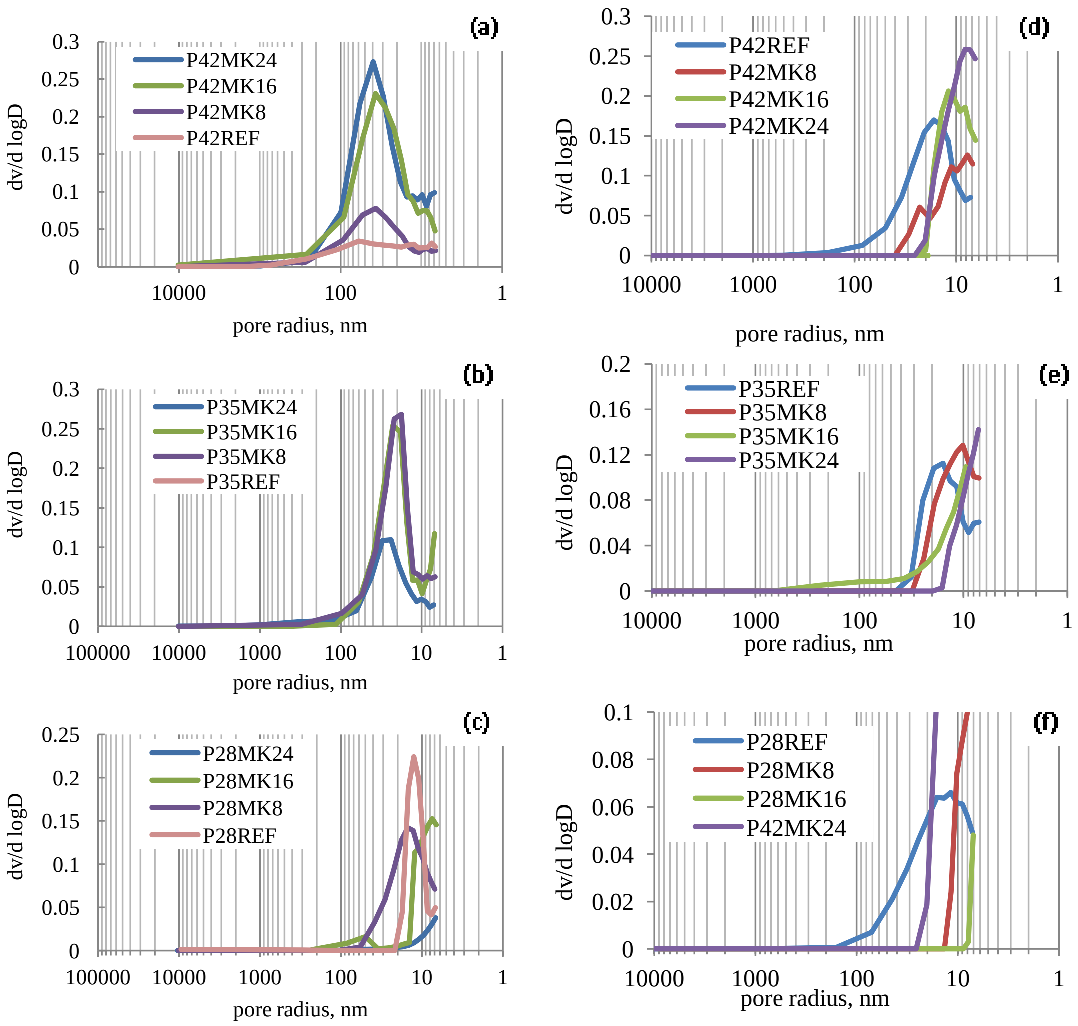

Fig. 5 dv/dlogD curves of paste samples from MIP analysis at 2 (a-b-c) and 28 (d-e-f) days

ratios (0.35 and 0.28), the use of 8% metakaolin increased the critical pore diameter, while further additions decreased significantly.

4. Effects of w/b ratio and metakaolin content on the mechanical properties

As pointed out above all the mechanical properties of concretes varies with both metakaolin content and w/b ratio. To clarify the effect of each parameter on these properties we performed regression analysis, where linear relationship between each parameter and the mechanical properties were established. To test whether the regression value (R) is significant at 95% confidence level, F test was performed. The results are summarized in Table 6, where value of mean F, if <0.05, indicates that the model terms are significant.

Table 5 MIP test results showing the 2 and 28 days porosities of the paste samples

	Cumulative intruded		Critical pore		Total porosity, %	
Time, days	2	28	2	28	2	28
P42	0.074	0.104	59.34	16.65	8.54	15.35
P42MK8	0.1239	0.0384	36.68	7.743	10.94	7.85
P42MK16	0.2419	0.0531	36.94	8.171	29.70	10.64
P42MK24	0.3082	0.0785	39.58	7.32	29.41	12.60
P35	0.1954	0.055	14.39	15.78	19.76	8.39
P35MK8	0.1308	0.0569	17.76	10.1	22.21	9.33
P35MK16	0.1222	0.0967	22.85	<6.711	21.81	9.64
P35MK24	0.1246	0.0427	23.87	<6.169	11.26	5.49
P28	0.0789	0.101	12.6	9.046	9.61	9.06
P28MK8	0.0879	0.0286	15.04	<7.16	12.48	3.90
P28MK16	0.0999	0.0047	7.49	<7.014	11.99	0.59
P28MK24	0.0586	0.0192	<6.77	<6.204	6.99	2.10

Table 6 Results of F-test showing the significance of correlation of both w/b ratio and metakaolin content (mk) with the mechanical properties

	R correlation	F	*mean(F)*
w/b vs. compressive strength	0.8137	19.5887	0.0013
mk content vs. compressive strength	0.3858	1.7489	0.2155
w/b vs. modulus of elasticity	0.6968	9.4400	0.0118
mk content vs. modulus of elasticity	0.4244	2.1969	0.1691
w/b vs. bending strength	0.7191	10.7096	0.0084
mk content vs. bending strength	0.2899	0.9178	0.3606
w/b vs. splitting tensile strength	0.8440	24.7585	0.0006
mk content vs. splitting tensile strength	0.3082	1.0494	0.3298
w/b vs. fracture energy	0.2431	0.6281	0.4465
mk content vs. fracture energy	0.7717	14.7210	0.0033
w/b vs. characteristic length	0.6820	8.6940	0.0146
mk content vs. characteristic length	0.2090	0.4567	0.5145

As is shown in Table 6, the correlation between w/b and compressive strength was significant, but there is no any meaningful linear variation between the metakaolin content and compressive strength. Furthermore, w/b ratio has been found to correlate with modulus of elasticity, bending and splitting tensile strength. Interestingly, the results show that no significant correlation is observed between the w/b ratio and fracture energy, while there is a meaningful correlation between the metakaolin content and fracture energy (with R and probability F values of 0.77 and 0.0033, respectively). Conversely, the characteristic length of concrete correlates with w/b ratio, but not with metakaolin content.

Table 7 Model fitting results for each response from regression analysis

	R value
f_c=358.85-1402.36*(w/b)+0.47*(mk)+1774.87*(w/b)^2	0.970
E=53.45-47.85*(w/b)+0.74*(mk)-0.03(mk)^2	0.897
G_f =76.8-0.82*(mk)	0.770
l_{ch} =20.28+81.53*(w/b)	0.685
p_{2days}=16.18+4.74 *(w/b)+6.90*(w/b)*(mk)	0.734
p_{28days}=-14.45+110.04* (w/b)-1.10*(mk)+1.69* (w/b) *(mk)-106.22*(w/b)^2 +0.02(mk)^2	0.899

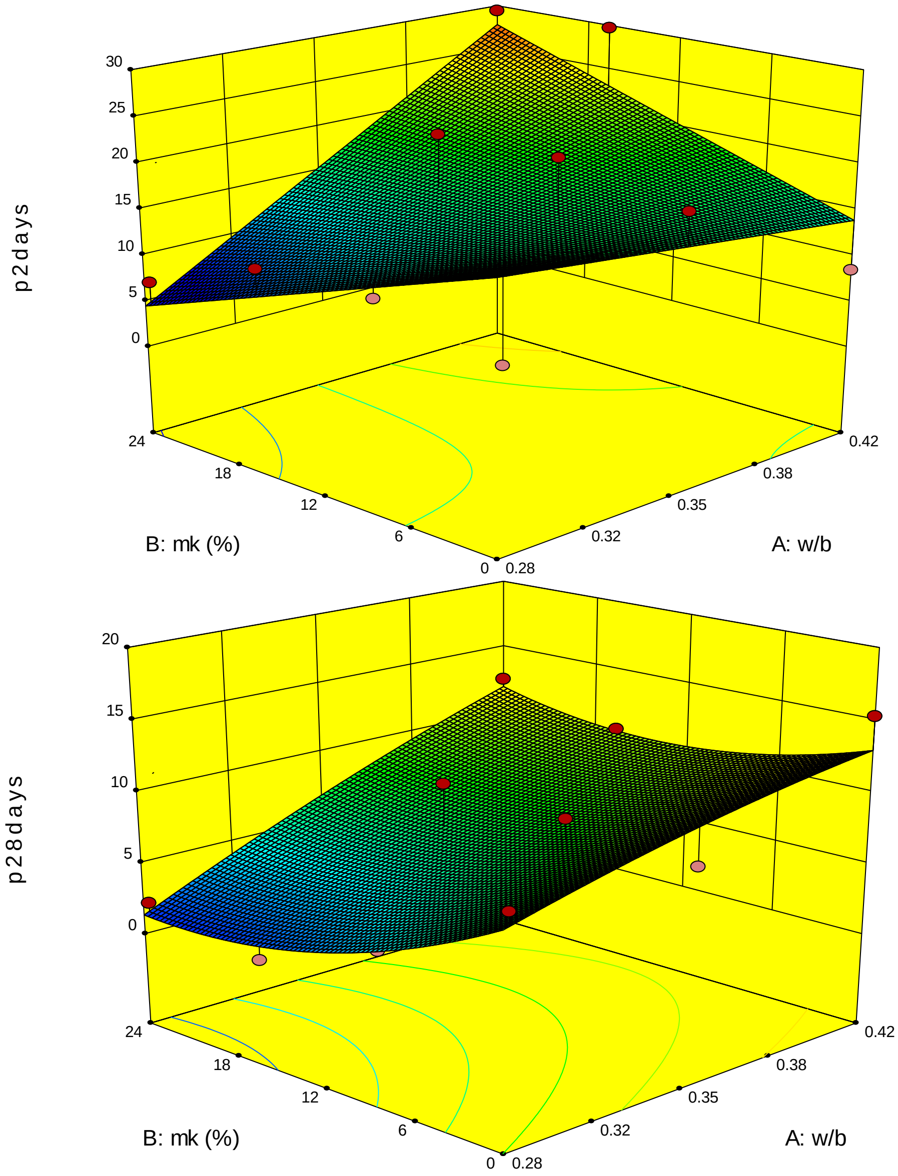

Fig. 6 Variation of 2 and 28 days total porosity with w/b ratio and metakaolin content

5. Optimization of water to binder ratio and metakaolin content

The experimental results demonstrate that the desired properties (e.g. high-strength and high-performance) in concrete cannot be achieved using the lowest w/b ratio and highest metakaolin content, suggesting that optimum values for both variables need to be defined using a more rigorous approach. However, to find out the optimum solutions for high-strength and high-performance concretes, the mechanical properties (with brittleness) and pore structure of concrete should also be considered. The compressive strength (f_c), fracture energy (G_F), modulus of elasticity (E), characteristic length (l_{ch}) were chosen for mechanical and fracture properties, whereas 2-days (p_{2days}) and 28-days total porosity (p_{28days}) values of paste samples were taken into account for durability issues. All these properties have been defined with respect to w/b ratio and metakaolin content. Then these factors were estimated through polynomial regression by applying analysis of variance.

A multi objective simultaneous optimization approach was applied by integrating the Response Surface Method (RSM). The details of RSM optimization technique and Response Surface Method are given in Akcay and Tasdemir (2009). The relevant ranges of the independent variables used in the modeling are as follows

$$\begin{gathered} 0.28 \leq w/b \leq 0.42 \\ 0\% \leq mk\ content \leq 24\% \end{gathered} \tag{3}$$

For two variables, the quadratic model can be determined for each of the responses using the following expression

$$y = b_0 + b_1\left({}^{w}/_{b}\right) + b_2(mk) + b_3\left({}^{w}/_{b}\right)^2 + b_4(mk)^2 + b_5\left({}^{w}/_{b}\right)(mk) \tag{4}$$

where b_0, b_1, b_2, b_3, b_4, and b_5 are the coefficients defined using analysis of variance.

A polynomial model for each of the parameters indicated above was generated using the experimental data from the twelve concrete series. The model fitting results for each response are listed in Table 7. The variations of 2 days and 28 days of total porosity with w/b ratio and metakaolin content are given in Fig. 6 to show the response surfaces.

Since optimization involves simultaneous evaluation of several responses, the desirability functions need to be obtained for each response, and then these functions can be simultaneously optimized to determine the best fittings (Derringer and Suich 1980; Akcay and Tasdemir 2009). The single composite response (D) was found using the following expression

$$D = (d_1 \times d_2 \times d_3 \times \ldots \times d_n)^{1/n} \tag{5}$$

where d and n define the geometric mean of the individual desirability functions and the number of responses, respectively. D is maximized over the feasible region of the design variables given in expression (5) (Derringer and Suich 1980). In order to calculate the maximum and minimum values for each response, the desirability function (d_j) can be calculated using the expressions (6) and (7), respectively.

$$d_j = \left\{ \begin{matrix} 0 \\ \left[\dfrac{Y_j - minf_j}{maxf_j - minf_j}\right]^{w_{tj}} \\ 1 \end{matrix} \right\} \quad and \quad \begin{matrix} Y_j \leq minf_j \\ 0 < d_j < 1,\ minf_j < Y_j \leq maxf_j \\ Y_j \geq maxf_j \end{matrix} \tag{6}$$

$$d_j = \left\{ \begin{matrix} 1 \\ \left[\dfrac{maxf_j - Y_j}{maxf_j - minf_j}\right]^{w_{tj}} \\ 0 \end{matrix} \right\} \quad and \quad \begin{matrix} Y_j \leq minf_j \\ 0 < d_j < 1, \; minf_j < Y_j \leq maxf_j \\ Y_j \geq maxf_j \end{matrix} \tag{7}$$

where Y_j is the fitted value, and $minf_j$ and $maxf_j$ stand for minimum and maximum values of j_{th} responses, respectively. The weighting factor of the j_{th} response is shown as w_{tj}. The optimization in this study was applied using the Design-Expert® program. In an aim to produce concrete with highest strength, less brittleness and lowest total porosity, we applied an optimization in which compressive strength and characteristic length were maximized and the total porosity was minimized simultaneously. The solution of this optimization gave the optimal solutions of the selected variables as: w/b ratio=0.28 and metakaolin content=10.2% (Fig. 7). The predicted response values were found as: compressive strength= 110.1 MPa, fracture energy= 68.7 N/m, characteristic length= 43.1 mm, 2 days total porosity= 12.5% and 28 days total porosity= 3.2%.

It is already known that the porosity is among the most important parameters in whole service life of concrete, considering especially the durability issues. A second optimization analysis was performed where the porosity at 2 and 28 days is considered to be at higher importance than the other responses. (i.e. w_{tj} = 5). In this case, the optimum solution gave w/b ratio of 0.28 and metakaolin content of 18.3%. The predicted response values are as follows; compressive strength= 113.9 MPa, fracture energy= 62.1 N/m, characteristic length= 43.1 mm, 2 days total porosity= 7.82%, 28 days total porosity= 1.4%. Using the approach presented above it is also possible to determine the optimum amount of metakaolin in concrete for any w/b.

5. Conclusions

The tests conducted in this study led us to reach the following conclusions:

• It has been found that with increasing amount of metakaolin a significant increase in bending strength of concrete with 0.42 water/binder ratios has been obtained. Thus, it can be said that with addition of metakaolin it is possible to improve the bending and splitting tensile strength, as well as the compressive strength of concrete especially in mixtures containing less amount of cement.

• With increasing water/binder ratio, the peak values of load-displacement curve of the reference concretes decreased significantly, while this effect was diminished with increasing amount of metakaolin. The primary effect on the fracture behavior of concrete with low amount of metakaolin has been found to be water/binder ratio, while with increasing amount of metakaolin the effects of metakaolin products become the dominant parameter. On the other hand, it has been seen that density of toughening mechanisms working on the descending branch after peak load of curve has been diluted with increasing amount of metakaolin.

• Fracture energies, calculated using the area under the load-displacement curve obtained from fracture test, is shown to have been affected by addition of metakaolin as even using 8% of metakaolin reduced the fracture energies compared to the reference concrete. However, there is no meaningful difference between the fracture energies of concretes with 16 and 24% metakaolin.

• Analysis of pore structures of paste phases of by Mercury Intrusion Porosimetry showed that increasing the amount of metakaolin reduced the critical pore size.

• The experimental design assigned using Response Surface Method provides a detail assessment of properties over the selected range of metakaolin content. It has been shown that

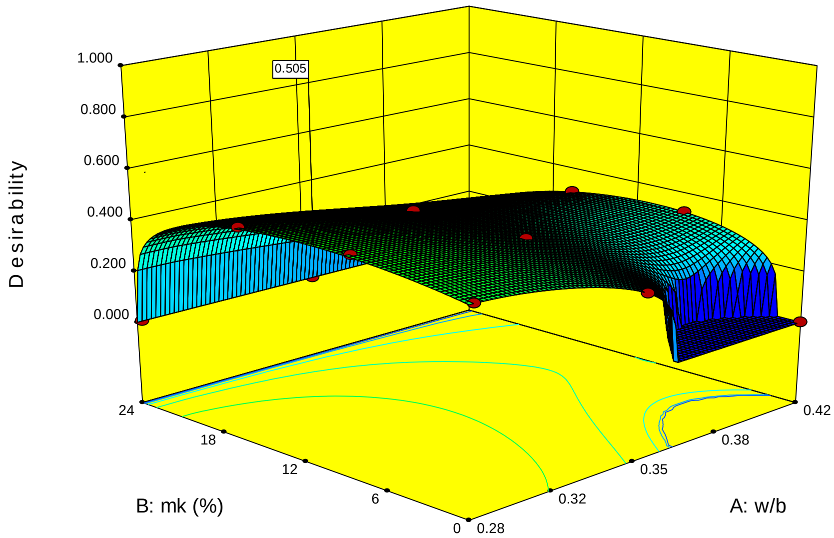

Fig. 7 Response surface of the composite desirability (D)

possible optimum solution can be obtained for preferred mechanical and fracture characteristics, as well as pore structure of concretes using variable amount of metakaolin.

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