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Durability of metakaolin concrete to sulfate attack

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Abstract

This study investigates the effect of metakaolin (MK) replacement of cement on the durability of concrete to sulfate attack. Three MK replacement levels were considered in the study: 5%, 10%, and 15% by weight of cement. The other experimental parameters investigated in the study were: water to binder ratio (0.5 and 0.6), initial moist curing period (3, 7, and 28 days), curing type (moist and autoclaving), and air content (1.5% and 5%). After the specified initial moist curing period, concrete specimens were immersed in 5% sodium sulfate solution for a total period of 18 month. The degree of sulfate attack was evaluated by measuring expansion of concrete prisms, compressive strength reduction of concrete cubes, and visual inspection of concrete specimens to cracks. The study showed that MK replacement of cement increased the sulfate resistance of concrete. The sulfate resistance of MK concrete increased with increasing the MK replacement level. The sulfate resistance of MK concrete at w/b ratio of 0.5 was found higher than that at w/b ratio of 0.6. Autoclaved MK concrete specimens showed superior sulfate resistance compared to moist cured ones. The pore volume of autoclaved MK concrete was found less than that of moist cured MK concrete. The air entrained MK concrete showed higher improvement in the sulfate resistance than the non-air entrained MK concrete. However, the air entrained plain concrete showed lower improvement in the sulfate resistance than the non-air entrained concrete.

Keywords: Metakaolin; Sulfate attack; Expansion; Concrete; Compressive strength; Autoclave

1. Introduction

Sulfate attack is one of the most aggressive environmental deteriorations that affect the long-term durability of concrete structures. The sulfate attack of concrete leads to expansion, cracking, and deterioration of many civil engineering structures exposed to sulfate environment such as piers, bridges, foundations, concrete pipes, etc. The sulfate ions in solution, which come from the soil, ground water, and seawater, are found in combination with other ions such as sodium, potassium, magnesium and calcium ions [1-5]. The sulfate attack is generally attributed to the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum and ettringite. The gypsum and ettringite formed as a result of sulfate attack is significantly more voluminous (1.2 to 2.2 times) than the initial reactants [6]. The formation of gypsum and ettringite leads to expansion, cracking, deterioration, and disruption of concrete structures. In addition to the

formation of ettringate and gypsum and its subsequent expansion, the deterioration due to sulfate attack is partially caused by the degradation of calcium silicate hydrate (C–S–H) gel through leaching of the calcium compounds. This process leads to loss of C–S–H gel stiffness and overall deterioration of the cement paste matrix [3].

The sulfate attack chemical interaction is a complicated process and depends on many parameters including concentration of sulfate ions, ambient temperature, cement type and composition, water to cement ratio, porosity and permeability of concrete, and presence of supplementary cementitious materials [7].

The incorporation of supplementary cementitious materials such as blast-furnace slag, fly ash, and silica fume as a partial replacement of ordinary cement has been found a beneficial technique of enhancing the resistance of concrete to sulfate attack [8–11,6].

Recently, there has been a growing interest in the use of high reactivity metakaolin (MK) as a supplementary cementitious material in concrete industry. Metakaolin (commercially available since the mid 1990s) is produced by calcining purified kaolinite clay at temperature ranging from 700 to 800 °C to drive

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Table 1
Physical properties of the cement and metakaolin used in the study

| Property | Cement | Metakaolin |
|--------------------------------------|--------|------------|
| Specific gravity | 3.15 | 2.5 |
| Blaine fineness (m ² /kg) | 330 | 12,000 |
| Average particle size (µm) | 12 | 1 |
| Color | Gray | White |

off the chemically bound water and destroy the crystalline structure [12-14]. Metakaolin is increasingly being used to produce high-strength, high-performance concrete with improved durability. Extensive research is reported in the literature concerning different properties of MK paste and concrete such as porosity, pore size distribution, pozzolanic reaction, compressive and flexural strength, and shrinkage cracking [15–18,13]. However, limited research is reported in the literature concerning the effect of MK on the resistance of concrete to sulfate attack. Khatib and Wild [19] have investigated the effect of cement type with different C₃A content on the resistance of MK mortar to sulfate attack under moist curing conditions. However, Khatib and Wild did not investigate the influence of other experimental parameters such as water to binder ratio, initial moist curing period, autoclaving curing, and air content on the resistance of MK concrete to sulfate attack. Metakaolin had been found effective in reducing the thaumasite-type of sulfate attack in concrete containing limestone filler [20].

This study was conducted at Jordan University of Science and Technology to investigate the effect of metakaolin (MK) replacement of cement on the resistance of concrete to sulfate attack under different experimental parameters including: MK replacement level, water to binder (w/b) ratio, curing type, initial moist curing period, and air content.

2. Experimental program

2.1. Materials

2.1.1. Cement

Locally available ordinary Portland cement (ASTM Type I) was used in the study. The physical properties and chemical composition of the cement are presented in Tables 1 and 2, respectively.

2.1.2. Coarse aggregate

The coarse aggregate used was crushed limestone. The coarse aggregate had a maximum aggregate size of 19 mm, water absorption of 1%, bulk specific gravity of 2.65, and bulk density of 1600 kg/m^3 .

2.1.3. Fine aggregate

The fine aggregate used was natural silica sand. The sand had a bulk specific gravity of 2.60, a fineness modulus of 1.8, and water absorption of 1.5%.

2.1.4. Metakaolin

The metakaoiln (MK) used was brought from Grace Construction Products. The MK was in dry uncompacted

powder state with white color, average silica (SiO_2) content of 52%, and Blaine fineness of 12,000 m²/kg. The physical properties and chemical composition of the MK are presented in Tables 1 and 2, respectively.

2.1.5. Superplasticizer

The superplasticizer used was based on sulfonate naphthalene formaldehyde condensate. The solid content and specific gravity of the superplasticizer were 30% and 1.25, respectively.

2.1.6. Air entraining admixture

A multi-component synthetic resin type of air entraining admixture was used in four concrete mixtures (I, J, K, and L) to increase the air content of MK concrete from 1.5% for non-air entrained concrete to 5% for air entrained concrete.

2.2. Mixtures details

Twelve concrete mixtures were prepared and used in this study according to ACI 211.1-91 procedure to investigate the influence of MK replacement of cement on the sulfate resistance of concrete. Two w/b ratios were used in the study: 0.5 and 0.6. Non-air entrained and air entrained concrete specimens were used to investigate the influence of air content on the sulfate resistance of MK concrete. Details of the concrete mixtures are presented in Table 3.

Concrete mixtures A, B, C, and D were non-air entrained, the w/b ratio was 0.5, and the MK replacement levels were 0%, 5%, 10%, and 15% by weight of cement, respectively. These concrete mixtures were used to investigate the effect of MK replacement level, initial moist curing period, and curing type on the durability of MK concrete to sulfate attack.

Concrete mixtures E, F, G, and H, were non-air entrained, the w/b ratio was 0.6, and the MK replacement levels were 0%, 5%, 10%, and 15% by weight of cement, respectively. These concrete mixtures were used to investigate the effect of w/b ratio on the durability of MK concrete to sulfate attack

Concrete mixtures I, J, K, and L were air entrained with average air contents of about 5%, the w/b ratio was 0.5, and the MK replacement levels were 0%, 5%, 10%, and 15% by weight of cement, respectively. These concrete mixtures were used to investigate the effect of air content on the durability of MK concrete to sulfate attack.

Table 2
Chemical composition of the cement and metakaolin used in the study

| | | • | |
|-------------------|--------|------------|--|
| Compound (%) | Cement | Metakaolin | |
| SiO ₂ | 20.5 | 52.2 | |
| Al_2O_3 | 5.6 | 44.6 | |
| Fe_2O_3 | 3.8 | 0.5 | |
| MgO | 2.1 | 0.1 | |
| CaO | 64.5 | 0.2 | |
| Na ₂ O | 0.2 | 0.3 | |
| K_2O | 0.2 | 0.2 | |
| SO ₃ | 2.1 | 0.1 | |
| Loss on ignition | 0.8 | 1.4 | |
| | | | |

Table 3
Proportions of concrete mixture (kg/m³) used in the study

| Mix | MK (%) | W/b | Cement (kg) | MK (kg) | W (kg) | CA (kg) | FA (kg) | SP (%) | AE (%) |
|-----|-----------|-----|-------------|------------|-----------|------------|------------|-----------|-----------|
| A | 0 | 0.5 | 380 | 0 | 190 | 1072 | 702 | 1.2 | _ |
| В | 5 | 0.5 | 361 | 19 | 190 | 1072 | 697 | 1.4 | _ |
| C | 10 | 0.5 | 342 | 38 | 190 | 1072 | 693 | 1.6 | _ |
| D | 15 | 0.5 | 323 | 57 | 190 | 1072 | 689 | 1.8 | _ |
| E | 0 | 0.6 | 317 | 0 | 190 | 1072 | 754 | 1.0 | _ |
| F | 5 | 0.6 | 301 | 16 | 190 | 1072 | 750 | 1.2 | _ |
| G | 10 | 0.6 | 285 | 32 | 190 | 1072 | 747 | 1.4 | _ |
| Н | 15 | 0.6 | 269 | 48 | 190 | 1072 | 743 | 1.6 | _ |
| I | 0 | 0.5 | 350 | 0 | 175 | 1072 | 674 | 1.0 | 0.20 |
| J | 5 | 0.5 | 332 | 18 | 175 | 1072 | 670 | 1.2 | 0.24 |
| K | 10 | 0.5 | 314 | 36 | 175 | 1072 | 667 | 1.4 | 0.28 |
| L | 15 | 0.5 | 296 | 54 | 175 | 1072 | 663 | 1.6 | 0.32 |

SP = Superplasticizer.

AE = Air entraining admixture.

Dosage of SP and AE admixtures are reported as percent by weight of binder. The amount of CA and FA are based on saturated-surface dry.

High range water reducer (superplasticizer) was incorporated in all concrete mixtures. The dosage of superplasticizer was increased with increasing the MK replacement level to keep the workability constant due to the high fineness of MK. The dosage of superplasticizer was also decreased with introducing air entraining admixture to maintain constant workability due to improving the workability with incorporating entrained air bubbles in fresh concrete mixtures.

2.3. Specimens preparation

The concrete specimens utilized in the study were: $75 \times 75 \times 300$ mm concrete prisms were used to measure the change in length and 100 mm cubes were used to measure the reduction in compressive strength with respect to strengths of control specimens cured in lime-saturated water solution. Casting of concrete specimens was conducted in two lavers. Each layer was compacted on a vibrating table to ensure good compaction and to reduce the air voids. Fresh concrete was poured into oiled steel molds and covered with wet burlaps for 24 h. Concrete specimens were then demolded, labeled as to the date of casting and mixture type, and stored in a limesaturated water solution tank for an initial moist curing period of 3, 7, or 28 days. Stainless steel locating discs were mounted using epoxy resins at the ends of the concrete prisms to allow accurate measurements of length change. Three concrete specimens were cast and tested for each test condition to obtain average values.

2.4. Test procedures

The concrete mixtures were mixed and prepared using a tilting drum mixer of 0.04 m³ capacity (ASTM C192-02). The workability of MK concrete was measured using the slump test (ASTM C143-03). The workability of all concrete mixtures was comparable with slump ranging from 7 to 9 cm. The air content of the fresh concrete was measured using the pressure method (ASTM C231-04). The air content of the fresh concrete mix-

tures was $1.5\pm0.1\%$ for non-air entrained concrete and $5\pm0.2\%$ for air entrained concrete.

The sulfate exposure testing procedure was conducted by immersing concrete specimens after the specified initial curing in a water tank containing 5% sodium sulfate solution at 23± 2 °C (ASTM C1012-04). Some control concrete cubes were kept in the lime-saturated water solution tank at 23 ± 2 °C for the compressive strength reduction determinations. This type of testing represents an accelerated testing procedure, which indicates the performance of a particular concrete mixture to sulfate attack. The sulfate solution was replaced whenever the pH value exceeded 9.5. The degree of sulfate attack was evaluated by measuring the expansion of concrete prisms, compressive strength of concrete cubes, weight change of concrete bars, and visual inspection of concrete specimens to cracks. Sulfate expansion and weight change measurements were conducted every two-month of sulfate exposure. The observed weight changes were found to be negligible and insignificant (within $\pm 0.10\%$). The expansion and compressive strength reduction criteria were found the most reliable measures to indicate the sulfate attack.

The compressive strength measurements were conducted at the end of the sulfate exposure period of 18 month using a uniaxial testing machine. The compressive strength reduction (CSR) was calculated as follows:

$$CSR(\%) = \frac{\sigma_{\rm m} - \sigma_{\rm s}}{\sigma_{\rm m}} \times 100$$

Where, $\sigma_{\rm m}$ is the average compressive strength (in MPa) of three concrete cubes moist cured for 18 month in lime-saturated water solution and $\sigma_{\rm s}$ is the average compressive strength (in MPa) of three concrete cubes immersed in 5% sodium sulfate solution for 18 month. Concrete specimens were taken out of testing water 4 h before testing and dried in air.

After crushing concrete cubes to determine the compressive strength, small bulk samples of the mortar portion weighing about 10 g were taken out from the middle of the crushed cubes for the measurements of volume of pores using mercury porosimetry. The specimens were desiccated to constant weight at 40 °C using silica gel that was changed daily.

Autoclaved concrete specimens were exposed to the sulfate environment after being exposed to high pressure steam curing (autoclave) at the age of 3 days for a period of 3 h using a pressure of 2 MPa. The periodical visual inspection and examination of concrete specimens have indicated the initial time to cracking as shown in Table 4. After the designated sulfate exposure period, the deterioration was classified on a

Table 4 Initial time (days) to cracking of MK concrete exposed to sulfate solution

| Mixture properties | MK replacement level | | | | |
|----------------------------|----------------------|-----|-----|-----|--|
| | 0% | 5% | 10% | 15% | |
| W/b=0.5 moist curing | 180 | 240 | 300 | 360 | |
| W/b=0.6 moist curing | 150 | 200 | 260 | 310 | |
| W/b=0.5 autoclaving curing | 300 | 500 | NC | NC | |

NC = No cracks were observed.

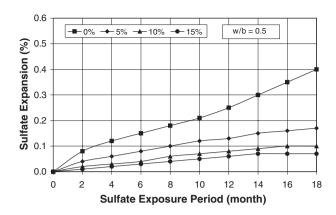


Fig. 1. Effect of MK replacement level on the variation of sulfate expansion with sulfate exposure period at w/b ratio of 0.5.

six-point scale ranging from 0 to 5. A rate of 0 indicates no deterioration while a rate of 5 indicates complete failure [9].

3. Results and discussion

Concrete resistant to sulfate attack should meet a criterion of low expansion and strength reduction, and little or no deterioration. The first cracks of plain and MK concrete specimens due to sulfate attack start to appear on the corners of concrete specimens (due to the sulfate intrusion from the two adjacent faces). Subsequently, cracking and spalling (depending on the experimental parameters) were propagated through the surface of the specimens.

3.1. MK replacement level

The effect of MK replacement level on the variation of sulfate expansion with sulfate exposure period at w/b ratios of 0.5 and 0.6 is shown in Figs. 1 and 2, respectively. Concrete specimens were non-air entrained and exposed to the sulfate environment after 28 days of initial moist curing. The expansion of MK concrete increased steadily and continuously with increasing sulfate exposure period due to the slow and continuous intrusion of sulfate ions into concrete specimens.

In general, the sulfate resistance of MK concrete was higher than that of plain concrete (without MK replacement). Additionally, the sulfate resistance of MK concrete increased with increasing the MK replacement levels. Plain concrete was not durable to sulfate attack reaching maximum sulfate expansion values after 18 months of sulfate exposure of 0.40% and 0.45% (complete disintegration and degradation) for concrete at w/b ratios of 0.5 and 0.6, respectively. The periodical visual inspection of plain concrete specimens have indicated that first cracks were observed after 180 and 150 days of sulfate exposure for concrete at w/b ratios of 0.5 and 0.6, respectively. The deterioration rating after 18 month of sulfate exposure assigned to plain concrete at w/b ratios of 0.5 and 0.6 was 4 and 5, respectively, indicating severe deterioration and failure of plain concrete specimens.

The 10% and 15% MK concrete at both w/b ratios used (0.5 and 0.6) showed excellent durability to sulfate attack and

reached maximum sulfate expansion values after 18 month of sulfate exposure of 0.10% and 0.07% for concrete at w/b ratio of 0.5, and 0.13% and 0.10% for concrete specimens at w/b ratio of 0.6, respectively. The visual inspections of MK concrete specimens have indicated that marginal deterioration was observed for the 10% and 15% MK. The initial time to cracking of the 10% and 15% MK concrete at w/b ratio of 0.5 was 300 and 360 days, respectively. The corresponding initial time of cracking of the 10% and 15% MK concrete at w/b ratio of 0.6 was 260 and 310 days, respectively. The deterioration rating after 18 months of sulfate exposure assigned to the 10% and 15% MK concrete at w/b ratio of 0.5 was 2 and 1. The corresponding deterioration rating assigned to the 10% and 15% MK concrete at w/b ratio of 0.6 was 3 and 2, respectively.

The 5% MK concrete showed intermediate durability to sulfate attack reaching maximum sulfate expansion values of 0.17% and 0.2% for concrete at w/b ratios of 0.5 and 0.6, respectively. The initial time to cracking was 240 and 200 days for concrete at w/b ratios of 0.5 and 0.6, respectively. The visual observation of MK concrete have showed that the severity of the deterioration was less intense in the 5% MK concrete specimens compared to 10% and 15% MK concrete specimens. The deterioration rating assigned to the 5% MK concrete was 3 and 4 (indicating moderate to severe deterioration) for concrete at w/b ratios of 0.5 and 0.6, respectively.

The increase in the sulfate resistance of MK concrete with increasing the MK replacement level is explained by the following mechanisms. First, the replacement of a portion of Portland cement with MK reduces the total amount of tricalcium aluminate hydrate in the cement paste matrix of concrete. The second mechanism is through the pozzolanic reaction between the MK and calcium hydroxide released during the hydration of cement, which consumes part of the calcium hydroxides. Thus, the quantity of expansive gypsum formed by the reaction of calcium hydroxide will be less in MK concrete than in plain concrete. Furthermore, the formation of secondary C-S-H by the pozzolanic reaction, although less dense than the primary C-S-H gel, is effective in filling and segmenting large capillary pores into small, discontinuous capillary pores through pore size refinement. Thus, the total permeability of concrete decreases [21]. In addition to the pozzolanic reaction, the filler

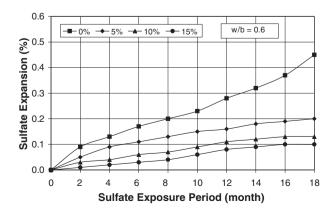


Fig. 2. Effect of MK replacement level on the variation of sulfate expansion with sulfate exposure period at w/b ratio of 0.6.

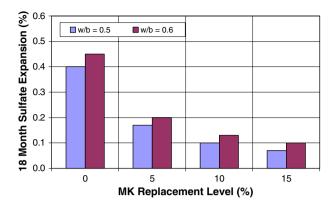


Fig. 3. Effect of w/b ratio on the 18 month sulfate expansion of MK concrete.

action of MK due to the fine particle size of MK (1 μ m) compared to the particle size of cement (12 μ m) further densifies the pore structure of MK concrete to enhance the resistance of MK concrete to sulfate attack [5].

3.2. Water to binder ratio

Water to binder ratio affects many properties of concrete such as pore size distribution, refinement of capillary pores, and compressive strength. Two w/b ratios were investigated in the study 0.5 and 0.6. The effect of w/b ratio of plain and MK concrete after 18 month of sulfate exposure on the sulfate expansion and compressive strength reduction is shown in Figs. 3 and 4, respectively. Metakaolin concrete at w/b ratio of 0.5 showed higher durability to sulfate attack (as indicated by lower expansion and strength reduction) than MK concrete at w/b ratio of 0.6. The maximum sulfate expansion values after 18 month of sulfate exposure and compressive strength reduction of MK concrete decreased with decreasing the w/b ratio. Fig. 5 shows the effect of w/b ratio on the visual deterioration rating of sulfate attack. The deterioration rating was higher for concrete specimens at w/b ratio of 0.6 compared to those at w/b ratio of 0.5.

The increase in the sulfate resistance of MK concrete with decreasing the w/b ratio may be attributed to the fact that the capillary pores volume decreased with decreasing the w/b ratio.

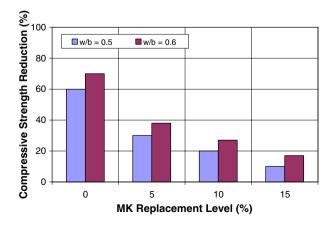


Fig. 4. Effect of w/b ratio on the compressive strength reduction of MK concrete.

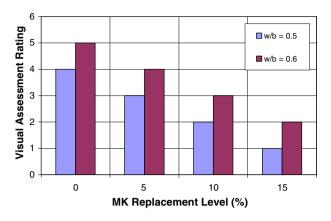


Fig. 5. Effect of w/b ratio on the visual assessment rating of MK concrete.

Thus, the total porosity and permeability of MK concrete decreased with decreasing the w/b ratio. Therefore, sulfate ions intruding MK concrete decreased with decreasing the w/b ratio and the sulfate attack became less.

3.3. Initial moist curing period

The initial moist curing period benefits concrete durability by providing additional strength development and increased pore refinement. The initial moist curing was achieved in this study by immersing concrete specimens at w/b ratio of 0.5 in a lime-saturated water solution tank for initial moist curing periods of 3, 7, or 28 days. No significant improvement in the sulfate resistance of MK concrete (as indicated by the expansion of concrete prisms and the compressive strength reduction of concrete cubes) was observed as a result of the longer initial moist curing period. This result is explained by the following facts. The intrusion of the sulfate ions into concrete is a very slow process. The hydration of cement takes place at a much faster rate than the sulfate intrusion, especially during the initial 28 days. MK concrete specimens cured for 3 and 7 days started hydration immediately after immersion in the sodium sulfate solution. The cement hydration process dominated over the sulfate intrusion during the initial moist curing period. Hence, the 3-day and 7-day cured MK concrete attained a dense pore structure similar to that of the 28-day cured MK concrete during the initial period of sulfate exposure. Therefore, MK concrete specimens cured for 3, 7, or 28 days indicated similar resistance to sulfate attack.

3.4. Curing type

The study investigated the effect of two different curing types (moist and autoclaving) on the sulfate resistance of MK concrete at w/b ratio of 0.5. Autoclaving curing was accomplished in this study by exposing concrete specimens at the age of 3 days to a high-pressure steam curing for 3 h at 2 MPa pressure using autoclave. Autoclaving curing provides high-strength and increases the durability of concrete and concrete at very early age. The autoclaved concrete specimens were $50 \times 50 \times 200$ mm prisms and 75 mm cubes. The effect of curing type of plain and MK concrete after 18 month of sulfate

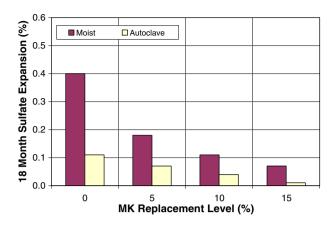


Fig. 6. Effect of moist and autoclaving curing on the sulfate expansion of MK concrete.

exposure on the sulfate expansion and compressive strength reduction is shown Figs. 6 and 7, respectively.

Autoclaved plain and MK concrete specimens showed superior sulfate resistance (as indicated by the very low sulfate expansion and strength reduction) compared to the moist cured concrete specimens. The sulfate expansion of the plain autoclaved concrete after 18 month of sulfate exposure was 0.11% compared to 0.4% for the moist cured plain concrete. On the other hand, the sulfate expansion of the autoclaved 15% MK concrete was only 0.01% compared to 0.07% for the moist cured 15% MK concrete.

Furthermore, the sulfate resistance of the autoclaved MK concrete increased with increasing the MK replacement level. The sulfate expansion of autoclaved concrete decreased from 0.11% for plain autoclaved concrete to 0.01% for the 15% MK concrete. The compressive strength reduction of the autoclaved concrete decreased also from 15% for plain autoclaved concrete to 3% for the 15% autoclaved MK concrete.

The periodical visual inspection and examinations of the 10% and 15% autoclaved MK concrete specimens did not show any visible cracks after 18 month of sulfate exposure. The deterioration rating of the 10% and 15% autoclaved MK concrete was zero (indicating no cracks and complete intact

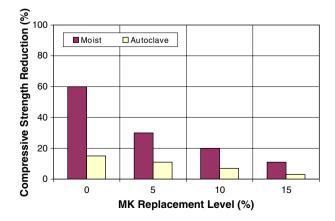


Fig. 7. Effect of moist and autoclaving curing on the compressive strength reduction of MK concrete.

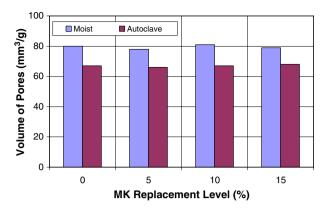


Fig. 8. Effect of moist and autoclaving curing on volume of pores of MK concrete

specimens). However, plain and 5% MK concrete specimens showed initial cracks after 300 and 500 days of sulfate exposure, respectively. The deterioration ratings were 2 and 1 for the plain and 5% MK concrete, respectively.

Fig. 8 shows the effect of curing type of plain and MK concrete on the volume of pores. No significant difference in the volume of pores was observed for different MK replacement levels for either moist or autoclaved concrete. However, the intruded pore volume for autoclaved concrete is found significantly less than that for moist concrete for all MK replacement levels. The average pore volume decreased with autoclaving curing from 80 to 67 mm³/g. Autoclaving curing reduced the total porosity of MK concrete compared to moist curing by about 19%. This result agrees well with many research studies found in the literature which reported that autoclaving curing reduced the porosity of concrete containing supplementary cementing materials compared to moist curing [22–25].

The superior resistance of autoclaved MK concrete to sulfate attack compared to moist cured MK concrete is attributed to many factors. The main and most important factor is that autoclaving curing using high pressure steam produce tricalcium aluminate hydrates more stable in the presence of sulfate ions than those formed in the moist cured concrete specimens [26]. The second factor is the reduction of pore volume of autoclaved concrete compared to the moist cured concrete as discussed

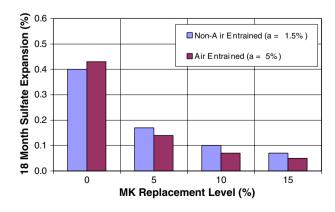


Fig. 9. Effect of air content on the sulfate expansion of MK concrete.

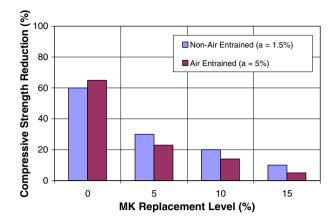


Fig. 10. Effect of air content on the compressive strength reduction of MK concrete.

above. The reduction of pore volume causes a reduction in the permeability of autoclaved concrete and consequently a reduction in the sulfate ions intruding into autoclaved concrete. The third factor is the fast reduction of calcium hydroxide in the cement paste as a result of the pozzolanic reaction. Further improvement in sulfate resistance is due to the increased strength of the autoclaved concrete, and also to the existence of cement hydrates in a well-crystallized form [21].

3.5. Air content

Entrained air increases the uniformity of the MK and mortar in concrete and improves the durability of concrete to freeze-thaw deterioration. The effect of air content of plain and MK concrete after 18 month of sulfate exposure on the sulfate expansion and compressive strength reduction is shown in Figs. 9 and 10, respectively. The air entrained MK concrete specimens showed higher improvement in the sulfate resistance than the non-air entrained ones. On the other hand, the air entrained plain concrete showed lower improvement in the sulfate resistance than the non-air entrained concrete.

The behavior of improving the sulfate resistance of the air entrained MK concrete compared to the non-air entrained MK concrete is explained that incorporating entrained air bubbles may increase the uniformity and homogeneity of MK in the cement paste matrix of concrete mixtures. Therefore, the efficiency of MK effect (pozzolanic reaction and filler action) within concrete specimens is increased. However, plain air entrained concrete showed decrease in the sulfate resistance due to increasing the porosity in the cement matrix, which increases the rate of sulfate ions intruding within concrete.

4. Conclusions

This study presents the results for the effect of MK replacement of cement on the resistance of concrete to sulfate attack. Based on the results obtained from this study, the following conclusions may be warranted:

 Metakaolin replacement of cement was found effective in improving the resistance of concrete to sulfate attack. The

- sulfate resistance of MK concrete increased with increasing the MK replacement level. Concrete containing 10% and 15% MK replacements showed excellent durability to sulfate attack.
- 2. The resistance of MK concrete at w/b ratio of 0.5 to sulfate attack was found higher than that of MK concrete at w/b ratio of 0.6
- 3. The initial moist curing period (3, 7, or 28 days) was found insignificant in improving the resistance of MK concrete to sulfate attack.
- 4. Autoclaved MK concrete showed superior sulfate resistance compared to moist cured MK concrete. The pore volume of the autoclaved plain and MK concrete was found less than that of the moist plain and MK concrete.
- 5. Increasing the air content (from 1.5% to 5%) improved the sulfate resistance of MK concrete to sulfate attack. However, plain concrete showed lower improvement in the sulfate resistance by increasing the air content.

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