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Effect of Microsilica and Water Proofer on Resistance of Concrete to Phosphoric Acid Attack

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ABSTRACT

This paper investigates the effect of microsilica (MS), water proofer (WP) and MS-WP contents on the durability of concrete to phosphoric acid attack. Three MS replacement levels and three WP mixes were considered in the study: 10%, 15% and 20% by weight of cement for MS and mixes of 0.4, 0.6 and 0.8 L for WP. The water to cement ratio was considered to be constant. The workability, durability of concrete to freezing thawing after 300 cycles, durability of concrete to phosphoric acid attack after 15 cycles of wetting and drying in phosphoric acid solution, compressive strength and modulus of rupture after 28 days were investigated. The degree of acid attack was evaluated by measuring the loss in weight. The study showed that the combined effect of MS-WP improved the durability of concrete to freezing thawing and to phosphoric acid attack without significantly reducing the compressive strength or modulus of rupture of the concrete. The optimum mix was 10% of MS replacement and 0.8 L of WP.

KEYWORDS: Phosphoric acid attack, Microsilica, Water proofer, Durability, Compressive strength.

INTRODUCTION

The economy of many countries in the world depends on the production of phosphoric acid from rock phosphate for use in agriculture and industry. The largest phosphorite mines are primarily found in the United States of America in North Carolina and Central Florida, and also in Africa and the Middle East, especially in Morocco, Tunisia, Togo, Saudi Arabia, Jordan and Iraq. The phosphoric acid is usually stored in concrete tanks. Significant deterioration of these tanks due to leakage of the acid could cause environmental and economical problems. Very high costs are involved in repairing such deteriorated structures in the world. Although the durability of concrete to resist phosphoric acid attack is an important subject, it is unfortunately not sufficiently covered in the literature. On the other hand, structures that deteriorate due to sulphate attack are widely covered by many researchers in the past decades (Zivica and Bajza 2001, 2002, 2004; Rozière et al., 2009; Fattuhi and Hughes, 1988). Neville (2004) summarized extensively all the aspects of external sulphate attack and presented conclusions and considerations of future improvements.

In the past few decades, industrial byproducts such as fly ash (Bonakdar and Mobasher, 2010; Wu and Naik, 2002) and silica fume (Durning and Hicks, 1991; Hooton, 1993; Roy et al., 2001; Aköz et al., 1999; Torii and Kawamura, 1994) have been used as mineral additives in cement and concrete to improve the resistance of concrete to attacks of different acids and salts. The use of these artificial pozzolans can achieve

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not only economical and ecological benefits but technical benefits as well. Nevertheless, it is also well known that mineral additives may reduce the strength of concrete. Lee at al. (2005) reported that silica fume enhances the resistance to sodium sulphate attack but causes a compressive strength loss of 15-20%.

Many researchers used corn cob ash (CCA) blended cement (Adesanya and Raheem, 2010) to investigate the durability of concrete to chemical attack involving H_2SO4 and HCl. The results indicated that the use of CCA blended cement reduces the water absorption of concrete, and the resistance to chemical attack was improved with the addition of CCA up to 15% replacement level, but this caused a decrease in permeability and a reduction in weight loss due to reactions of the specimens with HCl and H_2SO4 acid water.

Lately, newly manufactured sulfur polymer concrete (SPC), from recycled waste materials such as sulfur (by-product from oil industry), fly ash and desert sand, was used to resist the corrosion in acid and salt environments (Mohamed and El-Gamal, 2006). The results indicated that SPC has a high compressive strength, a low hydraulic conductivity and a high resistance to permeation of water.

Other researchers (Al-Akhras, 2006) investigated 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 the cement. The degree of sulfate attack was evaluated by measuring the expansion of concrete prisms and the compressive strength reduction of concrete cubes, as well as a 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.

Calcareous limestone aggregates were also used to improve concrete resistance against sulphuric acid attack (Chang et al., 2005). Cement containing ground granulated blast furnace slag and cement containing slag and silica fume or fly ash and silica fume were used. Concrete using limestone aggregates and cement containing silica fume and fly ash performed the best compared with using silicious aggregates.

In this paper, the durability of concrete to phosphoric acid attack was investigated. Microsilica (MS) and water proofer (WP) were used to study their effects on the resistance of concrete to phosphoric acid attack. Three MS replacement levels were considered in this paper; 10%, 15% and 20% by the weight of cement. Also, three levels of WP were adopted; low, medium and high levels of 0.4 L, 0.6 L and 0.8L, respectively. The effects of MS replacement content only and of WP content only, as well as the combined effects of MS-WP were investigated on many features of concrete. These features were: workability, durability to freezing thawing, durability to phosphoric acid attack, compressive strength and modulus of rupture after 28 days of the concrete. The durability of concrete to freezing thawing and acid attack was evaluated by measuring the loss in weight, in addition to a visual inspection of concrete specimens to cracks.

EXPERIMENTAL PROGRAM

Materials

Cement

Sulphate resisting cement (ASTM Type V) was used in the study.

Microsilica (MS)

The chemical composition and physical properties of microsilica (MS) and Ordinary Portland Cement (OPC) used are given in Table 1. The SiO_2 content was 20% and 91% in OPC and MS, respectively.

Aggregates

Table 2 shows grain size distribution and properties of the coarse and fine aggregates used. The coarse aggregates had a maximum aggregate size of 20 mm, a water absorption of 4% and a specific gravity of 2.60. The fine aggregates had a water absorption of 6.6% and a specific gravity of 2.49.

Table 1: Chemical composition and physical properties of OPC and microsilica

Item	OPC	Microsilica
SiO_2 (%)	20	91
Al_2O_3 (%)	4	0.7
Fe_2O_3 (%)	3	0.8
CaO (%)	63	0.3
Na_2O (%)	0.4	0.45
K_2O (%)	1	1.65
MgO (%)	2	1.15
Particle density (kg/m^3)	3150	2200
Bulk density (kg/m^3)	1300	700
Specific surface (g/ m^2)	0.35	23

Table 2: Grain size distribution and properties of aggregates

Grain size distribution of aggregates			Physical properties of aggregates		
Sieve size (mm)	**Fine passing (%)**	**Coarse passing (%)**		**Specific gravity**	**Water absorption (%)**
20	100	100	**Coarse**	2.60	4
12.7	100	27.8	**Fine**	2.49	6.6
9.5	100	11.0			
4.75	99.8	0			
2.36	79.8				
1.18	53.8				
0.6	36.9				
0.3	24.9				
0.15	10.4				
0.075	2.2				

Water Proofer (WP)

The water proofer (WP) used is based on a blend of long chain carboxylic acids to give maximum reduction in permeability. It is an amber coloured liquid with a specific gravity of 1.01 at 20 ^oC, a viscosity of 26cP at 20 ^oC, a freezing point less than -5 ^oC and a pH of 9.5.

Mixture Details

Sixteen concrete mixtures were prepared and used in this study to investigate the influence of MS, WP and MS-WP contents on the phosphoric acid resistance of concrete. The water/cement (w/c) ratio was constant for all mixes at about 0.64 and the cement used was sulphate resisting cement (Type V) as stated earlier. Details of the concrete mixes are presented in Table 3.

Mix M1 was the control mix containing 411 kg/m^3 of cement, as well as 555 and 1090 kg/m^3 of fine and coarse aggregates, respectively. Concrete mixes M2, M3 and M4 contained MS replacement levels at 10%, 15% and 20% by weight of the cement, respectively. Concrete mixes M5, M6 and M7 contained 0.4, 0.6 and 0.8 L of WP, respectively without any replacement levels of MS. Concrete mixes M8, M9 and M10 contained MS replacement levels at 10% and 0.4, 0.6 and 0.8 L of WP, respectively. Concrete mixes M11, M12 and M13 contained MS replacement levels at 15%

and 0.4, 0.6 and 0.8 L of WP, respectively. Finally, concrete mixes M14, M15 and M16 contained MS replacement levels at 20% and 0.4, 0.6 and 0.8 L of WP, respectively.

Table 3: Properties of concrete mixes used

Mix	**W/C**	**Cement (kg/m^3)**	**Micro Silica (MS) (%)**	**Water Proofer (WP) (L)**	**Fine aggregate (kg/m^3)**	**Coarse aggregate (kg/m^3)**
M1: CM	0.64	411	---	---	555	1090
M2: CM- MS10	0.64	400	10	---	540	1060
M3: CM- MS15	0.64	394	15	---	532	1144
M4: CM- MS20	0.64	389	20	---	525	1035
M5: CM- WP 0.4	0.63	410	---	0.4	554	1087
M6: CM- WP 0.6	0.63	409	---	0.6	552	1084
M7: CM- WP 0.8	0.62	408	---	0.8	551	1080
M8: CM- MS 10-WP 0.4	0.63	399	10	0.4	539	1058
M9: CM- MS 10-WP 0.6	0.62	401	10	0.6	541	1062
M10: CM- MS 10-WP 0.8	0.62	400	10	0.8	540	1060
M11: CM- MS 15-WP 0.4	0.63	395	15	0.4	533	1046
M12: CM- MS 15-WP 0.6	0.63	395	15	0.6	533	1047
M13: CM- MS 15-WP 0.8	0.62	396	15	0.8	534	1049
M14: CM- MS 20-WP 0.4	0.63	390	20	0.4	527	1034
M15: CM- MS 20-WP 0.6	0.62	389	20	0.6	525	1031
M16: CM- MS 20-WP 0.8	0.62	388	20	0.8	524	1030

CM = Control Mix.
MS = Micro Silica.
WP = Water Proofer.

Specimen Preparation

Conventional concrete specimens were utilized in the study. Cubes (150 x 150 x 150 mm) and (100 x100 x500 mm) beams were used for modulus of rupture determination. Casting of concrete specimens was conducted in two layers. Each layer was compacted on a vibrating table to ensure good compaction and to reduce air voids. Fresh concrete was poured into steel molds and covered with wet burlaps for 24 hours. Concrete specimens were then demolded, labeled as to the date of casting and mix type and stored in a water solution tank for an initial moist curing period of 3, 7 or 28 days. Three concrete specimens were cast and tested for each test condition to obtain average values.

Test Procedures

The concrete mixes were mixed and prepared using a tilting drum mixer of 0.04 m^3 capacity. The following tests were performed:

1. Slump test (ASTM C143) to measure the workability of all concrete mixes.
2. Durability of concrete mixes. This was done by two approaches:
   I. Applying 300 cycles of freezing and thawing for

all concrete mixes to measure the loss in weight.

II. Applying 15 cycles of wetting and drying in phosphoric acid to measure the loss in weight. The acid exposure testing procedure was conducted by immersing concrete specimens in a water tank containing phosphoric acid solution at 23± 2 °C. After a specified constant time, the specimens were un-immersed and dried. The procedure was repeated for 15 cycles. The durability of concrete to phosphoric acid attack was also evaluated using visual inspection of concrete specimens to cracks.

3. Compressive strength test after 28 days, where (150x 150 x 150 mm) cubes were tested.
4. Flexure test to measure the modulus of rupture after 28 days, where (100 x100 x500 mm) beams and a symmetrical two-point loading setup, with a beam span of 400 mm, were used.

RESULTS AND DISCUSSION

All concrete mixes were investigated for workability, durability after freezing thawing, durability after phosphoric acid attack, compressive strength and modulus of rupture in order to determine the effects of MS, WP and MS-WP contents.

Workability

The workability was measured using the slump test (ASTM C143) as stated earlier. The control mix M1 slump was measured to be 6.5 cm; i.e. the concrete can be classified as concrete with medium workability. Figs. 1, 2 and 3 show the relationship between the slump of concrete and MS, WP and MS-WP contents, respectively. As shown, the replacement of MS decreases the workability of concrete significantly as expected. These decreases are proportional to the increases in the contents of MS as shown in Fig.1. The reduction in workability is attributed to the fact that MS is very fine in nature and more absorbing. On the other hand, the workability increases for concrete mixes M5, M6 and M7 due to the addition of WP. The slump was increased 30% for mix M7 as shown in Fig.2.

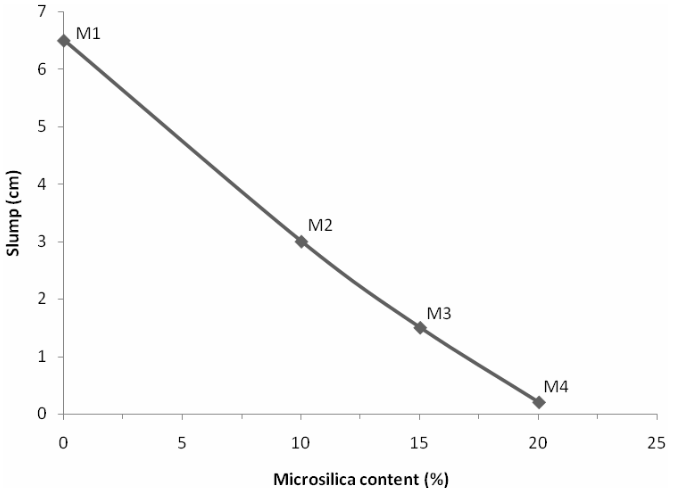

Figure 1: Relationship between MS content and the slump of concrete

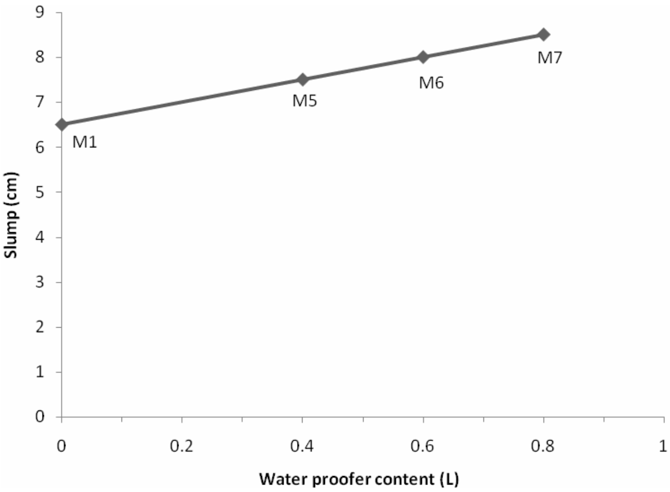

Figure 2: Relationship between WP content and the slump of concrete

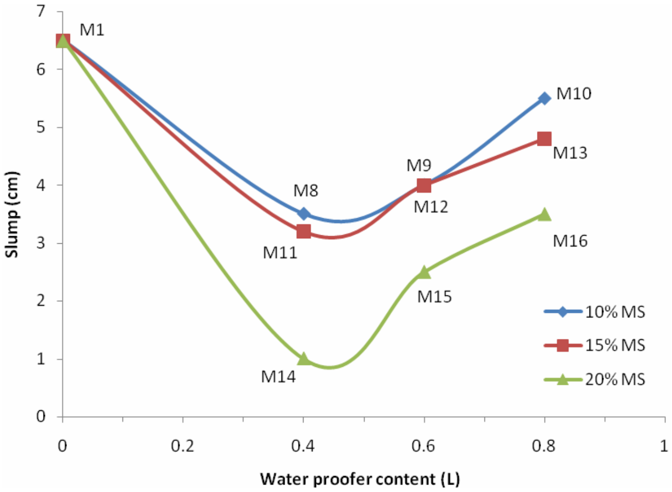

Figure 3: Relationship between MS-WP contents and the slump of concrete

The combined effect of MS-WP contents increases the workability compared with the effect of MS alone. Fig. 3 shows the increasing of workability for mixes M8 to M13. It also shows that the high contents of MS with WP; i.e. M14, M15 and M16 decrease the workability of the concrete keeping it as very low workable concrete.

Freezing and Thawing Resistance

The freezing and thawing resistance of concrete was measured by loss in weight after 300 cycles of freezing and thawing for all concrete mixes. Figs. 4, 5 and 6 show the relationship between loss in weight and MS, WP and MS-WP contents, respectively. The control mix M1 showed the least resistance to freezing and thawing, where the loss in weight was 1.69%. A close observation of Fig.4 exhibits that the MS content enhanced the durability of concrete to freezing and thawing. The loss in weight was enhanced by 58% for M2 and by 80% for M3. Also, Fig. 5 shows that WP enhanced the durability of concrete to freezing and thawing but less than MS. The loss in weight was enhanced by 42% for M5 and by 71% for M7.

The combined effect of MS-WP on durability of concrete to freezing and thawing was better than MS only and WP only as shown in Fig. 6. The loss in weight was enhanced from 69% to 92%. The minimum loss in weight was for 15% MS and the optimum was for concrete mix M13 with 0.13% loss in weight.

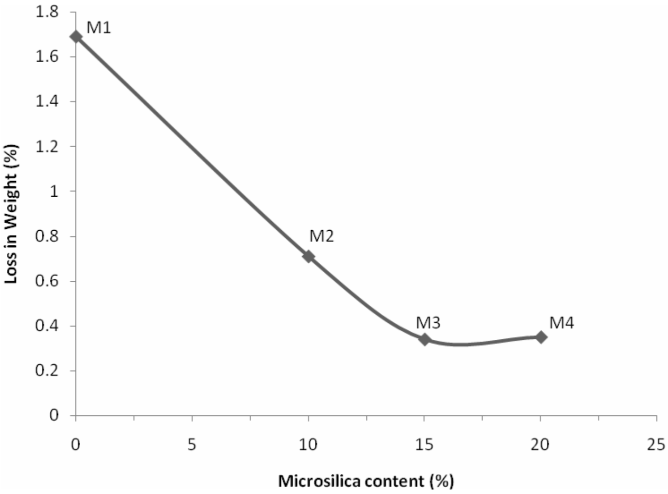

Figure 4: Relationship between loss in weight and MS content after 300 cycles of freezing and thawing

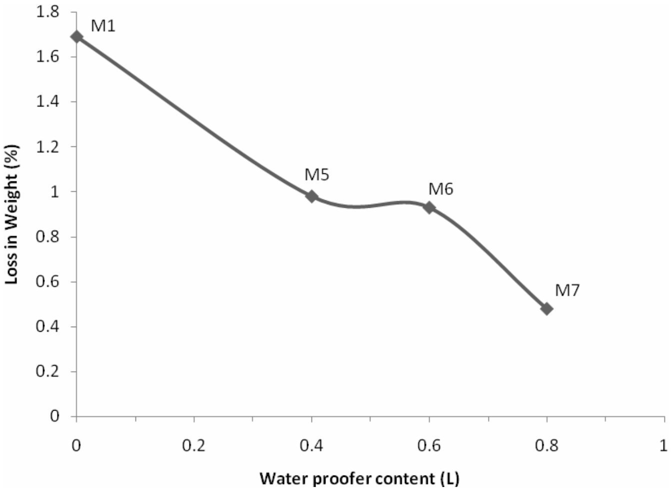

Figure 5: Relationship between loss in weight and WP content after 300 cycles of freezing and thawing

Phosphoric Acid Resistance

The durability of concrete to phosphoric acid attack was measured by the loss in weight after 15 cycles of wetting and drying in the phosphoric acid solution. Figs.

7, 8 and 9 show the relationship between loss in weight and MS, WP and MS-WP contents, respectively. As expected, the control mix M1 showed the least resistance to phosphoric acid attack; the loss in weight was measured to be 5.32%. The effects of MS, WP and MS-WP enhanced the durability of concrete to acid attack but with different proportions. The optimum loss in weight for MS mixes was for M3 with a value of 0.84% as shown in Fig. 7, while the optimum for WP mixes was 1.31% for M7 as shown in Fig. 8. On the other hand, the optimum loss in weight for MS-WP mixes was 0.71% for mix M10 as shown in Fig. 9. A close observation of Fig. 9 shows that although the high MS content with WP enhances the loss in weight compared to control mix M1, but it was the worst compared to low and medium MS replacement contents.

As a summary, the optimum resistance for phosphoric acid attack for all concrete mixes was for M8, M9 and M10 that have 10% MS and 0.4, 0.6 and 0.8 L of WP, respectively.

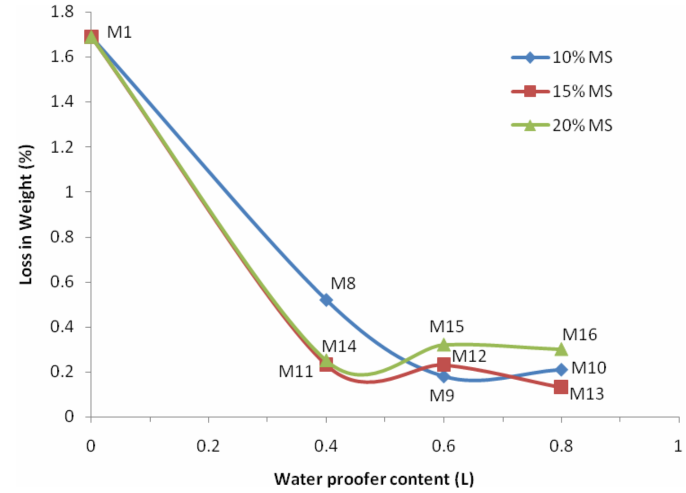

Figure 6: Relationship between loss in weight and MS-WP contents after 300 cycles of freezing and thawing

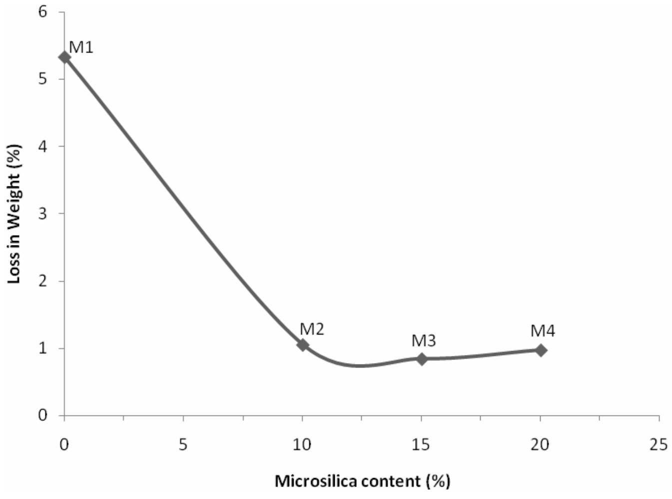

Figure 7: Relationship between loss in weight and MS content after 15 cycles of wetting and drying in phosphoric acid

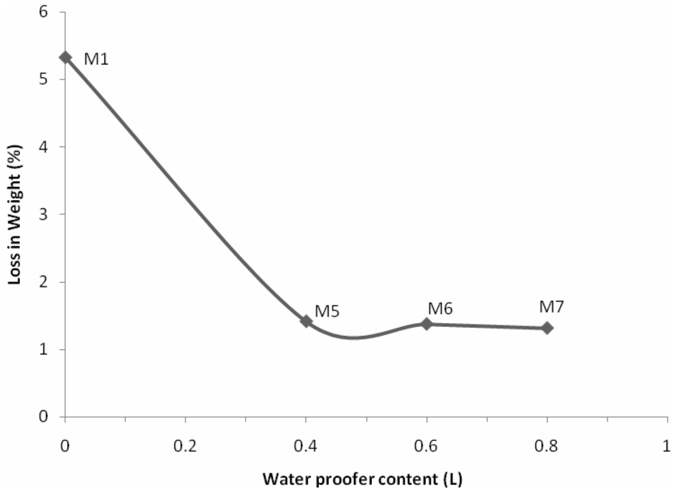

Figure 8: Relationship between loss in weight and WP content after 15 cycles of wetting and drying in phosphoric acid

Compressive Strength

The compressive strength after 28 days was reported for all the concrete mixes. The compressive strength for control mix M1 was 56.8 MPa. Figs. 10, 11 and 12 show the relationship between the compressive strength and MS, WP and MS-WP contents, respectively. The following observations were obtained:

1. The MS content increased the compressive strength. The maximum increase was 13.5% in mix M3.
2. The high levels of MS replacement; i.e. 20% MS, reduced the increase in the compressive strength down to 8%.
3. The effect of WP alone reduced the compressive strength as expected. The maximum decrease was 24% in mix M7.

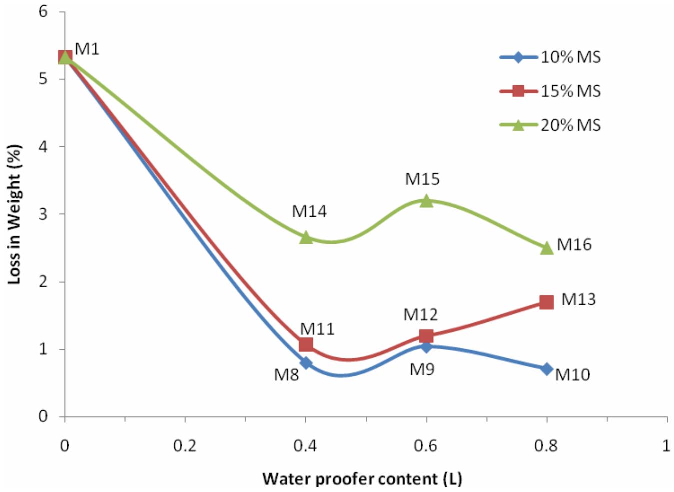

Figure 9: Relationship between loss in weight and MS-WP contents after 15 cycles of wetting and drying in phosphoric acid

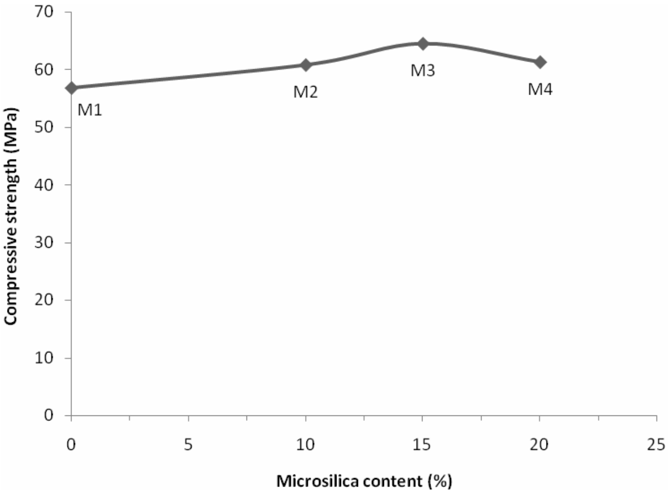

Figure 10: Relationship between compressive strength after 28 days and MS content

4. In general, the combined effect of MS-WP contents decreased the compressive strength. These decreases were not high as in the WP case. The maximum decrease was 21% in mix M16.
5. Low to medium MS replacement contents with WP; i.e. 10% and 15%, reduced the compressive strength very slightly compared with high MS contents.

Modulus of Rupture

The modulus of rupture was measured from the flexure test. Control concrete mix M1 has a modulus of rupture after 28 days of 5.3 MPa. Figs. 13, 14 and 15 show the relationship between modulus of rupture and MS, WP and MS-WP contents, respectively. The following observations were obtained:

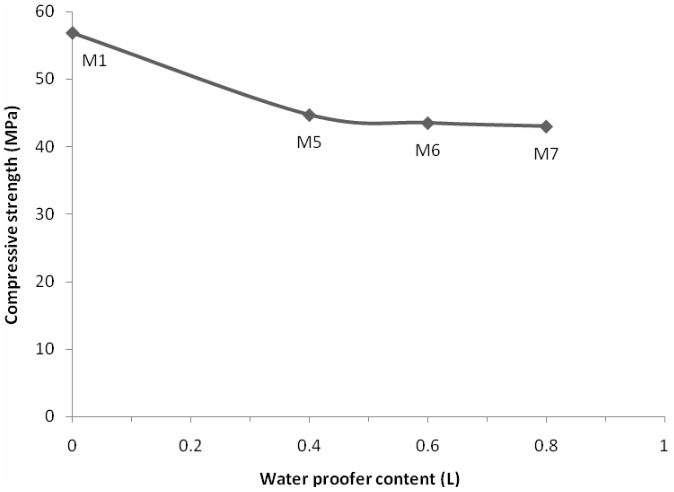

Figure 11: Relationship between compressive strength after 28 days and WP content

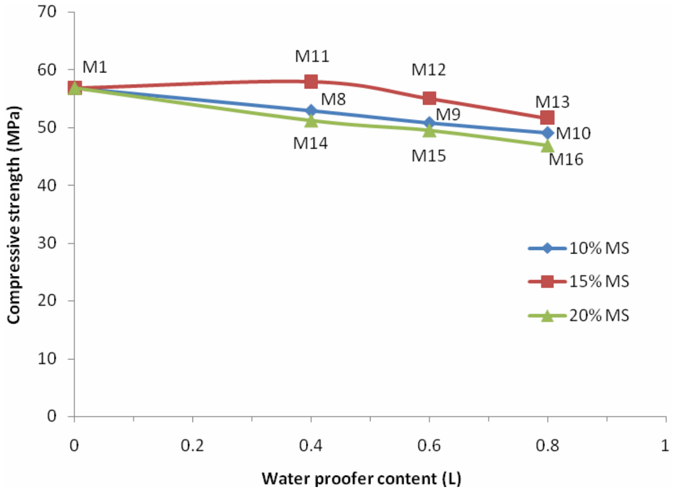

Figure 12: Relationship between compressive strength after 28 days and MS-WP contents

1. The effect of MS only increased the modulus of rupture from 4% to 13%.
2. The effect of WP only reduced the modulus of rupture from 37% to 26%.
3. The combined effect of MS-WP contents decreased the modulus of rupture slightly compared to WP only.
4. The optimum values of the modulus of rupture for all mixes were for M11, M12 and M13.

CONCLUSIONS

This study presents the results for the effects of microsilica (MS), water proofer (WP) and MS-WP contents on the resistance of concrete to phosphoric acid attack. Based on the results obtained from this research, the following conclusions can be drawn:

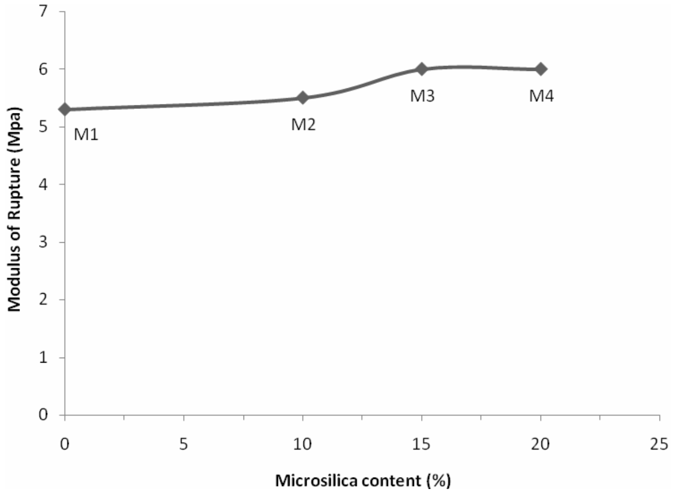

Figure 13: Relationship between modulus of rupture after 28 days and MS content

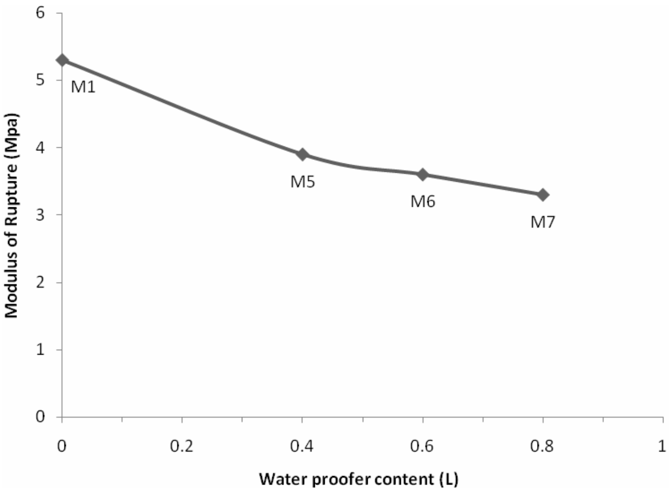

Figure 14: Relationship between modulus of rupture after 28 days and WP content

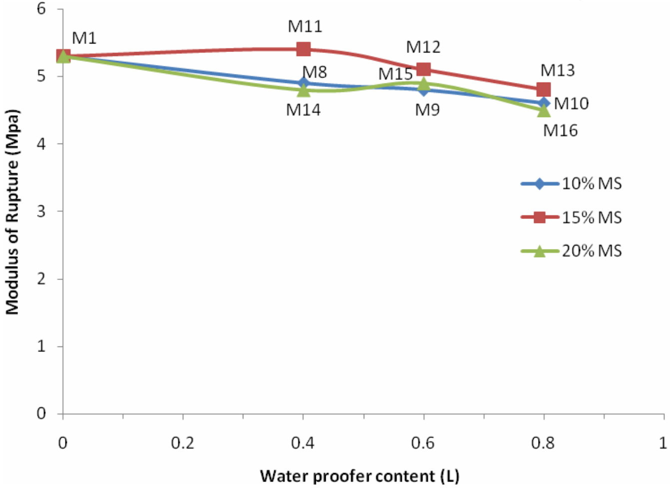

Figure 15: Relationship between modulus of rupture after 28 days and MS-WP contents

1. The use of MS only has a negative impact on the workability of concrete, especially for high replacement ratios, while the use of WP only increases the workability of concrete. This problem can be solved by the combined effect of MS-WP contents which provides medium workability for concrete.
2. The use of MS, WP and MS-WP contents enhances the durability of concrete to freezing and thawing. The optimum enhancement is by using 15% MS replacement with 0.8 L of WP.
3. The use of MS, WP and MS-WP contents enhances the durability of concrete to phosphoric acid attack. High MS content with WP is the worst compared to low and medium MS replacement contents with WP.
4. 10% MS and 0.4, 0.6 and 0.8 L of WP, respectively, are the optimum mixes for resistance to phosphoric acid attack.
5. The use of MS only increases the compressive strength and the modulus of rupture after 28 days.
6. The use of WP only and high MS only decrease the compressive strength and the modulus of rupture after 28 days.

7. The use of low to medium MS replacement contents with WP reduces very slightly the compressive strength and the modulus of rupture after 28 days.
8. The optimum mix to resist phosphoric acid attack has a medium workability and no major decrease on the compressive strength and the modulus of rupture after 28 days, with 10% of MS replacement and 0.8 L of WP.

REFERENCES

Adesanya, D.A. and Raheem, A.A. 2010. A study of the permeability and acid attack of corn cob ash blended cements. *Construction and Building Materials*, 24 (3): 403-409.

Aköz, F., Türker, F., Koral, S. and Yüzer, N. 1999. Effect of raised temperature of sulfate solutions on the sulfate resistance of mortars with and without silica fuma. *Cement and Concrete Research*, 29 (4): 537-544.

Al-Akhras, N. 2006. Durability of metakaolin concrete to sulfate attack. *Cement and Concrete Research*, 36 (9): 1727-1734.

Bonakdar, A. and Mobasher, B. 2010. Multi-parameter study of external sulfate attack in blended cement materials. *Construction and Building Materials*, 24 (1): 61-70.

Chang, Z., Song, X., Munn, R., and Marosszeky, M. 2005. Using limestone aggregates and different cements for enhancing resistance of concrete to sulphuric acid attack. *Cement and Concrete Research*, 35 (8): 1486-1494.

Durning, T.A. and Hicks, M.C. 1991. Using microsilica to increase concrete’s resistance to aggressive chemicals. *ACI Concrete International*, 13 (3): 42-48.

Fattuhi, N.I. and Hughes, B.P. 1988. The performance of cement paste and concrete subjected to sulphuric acid attack. *Cement and Concrete Research*, 18 (4): 545-553.

Hooton, R.D. 1993. Influence of silica fume replacement of cement on physical properties and resistance to sulfate attack, freezing and thawing and alkali-silica reactivity. *ACI Materials Journal*, 90 (2): 143-151.

Lee, S.T., Moon, H.Y. and Swamy, R.N. 2005. Sulfate attack and role of silica fume in resisting strength loss. *Cement and Concrete Research*, 27 (1): 65-76.

Mohamed, A. and El-Gamal, M. 2009. Hydro-mechanical behavior of a newly developed sulfur polymer concrete. *Cement and Concrete Research*, 31 (3): 186-194.

Neville, A. 2004. The confused world of sulfate attack on concrete. *Cement and Concrete Research*, 34 (8): 1275-1296.

Roy, D.M., Arjunan, P. and Silsbee, M.R. 2001. Effect of silica fume, metakaolin and low-calcium fly ash on chemical resistance of concrete. *Cement and Concrete Research*, 31 (12): 1809-1813.

Rozière, E., Loukili, A., El-Hachem, R. and Grondin, F. 2009. Durability of concrete exposed to leaching and external sulphate attacks. *Cement and Concrete Research*, 39 (12):1188-1198.

Torii, K. and Kawamura, M. 1994. Effects of fly ash and silica fume on the resistance of mortar to sulfuric acid and sulfate attack. *Cement and Concrete Research*, 24 (2): 361-370.

Wu, Z. and Naik, T. 2002. Properties of concrete produced from multicomponent blended cements. *Cement and Concrete Research*, 32 (12): 1937-1942.

Zivica, V. and Bajza, A. 2001. Acidic attack of cement based materials - a review: Part 1. Principle of acidic attack. *Construction and Building Materials*, 15 (8): 331-340.

Zivica, V. and Bajza, A. 2002. Acidic attack of cement-based materials - a review: Part 2. Factors of rate of acidic attack and protective measures. *Construction and Building Materials*, 16 (4): 215-222.

Zivica, V. 2004. Acidic attack of cement-based materials - a review: Part 3. Research and test methods. *Construction and Building Materials*, 18 (9): 683-688.