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Resistance to magnesium sulfate and sodium sulfate attack of mortars containing wheat straw ash

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Abstract

Magnesium and sodium sulfate resistance of mortars containing wheat straw ash (WSA) was investigated. WSA was obtained by burning of wheat straws in electrical furnace under controlled conditions. When this ash is rapidly cooled, a good pozzolanic material is obtained. In this study, resistance to magnesium sulfate and sodium sulfate attack of mortars containing different levels of WSA was investigated. Compressive and flexural strength, density and mass changes of mortar specimens in water and sulfate solutions were determined for 180 days. The strengths of mortars generally increased in magnesium sulfate solutions during the tests. However, decreasing strengths, after 56 days in solution at a concentration of 40,000 mg/l at the 24% replacement level, can be accepted as an indication of a negative development trend for later days. WSA replacement affected beneficially compressive strength of mortars in sodium sulfate solutions. When flexural strength results are considered, performance or Portland cement (PC)–WSA mortars are not satisfactory.

Keywords: Durability; Sulfate attack; Wheat straw ash

1. Introduction

Wheat straw ash (WSA) is obtained by the grinding of wheat straw burned in controlled electrical furnace and then cooled rapidly [1]. The amorphous SiO_2 content of this ash is high and it can be accepted as a pozzolanic material. WSA is finer than Portland cement (PC). It is known that fine pozzolans improve the properties of cement-based materials due to their pozzolanic properties and filler effect.

When cement-based materials are exposed to sodium sulfate attack, gypsum and ettringite are produced by chemical reactions of sulfate and $Ca(OH)_2$, C_3A [2–5]. Formation of gypsum plays an important role in the damage of material [4]. Gypsum results in softening of the material [2,6]. There is close relationship between the $Ca(OH)_2$ content and gypsum formation [4]. Ettringite formation results in cracking and expansion of the material. Expansion is related to the water absorption of crystalline ettringite [3,5]. The presence of a pozzolanic material results in an increase in the resistance to sodium sulfate attack [2,7–10]. On the other hand, effectiveness of pozzolanic material against sulfate attack is dependent on the maximum temperature reached during the producing of the pozzolan. Wild et al. [10] concluded that calcination temperature for clay below 900°C produces a marked loss in sulfate resistance when the pozzolanic product is partially replacing with cement in mortar.

Brucite, ettringite, and gypsum are formed in the case of magnesium sulfate attack on cement-based materials [11]. Brucite and CSH transform to non-cementitious MSH gel. The action of Mg^{+2} and SO_4^{-2} are largely independent [3]. The main damaging effect of magnesium sulfate solution is the decomposition of CSH gel to non-cementitious MSH [2,12].

Pozzolans react with $Ca(OH)_2$ and the result is additional CSH gel. This transformation leads to an increase in the resistance of the material to sodium sulfate attack but not to magnesium sulfate attack. CSH produced by the pozzolanic reaction is more susceptible to the magnesium sulfate attack [2,6,13]. Dependence of mortar properties on the magnesium sulfate attack is complicated. For different stages of sulfate attack, the resistance of mortar

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is dependent on the material properties and sulfate concentration [14].

In this paper, the effect of WSA replacement on the resistance of mortars to sodium sulfate (N) and magnesium sulfate (M) attack are reported.

2. Experimental procedure

The experimental study was carried out on mortar specimens. An ordinary PC and siliceous sand, according to RILEM guidelines, were used for the PC mortars. WSA was used as a partially replacing material of PC for the PC–WSA mortars. Cement and WSA properties are reported in Table 1. To produce WSA, wheat straws were cut into small pieces and burned in electrical furnace at 670°C for 5 h and then cooled rapidly outside the furnace, and ground. Details of this procedure were explained elsewhere [1]. Pozzolanic activity of WSA was determined according to Turkish standard (TS 25). According to this standard, mortar mixture containing lime, WSA, siliceous sand, and water was prepared, and the mortar was cast into the prismatic moulds. The specimens were kept in laboratory room for 24 h and in an oven at 55 ± 2°C for 6 days. Flexural and compressive strength tests were performed on the 7th day on three specimens. Mean values of the test results and the standard values are presented in Table 2. Results showed that the WSA is a pozzolanic material. In the PC–WSA blend mortars, the ash replaced 8% (B), 16% (C) and 24% (D) of the cement by mass. The sand/cement ratio was 3, and water/cementitious material ratio was 0.5. A superplasticiser was used in PCB, PCC and PCD mortars to have equal workability with the PC mortars. Prismatic specimens, 40 × 40 × 160 mm^3, were used for the flexural and compressive strength tests.

Table 1
Chemical and physical properties of PC and WSA

Chemical properties [%]	PC	WSA
SiO_2, soluble	20.60	54.24
SiO_2, insoluble	0.38	29.56
Al_2O_3	6.14	4.55
Fe_2O_3	3.72	1.05
CaO	63.65	12.54
MgO	1.29	2.39
SO_3	2.55	1.49
Ignition loss	1.42	7.22
Specific density [g/cm^3]	3.05	2.41
Blaine [cm^2/g]	3204	5520
Setting time [h]		
Initial	1.50	
Final	3.35	
Mineralogy components [%]		
C_3S[a]	40.18	
C_2S	28.83	
C_3A	9.98	
C_4AF	11.32	

[a] *S:* SiO_2, *C:* CaO, *A:* Al_2O_3, *F:* Fe_2O_3, *M:* MgO, *S:* SO_4, *H:* H_2O.

Table 2
Results of pozzolanic activity tests of WSA and standard values according to TS 25

Pozzolanic WSA	Flexural strength [N/mm^2]	Compressive strength [N/mm^2]
Standard Values (TS 25)	1	4
Ash at 670°C	3.0	11.6

After the mixtures were cast into the moulds, specimens were stored in laboratory conditions for 24 h and then transferred into the sulfate solutions.

Solution concentrations were 10,000 mg/l (N1, M1) and 40,000 mg/l (N4, M4) as SO_4^{-2}. The specimens consisted of 12 groups which were named according to the ash ratio (B, C, and D) and the solution in which they were stored (S, M1, M4 and N1, N4). Curing water and magnesium sulfate solution were renewed in periods of 14 days. Flexural and compressive strengths were determined at 0, 28, 56, 90, and 180 days of exposure. The mass of the specimens was measured every 14 days.

3. Results and discussion

Compressive and flexural strengths results of the specimens prior to sulfate attack are presented in Table 3. Relative results were calculated by dividing the results at any time of the 28 days values.

3.1. Water

The addition of WSA reduced the compressive strength at 28 days at all replacement levels (Fig. 1). However, at the 8% level, compressive strength increased steadily and reached the strength of the cement mortar after 180 days. This shows that pozzolanic reactions due to the presence of WSA progressed in a very slow rate. At the higher replacement level, compressive strengths of mortars did not show a steady increase except a surprising increase at 180 days for the specimens containing the highest amount of WSA. WSA addition affected the flexural strength beneficially at all replacement level at the first 28 days (Fig. 2). This beneficial effect diminished at later days for the replacement level of 16% and 24%. The rate of increase of all the specimens increased during the test (Fig. 3). The rate of increase was highest for the specimens containing 8% WSA. Mass increase was significant especially at the first few days.

Table 3
Physical and mechanical test results of the specimens prior to sulfate exposure

	PC	*PCB*	*PCC*	*PCD*
Compressive strength [N/mm^2]	56.15	50.52	45.10	40.00
Flexural strength [N/mm^2]	7.23	10.28	9.51	7.23
Density [g/cm^3]	2.06	2.06	2.01	2.04

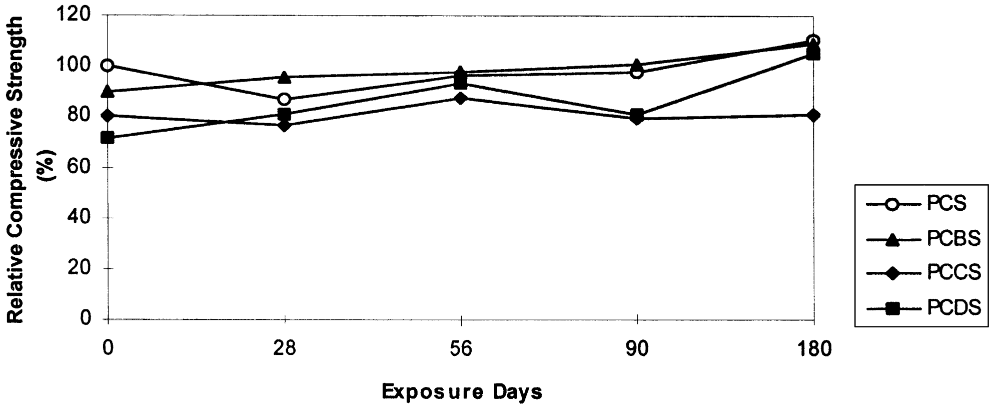

Fig. 1. Relation between compressive strength and exposure time in water.

3.2. Sodium sulfate solution

When the compressive strength results are considered, all the mixtures containing WSA showed good performance in sodium sulfate solution at 10,000 mg/l concentration for the whole testing period (Fig. 4). Mixture having highest amount of WSA showed the best performance. Similar performance could be seen for the concentration of 40,000 mg/l except among 28 and 90 days for the mortar containing 8% WSA (Fig. 5). Best performance was obtained for the replacement level of 16% WSA at the 180 days. However, WSA replacement

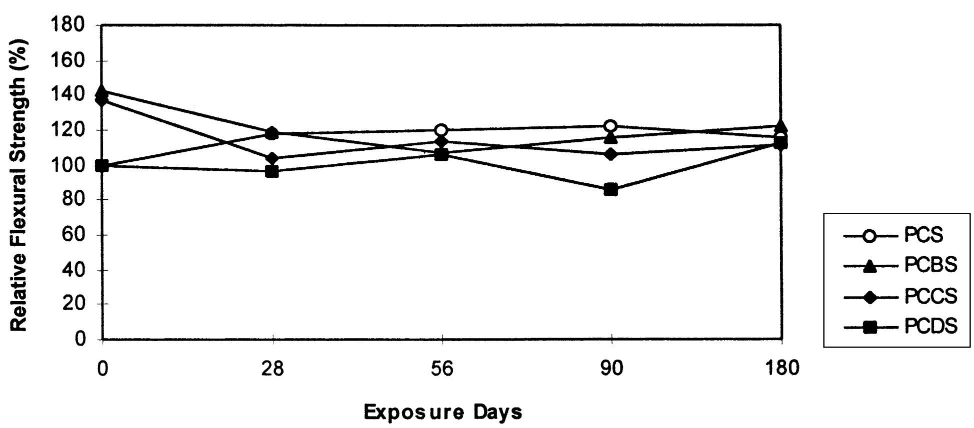

Fig. 2. Relation between flexural strength and exposure time in water.

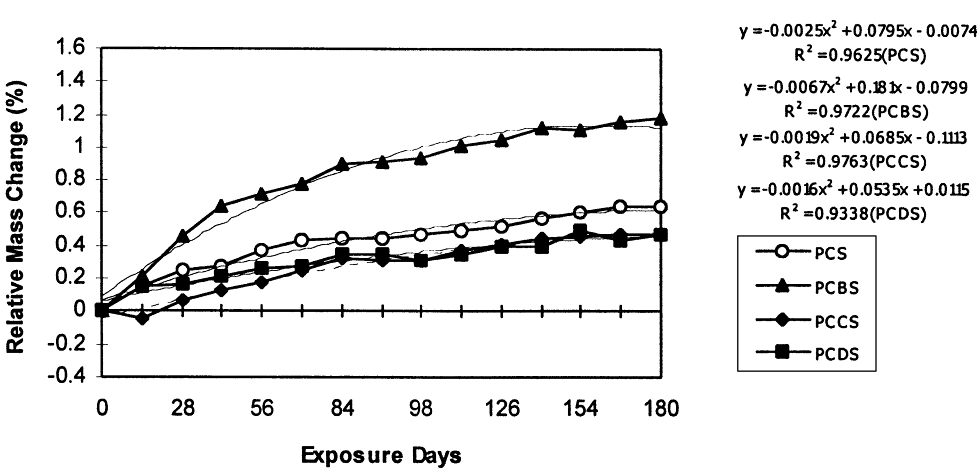

Fig. 3. Relation between relative mass change and exposure time in water.

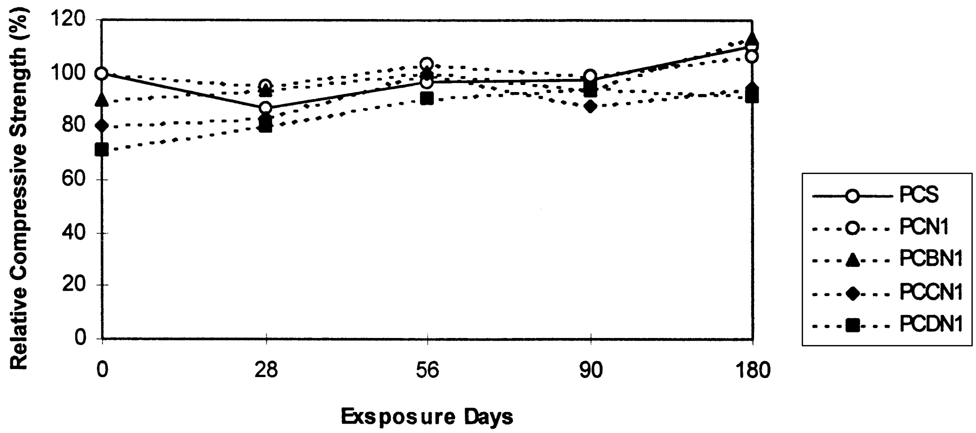

Fig. 4. Relation between compressive strength and exposure time in 10,000 mg/l concentration sodium sulfate solution.

seemed more effective against the sulfate attack at the lower sulfate concentration.

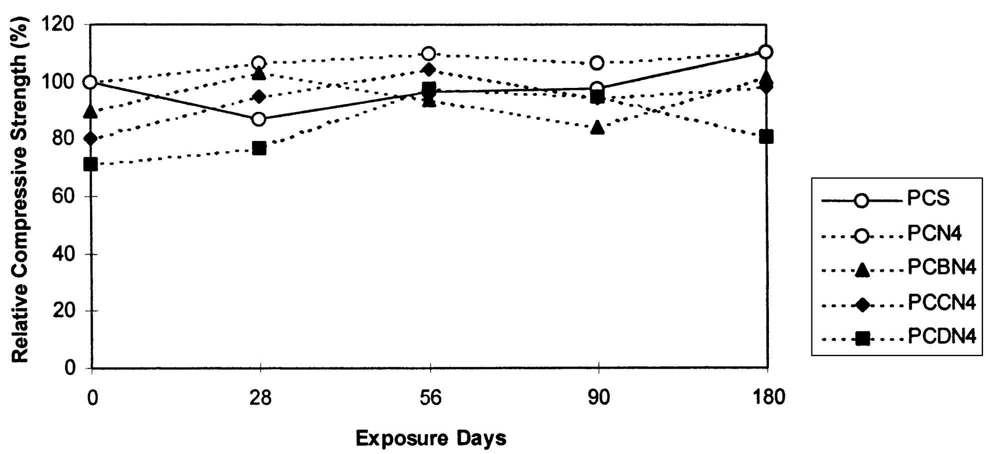

Fig. 5. Relation between compressive strength and exposure time in 40,000 mg/l concentration sodium sulfate solution.

Some decline in the flexural strength of the mortars containing 8% and 16% can be seen on the first 28 days of sulfate exposure (Figs. 6 and 7). However, cyclic changes can be observed after 28 days. When flexural strength results are considered, PC mortars showed better performance.

There was a significant mass increase on the first 40 days in sulfate solution of 10,000 mg/l and 14 days in 40,000 mg/l concentration for the specimens containing

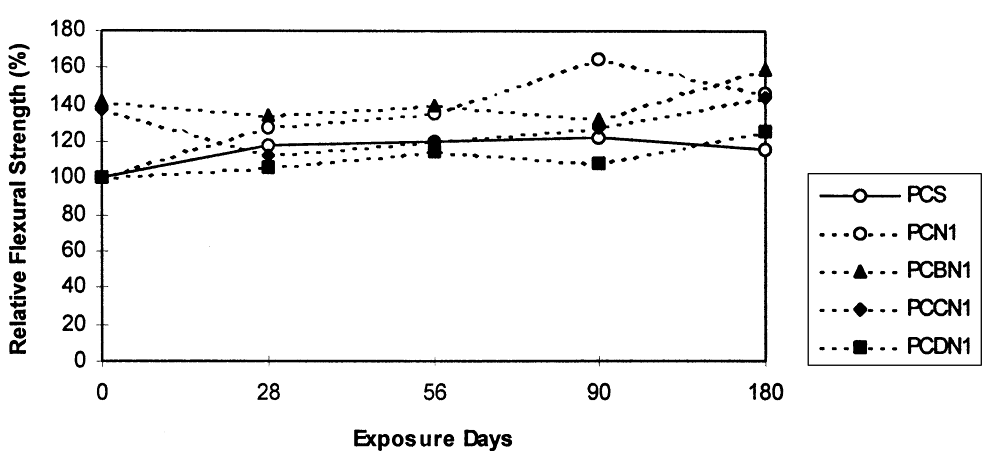

Fig. 6. Relation between flexural strength and exposure time in 10,000 mg/l concentration sodium sulfate solution.

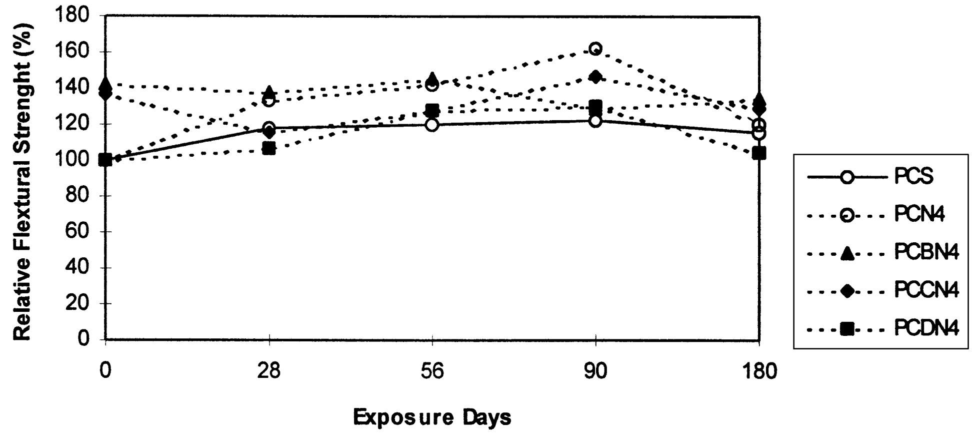

Fig. 7. Relation between flexural strength and exposure time in 40,000 mg/l concentration sodium sulfate solution.

8% WSA (Figs. 8 and 9). The mass increased steadily at a lower rate for both concentrations. However, mass increase rate was lower in solution of 40,00 mg/l concentration and at a tendency for decrease could be observed at the end of the testing period. On the other hand, there was a general steady increase in mass at a lower rate for the replacement level of WSA at 16% and 24% in lower sulfate concentration. After a slight mass increase on the first 56 days of

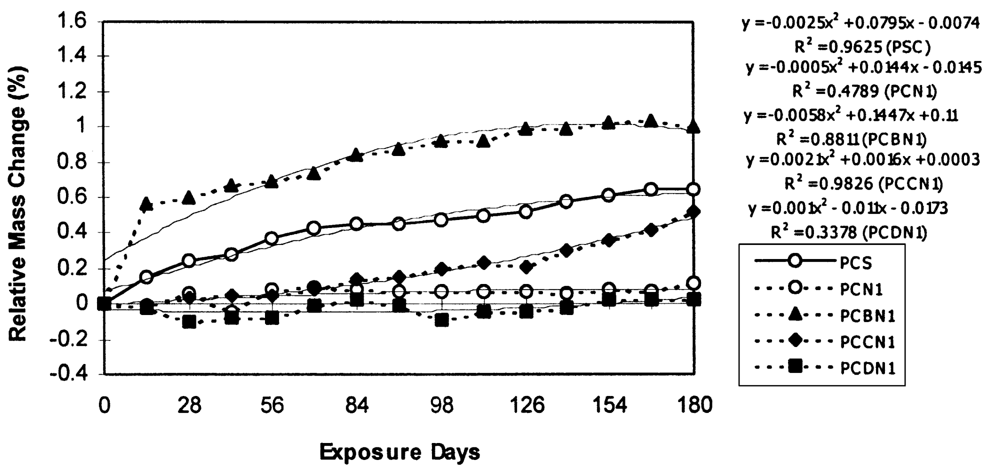

Fig. 8. Relation between relative mass change and exposure time in 10,000 mg/l concentration sodium sulfate solution.

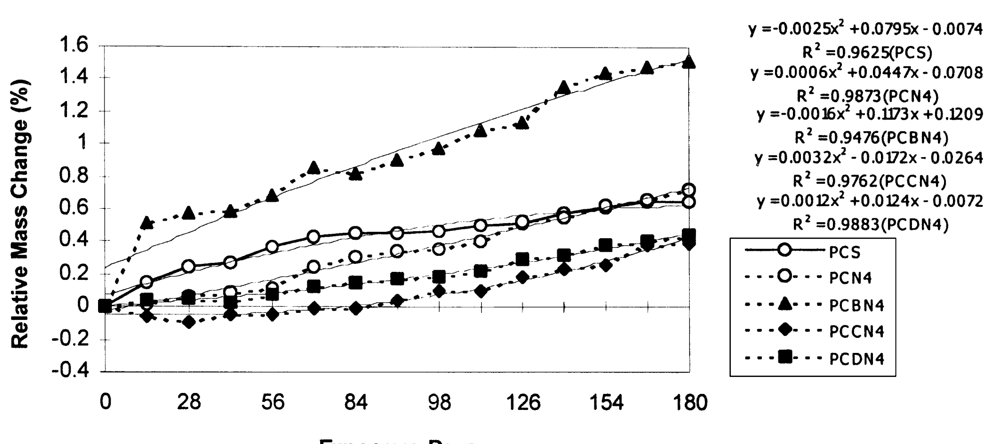

Fig. 9. Relation between relative mass change and exposure time in 40,000 mg/l concentration sodium sulfate solution.

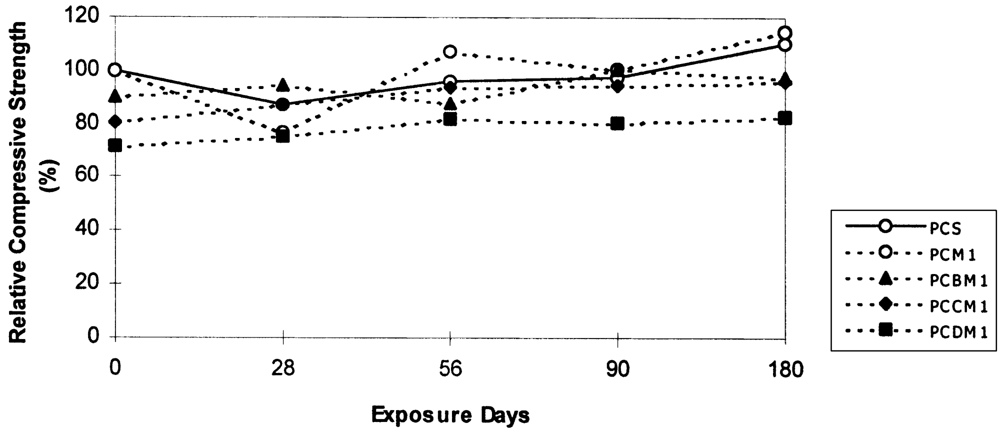

Fig. 10. Relation between compressive strength and exposure time in 10,000 mg/l concentration magnesium sulfate solution.

exposure, an accelerated increase could be seen for the 16% replacement level in 4000 mg/l concentration. At the highest amount of WSA, mass was almost the same until the end of the immersion period. Results showed that mass

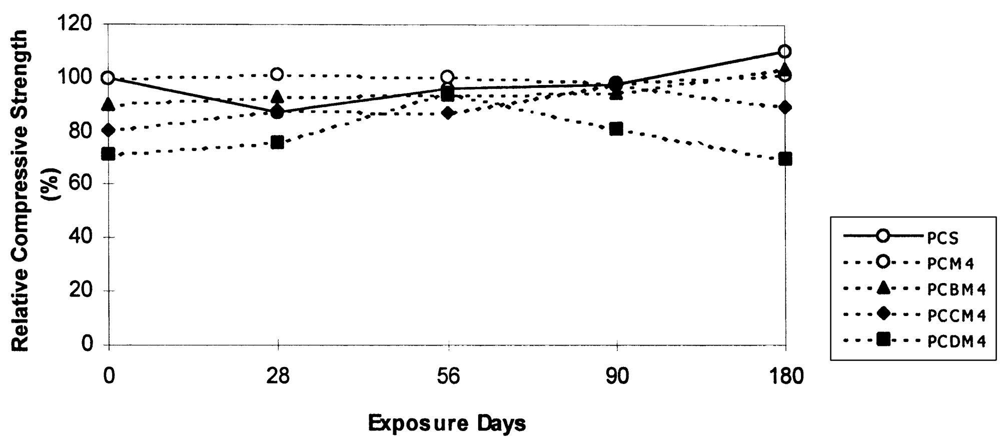

Fig. 11. Relation between compressive strength and exposure time in 40,000 mg/l concentration magnesium sulfate solution.

changes are dependent on the replacement level of WSA and sulfate concentration.

3.3. Magnesium sulfate solution

Compressive strength of all the mortars containing WSA was generally higher than the initial strength for the two sulfate concentrations (Figs. 10 and 11). Performance of these mixtures was comparable with PC mortars

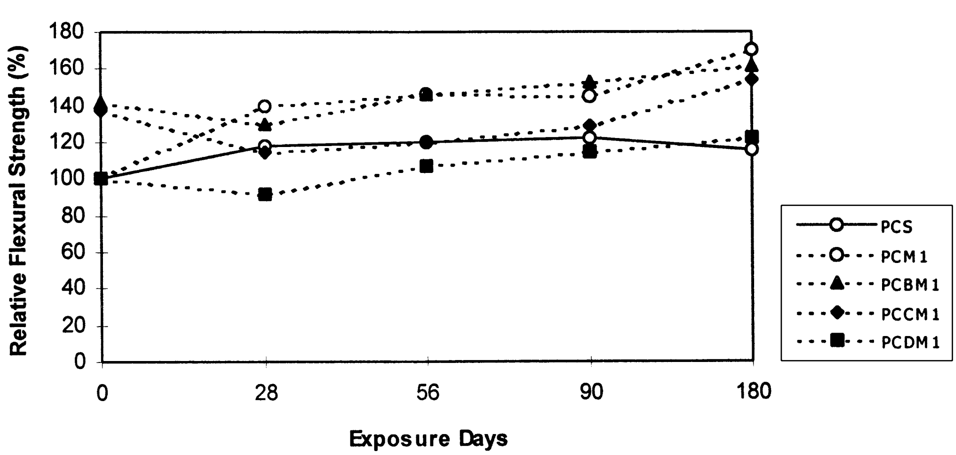

Fig. 12. Relation between flexural strength and exposure time in 10,000 mg/l concentration magnesium sulfate solution.

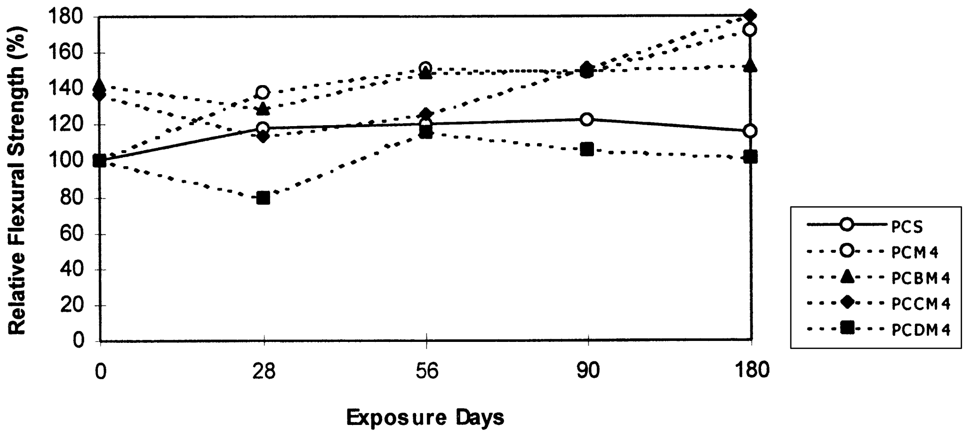

Fig. 13. Relation between flexural strength and exposure time in 40,000 mg/l concentration magnesium sulfate solution.

and was sometimes even better. Although the strength was lower for the PC–WSA mortars compared to PC pozzolanic reactions developed at a slow rate as mentioned above.

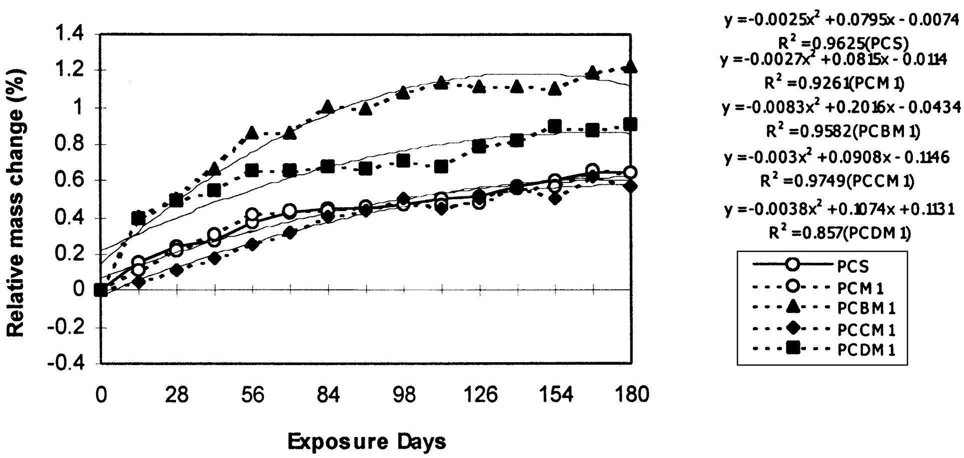

Fig. 14. Relation between relative mass change and exposure time in 10,000 mg/l concentration magnesium sulfate solution.

mortars, they showed a good performance in magnesium sulfate solutions. This can be attributed probably to

When the flexural strengths are considered, mortars containing WSA gained strength up to 180 days in the

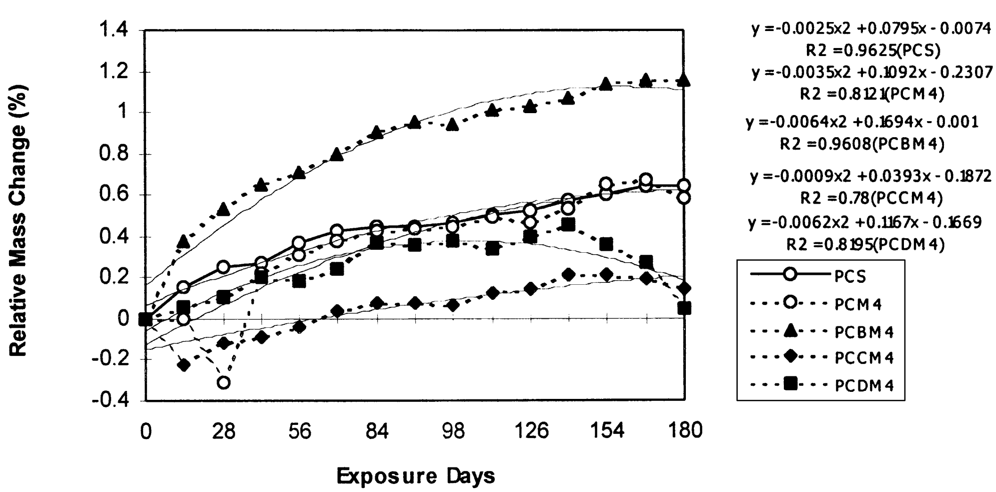

Fig. 15. Relation between relative mass change and exposure time in 40,000 mg/l concentration magnesium sulfate solution.

solution of 10,000 mg/l concentration (Fig. 12). Similar trend was observed in the higher sulfate concentration solution except 28 days for the 24% replacement level of WSA (Fig. 13). However, performance of PC mortars in sulfate solution was significantly better than the mixtures containing WSA.

The mass of the specimens generally increased in the solution of 10,000 mg/l concentration during the test. Mass increase was the highest for the specimens containing 8% WSA (Figs. 14 and 15). In magnesium sulfate solution at 10,000 mg/l concentration, mass increase of the specimens containing 8% and 24% WSA was higher compared to water curing for the PC–WSA mortars on the first days of exposure (Fig. 14). Thereafter, slight increases and decreases could be observed. Significant difference in mass change was observed for the mortars containing 16% WSA in the 10,000 mg/l solution. Sharp increase in mass on the first days for the 8% and 24% replacement level could not be observed for this replacement level whose mass increased almost linearly. Mass change of the specimens in the 40,000 mg/l concentration solution for the 8% WSA replacement level was similar to that in 10,000 mg/l solution (Fig. 15). On the other hand, mass change showed different trends for the higher replacement level of WSA for the higher sulfate concentration. Significant mass decrease could be observed at later days of sulfate exposure, especially for the 24% WSA replacement level.

Mass changes of cement-based materials in sulfate solutions are dependent on different physical and chemical processes. According to Lawrence [15], these processes are: hydration of binder, absorption of sulfate ions, withdrawal of water from the specimen due to osmotic forces, and leaching, and specimen disintegration. The first two processes lead to increase in mass and the latter to decrease. When cement-based materials are subjected to magnesium sulfate attack, calcium hydroxide converts to gypsum and brucite (magnesium hydroxide) [11]. Lobo and Cohen [13] reported that formation and deposition of brucite and gypsum result in mass gain in cement paste. They also claimed that mass gain was not observed in mortar specimens. However, their results indicated that there was a mass gain for a short period for the mortar specimens. Thereafter, a different mechanism affects the mass changes. CSH gel of cement hydration converts to gypsum. This leads to mass loss [2]. Brucite formation on the specimen faces protects the CSH gel from magnesium sulfate attack [2,13]. Mass change results in our experiments showed that factors leading to mass increase such as hydration and absorption of sulfate ions are dominant on the first days of sulfate exposure. Thereafter, mass decreasing factors gradually become effective. This trend is more evident at high concentration of magnesium sulfate and high level of WSA. In this research, any softening, cracking and spalling was not observed during the tests.

4. Conclusions

WSA replacement affected beneficially compressive strength of mortars in sodium sulfate solution at 10,000 and 40,000 mg/l. When flexural strength results are considered, performance of PC–WSA mortars is not better than the PC mortar. Mass changes in sodium sulfate solution are dependent on WSA replacement level and sulfate concentration.

Mortars containing WSA up to 24% of the cement by mass generally gained compressive and flexural strengths in magnesium sulfate solutions of 10,000 and 40,000 mg/l during the 180 days of immersion. Mortar mixture containing 8% WSA showed highest mass increase in water and magnesium sulfate solutions. At higher replacement levels, mass increase was lower and decrease could be observed after 140 days in concentration of 40,000 mg/l. Strength decrease after 56 days and mass decrease at later days in solution at concentration of 40,000 mg/l at the 24% replacement level can be accepted as an indication of a negative development at later days. However, to reach a final conclusion, experiments must be carried out for longer time periods.

Acknowledgments

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References

[1] H. Biricik, Pozzolanic properties of wheat straw ash and effects on durability of mortar, PhD Thesis, The Institute for Graduate Studies in Science and Technology of Yildiz Technical University, 1995.

[2] M.D. Cohen, A. Bentur, Durability of Portland cement–silica fume pastes in magnesium sulfate and sodium sulfate solutions, ACI Mater J 85 (1988) 148–157.

[3] R.S. Gollop, H.F.W. Taylor, Microstructural and microanalytical studies of sulfate attack: I. Ordinary Portland cement paste, Cem Concr Res 22 (1992) 1027–1038.

[4] J.W. Wang, Sulfate attack on hardened cement paste, Cem Concr Res 24 (4) (1994) 735–742.

[5] P.K. Mehta, Mechanism of sulfate attack on Portland cement concrete — another look, Cem Concr Res 13 (1983) 401–406.

[6] K. Torii, M. Kawamura, Effects of fly ash and silica fume on the resistance of mortar to sulfuric acid and sulfate attack, Cem Concr Res 24 (1994) 361–370.

[7] P.J. Tikalsky, R.L. Carrasquillo, Influence of fly ash on the sulfate resistance of concrete, ACI Struct J 89 (1992) 69–75.

[8] K. Torii, K. Taniguchi, M. Kawamura, Sulfate resistance of high fly ash content concrete, Cem Concr Res 25 (4) (1995) 759–768.

[9] P.S. Mangat, J.M. Khatib, Influence of fly ash, silica fume, and slag on sulfate resistance of concrete, ACI Mater J 92 (1995) 542–552.

[10] S. Wild, J.M. Khatib, M. O'Farrell, Sulphate resistance of mortar, containing ground brick clay calcined at different temperatures, Cem Concr Res 27 (5) (1997) 697–709.

[11] D. Bonen, M.D. Cohen, Magnesium sulfate attack on Portland cement paste: I. Microstructural analysis, Cem Concr Res 22 (1992) 169.
[12] R.S. Gollop, H.F.W. Taylor, Microstructural and microanalytical studies of sulfate attack: IV. Reactions of a slag cement paste with sodium and magnesium sulfate solutions, Cem Concr Res 26 (7) (1996) 1013–1028.
[13] C. Lobo, M.D. Cohen, Magnesium sulfate attack on Portland cement with silica fume pastes and mortars, CANMET/ACI International Workshop on the Use of Silica Fume in Concrete, Washington, DC, (1991) 391–395.
[14] F. Türker, F. Aköz, S. Koral, N. Yüzer, Effects of magnesium sulfate concentration on the sulfate resistance of mortars with and without silica fume, Cem Concr Res 27 (2) (1997) 205–214.
[15] C.D. Lawrence, The influence of binder type of sulfate resistance, Cem Concr Res 22 (1992) 1047–1058.