Construction and Building Materials xxx (2009) xxx–xxx

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes

F. Pacheco-Torgal [a,*], Said Jalali [b,1]

[a] University of Minho, C-TAC Research Unit, 4800 Guimarães, Portugal
[b] University of Minho, Department of Civil Engineering, 4800 Guimarães, Portugal

ARTICLE INFO

Article history:
Received 10 April 2009
Received in revised form 30 June 2009
Accepted 5 August 2009
Available online xxxx

Keywords:
Precast concrete
Polymer
Impregnation
Addition
Sulphuric acid
Sulphate resistant cement
Concrete
Fly ash
Styrene–butadiene
Melamine

ABSTRACT

Classic approaches to polymer-modificated Portland cement based materials usually forget the specific nature of the precast concrete industry and also the economic impacts of each technical option. This manuscript report results of a wider investigation which aims to understand what is the best option for the concrete pipe industry as far as sulphuric acid resistant is concerned, polymer addition or polymer impregnation. Results show that the use of polymer addition it is not economically attractive when compared to polymer impregnation. The increase of costs per meter of pipe is too high. The use of polymer impregnation enhances the chemical resistance of concrete considerably. Furthermore, it is economically viable, especially for smaller diameters. Results also show that using sulphate resistant cements improve the chemical resistance without cost increase.

1. Introduction

The use of polymers in concrete goes back as far as 1923 when for the first time a patent was issued for a concrete floor with natural latex, being that Portland cement was used only as filler. It was only in 1924 that was issued the first patent on hydraulic binders modified with polymers [1]. However, only in the 1950s appeared the first uses of concrete modified with polymers, particularly in the rehabilitation of concrete structures [2]. At present three kinds of polymer based concrete can be separated due to their different nature. One group is related to polymer modified concrete – PMC or "polymer cement concrete" – PCC and is composed of aggregates and a binder matrix where phases generated by the hydration of Portland cement coexists with polymeric phases. Another group is related to polymer impregnated concretes – PIC, in which concretes are impregnated with a monomer of low viscosity, usually of methyl methacrylate in order to fill its porous structure. A third group is related to polymer concrete – PC, this group is composed of aggregates and a polymer matrix without Portland cement [3]. For PMC, additives are added to concrete during the mixing stage, usually in the form of a colloidal suspension of latex, powder, or as water-soluble polymers or liquids, and the literature usually refers to more used the polymer of styrene–butadiene (SBR) of polyacrylic-ester (PAE), polyethylene vinyl acetate (EVA). These materials are know to possess superior durability over ordinary Portland cement concrete, assessed by resistance to acid attack [4–6], resistance to action of ice-melting [7], resistance to diffusion of chlorides [8]. The explanations for this difference in behaviour are due to one hand, to a lower porosity of the formation of a polymer film inside the pores [9] and to a low permeability to water access [10]. Several authors show that polymer impregnation of concrete materials may lead to an increase durability depending of the type of polymers that are used [11–13]. Nevertheless, there are not studies that could help to understand what is the best option economically speaking, i.e., polymer addition or polymer impregnation are both to merit as far as industrial production is concerned? In this manuscript technical and economic data are presented in order to help a better judgment about the previous question. The use of two sulphate resistant cements and fly ash addition are also tested about their technical and economic performance.

2. Experimental work

The experimental work is based in eight mixtures (four mortar and four concrete mixtures). The first and second sets of mortar mixtures are meant to assess the performance respectively of polymer modified mortars and polymer impregnated mortars. The third set evaluates the performance of sulphate resistant

* Corresponding author. Tel.: +351 253 510200; fax: +351 253 510213.
E-mail addresses: torgal@civil.uminho.pt (F. Pacheco-Torgal), said@civil.uminho.pt (S. Jalali).
1 Tel.: +351 253 510200; fax: +351 253 510213.

0950-0618/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.conbuildmat.2009.08.001

Please cite this article in press as: Pacheco-Torgal F, Jalali S. Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes. Constr Build Mater (2009), doi:10.1016/j.conbuildmat.2009.08.001

Table 1
Characteristics of aggregates.

Characteristics	Fine sand (0–1 mm)	Sand (2–3 mm)	Coarse aggregates (5–15 mm)	Coarse aggregates (15–25 mm)
Density (kg/m^3)	2542	2538	2634	2664
Water absorption by immersion (%)	1.2	0.9	1.4	0.7
Faury fineness modulus	1.644	3.478	4.873	6.292

Table 2
Chemical, physical and mechanical properties of the ordinary Portland cement and fly ash.

	CEM 32.5 IV	CEM 42.5 I SR-MR	CEM 42.5 II	Fly ash
Chemical compositions (%)				
LOI	3.38	2.61	4.95	3.30
SiO_2	33.57	20.32	18.50	54.48
Al_2O_3	15.46	4.34	5.00	25.76
Fe_2O_3	5.63	4.26	2.90	8.43
CaO (total)	36.08	62.26	62.80	2.56
MgO	2.56	2.72	1.40	2.14
Na_2O	–	–	0.30	0.71
NO_3	–	–	0.70	–
SO_3	2.00	2.46	2.75	0.47
TiO_2	–	–	–	1.14
K_2O	–	–	–	3.13
P_2O_5	–	–	–	1.10
MnO_2	–	–	–	0.08
Cl	–	–	0.01	–
CaO (free)	0.95	1.22	–	–
Mineral composition (%)				
Clinquer	55	96	80	–
Fly ash	41	–	14	–
Limestone filler	4	4	6	–
Physical characteristics				
IR (%)	33.15	0.19	0.70	–
Blaine (cm^2/kg)	4405	4007	3700	–
Setting time				
Initial	4 h10 m	3 h42 m	2 h30 m	–
Final	5 h10 m	4 h30 m	3 h49 m	–
Compressive strength (MPa)				
1 Day	–	–	19.0	–
2 Days	16.8	28.8	28.0	–
7 Days	26.9	43.3	–	–
28 Days	36.0	51.9	52.0	–

cements based mortars and the fourth evaluates the influence of using fly ash based mortars. The characteristics of the aggregates used to make the four sets of mortar mixtures and the four concrete mixtures are shown in Table 1. The binders used in the experimental work are shown in Table 2. For the first and second set, five mortars mixtures were made with two different W/C ratios and two different melamine percentages (Table 3). Mixtures with a melamine percentage of 0.8 and a W/C ratio of 0.5 where named M_0.8_0.5. Mortar specimens with $40 \times 40 \times 40$ mm^3 were moulded and cured under water at 40 °C during 9 days which correspond to 28 days curing at 18 ± 1 °C. For the second set of mixtures specimens were impregnated with melamine and they were cured in air during 48 h to allow melamine to polymerize at laboratory temperature. The impregnation process was carried out by gravity at laboratory temperature. The third mixture includes two control compositions with different cements (Control SR-MR and Control 32.5IV) and the same composition where impregnated with melamine (Control SR-MR_MI and Control 32.5IV_MI). The fourth set includes a composition with 20% fly ash (Control Fly ash) and a composition impregnated with melamine (Control Fly ash_MI). Concrete mix proportions are shown in Table 4. Three modified polymer mixtures were made. PM_M_2 stands for 2% melamine addition, PM_SK_10 for 10% styrene–butadiene latex addition and PM_PCI_10 for 10% styrene–butadiene emulsion addition. The resistance to the acid attack was tested by immersion of concrete specimens in sulphuric acid solution (pH = 0.7). After curing time, i.e., 28 days, the concrete specimens were exposed to sulphuric acid while the reference specimens were conditioned in water. Chemical resistance was assessed by an evaluation on compressive strength and weight reduction. The exception was for concrete specimens that were testes only by weight reduction. Concrete samples were taken from concrete pipes. The compressive strength was determinate following the ISO 4012.

Table 3
Mortar mix proportions.

	Cement (g)	Sand (2–3 mm) (g)	Melanines (ml.)		Water (ml.)	W/C
			Solid	Liquid		
1° and 2° set						
Control	450	1350	0		225	0.5
M_0.8–0.5	450	1350	3.8		221.2	
			0.8	3		
M_0.8–0.4	450	1350	3.8		177	0.4
			0.8	3		
M_2.0–0.5	450	1350	9		216	0.5
			1.9	7.1		
M_2.0–0.4	450	1350	9		171	0.4
			1.9	7.1		
3° set						
Control I SR-MR	450	1350	–	–	225	0.5
Control 32.5 IV			–	–		
4° set						
Control 42.5 II with 20% of fly ash	450	1350	–	–	225	0.5

Table 4
Concrete mix proportions per cubic meter of concrete.

Components	Concrete mix			
	Control	PM_M_2	PM_SK_10	PM_PCI_10
Cement 32.5 (kg)	320.0	320.0	320.0	320.0
Fine sand (0–1 mm) (kg)	600.0	600.0	600.0	600.0
Sand (2–3 mm) (kg)	600.0	600.0	600.0	600.0
Coarse aggregate 5/15 (kg)	800.0	800.0	800.0	800.0
Coarse aggregates 12/15 (kg)	400.0	400.0	400.0	400.0
Admixture (l)	–	6.40	85.70	77.70
Water (l)	227.0	212.0	162.0	162.0
A/C	0.709	0.663	0.506	0.506
Solid polymer/C	–	0.004	0.096	0.092

3. Results and discussion

3.1. Polymer addition

Weight reduction of melamine modified mortars is shown in Fig. 1. With the exception of the mixture with 2% melamine addition and a W/C = 0.4 (M_2.0–0.4) mixtures perform better than the control mixture. It seems that for the 0.8% polymer addition there is not much difference using a W/C = 0.4 or a W/C = 0.5. But for the 2% melamine addition a decrease in W/C ratio from 0.5 to 0.4 brings a worst performance for all curing ages. Using melamine addition is responsible for minor weight reductions when a comparison with the control mortar is made between 9% and 18%. Compressive strength of polymer modified mortars is shown in Fig. 2. Except for the case of the mixture with 2% of melamine and a W/C = 0.4 it could be said that melamine addition is not an effective addition to increase sulphuric acid resistance. But the fact is that the mixture with the best performance is the mixture that had the higher weight loss. Since weight loss seems to be a more accurate measure of chemical resistance the results of compressive strength should be viewed with caution. The other three mixtures performed worst than the control mixture. It is not possible to say that compressive strength reduction is influenced by the water/cement ratio. When a polymer percentage of 0.8 is used reducing water ratio increases strength reduction but when the polymer percentage is 2% a decrease of W/C ratio is associated with a minor strength reduction. For the concrete specimens all mixtures with

Please cite this article in press as: Pacheco-Torgal F, Jalali S. Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes. Constr Build Mater (2009), doi:10.1016/j.conbuildmat.2009.08.001

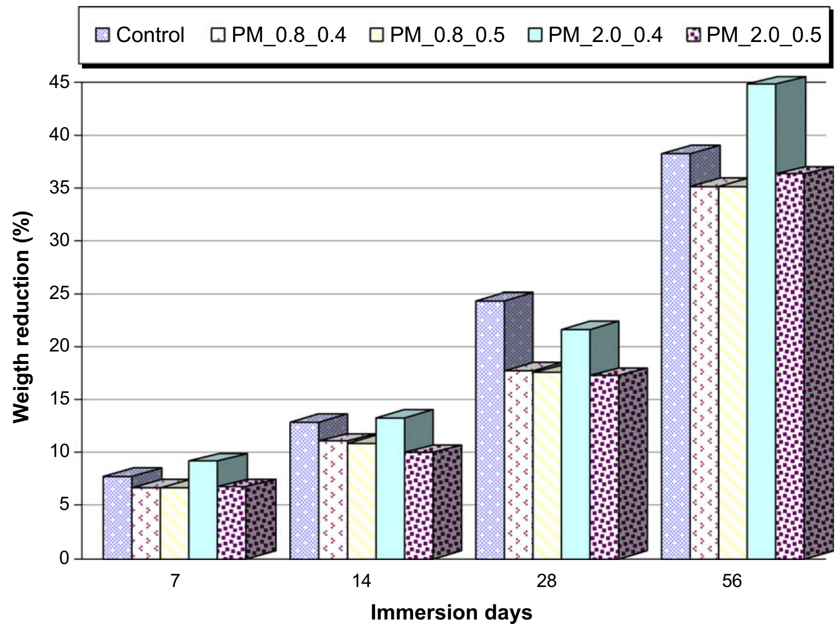

Fig. 1. Weight reduction of polymer modified mortars.

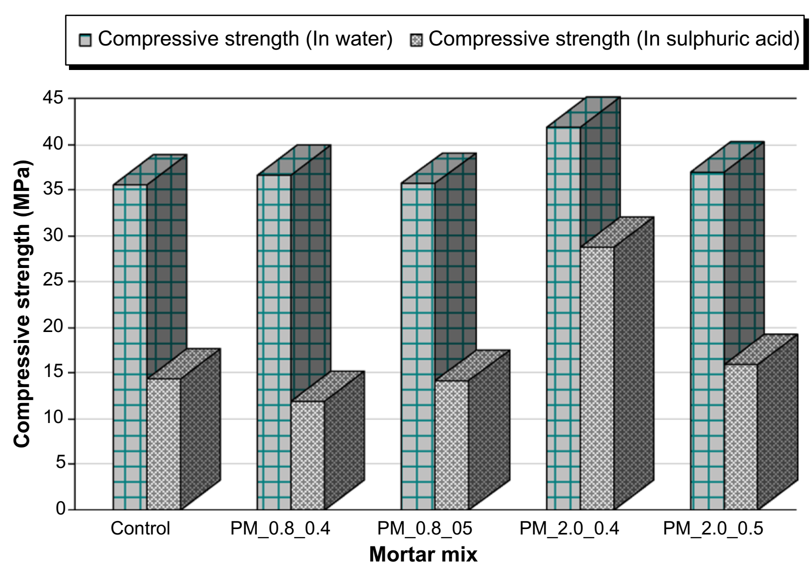

Fig. 2. Compressive strength of polymer modified mortars.

polymer addition performs worst than the control mixture (Fig. 3). The weight reduction is very dependent on the polymer type and form the time exposed to acid solution. Although melamine addition performed better for 7 days it had the worst performance for 14 and 28 days.

3.2. Polymer impregnation

Strength reduction is far lower for polymer impregnation than for polymer addition (Fig. 4). The best compressive strength result is obtained by the mixture with a 0.8 melamine percentage that has the same performance of the control mortar. Increasing melamine to 2% leads to a higher strength loss (45.5–65.6%). Compressive strength reduction seems to be influenced by the water/cement ratio. Reducing the W/C ratio from 0.5 to 0.4 is responsible for a major compressive strength reduction. For polymer impregnated mortars results show that all mixtures perform worst than the control mixture (Fig. 5). Nevertheless, polymer impregnation performs better than polymer addition. For 7 days all specimens had a weight reduction below 5%. Fig. 6 shows the compressive strength of mortars mixtures made with sulphat resistant cements and fly ash. The results shows that fly ash addition leads to a

Please cite this article in press as: Pacheco-Torgal F, Jalali S. Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes. Constr Build Mater (2009), doi:10.1016/j.conbuildmat.2009.08.001

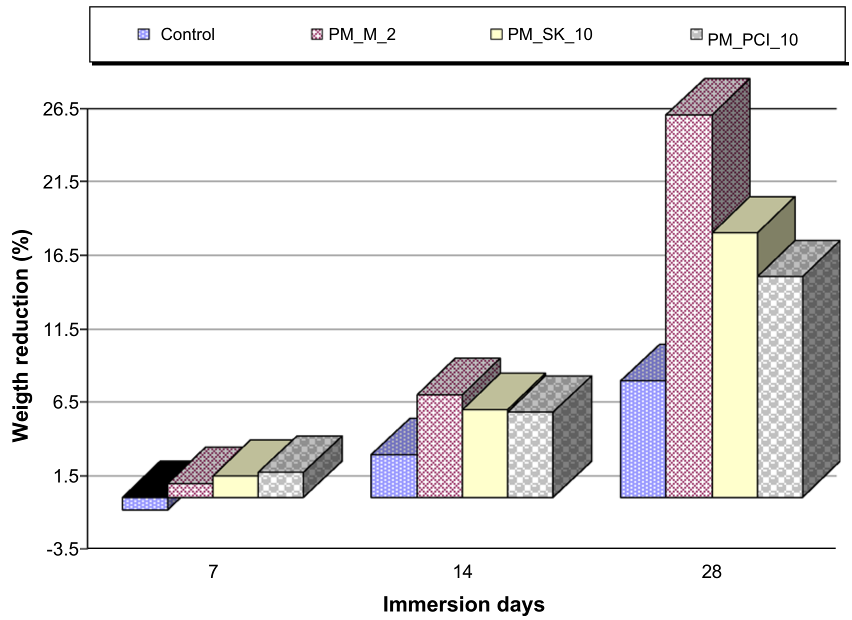

Fig. 3. Weight reduction of polymer modified concrete.

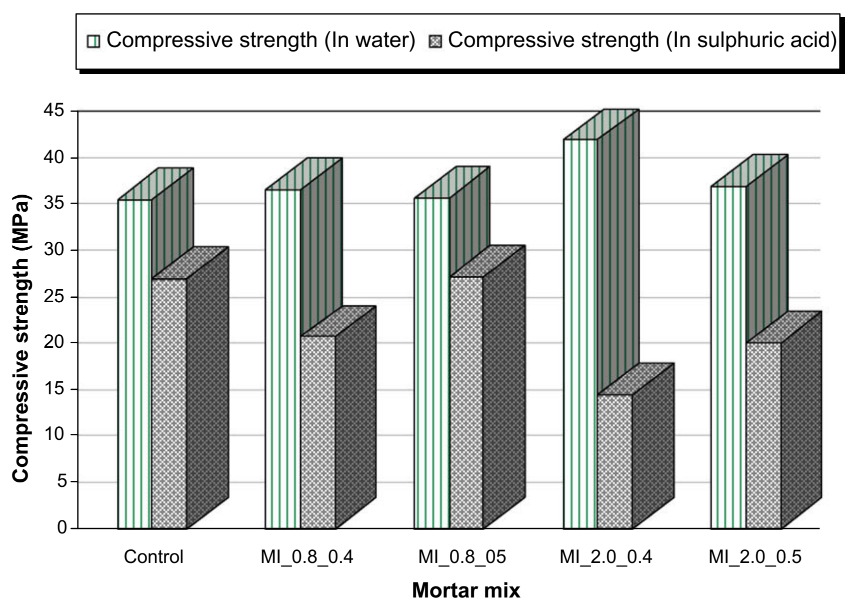

Fig. 4. Compressive strength of polymer impregnated mortars.

compressive strength reduction higher than the control mixture meaning that it does seems a good solution to improve resistance to acid attack. The use of sulphate resistant cements (SR-MR and 32.5IV) seems to be a good option since both improve chemical resistance to acid attack. Fig. 7 confirms that fly ash addition is not an option regarding chemical resistance of Portland based products. Results from acid immersion versus time shows that cement 32.5IV is more effective than SR-MR. Mortar specimens made with that particular cement and impregnated with polymer have not any weight reduction at least in the first 28 days. Nevertheless, that behaviour is independent of polymer impregnation. For concrete specimens (Fig. 8), weight reduction results show that polymer impregnation performance is influenced by the polymer type. Being that the minimum weight loss takes place when the melamine impregnation was used.

3.3. Economic evaluation

Precast concrete production with polymer addition it is not a viable solution since it implies a very high cost (Table 5). Polymer impregnated concrete has much lower costs especially for small pipe diameters (Table 6). Using sulphate resistant cements are also a good option since they have a high chemical resistance without cost increase (Table 7).

Please cite this article in press as: Pacheco-Torgal F, Jalali S. Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes. Constr Build Mater (2009), doi:10.1016/j.conbuildmat.2009.08.001

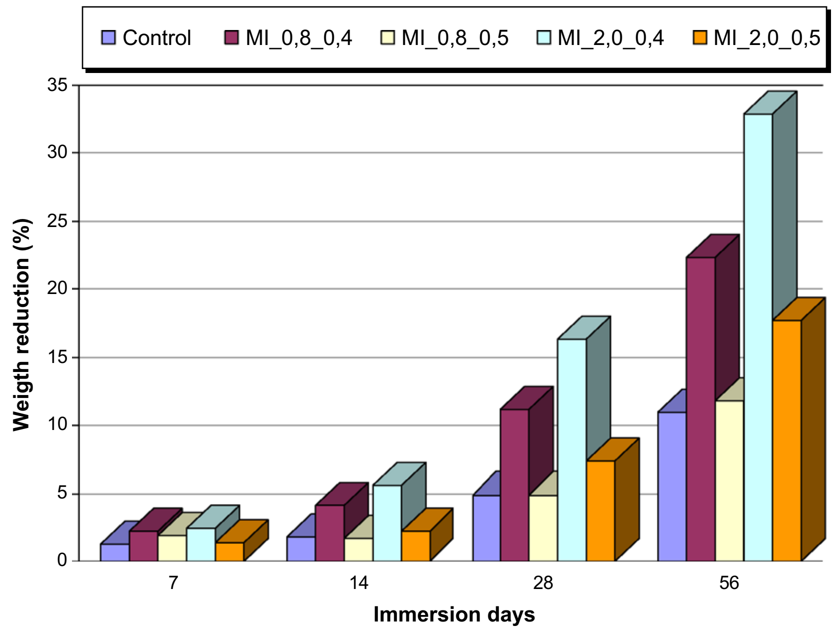

Fig. 5. Weight reduction of polymer impregnated mortars.

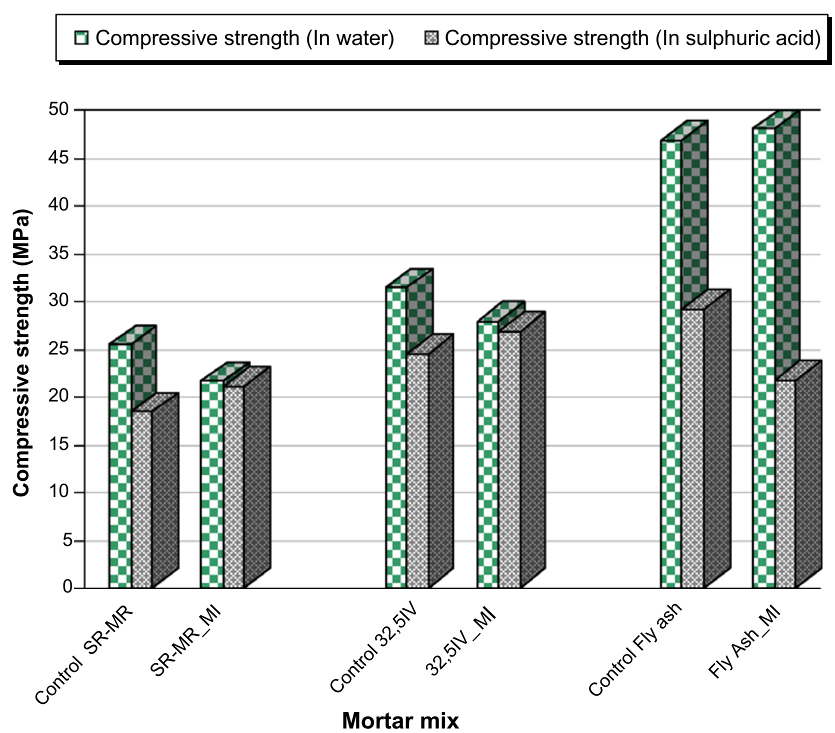

Fig. 6. Compressive strength of mortars mixtures made with sulphate resistant cements and fly ash. Control mixtures versus impregnated mixtures (MI).

4. Conclusions

This study presents investigations about sulphuric acid resistance of polymer modificated, and fly ash cement concretes. Based on the experimental results the following conclusions can be drawn. The use of concrete with polymer addition during the mixing phase showed minor beneficial effect on the durability and acid resistance of concrete pipes. Furthermore, this solution is not economically attractive because the increase of costs per meter of pipe is too high. Concrete with polymer impregnation performs better than concrete with polymer addition. The use of polymer impregnation process enhances the chemical resistance of hardened concrete. This solution is economically viable, especially for smaller diameters. The use of special cements has a positive impact on

Please cite this article in press as: Pacheco-Torgal F, Jalali S. Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes. Constr Build Mater (2009), doi:10.1016/j.conbuildmat.2009.08.001

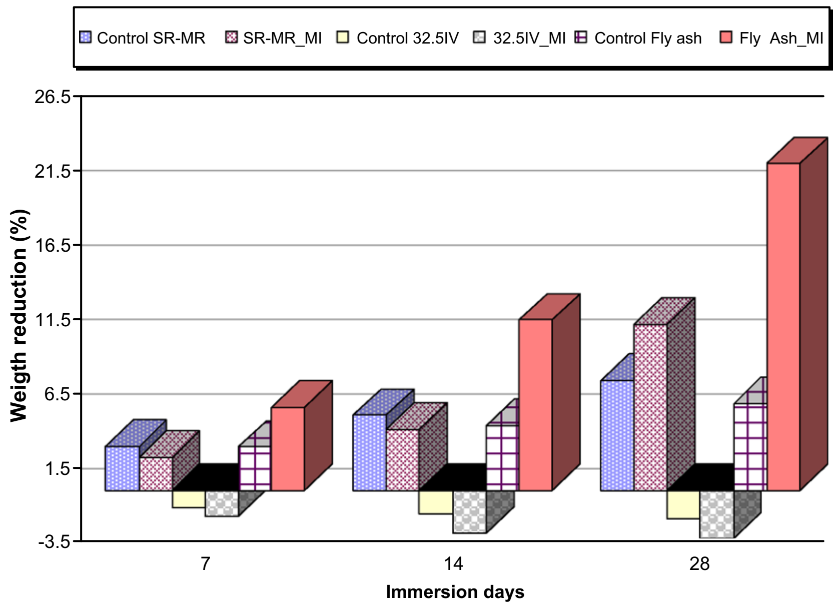

Fig. 7. Weight reduction of of mortars mixtures made with sulphate resistant cements and fly ash. Control mixtures versus impregnated mixtures (MI).

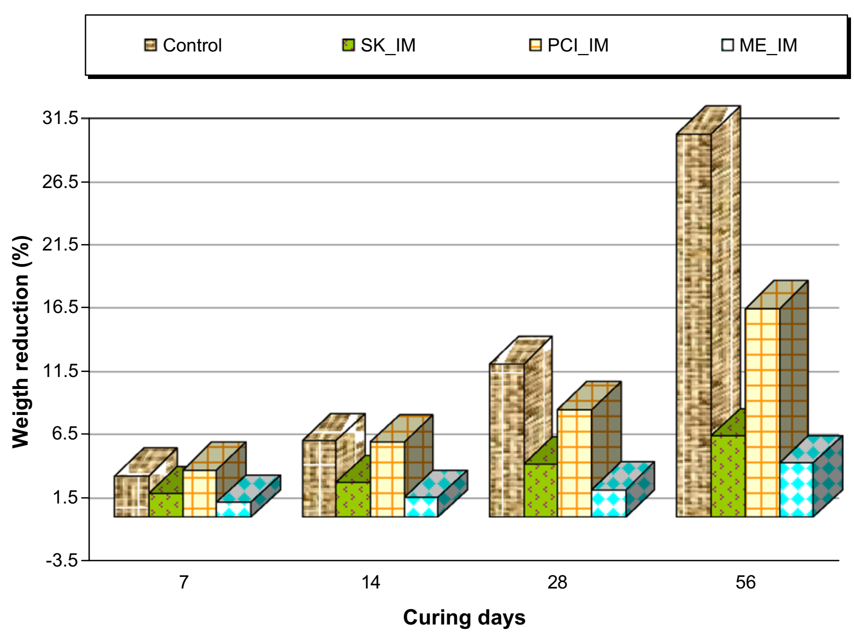

Fig. 8. Weight reduction of polymer impregnated concrete.

Table 5
Polymer modified concrete pipe costs.

Pipe diameter (m)	0.15	0.2	0.25	0.3	0.4	0.5	0.6
Pipe volume (m^3)	0.011775	0.01884	0.02355	0.02826	0.05024	0.0785	0.11304
Current coating cost/pipe (euro)	3.00	3.35	4.00	4.20	5.85	6.80	7.95
Current coating cost/m^3 (euro)	254.78	177.81	169.85	148.62	116.44	86.62	70.33
Liters of styrene–butadiene latex per m^3 (l)	28	20	19	17	13	10	8
Liters of styrene–butadiene emulsion per m^3 (l)	61	42	40	35	28	21	17
Liters of melamine per m^3 (l)	150	105	100	87	68	51	41

Please cite this article in press as: Pacheco-Torgal F, Jalali S. Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes. Constr Build Mater (2009), doi:10.1016/j.conbuildmat.2009.08.001

Table 6
Polymer impregnated concrete pipe costs.

Pipe diameter (m)	0.15	0.2	0.25	0.3	0.4	0.5	0.6
Cost/ml (euro)	4.95	5.25	7.90	8.40	10.40	15.00	19.00
Weight (kg)	44	54	70	105	165	245	325
Current coating cost (euro)	3.00	3.35	4.00	4.60	6.25	7.30	8.35
Styrene–butadiene latex absorption (l)	2.9	3.6	4.7	7.0	11.0	16.3	21.6
Styrene–butadiene latex impregnation cost (euro)	26.33	32.32	41.90	62.84	98.75	146.63	194.51
Cost increase with styrene–butadiene latex (%)	778	966	1263	1941	3083	4644	6205
Styrene–butadiene emulsion absorption (l)	3.17	3.89	5.05	7.57	11.90	17.66	23.43
Styrene–butadiene emulsion impregnation cost (euro)	13.32	16.35	21.20	31.80	49.97	74.19	98.42
Cost increase with styrene–butadiene emulsion (%)	344	388	430	591	699	916	1079
Melamine absorption (l)	1.95	2.40	3.11	4.66	7.33	10.88	14.43
Melamine impregnation cost (euro)	33.2	40.8	52.8	79.3	124.5	184.9	245.3
Cost increase with melamine (%)	11	24	43	111	207	373	539

Table 7
Concrete pipes made with sulphate resistant cements.

Pipe diameter (m)	0.15	0.2	0.25	0.3	0.4	0.5	0.6
Pipe volume (m^3)	0.011775	0.01884	0.02355	0.02826	0.05024	0.0785	0.11304
Current coating cost (euro)	3.00	3.35	4.00	4.20	5.85	6.80	7.95
Cement/pipe (kg)	3.768	6.0288	7.536	9.0432	16.0768	25.12	36.1728
Cement/pipe cost (euro)	0.53	0.84	1.06	1.27	2.25	3.52	5.06
Cement SR-MR/pipe cost (euro)	0.53	0.85	1.06	1.28	2.27	3.54	5.10
Cost increase (euro)	0	0.01	0.01	0.01	0.02	0.03	0.04
Cement type 32.5 IV/pipe cost (euro)	0.46	0.74	0.93	1.11	1.98	3.09	4.45
Cost increase (euro)	−0.06	−0.1	−0.13	−0.15	−0.27	−0.43	−0.61

the quality of concrete. If the sulphate resistance is the aim, such cements are highly recommended because no increase in costs or procedures of fabrication is involved.

References

[1] Ohama Y. Polymer-based admixtures. Cem Concrete Compos 1998;20:189–212.
[2] Storte M. Látex estireno-butadieno. Aplicação em concretos de cimento polímero. Dissertação de Mestrado, Escola Politécnica da Universidade de S. Paulo; 1991.
[3] Fowler DW. Polymers in concrete: a vision for the 21st century. Cem Concr Compos 1999;21:449–52.
[4] Shaker FA, El-Dieb AS, Reda MN. Durability of styrene–butadiene latex modified concrete. Cem Concr Res 1997;27:711–20.
[5] Monteny J, Belie N, Vincke E, Verstraete W, Taerwe L. Chemical and microbiological tests to simulate sulphuric acid corrosion of polymer-modified concrete. Cem Concr Res 2001;31:1359–65.
[6] Monteny J, Belie N, Vincke E, Verstraete W, Taerwe L. Simulation of corrosion in sewer systems by laboratory testing. In: Proceedings of the fib-symposium concrete and environment, Berlin, Germany; 2001. p. 91.
[7] Chmielewska B. Adhesion strength and other mechanical properties of SBR modified concrete. In: 12Th International congress on polymers in concrete, Chuncheon, Korea; 2007. p. 157–66.
[8] Yang Z, Shi X, Creighton A, Peterson M. Effect of styrene–butadiene rubber latex on the chloride permeability and microstructure of Portland cement mortar. Constr Build Mater 2008;23:2283–90.
[9] Rossignolo J. Porosity and calcium hydroxide content of portland cement pastes with active sílica and SBR látex. Revista Matéria 2005;10:437–42 [only in Portuguese].
[10] Neelamegan M, Dattatreya J, Harish K. Effect of latex and fibber addition on mechanical and durability. Properties of sintered fly ash ligthweigth aggregate concrete mixtures. In: 12th international congress on polymers in concrete, Chuncheon, Korea; 2007. p. 113–21.
[11] Moreira P, Aguiar José B. Aires Camões – Systems for superficial protection of concrete. In: ISPIC 2006 International symposium on polymers in concrete, Guimarães, Portugal; 2006. p. 225–36.
[12] Ogawa H, Kano K, Mimura T, Nagai K, Shirai A, Ohama Y. Durability performance of barrier penetrants on concrete surfaces. In: 12th International congress on polymers in concrete, Chuncheon, Korea; 2007. p. 373–82.
[13] Shirai A, Kano K, Nagai K, Ide K, Ogawa H, Ohama Y. Basic properties of barrier penetrants as polymeric impregnants for concrete surfaces. In: 12th International congress on polymers in concrete, Chuncheon, Korea; 2007. p. 607–15.

Please cite this article in press as: Pacheco-Torgal F, Jalali S. Sulphuric acid resistance of plain, polymer modified, and fly ash cement concretes. Constr Build Mater (2009), doi:10.1016/j.conbuildmat.2009.08.001