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The physical and chemical effects of long-term sulphuric acid exposure on hybrid modified cement mortar

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ABSTRACT

The properties of a hybrid modified cement mortar (HM) after 5 years storage in a sulphuric acid solution were studied. HM was made by mixing ordinary portland cement (OPC), sand and water and subsequently adding Na_2SiO_3 (water glass), Na_2SiF_6, polyvinyl acetate, lignosulphonate, and tributylphosphate. A control mortar (CM) was prepared by mixing OPC, sand, and water. The compressive strength losses after sulphuric acid attack were measured. The microstructures of HM and CM after sulphuric acid attack were observed and analyzed by using scanning electron microscopy (SEM), and the porosity and the pore size distribution were measured by using mercury intrusion porosimetry (MIP). Fourier-transform infrared (FT-IR) spectroscopy was utilized to determine the phases present in HM and CM after sulphuric acid attack. Test results show that many cracks appeared in the near-surface region and many needle-like crystals in the centre region of CM after 5 years sulphuric acid exposure, leading to a higher porosity of 28.6% and a higher strength loss of 50.6%. By contrast, a basically monolithic structure was kept in HM after 5 years sulphuric acid exposure, resulting in a lower porosity of 13.3% and a lower strength loss of 27.4%.

1. Introduction

In many parts of the world, most expenditure on sewerage is allocated for improving the structural performance and capacity of the existing network. Most collapses and stoppages of sewers are the results of sulphuric acid attack. This is because sulfur containing compounds in sewage are decomposed by anaerobic bacteria producing H_2S, which is either dissolved in water or metabolized with oxygen by aerobic bacteria to produce sulphuric acid. The sulphuric acid attack is also supplemented by the potential discharge of sulphuric acid from the chemical industry [1,2]. Good sulphuric acid resistance, therefore, is essential for sewers[3,4]. In order to obtain a higher sulphuric acid resistant mortar at a low cost, a Na_2SiO_3 and five polymer latexes were chosen to produce five kinds of modified cement mortars in a previous experimental study [4], in which the Na_2SiO_3–polyvinyl acetate latex hybrid modified cement mortar (HM) had been found to be the best. The modified effect of HM is similar to that of the other research [5].

In order to understand the long-term behavior of HM under sulphuric acid attack, in this paper, two kinds of mortars, namely HM and CM (control mortar), were made and stored in a sulphuric acid solution up to 5 years. The morphology and microstructure of the corroded mortars were observed by scanning electron microscopy (SEM), and the porosity and pore size distribution were measured using mercury intrusion porosimetry (MIP). The phases present after sulphuric acid attack were analyzed with Fourier-transform infrared (FT-IR) spectroscopy. Compressive strength losses were also measured.

2. Methods

2.1. Materials

A Na_2SiO_3 with a specific gravity of 1.44 g/cm^3 and a viscosity index of 1.6 mPs a, was chosen, and a Na_2SiF_6 was taken as the hardener of Na_2SiO_3. OPC, fly ash, and sand with a fineness modulus of 2.35 were also used. The chemical composition and physical properties of the cement and fly ash are presented in Table 1. A commercially available lignosulphonate was used as the superplasticizer and tributylphosphate was used as the antifoaming agent. A polyvinyl acetate latex with a pH value of 9.0 and a specific gravity of 1.19 g/cm^3 was used.

2.2. Experimental program

The mix proportions of HM and CM are presented in Table 2. In the experiment, materials for HM were mixed in the following order. Water, cement, and sand were mixed for 2 min. In a separate

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Table 1
Chemicalcomposition and physical properties of OPC and fly ash.

Chemical analysis (wt.%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	LOI	Total percentage	Specific surface, Blaine (m^2/kg)	28 days Compressive strength (Mpa)
OPC	19.5	4.4	6.22	65.9	1.5	1.09	0.30	1.43	100	462	45.9
Fly ash	52.5	19.1	8.2	14.7	1.98	0.35	0.48	3.6	100	565	–

Table 2
Mix proportions by weight of HM and CM.

Material	HM	CM
OPC	100	100
Na_2SiO_3/ Lignosulphonate[a]	7/0.05	
Na_2SiF_6	1.05	
Polyvinyl acetate latex	3	
Lignosulphonate	0.5	
Tributylphosphate	6	
Fly ash	15	15
Sand	200	200
Water	55	55

[a] Soluble glass and Lignosulphonate were mixed before producing modified mortar.

container polyvinyl acetate latex, Na_2SiO_3 and fly ash were premixed for 2 min. Tributylphosphate in the amount of 0.15 vol% of polymer latex was added to the mix. Then, the two mixtures combined with a further 5 min mixing until a uniform mortar was obtained.

As shown in Table 2, two groups of specimens, namely HM and CM, were made, and each group of specimens was composed of eighteen 31.5 × 31.5 × 50 mm prisms. Six prisms from HM and CM were used solely to determine the compressive strength after 28 days. Another six prisms were cured in air up to 5 years. The remaining six prisms were immersed into a 1% sulphuric acid solution with a volume of 10 L at room temperature up to 5 years. The sulphuric acid solutions were exchanged at intervals of 30 days.

2.3. Specimen characterization

2.3.1. Compressive strength

The compressive strengths of HM and CM were measured after 28 days curing and again after 5 years exposure to the atmosphere and sulphuric acid solution.

2.3.2. SEM

Morphology and microstructure of HM and CM samples were observed by using a Philip XL 30 scanning electron microscope with an EDX analyzer at an accelerating voltage of 25 kV. The samples after sulphuric acid attack were dried in a vacuum-dried oven at 50 °C for 24 h, and sputter coated with 100 A of Au–Pd prior to imaging.

2.3.3. Porosity and pore size

The porosity and pore size distribution of HM and CM were determined using an AUTOSCA-10 MIP with a measure range of 2–5000 nm radius. The maximum pressure of the porosimeter was 600 MPa, values of 140° and 480.0 N/cm^2 were used for the contact angle and mercury surface tension, respectively. Six HM and six CM samples were dried in a vacuum-dried oven for 24 h before MIP.

2.3.4. FT-IR Spectroscopy

Samples of HM and CM were prepared for FT-IR spectroscopy by drying to a constant weight, ground to pass through a 45 μm sieve and coated on a KBr pellet. FT-IR spectra were subsequently collected in the mid-region (400–5000 cm^{-1}) using a Nicolet 5DXC FT-IR spectrometer at a resolution of 4 cm^{-1} with an accumulation of 4000 scans. The unmodified cement mortar cured under a normal atmosphere up to 5 years. UCM (air-cured CM) was also prepared for FT-IR spectroscopy.

3. Results and discussion

Three colored zones could be identified in HM and CM after 5 years in sulphuric acid (Fig. 1). The near-surface zone was white in color and reached a depth of 50 mm in HM and 75 mm in CM due to corroding. The transition zone was the part of mortar where color changed from gray to white with a depth of 3–4 mm indicating partial corrosion. The centre zone was gray in color, appearing to be uncorroded.

3.1. Mechanical properties

The compressive strength test results of HM and CM mortars with and without sulphuric attack are presented in Table 3. The strength test results indicate HM has a higher resistance to sulphuric acid attack, with a strength loss of 29.4% compared to 50.6% for CM. It should be noted that the strengths are an indication of the combined resistance of zones A, B, and C, since the microstructure is affected non-uniformly through the specimen volume with the near-surface zones more affected. It should also be mentioned that specimen size effect had not been included in this test. If large size specimens were used, the strength losses would be lower.

3.2. Morphology and microstructure

Three HM and three CM samples with a size of 1 × 1 × 1 cm were taken at three regions (the near-surface zone, the transition zone, and the centre zone) as shown in Fig. 1 for SEM.

Portlandite, gypsum, ettringite or other phases could not be identified in Zone A, which was characterized by numerous interconnecting cracks for CM under sulphuric acid attack up to 5 years (Fig. 2), probably because the reaction products of $H_2SO_4$and portlandite had dissolved in water. The observed cracks were generally 20 μm in length and 2 μm in width, with the largest one being 80 μm long and 2 μm wide. Similarly for HM, portlandite, gypsum, ettringite or other phases were not observed in the near-surface zone A and contained cracks (Fig. 3), although these were generally smaller, measuring generally 2 μm in length and 1 μm in width. A key difference between Zone A in CM and HM was the develop-

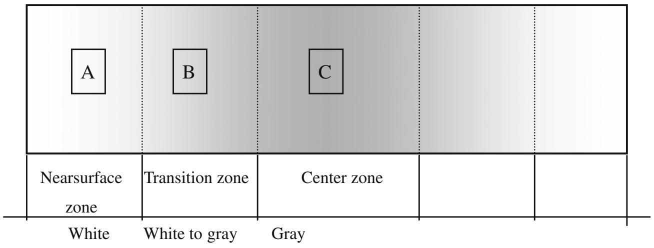
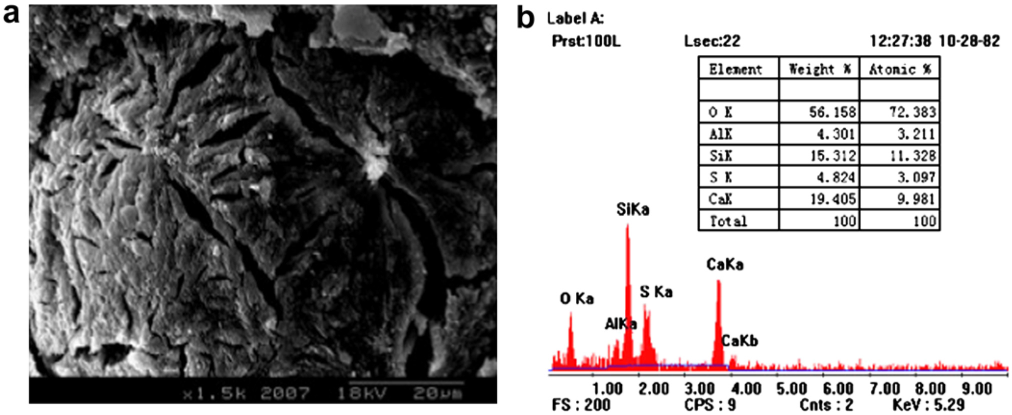


Fig. 1. Schematic representation on the three zones (labeled A, B, C) identified in HM and CM after 5 years exposure to sulphuric acid.

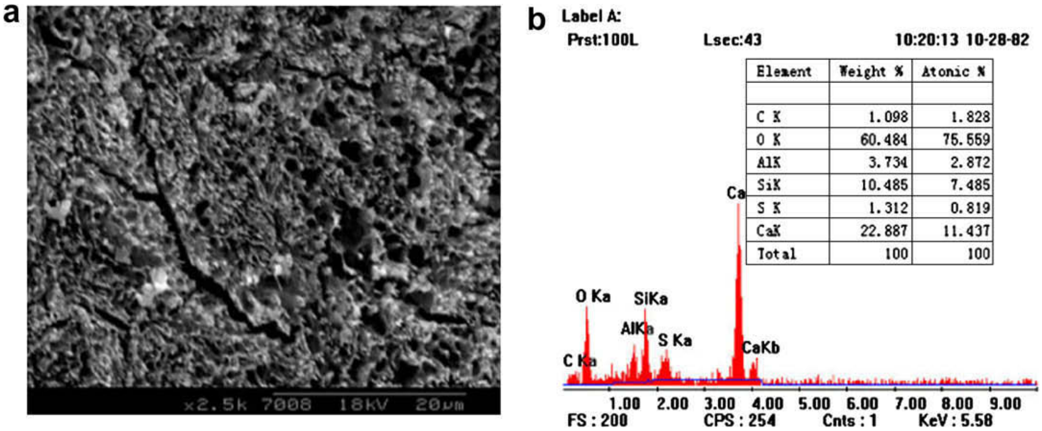
Table 3
Compressive strengths of HM and CM cured in air (28 days and 5 years) and sulphuric acid (5 years).

Sample	Compressive strength after 28 days cured in air (MPa)	Compressive strength after 5 years cured in air (MPa)	Compressive strength after 5 years stored in sulphuric acid solution (MPa)	Strength loss after 5 years sulphuric attack (%)
HM	20.7 ± 5.3%	24.8 ± 4.2%	17.5 ± 5.8%	29.4
CM	20.3 ± 4.7%	23.5 ± 2.6%	11.6 ± 4.5%	50.6



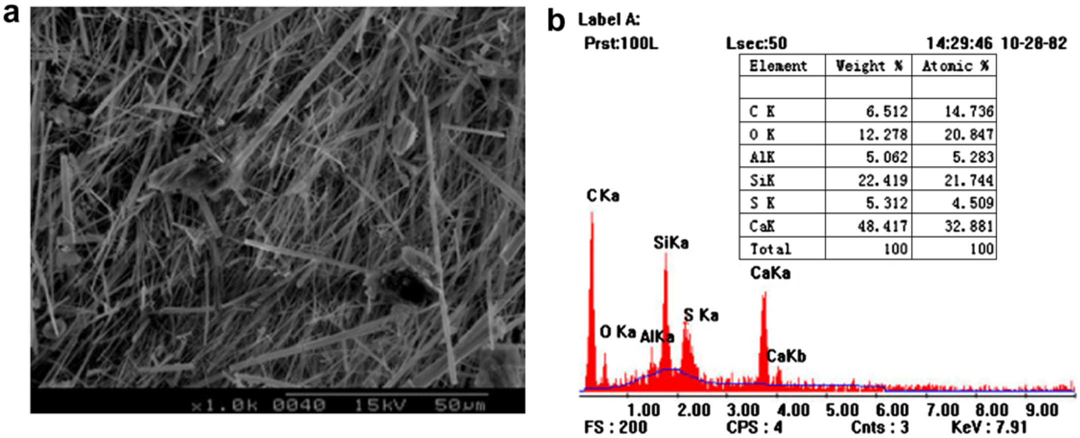
Element	Weight %	Atomic %
O K	56.158	72.383
AlK	4.301	3.211
SiK	15.312	11.328
S K	4.824	3.097
CaK	19.405	9.981
Total	100	100

Fig. 2. SEM images and EDX analysis of zone A for CM after 5 years exposure to sulphuric acid.



Element	Weight %	Atomic %
C K	1.098	1.828
O K	60.484	75.559
AlK	3.734	2.872
SiK	10.485	7.485
S K	1.312	0.819
CaK	22.887	11.437
Total	100	100

Fig. 3. SEM images and EDX analysis of zone A for HM after 5 years exposure to sulphuric acid.



Element	Weight %	Atomic %
C K	6.512	14.736
O K	12.278	20.847
AlK	5.062	5.283
SiK	22.419	21.744
S K	5.312	4.509
CaK	48.417	32.881
Total	100	100

Fig. 4. SEM images and EDX analysis of zone B for CM after 5 years exposure to sulphuric acid.

ment of a netlike film in the latter. The development of coherent polymer films has been found elsewhere [6] to be not well development, in a modified mortar, therefore the formation of the netlike film in HM may be explained by the interaction of Na_2SiO_3 and polyvinyl acetate latex. The chemical analyses performed by EDX in the near-surface zone A for HM and CM are shown in Fig. 2b and 3b, indicating the different Ca/Si, carbon, and sulfur percentage. For CM, a low Ca/Si atomic ratio and a high atomic sulfur percentage were found, probably because $CaSO_4 \cdot \chi H_2O$, the reaction product of C—S—H and H_2SO_4, dissolved in water, leading to the loss of Ca from C—S—H.

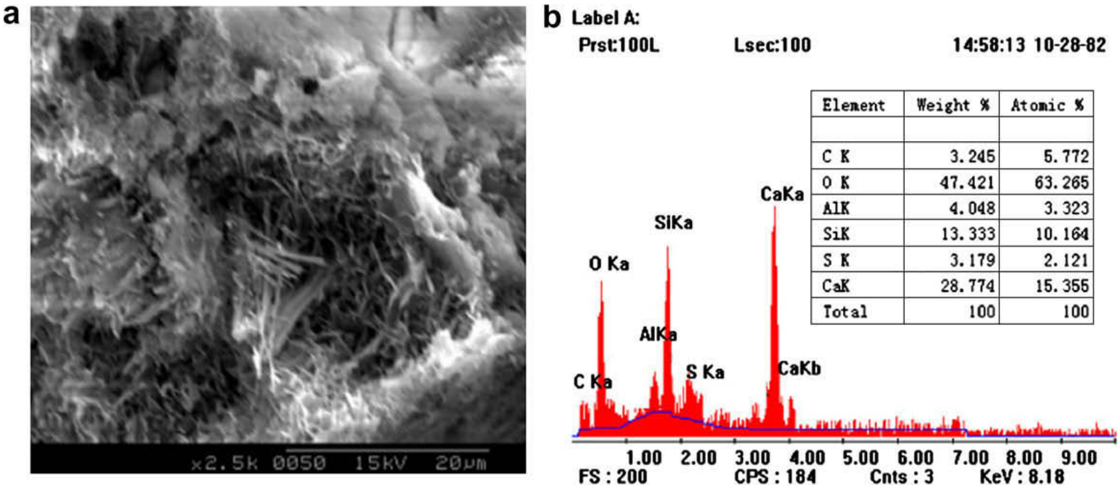
Fig. 4 shows that the dominance needle-like crystals in zone B for CM, the crystals were generally 50 μm long, with the largest one being 100 μm long and 1 μm wide. Some needle-like crystals (generally 10 μm long) were also observed in zone B for HM (Fig. 5). A netlike film can be seen in the zone B for HM. The chemical analyses performed by EDX in zone B for HM and CM are shown in Fig. 4b and 5b indicate that the samples contain sulfur and carbon containing compounds. Evidence suggests that the crystals may be a mixture of ettringite and thaumasite which is in agreement with the research result of Brown and Hooton [7].

In zone C for CM (Fig. 6), needle-like crystals about 5 μm long can be observed; the number and the length of the crystals, however are less than those in zone B. As shown in Fig. 7, no needle-like crystals can be found, and a polymer film can be observed in zone C for HM, indicating a denser microstructure compared with CM. The chemical analyses of zone C performed by EDX for HM and CM are shown in Fig. 6b and 7b; for UMHM, sulfur atomics were found, indicating that a sulphuric acid attack had already happend; while in the case of HM, carbon atomics were found, suggesting the presence of polymer compounds.

3.3. FT-IR Spectroscopy

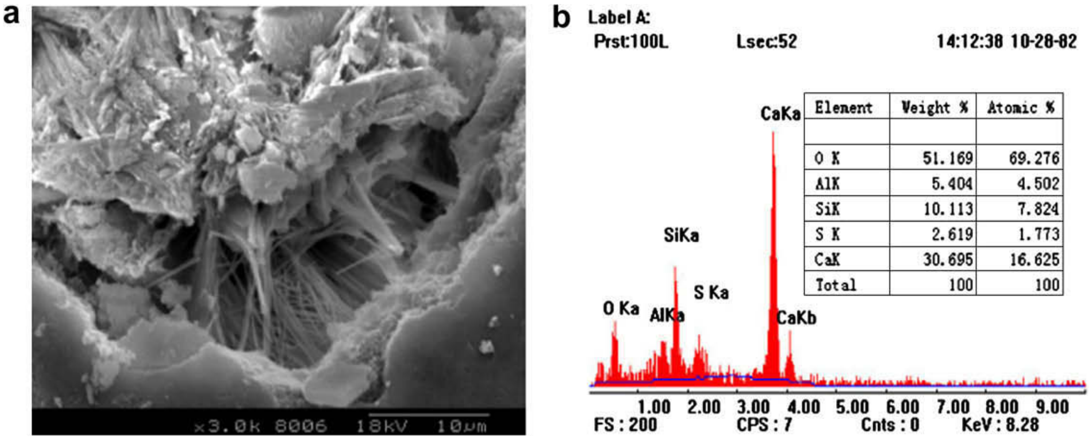
Three HM and three CM samples were taken at each transition zone for FT-IR spectroscopy. The FT-IR spectrum of U CM (air-cured CM)showed bands at 3643, 3436, 1632, 1428, 980, 779, 678, and 457 cm^{-1} (Curve A, Fig. 8), respectively. According to Geidel et al. [8], the band observed at 980 cm^{-1} can be assigned to Si—O stretching modes of silanol groups in the C—S—H phase present in the cement; the absorption band due to O—H stretching in $Ca(OH)_2$ is present at 3643 cm^{-1}. According to Ghosh [9], the bands at 1632 and 3436 cm^{-1} can be explained by the presence of calcium sulphate in the form of ettringite (mono and trisulphate) in the cement; the bands at 779 cm^{-1} and 678 cm^{-1} are consistent with β-C2S and α-C2S phases, respectively.

The spectrum of CM (Table 4) showed bands at 3608, 3552, 3410, 1620, 1426, 1153, 1096, 1007, 874, 797, 779, 661, 601, and 461 cm^{-1}, respectively. The majority of these bands can be explained by the presence of $CaSO_4 \cdot \chi H_2O$ (the spectrum of $CaSO_4.2H_2O$ shows bands at 1000, 492, 1131, 1142, 602–669, 3555, and 1690 cm^{-1} or 1006, 413, 1118, 1138, 3500, and 1629 cm^{-1}, respec-



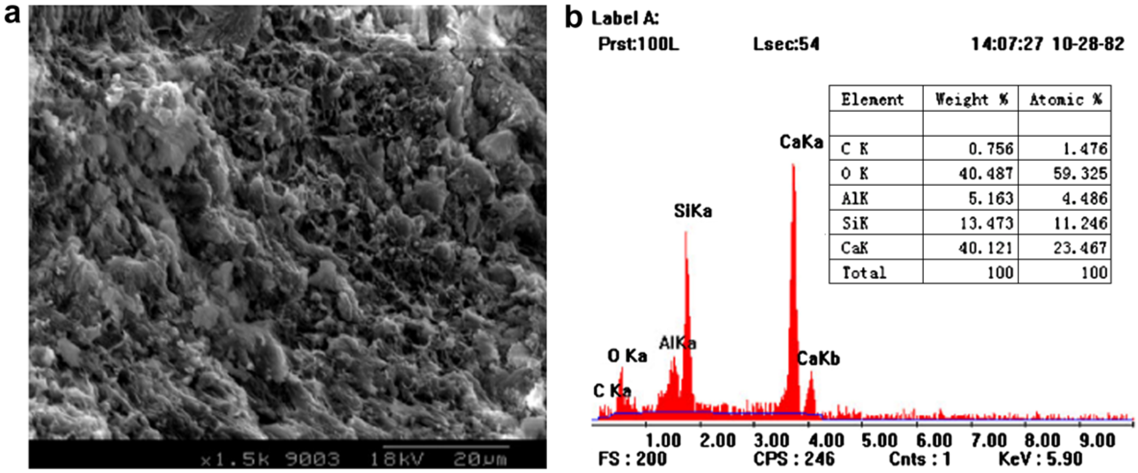
Element	Weight %	Atomic %
C K	3.245	5.772
O K	47.421	63.265
AlK	4.048	3.323
SiK	13.333	10.164
S K	3.179	2.121
CaK	28.774	15.355
Total	100	100

Fig. 5. SEM image and EDX analysis of zone B for HM after 5 years exposure to sulphuric acid.



Element	Weight %	Atomic %
O K	51.169	69.276
AlK	5.404	4.502
SiK	10.113	7.824
S K	2.619	1.773
CaK	30.695	16.625
Total	100	100

Fig. 6. SEM image and EDX analysis of zone C for CM after 5 years exposure to sulphuric acid.



Element	Weight %	Atomic %
C K	0.756	1.476
O K	40.487	59.325
AlK	5.163	4.486
SiK	13.473	11.246
CaK	40.121	23.467
Total	100	100

Fig. 7. SEM image and EDX analysis of zone C for HM undergone after 5 years exposure to sulphuric acid.

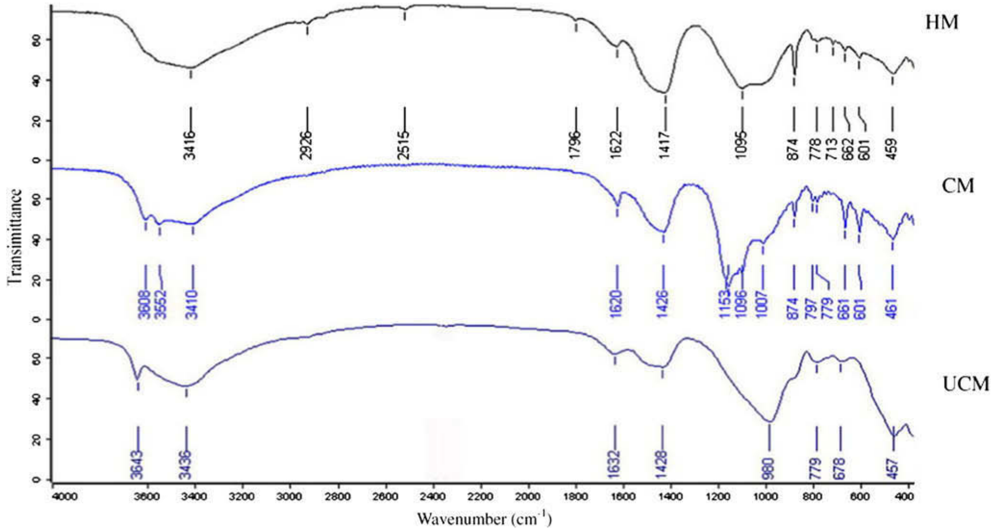


Fig. 8. FT-IR spectra of UCM (CM air cured for 5 years), CM and HM after 5 years exposure to sulphuric acid.

tively; the spectrum of $CaSO_4.1/2H_2O$ shows bands at 1012, 465, 1158, 1120, 3615, and 1629 cm^{-1}, respectively [10,11]). The absence of the band at 3643 indicates the loss of portlandite by its dissolution in sulphuric acid.

The IR spectrum of HM (Curve C, Fig. 8) showed bands at 3416, 2926, 1622, and 1417 cm^{-1}, indicating the presence of polymer latex. Polymer latex accounts for the broad hydroxyl band centred at about 3400 cm^{-1}, the C—H absorptions at 2926 cm^{-1}, and the carboxylate group absorptions at 1622 and 1417 cm^{-1}.

3.4. Porosity and pore size distribution

The porosity test results for HM and CM after 5 years sulphuric acid attack are shown in Table 5. The total porosity of HM was 13.25%. It was much lower than that of CM (28.62%), indicating a denser structure for HM. Moreover, the pores with a size $d \geqslant 50$ nm in HM are 3.98%, about 20.32% in that of CM. Mean volume pore radius (MVPR) refers to the minimum radius of pores when half of the total intrusion has taken place. The MVPR value of HM is about 11.26 nm, but the MVPR value of CM is much higher, about 31.20 nm. It should be noted that the measured porosities and pore size distributions were an indications of the combined resistance of zones A, B, and C, since sulphuric acid attack caused non-uniform changes in porosity through the specimen thickness with the surface regions obviously more affected.

Table 4
Characteristic transmittance bands for UCM, CM and HM.

UCM	CM	HM	Assignment
3643	3608		OH bending in C—S—H
3438	3552		OH bending in C—S—H
	3410	3414	OH bending in C—S—H
		2926	C—H vibration in R_1COOR_2
		2515	
		1796	C=O vibration in R_1COOR_2
1632	1620	1622	O—H bending of water
1428			CO_3^{2-} vibration
		1417	
	1153		
980	1096	1096	
	1007		SiO stretching
779	874	874	CO_3^{2-} vibration
	797		
	779	778	
678		713	
	661	662	AlO_6 vibration
	601	601	SO_4 vibration in $CaSO_4{\cdot}\chi H_2O$
457	456	459	SiO_4 vibration in C—S—H

Table 5
Porosity, mean radius and pore size distribution of HM and CM.

Sample	Total intruded vol (cm^3/g)	Mean radius (nm)	Apparent density (g/cm^3)	Porosity (2 nm < d^a < 5nm) (%)	Porosity ($d \leqslant 10$ nm) (%)	Porosity (10 nm < d < 50 nm) (%)	Porosity ($d \geqslant 50$ nm) (%)
CM	0.1655	31.60	1.729	28.62	2.29	6.01	20.32
HM	0.0727	11.26	1.823	13.25	5.30	3.97	3.98

[a] *d* is the mean pore diameter.

4. Conclusions

Based on the results of the experiments, the following conclusions can be drawn:

1) After 5 years sulphuric acid attack, the compressive strength loss of Na_2SiO_3–polyvinyl acetate latex modified mortar (HM) was 29.4%, whereas the control mortar (CM) had a higher strength loss of 50.6%.
2) After 5 years sulphuric acid attack, three distinct zones (near-surface zone – Zone A, transition zone – Zone B, and central zone – Zone C) could be identified for HM and CM. For CM, Zone A was characterized by SEM as being heavily cracked, Zone B containing a mass of needle-like crystals, and Zone C having a few cracks. For HM, a netlike film could be found in all three Zones, with less cracking and the same crystals identified in CM, but in smaller quantities.
3) The possible interaction between Na_2SiO_3 and polyvinyl acetate, interpreted from the FT-IR spectra, leads to the formation of the netlike film in the HM, making HM more resistant to sulphuric acid attack than CM.
4) The porosity of HM was 13.25%, while the porosity of CM was about 28.62%. The netlike film may be the main reason for decreasing the porosity of HM.

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