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Effects of hydroxyethyl cellulose and oxalic acid on the properties of cement

N.K. Singh[a,*], P.C. Mishra[a], V.K. Singh[b], K.K. Narang[c]

[a]*Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005, India*
[b]*Department of Ceramic Engineering, Institute of Technology, Banaras Hindu University, Varanasi-5, India*
[c]*Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi-5, India*

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Abstract

Effects of hydroxyethyl cellulose (HEC), oxalic acid and their binary mixtures {1:1, 1:2, 1:3 and 1:4 (by mass)} on the properties of ordinary Portland cement have been studied using up to 4% admixtures. Variations in setting time, heat of hydration, strength, hardness and fracture toughness have been determined. FT-IR and XRD have been utilized to determine the phase compositions of the material. Corrosion resistance against H_2SO_4, HCl and seawater has been studied by determining the loss in mass of cement mortars. It was found that HEC acts as a retarder and oxalic acid as an accelerator. The binary mixture (1:3) has increased the heat of hydration, strength, hardness, fracture toughness and corrosion resistance. Interaction between HEC, oxalic acid and cement hydration products takes place, and new phases are formed in the presence of water, which lead to the formation of stronger bonds and the sealing of the pores in the resulting product causing decreased water absorption as compared to ordinary Portland cement.

Keywords: Admixture; Curing; X-ray diffraction; Microstructure; Polymer-modified cementitious system

1. Introduction

Lime is one of the products formed during the hydration of cement. Over time, this lime reacts with environmental pollutants and forms soluble salts, which ultimately leach out from the material and creates holes. Consequently, these holes spread widely and weaken the whole structure. To prevent this deterioration, an admixture can be introduced with cement, which is able to check the formation of soluble calcium salt by the reaction with free calcium hydroxide.

Several papers related to polymer-modified cements in the field of macrodefect-free (MDF) systems have been published [1–3]. Water-soluble, cellulose-based polymers such as hydroxymethyl cellulose (HMC) [4], hydroxypropyl methyl cellulose (HPMC) [5] and carboxymethyl cellulose (CMC) have been reported as high-performance materials for plastering and for using in the underwater concrete works. However, the water-soluble, polymer-modified cementitious system shows late setting and gives strength after a long curing period in comparison to neat cement. A suitable quantity of accelerator along with the polymer may be added to enhance the rate of setting reaction in the mixes. The accelerator, if added in higher proportion with cement, may cause cracking in the long run due to the formation of soluble salts with free calcium and aluminium ions [6]. The selection of a less aggressive and more stable accelerator would be beneficial to such type of modification. Oxalic acid is a weak acid and is reported to act as an accelerator for cement hydration reaction [7]. This may also be helpful in the formation of a protective electrical double-layer film around the cement particle during gel state [8]. The insoluble salts of calcium and aluminium formed by oxalic acid are not aggressive for hydrated cement [9]. One percent addition of various carboxylic acids (i.e., oxalic acid) acts as a very good binder for free calcium ions present in the cement gel [10] because of the formation of an insoluble protective film of calcium oxalate, which also shows the thermal stability. The anticorrosive behavior of 1N oxalic acid solution for high-alumina cement is also reported [6,7].

In the field of polymer-modified cement, there is no work reported on the combined effect of hydroxyethyl cellulose

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* Corresponding author. Tel.: +91-542-2318529; fax: +91-542-236-8174.

E-mail address: nksingh@banaras.ernet.in (N.K. Singh).

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Table 1
Chemical compositions of cement

Constituent	%
CaO	62.30
SiO_2	19.55
Al_2O_3	4.02
Fe_2O_3	3.74
MgO	3.10
SO_3	2.22
K_2O	0.48
Na_2O	0.21
Loss on ignition	2.10

Table 2
Physical properties of cement[a]

Density (g/cm^3)	Blaine's specific surface (cm^2/g)	Soundness	
		Le Chatelier(mm)	Autoclave (%)
3.16	3250	10	0.8

[a] See Tables 4 and 5 for other properties of cement.

(HEC) and oxalic acid, which act as a retarder–accelerator system. Therefore, the aim of the present work is to study the effect of HEC–oxalic acid[1] mixtures as an admixture of ordinary Portland cement. Both of these admixtures are water soluble and give slight turbidity when present together in aqueous medium, which can be easily mixed with cement. The presence of the desired quantity of oxalic acid might compensate for the lowering in the rates of setting and hardening due to HEC addition in ordinary Portland cement.

2. Materials

2.1. Cement

Ordinary Portland cement (43-grade) was obtained from Maihar cement factory. The chemical compositions of the cement are given in Table 1 and the physical properties in Table 2.

2.2. Fine aggregate

Sand, less than 1 mm in size, was obtained from the Sone River. The physical properties of the sand are given in Table 3.

2.3. Admixtures

Reagent-grade HEC and oxalic acid were used in the present experiments. The constitutional formula of HEC is shown in Fig. 1.

3. Testing procedures

3.1. Setting time test

The setting time experiment was performed using a standard Vicat apparatus as per IS 4031. Admixtures were dissolved in the required volume of water for preparing the cement paste. The experiment was performed at 27 ± 2 °C.

3.2. Test on heat of hydration

Heat of hydration of 3-, 7-, 28- and 91-day-cured specimens was determined by calorimetric method as per IS 4031, using a Beckmann thermometer and a constant-speed stirrer arranged in a thermos flask. Reagent-grade zinc oxide was utilized for calibrating the thermoelectric calorimeter. Cement and hydrated cement with and without admixture were dissolved in 1:4 mix of 40% hydrofluoric acid and 2N nitric acid.

3.3. Compressive and tensile strength tests

The compressive and tensile strength tests were carried out as per IS 269. The compressive strength was determined on cube specimens with 50-cm^2 cross-sectional area using 1:3 cement–sand mix. The tensile strength was determined using standard briquette specimens cured under similar condition of temperature and humidity. Water (11.5%) was taken for preparing the mortar in which the admixtures were dissolved. The mortar was placed in six moulds for each test. These were kept in 90% relative humidity (RH). After 24 h, specimens were demoulded and again placed at 90% RH for 7, 28 and 91 days for curing at 27 ± 2 °C to maintain proper humidity for hydration. Water curing was not chosen in order to prevent leaching out of the polymer from the specimens before complete interaction with cementitious phases.

3.4. Microhardness test

For testing the hardness number, a Vickers hardness tester (Blue Star, Model No. w p m 250) for 50 and 100 N and a microhardness tester (Wilson Tukon, Model No. 2377) for 5- and 10-N load were used for 91-day-cured polished speci-

Table 3
Physical properties of sand

Grading						Density (g/cm^3)	Water absorption (%)	Loss on ignition (%)
Size (μm)/(%)								
− 1000 + 710	− 710 + 500	− 500 + 355	− 355 + 300	− 300 + 255	− 255 + 200			
36.01	20.93	30.38	9.12	3.42	0.24	2.83	1.89	0.26

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[1] HEC and oxalic acid in different mix proportions (1:1, 1:2, 1:3 and 1:4) by mass.

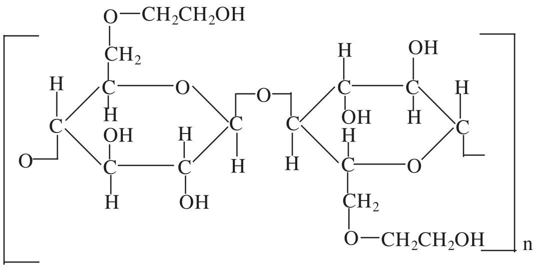


Fig. 1. Constitutional formula of HEC.

mens, adopting the preparation method as used in fracture toughness test. The hardness of materials was determined by indentation method as per ASTM (10) using the following formula:

$$H = \frac{1.854 \times P}{D^2}$$

where H = Vickers hardness, P = indentation load and D = diagonal of the indentation square.

3.5. Fracture toughness test

Fracture toughness was tested by a universal testing machine (Shimadzu AGS-5KND) under a three-point bending system as per ASTM (10) using a span length of 20 mm and a crosshead speed of 0.5 mm/min. Six specimens for each set were prepared. In the preparation of each specimen, 9.5 g of dry cement and 0.3% water with and without the admixture were mixed in an agate mortar for 1 min. The mixture was poured into a mould (10 × 20 × 50 mm) on which a 15-MPa load was applied for 1 min. After demoulding, a notch of 1.1-mm depth was made in the middle of the specimen length. The specimens were placed in a humidity chamber at 90% RH and 27 ± 2 °C. As the significant role of optimum contribution of admixtures was observed at late age of curing, only 91-day-cured specimens (rectangular-beam specimens, 10 × 10 × 50 mm) were chosen for hardness measurement. Fracture toughness values were determined by using the following formula:

$$K_{IC} = \frac{PqSf(a/w)}{B(W)^{3/2}}$$

where K_{IC} = fracture toughness, Pq = load, a = notch depth, B = breadth, W = width, S = span length and $f(a/w)$ = function of a/w.

3.6. Water absorption test

Water absorption studies have been carried out on the cube specimens with 25-cm^2 cross-sectional area using 1:3 cement–sand mortar [11]. Mortar was prepared adopting the mixing condition of compressive strength specimens, applying 15-tonne load by hydraulic press. After demoulding, specimens were placed under 90% RH and 27 ± 2 °C for 180 days.

3.7. Corrosion resistance test

Corrosion studies have been carried out by mass loss method [11] on the same cube specimens that were prepared for water absorption test. Reagent-grade sulfuric acid (0.1 and 1 N) and hydrochloric acid (0.1 and 1 N) and Arabian seawater were used as corrosive media. Only 91-day-cured dry specimens were used for corrosion studies.

3.8. Infrared spectroscopic test

The FT-IR spectra of 91-day hydrated neat cement and polymer-modified cement pastes were taken in KBr medium in the 4000–400 cm^{-1} region [12].

3.9. X-ray diffraction (XRD) test

XRD patterns of the hydrated cement and polymer-modified cements were recorded on an X-ray diffractometer using CuKα radiation with Ni filter. Intensity and d values were compared with the values given in JCPDS (9).

3.10. Microscopic test

The microstructures of the specimens were obtained using a microscope (Leica DMLM) attached with a camera (Leica MPS 30).

4. Test results and discussion

4.1. Setting time

The initial and final setting times of cement with HEC, oxalic acid and various proportions of HEC and oxalic acid mixtures in 1:1, 1:2, 1:3 and 1:4 (by mass) ratio up to 4% addition in cement are given in Table 4. The initial and final setting times of neat cement paste were found to be 130 and 230 min. The initial and final setting times of cement with HEC for lower addition (0.05%) were observed as 150 and 250 min and for higher additions (4%) were 647 and 715 min, respectively. Oxalic acid from 0.5% to 4% acts as an accelerator. However, it acts as a retarder if present below 0.05%.

Generally, organic polymers act as retarders, and have distinct behavior towards the setting of cement [13]. The setting time of cement may be varied according to the physical and chemical properties of organic polymers such as solubility, viscosity, chain length, polarity and functional group(s). HEC is a derivative of cellulose (a long-chain polymer which is a member of the carbohydrate group). It is reported [14] that, generally, organic retarders contain the H-C-OH group in their molecules, which retards the rate of adsorption of H_3O^+ ions on cement universal surface, and slows the setting reactions. The set retardation [15] may primarily be due to the retardation of the hydration of C_3S

Table 4
Setting time of cement in the presence of HEC, oxalic acid and various proportions of HEC–oxalic acid in different quantities

Type of admixture	Admixture content (%)	Setting time (min)	
		Initial set	Final set
HEC	0.0	130	230
	0.05	150	250
	0.1	195	275
	0.25	250	370
	0.5	325	415
	1	360	440
	2	475	550
	4	647	715
Oxalic acid	0.05	135	235
	0.1	145	238
	0.25	150	240
	0.5	125	235
	1	110	230
	2	90	150
	4	65	100
HEC–oxalic acid {1:1(by mass)}	0.05	140	245
	0.1	145	252
	0.25	165	280
	0.5	215	350
	1	285	395
	2	365	435
	4	435	515
HEC–oxalic acid {1:2(by mass)}	0.05	135	240
	0.1	140	247
	0.25	155	365
	0.5	185	315
	1	250	385
	2	305	415
	4	370	460
HEC–oxalic acid {1:3(by mass)}	0.05	130	235
	0.1	135	250
	0.25	138	265
	0.5	160	285
	1	188	320
	2	204	360
	4	245	415
HEC–oxalic acid {1:4(by mass)}	0.05	130	230
	0.1	135	233
	0.25	142	235
	0.5	155	257
	1	150	250
	2	115	200
	4	85	185

through the adsorption of the organic admixture onto calcium hydroxide. Steinour [16] considered that the organic agents are adsorbed by hydrogen bonds through their hydroxyl groups. The hydroxyl group, being polar and hygroscopic in nature, thus diminishes the amount of water available for the hydration of silicate. It seems that the retardation process in the presence of HEC is due to the chemical interaction among C_3A, C_2S, C_3S and polar functional groups of organic polymer to yield amorphous materials, which are scattered between the crystalline masses of cement paste. They might be quite insoluble and not removable from the stiffened mass.

Oxalic acid is reported as an accelerator [6,7] because its carboxylate ions [17] have a strong tendency to form ionic bonds with free lime and calcites of cement and form calcium oxalate. The present experiment is unable to explain the exact mechanism of retardation by oxalic acid when it is present in small amount in cement. Lea [18] has reported the same retardation behavior with acetic acid when present in small amount in cement. It seems probable that the setting behavior of cement may vary with the concentration of oxalic acid as found for acetic acid. The similarity of oxalic acid and acetic acid might be because both are aliphatic carboxylic acids. The combined effect of retarder and accelerator was observed with cement–{HEC–oxalic acid} mixtures. The mix proportions of HEC and oxalic acid in the ratios of 1:1, 1:2, 1:3 and 1:4 have the tendency to lower the setting time, which increases from 1:1 to 1:4. The lower setting time for a cement–{HEC–oxalic acid (1:4)} mixture as compared to the neat cement paste shows an immoderate amount of accelerator (oxalic acid) used in the mix. The basic objective of this work is to decrease the retardation effect of HEC to some extent by using oxalic acid. Hence, cement–{HEC–oxalic acid (1:3)} mixtures have been preferred for the present studies.

4.2. Heat of hydration

Heat of hydration of hydrated cement (without admixture) obtained at 3, 7, 28 and 91 days of curing periods were 259.57, 326.41, 364.11 and 439.35 J/g, respectively. Table 5 shows the heat of hydration of cement pastes with different quantities of admixtures: HEC and oxalic acid separately and a mixture of HEC–oxalic acid (1:3).

In cement–HEC mixes, the heat of hydration increases with increasing admixture content up to a certain extent, and then decreases. The optimum concentration of HEC for the maximum heat of hydration differs for different curing periods. In cement–oxalic acid mix, it was observed only in higher admixture content for all respective ages of curing, whereas in the mixes of cement–{HEC–oxalic acid (1:3)}, the heat of hydration increases with increasing admixture contents. It is reported [19] that for hydroxylated carboxylic acids, carbohydrates and polysaccharides, the heat of hydration may be higher at early ages. It seems that at early hydration, the unhydrated cementitious phases actively participated in hydration; thus, the tendency to react with a small amount of admixture is stronger and slows with late ages. The observation shows that the HEC–oxalic acid (1:3) mixture increases the heat of hydration with increasing concentration of admixture (HEC–oxalic acid, 1:3). This is in accord with the expectation because in HEC–oxalic acid (1:3), HEC is already in lower quantity and oxalic acid in higher quantity. Both of these are expected to increase the heat of hydration as is evident from the values observed in the presence of HEC and oxalic acid separately.

Table 5
Properties of cement in the presence of HEC, oxalic acid and HEC–oxalic acid (1:3)

Type of admixture	Admixture content (%)	Heat of hydration (J/g)				Compressive strength (MPa)			Tensile strength (MPa)			Indentation hardness (MPa)				Fracture toughness (MPa $m^{1/2}$)		Water absorption (%)	Corrosion resistance				
																			Mass loss (%)				
																			H_2SO_4/4 days		HCl/4 days		Seawater/91 days
		Age (days)				Age (days)			Age (days)			Load (N)				Age (days)			Concentration		Concentration		
		3	7	28	91	7	28	91	7	28	91	5	10	50	100	28	91	–	0.1N	1.0N	0.1N	1.0N	–
HEC	0.00	259.57	326.41	364.11	439.35	31.93	43.73	58.50	2.98	3.92	5.36	6.26	6.38	6.64	6.13	0.62	1.03	9.33	1.15	6.24	4.95	8.61	3.48
	0.10	266.39	328.79	365.03	440.94	30.80	44.10	58.88	2.88	3.99	5.42	6.74	6.77	6.96	6.43	0.74	1.22	–	–	–	–	–	–
	0.25	277.97	331.59	368.17	442.57	30.53	44.61	59.70	2.79	4.10	5.54	7.22	7.26	7.16	7.00	–	–	–	–	–	–	–	–
	0.50	285.49	335.82	369.34	446.17	28.89	45.17	60.85	2.70	4.33	5.75	8.06	8.42	8.76	8.38	0.87	1.58	8.81	0.80	5.83	4.30	8.22	3.40
	1.00	273.49	348.61	372.56	450.39	26.87	42.15	63.72	2.48	3.81	5.95	10.18	11.24	11.65	12.52	1.12	1.88	6.43	0.42	5.18	2.84	7.87	2.34
	2.00	244.44	327.83	387.19	453.94	24.03	39.21	67.97	1.86	3.61	6.37	14.21	13.26	12.08	11.27	1.02	1.98	6.23	0.28	4.87	2.44	6.98	2.13
	3.00	237.00	315.50	370.51	444.33	20.40	26.23	62.00	1.67	2.53	5.22	12.34	12.24	11.30	11.00	–	–	–	–	–	–	–	–
	4.00	229.06	309.06	355.63	430.03	18.80	29.03	57.81	1.47	2.49	4.92	7.96	8.54	8.63	7.61	0.66	1.74	6.89	0.3	5.17	2.06	7.68	1.70
Oxalic acid	0.10	262.25	328.08	365.95	439.44	31.98	43.80	58.50	2.98	3.90	5.30	6.84	7.15	6.99	6.56	0.63	1.13	–	–	–	–	–	–
	0.25	264.92	329.71	369.88	440.27	32.09	43.95	58.42	3.11	3.91	5.22	7.12	7.26	7.20	7.19	–	–	–	–	–	–	–	–
	0.50	274.75	332.93	371.68	441.40	32.72	44.40	59.70	3.18	4.23	5.36	7.54	8.37	9.27	8.87	0.73	1.26	9.35	0.58	6.13	3.87	7.86	3.13
	1.00	289.71	339.49	379.33	443.91	33.43	46.97	61.14	3.31	4.40	5.51	8.40	9.2	10.81	11.53	0.87	1.42	9.56	0.23	4.63	2.32	6.22	2.70
	2.00	319.89	352.91	394.59	447.26	34.98	49.04	64.13	3.39	4.62	5.96	9.44	9.58	11.01	12.20	0.98	1.54	9.84	0.15	3.05	1.84	5.53	2.04
	3.00	331.59	361.57	398.56	453.73	35.00	49.50	64.60	3.45	4.50	5.80	8.46	8.59	8.65	8.65	–	–	–	–	–	–	–	–
	4.00	345.26	367.12	399.52	453.65	37.13	46.83	62.09	3.50	4.48	5.69	7.45	8.61	9.18	9.88	0.64	1.45	10.40	0.06	2.64	1.88	5.03	1.53
HEC–oxalic acid {1:3 (by mass)}	0.1	261.16	326.41	364.11	439.61	32.00	43.80	58.50	3.00	4.08	5.30	6.54	6.67	6.60	6.22	0.65	1.16	–	–	–	–	–	–
	0.25	262.75	327.00	364.87	439.61	32.53	43.54	58.34	2.91	4.13	5.32	7.00	7.23	7.11	7.09	–	–	–	–	–	–	–	–
	0.5	265.97	327.83	365.66	440.69	31.99	44.78	58.49	2.90	4.23	5.48	7.38	7.67	7.49	6.85	0.79	1.48	9.21	1.11	6.03	4.20	8.00	3.45
	1.0	272.11	329.34	367.29	442.11	31.20	44.68	59.51	2.68	4.35	5.64	8.46	8.84	9.72	9.80	0.92	1.68	7.44	0.67	4.37	2.96	6.92	2.84
	2.0	284.95	336.99	370.55	444.96	30.49	45.70	62.97	2.56	4.40	5.91	11.37	11.71	12.70	13.02	1.07	1.83	6.63	0.31	4.07	2.48	5.18	2.03
	3.0	297.65	343.76	377.03	447.76	29.03	46.53	63.90	2.52	4.50	5.94	11.88	12.13	12.53	12.70	–	–	–	–	–	–	–	–
	4.0	310.36	349.53	390.11	450.60	28.71	47.12	66.20	2.42	4.53	5.99	12.96	12.90	13.20	13.25	0.93	1.90	5.50	0.44	3.20	1.12	5.80	1.89

4.3. Compressive and tensile strengths

The compressive and tensile strengths of cement are based on an average test of six specimens in each condition. The compressive strengths of cement (without admixture) at 7, 28 and 91 days were observed as 31.93, 43.73 and 58.50 MPa, and the maximum tensile strengths were 2.98, 3.92 and 5.36 MPa, respectively. Table 5 shows the average compressive strength values for cement in the presence of HEC, oxalic acid and HEC–oxalic acid (1:3). For the cement–HEC mixes, maximum compressive strengths at 7, 28 and 91 days were observed to be 30.53, 45.17 and 67.97 MPa and maximum tensile strengths were 2.79, 4.33 and 6.37 MPa, respectively, for 0.25%, 0.5% and 2% admixture contents (by mass of cement). For cement–oxalic acid mixes, the compressive strengths were observed as 37.13, 49.04 and 64.13 MPa and tensile strengths 3.50, 4.62 and 5.96 MPa, respectively, for 4%, 2% and 2% additions of oxalic acid at the respective ages of curing. For cement–{HEC–oxalic acid (1:3)} mixes, the maximum compressive strengths given by HEC–oxalic acid (1:3) contents of 0.25%, 4% and 4% at 7, 28 and 91 days, were observed as 32.53, 47.12 and 66.20 MPa, respectively, and the maximum tensile strengths were 2.91, 4.53 and 5.99 MPa, for the same contents and ages of curing.

The strengths of cement–HEC and cement–oxalic acid mixes obtained using the optimum amount of HEC and oxalic acid for early and late curing were observed to be different. For 7-day curing, lower concentration (0.25%) of HEC and higher concentration (4%) of oxalic acid were found to be more effective, whereas at 91-day curing, higher concentration (2%) of HEC and lower concentration (2%) of oxalic acid were more effective. For cement–{HEC–oxalic acid (1:3)} mixes, 4% addition of HEC–oxalic acid (1:3) gave excellent compressive strength at 28-day curing, which may be due to the presence of oxalic acid in higher amount and HEC in lower amount (1%). The above finding has been confirmed by the data of HEC and oxalic acid alone. The maximum strength at 91 days was also observed for the 4% addition of HEC–oxalic acid (1:3). The result shows that 2% HEC alone can be used in cement for 91-day strength, which can be modified for 28-day strength by the addition of 4% HEC–oxalic acid (1:3). This result suggests that the carboxylic acid group increases the early strength of cement.

4.4. Indentation hardness

The hardnesses of 91-day-cured cement on 5-, 10-, 50- and 100-N loads were observed as 6.26, 6.38, 6.64 and 6.13 MPa, respectively. The hardnesses of 91-day-cured specimens of cement–HEC, cement–oxalic acid and cement–{HEC–oxalic acid (1:3)} are given in Table 5. After 91-day curing, the different percent additions of cement–HEC mixes show different hardness values on different loads (5, 10, 50 and 100 N). Applying 1% HEC mix on 5-, 10-, 50- and 100-N loads has shown hardnesses of 10.18, 11.24, 11.65 and 12.52 MPa, respectively, and presented better hardness with increasing loads.

For 2% HEC mix, a better performance of hardness was observed on 5 N (14.21 MPa). In cement–oxalic acid mix, the hardness of materials increased up to 2% oxalic acid addition. The maximum hardness values of 2% oxalic acid mix on 5, 10, 50 and 100 N were observed as 9.44, 9.58, 11.01 and 12.08 MPa, respectively.

The hardness of cement–{HEC–oxalic acid (1:3)} mixes was found to increase with increasing contents of HEC and oxalic acid up to 4%. The specimen containing 4% {HEC–oxalic acid (1:3)} has given excellent load-bearing capacity. The hardnesses on 5-, 10-, 50- and 100-N loads were observed as 12.96, 12.90, 13.20 and 13.25 MPa. This shows that HEC and oxalic acid in 1:3 mix system interact with cementitious phases more strongly as compared to the system where they are added separately. The microstructure of cement–{HEC–oxalic acid (1:3)} shows a homogeneous interaction with cementitious phases. It may be concluded that the increased hardness in such specimens is due to the formation of new product(s). The possible mechanism, which may lead to increased hardness, may be related to the mechanism responsible for higher toughness, discussed under fracture toughness properties of cement.

4.5. Fracture toughness

The fracture toughness values of cement (without admixture) at 28 and 91 days were observed as 0.62 and 1.03 MPa $m^{1/2}$, respectively. The average fracture toughness of cement–HEC, cement–oxalic acid and cement–{HEC–oxalic acid (1:3)} mixes for different compositions is given in Table 5. For cement–HEC mixes, the maximum fracture toughness values at 28 and 91 days are 1.12 and 1.98 MPa $m^{1/2}$, which were observed by 1% and 2% admixture contents, respectively. In the case of cement–oxalic acid mixes, they were observed as 0.98 and 1.54 MPa $m^{1/2}$ by 2% addition. Cement–{HEC–oxalic acid (1:3)} mixes have given excellent fracture toughness with respect to cement (without admixture). The maximum fracture toughness values at 28 and 91 days were observed as 1.07 and 1.90 MPa $m^{1/2}$ by 2% and 4% addition, respectively, of HEC–oxalic acid (1:3).

The observation shows that the toughening of cement improved by the addition of HEC is better than that of oxalic acid alone. In the case of cement–{HEC–oxalic acid (1:3)} mix, it was found to be toughest in comparison to HEC and oxalic acid alone, justifying other tests of strength measurement. The possible factors behind the toughening mechanism are the attractive forces produced between different admixtures and hydrated cementitious particles. The observed values also justify the use of optimum concentration of admixture(s) in giving maximum compressive and tensile strengths. It seems that the higher toughness values, which were observed for longer curing period, result from alternative forces developed between the polymer and cementitious materials caused by hydrodynamic forces [20]. Hydrodynamic forces are of repulsive nature, which appear when the cementitious particles try to move against the viscosity of the polymer solution during setting time. These forces slowly change into an electrostatic attractive force as the curing period increases. Some workers have suggested [21,22] that the electrostatic forces are operative in dry atmosphere when the crack faces become charged during fracture. It is also possible that the same polymer molecules act as bridging forces [23] between more than one cementitious particle at the same time, thereby forming a link that holds the particles with hydrogen/chemical bonding. The forces may resist [24] the crack propagation. The effect that the presence of polymer can have on surface forces is varied and subtle, and it is not possible to describe them in detail. Details about the theory are given by Napper [25]. A descriptive account of the surface forces and their action in ceramic materials and different contributions to the forces with particular attention paid to the above mechanism are given by Horn [26].

4.6. Water absorption

Polymer-modified mortars have a structure in which the large pores can be filled by polymers or sealed by cementitious polymer films. This effect increases with an increase in admixture to cement ratio. These features are reflected in reduced water absorption in comparison to ordinary cement mortars. Table 5 shows the 48-h water absorption of 91-day cured cement mortars with HEC, oxalic acid and HEC–oxalic acid (1:3) mixes. Water absorption of cement mortar (without admixture) was observed as 9.33%. In the cement–HEC mixes, 2% admixture content has given minimum water absorption (6.23%) with respect to cement, whereas with 4% admixture content, it was found slightly increased. In the cement–oxalic acid mixes, the water absorption increased with increasing admixture content up to 4%, showing poor water resistance as compared to the cement mortars.

The mixes of cement–{HEC–oxalic acid (1:3)} have given excellent water-reduction property with an admixture content of 4%. The microstructures of cement–{HEC–oxalic acid (1:3)} mix specimen (without sand) in Fig. 4 show the deposition of filmlike materials inside the pores and on the surfaces. It seems that HEC and oxalic acid, if present together in the cement, produce a new composite material, which seals the porosity of cement and reduces the water absorption of mortars.

4.7. Corrosion behavior

The results of corrosion resistance tests of cement–HEC, cement–oxalic acid and cement–{HEC–oxalic acid (1:3)} mixes are given in Table 5. The mass losses (mass %) of cement specimens (without admixture) after 4 days in 0.1 and 1 N H_2SO_4 were observed as 1.15% and 6.25%, respectively. The mass losses in 0.1 and 1 N HCl were 4.95% and 8.61%, respectively. After 91-day immersion in seawater, the mass loss was observed to be 3.48%.

The sulfuric acid forms gypsum with calcium hydroxide and ettringite with calcium aluminate [27]. Chandra [28] has described the attack of HCl as a reaction occurring in layers forming distinct zones, and found that HCl dissolution of calcium hydroxide was three times more than that of H_2SO_4. The influence of seawater was studied by Conjeaud [29] and Regourd [30]. They reported that the seawater corrosion is a net effect of several salts like NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$ and bicarbonates present in seawater. The attack of chloride from NaCl and $MgCl_2$ was observed on aluminates of cement phases, which form monochloroaluminate, $C_3A\cdot CaCl_2\cdot 10H_2O$. They also transform C-S-H fibers into a more porous reticular network. The development of porosity in cement is probably due to the leaching out of the above monochloroaluminate.

The data show that 2% HEC-mixed cement mortar has given minimum corrosion against H_2SO_4 (0.1 and 1 N). In 0.1 N HCl, the minimum corrosion was observed for 4% HEC mix, whereas 2% mix has given minimum corrosion with 1 N HCl. The minimum corrosion against seawater was found with 2% HEC mix. The minimum mass loss of HEC mix in 0.1 N H_2SO_4, 1 N H_2SO_4, 0.1 N HCl, 1 N HCl and seawater were observed as 0.28, 4.87, 2.06, 7.68 and 1.70, respectively.

It was found that 4% oxalic-acid-mixed cement mortar shows excellent corrosion resistance against H_2SO_4 (0.1 and 1 N). In 0.1 N HCl, 2% oxalic acid mix has given minimum corrosion, whereas in 1 N HCl, it was observed for 4% mix. The seawater corrosion was found minimum with 4% oxalic acid mix. The minimum mass loss of oxalic acid mix in 0.1 N H_2SO_4, 1 N H_2SO_4, 0.1 N HCl, 1 N HCl and seawater were 0.06, 2.64, 1.84, 5.03 and 1.53, respectively.

The mortars of cement–{HEC–oxalic acid (1:3)} mixes have given minimum corrosion in 0.1 N H_2SO_4 and 1 N HCl, whereas 4% mix showed minimum value in 1 N H_2SO_4, 0.1 N HCl and seawater.

The polymer-modified cements are reported [31] to be corrosion resistant with corrosive media. It seems that in polymer-modified systems, the pores are reduced and filled with polymer or reaction product(s). The microstructures of the mixes (without sand) are shown in Fig. 4, which shows the reduced porosity and filling or sealing of cement pores with polymers, and their new reaction product(s) formed, which reduce the capillary system and effect the resistance against the corrosive media.

4.8. IR spectra

The IR spectra of 91-day hydrated cement (with and without admixtures) are shown in Fig. 2. The spectrum of 91-day hydrated cement specimen shows bands at 3645, 3445, 1613, 1417, 968, 875 and 530 cm^{-1}. Several workers have reported the spectra of hydrated products of cement phases, which revealed that the bands observed in the range

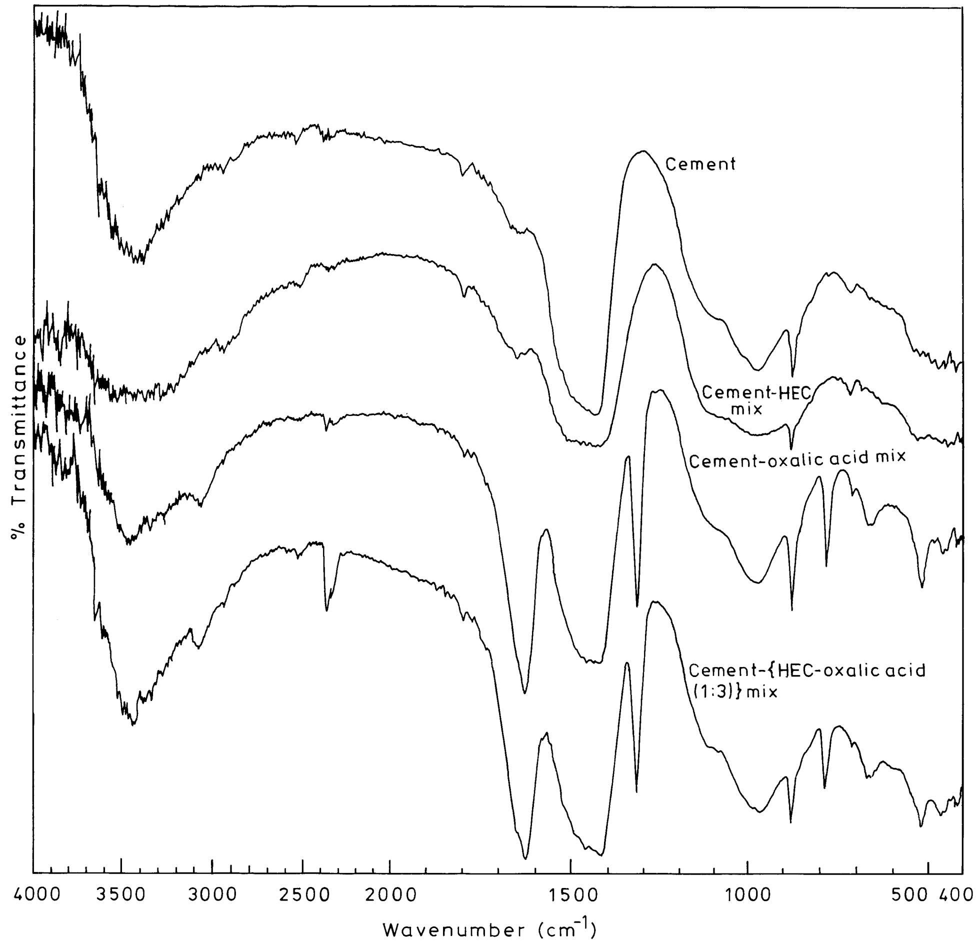


Fig. 2. FT-IR spectra of 91-day hydrated specimens.

of 700 to 1200 cm^{-1} are lost when C_3S is hydrated [12]. The band observed at 968 cm^{-1} is due to the higher shifting of anhydrous phase [12] and/or υ_3(Si–O) absorption bands of C_2SH_2 and C-S-H (B) type phases present in the cement [12]. The absorption band due to υ(OH) of $Ca(OH)_2$ is present at 3645 cm^{-1}. The bands at 1635 and 3445 cm^{-1} are due to the presence of calcium sulphate in the form of ettringite (mono and trisulphate) in the cement. The band at 875 cm^{-1} is consistent with γC_2S and βC_2S phases. The band at 1417 cm^{-1} shows the presence of carbon dioxide.

The spectrum of cement–HEC mix shows bands of cement phases at 3645, 3420, 1647, 1512, 1435, 981, 875 and 520 cm^{-1}. The band due to $CaSO_4$ of ettringite phase of cement at 3445 cm^{-1} appears with a negative shift of 25 cm^{-1}, indicating the interaction of HEC with the ettringite phase of the cement. The appearance of a new band at 1512 cm^{-1} (not present in pure HEC) indicates the formation of a new product in the cement–HEC mix cement. The υ_4 band of $[SiO_4]^{4-}$ at 530 cm^{-1} in cement appears at 520 cm^{-1}, indicating the interaction of HEC with the C-S-H phases of the hydrated cement.

The IR spectrum of cement–oxalic acid mix shows bands at 3468, 3059, 1625, 1458, 1320, 978, 783, 669 and 518 cm^{-1}. The presence of a band at 1458 cm^{-1} in a 91-day hydrated oxalic acid mix shows the possibility of the formation of calcium oxalate [12]. The presence of oxalate is further supported by three new bands at 783, 1320 and 1625 cm^{-1} due to δ(O–CO) + υ(CaO). The υ_4 band of $[SiO_4]^{4-}$ at 530 cm^{-1} in cement is present in the oxalic acid mix with a negative shift of 14 cm^{-1}.

The IR spectrum of cement–{HEC–oxalic acid (1:3)} mix shows bands at 3435, 1622, 1417, 1320, 964, 864, 783, 657 and 518 cm^{-1}. The υ(OH) band of pure HEC at 3458 cm^{-1} appears with a negative shift in the above mix at 3435 cm^{-1}, indicating the possibility of interaction between the $-CH_2OH$ group of HEC with $Ca(OH)_2$ (free lime) in the presence of oxalic acid. All bands of calcium oxalate (which were observed in the oxalic acid mix system) are also present in the cement–{HEC–oxalic acid (1:3)} system. The υ_4 band of $[SiO_4]^{4-}$ appears with a negative shift of 12 cm^{-1}, indicating the interaction of HEC and oxalic acid together with C-S-H phases of cement.

4.9. X-ray diffraction

X-ray diffractograms of 91-day hydrated cements (with and without admixture) show important peaks of cementi-

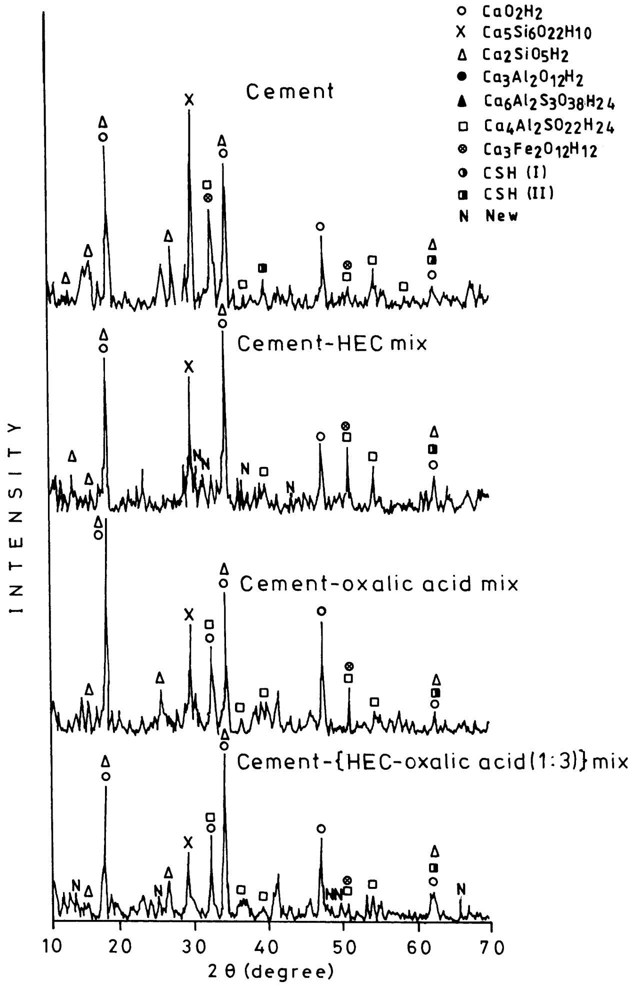


Fig. 3. XRD of 91-day hydrated specimens.

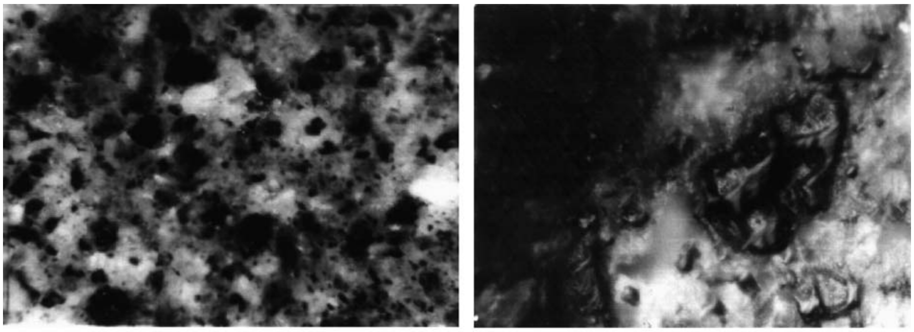
tious phases. Fig. 3 shows the XRD patterns of 91-day hydrated cement specimens [cement, cement–HEC mix, cement–oxalic acid mix and cement–{HEC–oxalic acid (1:3)}].

Important phases detected using JCPDS(9) in cement were $Ca_2SiO_3(OH)_2$ at $d=7.98$, 5.61, 4.92, 3.33, 2.62, 2.18, 1.48 Å; $Ca_2Al_3Fe_3Si_3O_{13}H$ at $d=3.02$ Å; $Ca_3Fe_2O_{12}H_2$ at $d=5.15$, 2.77, 2.15, 1.76 and 1.48 Å; $Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O$ at $d=3.33$, 3.09, 3.02 and 2.77 Å and free lime at 2.62, 2.18, 2.10, 1.92, 1.79, 1.68 and 1.53 Å. The ettringite (monosulphate: $3CaO \cdot Al_2O_3 \cdot CaSO_413H_2O$) appeared in 91-day hydrated specimens. XRD results show some important information about the above mixes after 91-day curing. XRD of the above mixes display some new peaks, which show the possibility of the formation of new product(s). Some cementitious phases disappeared and a few appeared in low intensities, which show the interaction of different mixes with cementitious phases.

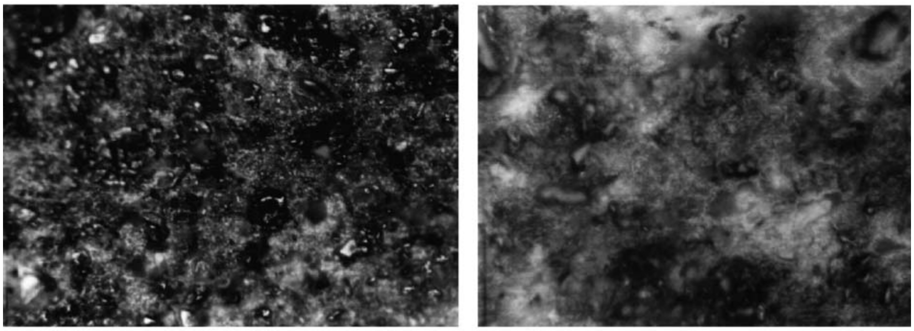
In cement–HEC mix, a few new peaks have appeared at $d=2.69$, 2.49, 2.46 and 2.01 Å, which show the possibility of the formation of new product(s). No peaks have disappeared whereas a few other peaks appeared with low intensities as compared to 91-day hydrated cement at $d=5.15$, 4.92, 3.49, 3.33, 2.77, 2.18, 2.15 and 2.10 Å. These peaks correspond to $Ca_3Fe_2O_{12} \cdot H_2$, $Ca_2Al_2(OH)_{12}$; $Ca(OH)_2$, $CaSiO_3(OH)_2$, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; $CaSi_2O_52H_2O$; $Ca_5Si_2O_8(OH)_2$, $Ca_2SiO_3(OH)_2$; $Ca_3Fe_2O_{12}H_2$ and $Ca_4Si_3O_7(OH)_2$ phases, respectively. The peaks at $d=3.09$, 3.02, 2.62, 2.31 and 1.79 Å have appeared with increased intensities for the possible phases: $Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O$; $Ca_2Al_2Fe_3Si_3O_{13}H$; $Ca_6Si_6O_{17}(OH)_2$, $Ca_2SiO_3(OH)_2$; $Ca(OH)_2$, $Ca_4Si_3O_6(OH)_2$, $Ca_3Al_2(OH)_2$ and $Ca_2SiO_5H_2$, $Ca(OH)_2$, respectively. In the cement–oxalic acid mix, a few new peaks appeared at $d=5.92$, 3.46, 2.34 and 1.97 Å, which are assigned to calcium oxalate as a new product with mixes. It may be due to the reaction of calcareous phases and oxalic acid in the presence of water. The peaks at $d=5.15$, 1.68 and 1.48 Å have appeared with low intensities. These peaks are assigned to $Ca_3Fe_2O_{12}H_2$, $Ca_3Al_2(OH)_{12}$, $Ca(OH)_2$ and $Ca_2SiO_5H_2$ phases, which show that the oxalic acid reacts more actively with calcium aluminate and calcium ferrite phases and less with calcium silicate phases of the cement. The peaks at $d=4.92$, 2.96 and 2.31 Å have appeared with increased intensities as compared to the hydrated cement, which are assigned to $Ca(OH)_2$, $Ca_2SiO_3(OH)_2$, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; $Ca_4Si_3O_6(OH)_2$ and $Ca_3Al_2(OH)_{12}$, $Ca_4Si_3O_6(OH)_2$ phases, respectively. In 4% admixture content of cement–{HEC–oxalic acid (1:3)} mix specimen, both 1% HEC and 3% oxalic acid (as a binary admixture) have given maximum strength. Some new peaks have appeared in the XRD patterns of this system, which were neither present in cement–HEC mix nor in cement–oxalic acid mix. These peaks are at $d=6.18$, 5.05, 4.71, 3.52, 1.87, 1.82 and 1.49 Å. It seems that HEC and oxalic acid in the mix system reacted commonly with cementitious phases and formed new compound(s) as a composite material(s). Some new peaks, which appeared in the HEC mix, disappeared in cement–{HEC–oxalic acid (1:3)} mix. The presence of peaks at $d=2.53$, 2.49, 2.46 and 2.41 Å shows the dominant reactivity of oxalic acid over HEC. The peak of lime at $d=4.92$ Å appeared with decreased intensity in cement–HEC mix but with increased intensity in cement–oxalic acid mix. It is also present with decreased intensity in cement–{HEC–oxalic acid (1:3)} mix. It seems that the mixture of HEC and oxalic acid plays an important role in cement mixes. HEC and oxalic acid, when present in cement, balance the opposite properties of each other (HEC as a retarder and oxalic acid as an accelerator).

4.10. Microstructural observation

Fig. 4 shows the microstructures of 91-day hydrated cement (with and without admixtures) at 500 × magnification. Fig. 4A represents the microstructures, which show clear pores on the surface. Fig. 4B exhibits the densified polymer film network around the hydrated cementitious



(A) Cement **(B) Cement-HEC mix**



(C) Cement-oxalic acid mix **(D) Cement-{HEC-oxalic acid (1:3)} mix**

Fig. 4. Microstructures of 91-day hydrated specimens.

phases. Fig. 4C shows the effect of oxalic acid on cement, which may be responsible for high water absorption. A new reaction product (probably calcium oxalate) is dispersed on the surface and inside the pores. Fig. 4D exhibits the effect of the HEC–oxalic acid (1:3) mixture. There is a significant difference in the surface structure of cement–{HEC–oxalic acid (1:3)} mix as compared to the cement–HEC and cement–oxalic acid separately, as microstructures show the presence of a new composite material inside the pores. The pores of the surface are sealed by the uniform patches, which is due to the formation of a new reaction product formed by HEC and oxalic acid in a particular ratio (1:3).

5. Conclusions

The binary mixture of up to 4% HEC–oxalic acid (1:3, by mass) added to cement has given setting time values close to the values for the cement test and increased the heat of hydration, strength, hardness and fracture toughness in comparison to the values for ordinary Portland cement. The cement mortar containing the above binary mixture has shown reduced water absorption and improved corrosion resistance against mineral acids and seawater due to the sealing of the pores. Interaction between components of admixture and various hydrated cementitious phases has produced strong bonds, which is expected to give a more durable material as compared to ordinary Portland cement.

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