

Acrylonitrile Monomer Modified Cement Products

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Effect of acrylonitrile monomer addition to the ordinary cement on the properties like heat of hydration, setting time, compressive and tensile strength has been studied by adding 0.1 to 5.0 per cent additive by weight of cement. Hardness of the products has been tested using Vickers indentation method. Bending strength and fracture toughness of the cementitious bond have been determined by using three point bending system. The corrosion resistance of different modified products has been tested against the sea water and 0.1 and 1.0 N HCl and H₂SO₄ respectively. Water absorption/open porosity of different samples has also been determined and microstructures of the polished specimen taken.

It was observed that the compressive and tensile strengths, hardness, toughness and corrosion resistance increase up to 3.0 per cent acrylonitrile addition in the ordinary Portland cement. Polymeric/monomeric phase is interspersed in the cement and causes decrease in the water absorption/open porosity of the modified cement products. The chemical interaction between functional group of organic material and hydrating cement phases causes the formation of new phases which cause some more bond formation in addition to cement bonds leading to the increase in strength.

Keywords : Ordinary Portland cement, acrylonitrile, fracture toughness, microstructure.

1. Introduction

Recent advances in the field of cement products are related to the use of admixtures specially those of organic materials like monomer/polymers added in small quantities to modify the properties of cement products. Cement polymer composites are materials, which are made by partial replacement of hydraulic cement by organic binders. Composites based on polyvinyl acetate [1] were developed four decades earlier. Since then continuous research [2] to develop new polymers have resulted in potentially improved latexes like styrene-butadiene, rubber-latex etc., which are now widely used. The properties of the composites are related to the nature and quantity of the monomer/polymer used. The addition of water-soluble organic materials permits the formation of highly

workable paste with very little water. The additive acts as lubricant facilitating close packing of various constituents, which are then held tightly together causing higher strength and toughness observed in the modified cement products. Acrylonitrile has $-CH_2$ and $-CN$ functional groups which on hydrolysis are likely to interact with cement phases forming new products, which remain dispersed uniformly in the rest of the materials modifying the physical and mechanical properties of the product. The increase in mechanical properties is not only because of the physical interaction between the cement and polymer producing a dense microstructure with very low porosity but also because of chemical interaction [3] between the cement phases and the functional groups present in the additive.

Our aim is to probe and produce corrosion resistance high strength cement products, which can give longer life to the structures and other products. Cement-polymer mixes are also useful as protective coatings over the ancient monuments, which are now deteriorating fast in the present polluted environment. The present work reports the effects of acrylonitrile on the properties of ordinary cement. The phase composition has been determined by IR and XRD studies [4]. Setting time, heat of hydration, flexural strength, fracture toughness, hardness and microstructure were determined by using neat cement samples and compressive and tensile strength, water absorption and corrosion resistance were determined using cement mortar [5].

2. Experimental

The cement used was ordinary Portland cement of 43 grade. The sand used was from the Sone River (Less than 1 mm. size). Seawater was taken from the Arabian Sea for corrosion studies. Analytical reagent grade acrylonitrile, zinc oxide, nitric acid, sulfuric acid, hydrofluoric acid and hydrochloric acid were used in the present experiments. Infrared spectra of neat cement and also with acrylonitrile (cured for 90 days) were recorded on JASCO, Tokyo, Japan, FT/IR-5300 using KBr medium in the region of $4000-400\text{ cm}^{-1}$. X-ray diffraction (XRD)

patterns of neat hydrated cement and modified cement containing additive were recorded on X-ray diffractometer (RICH SEIFERT Co. GmbH & COKGD-2076, Germany, model no. ID-3000) using Cu-K α radiation with Ni filters. Intensity and d-values of observed peaks were compared with the values given in JCPDS cards [4] for different phases of cement. The initial and final setting times of cement with and without additive were determined as per the Bureau of Indian Standards [5]. For the determination of heat of hydration, additive dispersed in water was mixed with cement and the paste so obtained was filled in specimen tubes (20×20 mm) corked and then sealed with wax. They were stored in a vertical position at 27 ± 2 °C in 90% relative humidity. The heat of hydration was obtained from the difference of the heat of solution of un-hydrated and hydrated cement samples. The calorimeter consisted of assembly of units as per the Bureau of Indian Standards [5], which was calibrated with analytical reagent grade zinc oxide. For the determination of compressive strength [5], cube samples with 50 cm² cross section were prepared containing 0.5 to 5.0% additive by weight of cement using a vibrating machine [AIMIL 416, Associated Instrument Manufacturers, India (P) Limited, New Delhi]. Samples were kept with mould in 90% relative humidity at 27±2 °C for the first 24 hours and then demoulded and kept in chamber at the same humidity and temperature for 7, 28 and 90 days curing at 27±2 °C. For the determination of tensile strength, standard briquettes with 0.5 to 5.0 per cent additive were prepared using 1:3 cement-sand mix (by mass) and cured as above. Hardness of neat cement samples with and without additive was determined using the Vickers indentation method (using a pyramidal square-based diamond indenter with an optical angle at 136°: $H = P/A = 2p \sin \theta/2/d^2$, where $\theta = 136^\circ$, angles of Vickers indenter). Six indentations were done for determining the average hardness value of samples in each condition of load. Flexural strength and fracture toughness were determined [5] on rectangular (1×1×5 cm³) bar samples under a three point bending fixture using Universal Testing Machine (Shimadzu, Tokyo, Japan). Toughness was determined using a single-edge notched beam (SENB) at 20 mm span length and cross head speed of 0.5 mm/min. Water absorption was

determined using cube samples with 25 cm² cross-section area. Resistance to corrosion in five aggressive media (0.1 and 1.0 N H₂SO₄, 0.1 and 1.0 N HCl and sea water) was determined on cube mortar specimens (25×25×25 cm³) containing 0.5 to 5.0% additive. The microstructures of the specimens were obtained using a reflecting microscope (Leica-DMLM) attached with a camera (Leica MPS30 CH-Herzbergg, Switzerland).

3. Results and discussion

3.1 IR spectra

Ordinary cement constituents e.g. C₃A and C₁₂A₇ react with water to produce hydrates like CAH₁₀, C₂AH₈ and C₃AH₆ and calcium silicates e.g. C₃S and C₂S (C=CaO, A=Al₂O₃, H=H₂O and S=SiO₂) to produce C-S-H_I, C-S-H_{II} and C₅S₆H₅ etc. CH is formed as a dominant phase in the beginning of the hydration process. It interacts with hydration reaction intermediates for producing the calcium aluminate and silicate hydrates and thus its content decreases with time of hydration. In presence of acrylonitrile which contains functional groups like -CN and -CH₂, some new phases are also formed on interaction with CH and other products of hydration. Infrared spectra of the 90 days hydrated neat cement and cement hydrated with 3% of acrylonitrile are shown in Fig.1. It shows that the bands between 972 and 3645 cm⁻¹ are because of hydrated calcium aluminates and between 3437 and 3645 cm⁻¹ are predominantly due to water molecule or OH group vibration from Ca (OH)₂ and other hydrates present in the systems. The bands between 453 and 873 cm⁻¹ are quite broad and not properly resolved. They may be due to the Si-O and Al-O stretching vibration of silicate and aluminate groups. The bands between 800 and 972 cm⁻¹ are strong and broad indicating polymeric silicate (SiO₄) and aluminate group vibrations. The band observed at 972 cm⁻¹ is due to the higher shifting of absorption band [3] of C₂SH₂ and C-S-H phases present in cement. The bands between 1500 and 2000 cm⁻¹ are not very well resolved. The bands at 1637 cm⁻¹ may be because of monosulfate group, which indicates the heterogeneous character of the materials involving cement components and the gypsum, which are hydrated, and their

infrared bands overlap [3]. As compared to the infrared absorption band of hydrated cement, some new bands were detected in the samples hydrated with acrylonitrile. Three new bands were observed at 2926, 2854 and 1245 cm^{-1} in the mix which may be because of $-\text{CH}$ stretching vibration of $-\text{CH}_2$ group and at 1797 cm^{-1} because of $-\text{CN}$ stretching vibration present in the acrylonitrile. The bands at 3439 and 1633 cm^{-1} may be because of O-H stretching and monosulfate group, at 993 cm^{-1} because of C-S-H group and at 713 cm^{-1} may be because of C_4AH_{13} group.

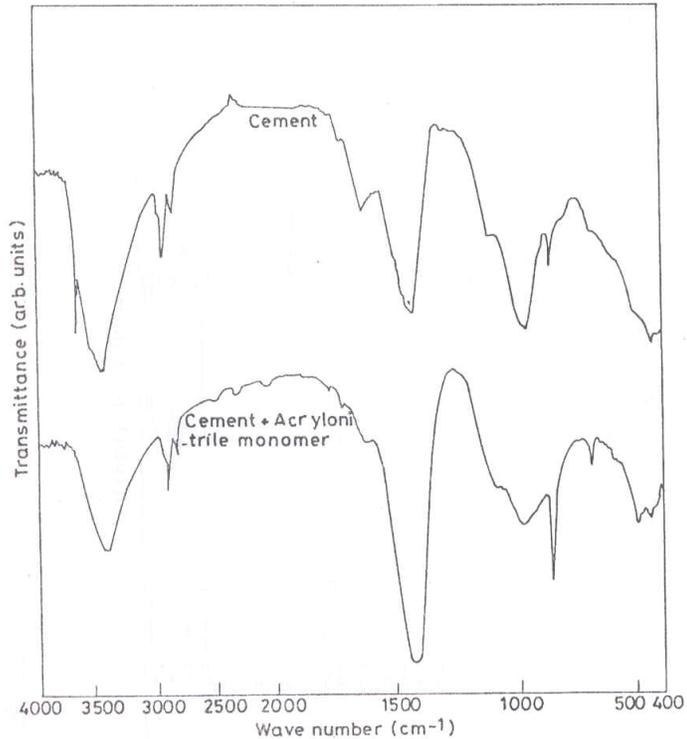


Fig. 1 - IR of 90 days hydrated cement and cement containing 3% of acrylonitrile

3.2 X-ray diffraction

X-ray diffraction patterns of 7, 28 and 90 days cured hydrated cement show the important peaks of above cementitious phases formed during hydration (Fig.2A, B & C). The peak intensity of tobermorite phase ($\text{C}_5\text{S}_6\text{H}_5$) at $2\theta=29.39^\circ$ ($d=3.03\text{\AA}$) increases from 26 to 93 with increase in hydration time from 7 to 90 days. The peaks of trisulfate phase ($\text{C}_3\text{A}.3\text{CaSO}_4.32\text{H}_2\text{O}$) were detected at $2\theta=15.73^\circ$ ($d=5.62\text{\AA}$), 24.29° (3.66\AA), 25.13° (3.53\AA), and 26.60° (3.34\AA) in 7 days hydrated cement sample while the peaks of monosulfate ($\text{CA}. \text{CaSO}_4.11\text{H}_2\text{O}$) appeared at $2\theta=19.90^\circ$ ($d=4.45\text{\AA}$) and 34.84° (2.48\AA) in 28 days cured samples and $2\theta=32.99^\circ$ ($d=3.86\text{\AA}$) and 36.95° (2.43\AA) in 90 days hydrated cement sample. Important phases detected in 90 days cured cement samples were $\text{Ca}_2\text{SiO}_5\text{H}_2$ at $2\theta=11.10^\circ$ ($d=7.59\text{\AA}$), 15.81° (5.59\AA), 34.12° (2.62\AA) and 50.82° (1.79\AA),

Ca₃Al₂O₁₂H₁₂ at 2θ=32.27° (2.77 Å), Ca₃Si₆O₂₂H₁₀ at 2θ =29.38° (d=3.03 Å) and Ca₃Fe₂O₁₂H₁₂ at 2θ=51.88° (d=1.76 Å) and 2θ=62.57° (d=1.48 Å). The ions or molecules formed during the hydration of cement control the formation of cement-acrylonitrile products. The relative intensities of the peaks corresponding to hydrated cement phases were altered and a few new peaks were detected along with the disappearance of some of the peaks shown in 90 days hydrated neat cement samples. In the Cement-3% acrylonitriles mix, XRD pattern (Fig.2D) has shown that new peaks appear at 2θ=18.79° (d=4.71Å) may be because of Ca(CN)₂ phase. The peaks of hydrated cement phases e.g. C-S-H_{II} at 2θ=41.32° (d=2.18Å), Ca₃Al₂O₁₂H₁₂ at 49.80° (1.82Å) and 26.60° (d=3.34 Å), Ca₂SiO₅H₂ at 2θ=62.46° (d=1.48 Å) and monosulfate at 32.20° (2.77Å) have increased intensities as compared to their intensities in 90 days hydrated neat cement. Some of the peaks of 90 days hydrated cement were adversely affected by the

acrylonitrile addition and their intensities were considerably reduced e.g. peak of hydrated lime at 2θ=18.03° (d=4.90Å) and 47.15° (1.92 Å), peak of Ca₂SiO₅H₂ at 2θ=15.86° (d=5.59Å) and 34.39° (2.62 Å) were reduced from 46 to 19 and 25 to 13 and from 25 to 19 and 43 to 34 respectively.

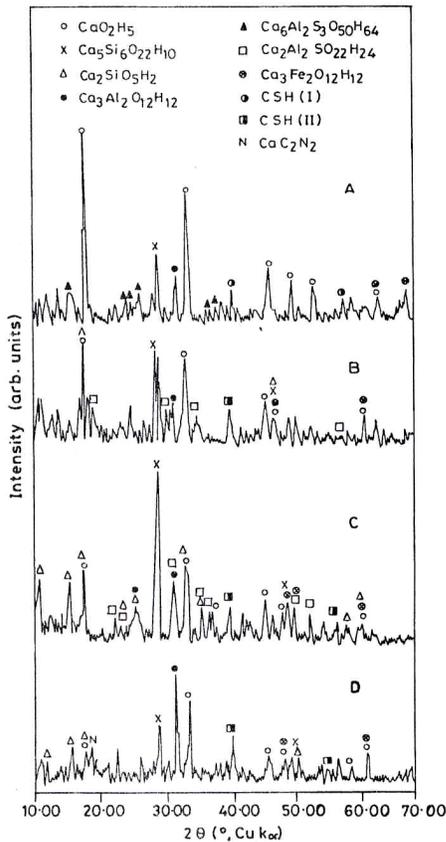


Fig. 2 - X-ray diffraction pattern of cement hydrated for (A) 7 days, (B) 28 days, (C) 90 days and (D) 90 days hydrated cement containing 3% acrylonitrile

3.3 Setting time

The calcium silicate hydrate e.g. C-S-H_I, C-S-H_{II} and tobermorite formed are distributed in the cement paste in different stages of hydration varying both in composition and degree of crystallinity. The calcium silicates have been shown to have tetrahedral (SiO₂(OH)₂)²⁻ structure having accessible sites for the interlocking of hydrates. The gel structure of the

tobermorite phases and the interlocking of hydrated aluminates and silicates bring about the stiffening of the paste and are responsible for setting of cement paste. The setting time of cement containing 0.5 to 5.0 % acrylonitrile are given in Table 1. The value of initial setting time and final setting time of cement was found to be 130 and 230 minutes respectively.

Table 1 Setting time and heat of hydration of cement in the presence of crylonitrile

<i>acrylonitrile</i> Mass %	Setting time (min)		Heat of hydration (J/g) at			
	Initial	Final	3-days	7-days	28-days	90-days
0.00	130	230	259.57	326.41	364.11	439.95
0.25	-	-	261.91	327.37	367.38	440.61
0.50	109	206	264.30	328.33	370.68	441.90
1.00	98	188	269.02	330.22	377.32	444.50
2.00	-	-	278.51	334.02	390.62	449.72
3.00	82	159	279.60	344.00	396.01	451.60
5.0	65	123	272.91	326.58	391.47	447.34

It is evident from the table 1 that when acrylonitrile is mixed with cement, it acts as an accelerator and the initial setting time was reduced from 109 to 65 and final setting time from 206 to 123 minutes with 0.5 to 5.0 % addition. It seems that the acceleration process in the presence of acrylonitrile is due to the chemical interaction between hydrated cement phases and functional groups of additive to yield amorphous materials, which are scattered and interspersed in the hydrated masses of cement paste.

3.4 Heat of hydration

When cement reacts with water, the process is accompanied by the evolution of heat, which leads to the decrease in the energy of the system. The magnitude of the strength developed during hardening depends essentially on the nature and reactivity of phases, the rate of their interaction with water, the rate of formation of new phases and the nature of their hardening structures. The relation between the structural peculiarities of cement minerals and their reactivity with water can be interpreted by the measurement of heat of hydration. Several of the properties important to the user of Portland cement and other hydraulic materials are direct

result of the hydration reactions taking place between the components of cement and water. The measurement of heat of hydration is accepted to be simple and reliable method for the evaluation of hydration reaction. The heat of hydration can also be correlated with the heat of solution.

The difference in the heat of solution of anhydrous and hydrated cement can be taken as a measure of the heat of hydration [5]. The values of heat of hydration of cement were 259.57, 326.41, 364.11 and 439.95 Jg⁻¹ for samples hydrated for 3, 7, 28 and 90 days, respectively. The heat of hydration of cement-acrylonitrile mixes varied with the concentration of additive as well as curing period (Table 1). It seems that during early hydration period, the un-hydrated cement phases actively participated in hydration, so the tendency to react with small amount of additive is stronger which slows down at later stages. For cement-acrylonitrile mixes, the heat of hydration increases with increasing additive

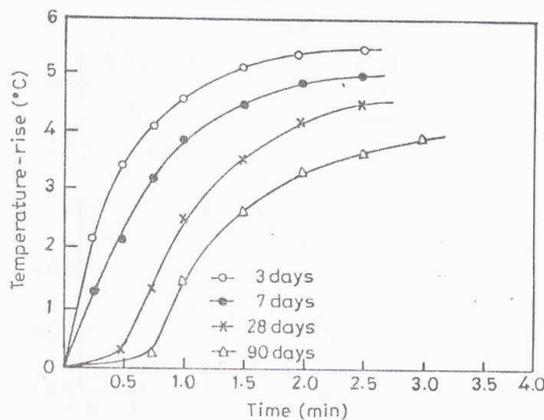


Fig.3 Temperature rise during the dissolution

contributes to the development of strength. The strength is caused by the intergrowth and welding together of the splines of calcium silicate hydrate and other phases in set Portland cement. The compressive strength and tensile strength of cement at 7, 28 and 90 days are given in Table 2. In cement-acrylonitrile mixes, the values were found to increase with 0.5, 1.0 and 3.0 % additive. It also shows the tensile strength of cement mortar cured for 7, 28 and 90 days with 0.5, 1.0, 3.0 and 5.0 % acrylonitrile. The values of compressive and

content up to 3.0% and thereafter a little lower values have been with 5.0 % addition at all the ages.

3.5 Compressive and tensile strengths

When water is mixed with cement, hydrated phases are formed and the interlocking of different phases

Table 2 Properties of cement in the presence of acrylonitrile

Additive content (%)	Compressive strength (MPa)			Tensile strength (MPa)			Indentation hardness (MPa)	Fracture toughness (MPa.m ^{1/2})		Flexural strength (MPa)	Water absorption (%)
	at			at			at	at			
	7 days	28 days	90 days	7 days	28 days	90 days	50 (N)	28 days	90 days	90 days	90 days
0.00	31.60	43.32	58.10	2.77	3.81	5.13	6.64	0.62	1.06	8.67	9.93
0.50	34.09	45.61	58.89	3.81	4.68	6.04	7.00	0.89	1.35	9.03	9.64
1.00	35.62	47.24	59.09	4.32	4.82	6.30	7.90	0.95	1.58	12.20	9.43
3.00	36.13	48.67	59.13	4.87	4.99	6.37	8.50	1.40	1.83	12.56	9.06
5.00	32.69	45.91	58.43	4.39	4.80	6.09	7.46	1.00	1.38	11.93	9.18

tensile strengths increase up to 3.0 % additive. Although lower values are obtained for cement-5.0% acrylonitrile mix, they were still higher than the strength of unmodified cement at all the ages. Cement is weak when tested under tension and therefore it is reinforced with steel or other materials. Acrylonitrile has been found to increase the tensile strength of modified products. In the composite so developed, the products of this organic additive probably act as a reinforcing component and causes increase in the tensile strength. The products between the hydrating cement phases and the functional groups of the organic material (e.g. $\text{Ca}(\text{CN})_2$) remain interspersed in the modified cement composite and helps further in increasing the tensile strength.

3.6 Indentation hardness

With progress in setting reactions, new bonds are formed in cement products and their strength as well as hardness increase. Acrylonitrile present in the products contributes additional bonds, which causes further increase in the hardness values. Hardness (H) values were calculated by the equation $H = 1.854 P/d^2$ in which the values of the diagonal length (d) and the applied indentation load (P) were substituted. The hardness of 90 days cured cement on 50 N load is shown in table 2. Lowering in the values may be because of low hardness of products at higher concentration of additive and flow generated in bonds.

Samples with 3% acrylonitrile in cement gave hardness values of 8.5 MPa at 50 N loads, which was found to be highest under the experimental conditions. Table 2 shows that the hardness values increase with 0.5 %, 1.0 % and 3.0 % acrylonitrile mixed in the cement. The hardness value obtained was lower with 5.0% acrylonitrile addition as compared to 3.0 % but it was higher than the unmodified cement.

3.7 Flexural strength and fracture toughness

The flexural strength (FS) of neat cement samples, as calculated by equation $FS = 3WL/2bd^2$ (where, W=fracture load, L=span of the bar between the two supporting edges, b=width of the sample and d=depth of the sample at the fracture plane) was 8.82 MPa after curing for 90 days. The flexural strength values obtained with 0.5, 1.0, 3.0 and 5.0% acrylonitrile are shown in table 2. These values increase with increasing concentration of acrylonitrile up to 3.0 % additive in cement. 5.0 % addition of acrylonitrile in cement has given slightly lower values than the values obtained with 3.0% additive but these were still higher than the neat cement FS values. The fracture toughness values (K_{1C}) of 28 and 90 days hydrated neat cement samples were 0.62 and 1.06 $Mpa.m^{1/2}$ respectively, as calculated by equation $K_{1C} = PqS f(a/w)/BW^{3/2}$ (where Pq =Fracture load in Newton, S =Span length, B =Width of the sample, W =Depth of the sample and a =Notch depth in cm). The average fracture toughness of cement containing 0.5 to 5.0 % acrylonitrile is shown in Table 2. 3.0 % additive has given good resistance to crack propagation against the applied load as evidenced by a value of toughness equal to 1.51 as compared to 1.03 $Mpa.m^{1/2}$ of neat cement.

3.8 Water absorption

Cement mortar and concrete absorb water because of their porosity when they are brought in contact with water. The water absorption in 90 days-cured cement-mortar was 9.93% by weight. Water soluble organic materials find their place on the surface of the components of the cement mortar and concrete. They can also

fill the void/pore space and reduce the porosity. Table 2 also shows the water absorption of cement-acrylonitrile mortars containing 0.5 to 5.0-wt % additive. The values of water absorption decreased with increasing concentration of acrylonitrile up to 3.0% as compared to unmodified cement mortar. Acrylonitrile-modified cement mortars have a structure in which the pores micro pores and other flaws are filled by polymers/monomer or sealed by polymer-cement composite material and water absorption/porosity is reduced.

3.9 Corrosion resistance

The organic compounds by acting as a continuous reinforcing network [3] or by interaction with the hydrated cement enhance the corrosion resistance properties of the composite. The weight loss in 90 days cured ordinary cement-mortar, after 4 days immersion in 0.1 and 1.0 N H₂SO₄ were 1.15 and 6.24 %, respectively.

The data shows that the loss decreases with

Table 3 Corrosion Table resistance

increasing concentration of acrylonitrile in cement up to 3.0% after 4 days immersion in 0.1 and 1.0 N H₂SO₄, respectively. The new phases present in modified products resist the corrosive action of acids. The higher values of weight loss in ordinary cement-mortar with 0.1 and 1.0 N HCl were also decreased with acrylonitrile addition in cement (table 3). The value of weight loss in ordinary cement-mortar after one-month

Additive content (Mass %)	Corrosion resistance				
	Mass loss (%)				
	H ₂ SO ₄ /4d		HCl/4d		Sea water/ 90d
	Conc.		Conc.		
	0.1 N	1.0 N	0.1N	1.0N	-----
0.00	1.15	6.24	4.95	8.61	3.46
0.50	0.87	5.46	3.36	7.80	3.24
1.00	0.38	4.89	3.30	7.72	2.68
3.00	0.33	4.21	3.25	7.65	2.30
5.00	0.41	4.32	3.28	7.69	2.38

immersion in seawater (3.46%) was also reduced as shown in table 3; which shows that the cement-acrylonitrile mortar is also more resistant to seawater. The decreases in weight loss with increasing concentration of additive in cement i.e. the improvements in the corrosion resistance properties might be ascribed to the filling of pores/voids and non-corrosive nature of cement-acrylonitrile products. Microscopic examinations of the composite revealed the presence of monomer/polymer in capillary canals, pores and micro pores of the hydrated

cement samples. Acrylonitrile functional groups ($-\text{CH}_2$ and $-\text{CN}$) on hydrolysis are likely to interact with hydrating cement phases forming new products (e.g. $\text{Ca}(\text{CN})_2$), which remain dispersed uniformly in the rest of the materials modifying the physical and mechanical properties of the product. Cement phases may accommodate only upto 3.0% acrylonitrile functional groups in their interaction and no further improvement is seen with higher additive content.

4. Conclusions

1. The addition of acrylonitrile alters the physical properties like setting time, heat of hydration, strength, hardness, toughness etc. of ordinary cement. The studies indicate that monomer/polymer modified cement posses higher strength compared to ordinary neat cement.
2. The values of strength, hardness and toughness of cement with 3.0% acrylonitrile were found to be higher than those of the other percentages of additive as well as neat cement. The organic material interspersed in the hydrated cement may lead to the formation of cross-links among the grains solidified in originally free space. Densification of the resulting product causes a decrease in porosity and an increase in the strength of the product.
3. Cement with 3.0% acrylonitrile was found to be more corrosion resistant as compared to other percentages of additive as well as neat cement in the different corrosive media studied.

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