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Properties of plain and latex modified Portland cement pastes and concretes with and without superplasticizer

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Abstract

This paper deals with the effects of latex concentration on the workability and strength characteristics of Portland cement pastes with and without superplasticizer. Durability assessments are made by immersing these pastes in 5% Na_2SO_4 and 2.5% NaCl solutions. From the results obtained, it is found that the superplasticizer and superplasticizer–latex combinations may improve the workability of the Portland cement pastes. The Portland cement pastes with superplasticizer have much higher strengths than the latex modified Portland cement pastes with and without superplasticizer. In general, curing in lime-saturated water adversely affect the strength of the pastes containing latex from about 28 days onwards. In the durability test, the resistance of latex modified Portland cement pastes with and without superplasticizer to NaCl is decreased. Degradation mechanism depends on the characteristics of the corrosive medium as well as the resistance of the material itself to the resulting chemical action. The character of strain–stress data of latex modified concretes becomes more prominent as the latex concentration increases. These data are anomalous when compared with the data normally observed for concretes without admixture. The proposed equations are found adequate to describe the stress–strain behaviour of latex modified concretes in compression. These equations can also be applied in calculating the initial modulus of elasticity and proportional limit in the case of polymer modified concretes, which exhibit non-linear behaviour at high stress.

Keywords: Cement paste; Concrete; Superplasticizer; Compressive strength; Durability

1. Introduction

Polymer latexes are known to affect the physical, mechanical and durability properties of Portland cement paste, mortar and concrete. The magnitude of this effect is dependent on the type of latex and the latex concentration in the mixture. Latexes, most notably those based upon liquid rubber such as styrene–butadiene rubber, have been employed to dramatically increase the tensile and flexural strength [1,2]. However, latexes frequently provide improvements in these strength parameters when incorporated in concentration levels greater than a critical value. On the other hand, an increase in latex concentration can substantially diminish the compressive strength by reducing the quantity of Portland cement in the mixture. This disadvantage together with an increase in viscosity, which is likely to influence the workability of the paste, obviously requires serious consideration. A wide variety of superplasticizers have been considered for use, in combination with styrene–butadiene, so as to impart property modifications. In a study [3], the combination of styrene–butadine with a melamine based superplasticizer has been shown to produce Portland cement concretes having a better slump retention than those obtained with styrene–butadiene alone. This method can also be successful in increasing the compressive strength of latex modified concrete up to similar levels to that obtained for Portland cement concrete without admixture. In addition to the drawbacks mentioned above, Portland cement pastes containing latex offer the advantage of a fairly limited degree of chemical stability when subjected to a chemical attack. However, the work of Ohama et al. [4] has shown that the incorporation of alkyl

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alkoxy silane into the styrene–butadiene rubber latex modified Portland cement concrete can substantially elevate durability while having a relatively minor influence on compressive strength.

The most notable advantage achieved by the use of styrene–butadiene rubber latex is the improvement in toughness. The addition of this type of latex in appropriate concentrations clearly transforms an essentially brittle Portland cement paste into one exhibiting ductile characteristics. In fact, these characteristics do not only belong to one particular class of latex. Other possible copolymers can also be used to provide specific properties. Much of this work is concerned with assessing the influence of methacrylic acid ester–styrene copolymer on the strength and durability characteristics of Portland cement pastes with and without superplasticizer. In addition, statistical analysis was used as a means of studying the stress–strain behaviour of natural rubber latex modified Portland cement concretes containing superplasticizer. This analysis was done with a restricted set of data thought to be more representative of these types of concretes.

2. Materials and method

The plain pastes (without admixture) were prepared using ordinary Portland cement with water contents adjusted to yield an indentation depth of 34±1 mm as determined by Vicat probe. The w/c ratio of plain Portland cement paste was found to be 0.36. The same method was also used to determine the w/c ratio of superplasticized pastes. The superlasticizer is sulfonated melamine formaldehyde condensate; it was used in amounts from 0.2% to 0.8% by weight of Portland cement. The latex modified Portland cement pastes were prepared by adding methacrylic acid ester–styrene copolymer in amounts of 1.75% to 7% of the weight of Portland cement. These values represent the total amount of solid of the organic admixtures. In the pastes made with a combination of latex and superplasticizer, the optimum superplasticizer to cement ratio was found by the aid of Vicat test to be 0.2%. This is the most widely used method of determining the water requirement of polymer modified plasters made from gypsum paste. The apparatus and procedure are simple and the experimental conditions are near to those of practical usage. This test is also considered to be suitable for Portland cement paste containing lower amount of latex or superplasticizer. The compatibility of latex with superplasticizer was determined conveniently by following the change in the film forming abilities of samples in a laboratory condition held at constant temperature and relative humidity (20±2 °C and 65% RH). This test was also used to evaluate the effect of lime-saturated water on the performance of latex dispersion with and without superplasticizer. The tensile strengths of samples were measured for determining the elasticity of the film. These measurements were all made on dog-bone samples of 1 mm in thickness, 12 mm in width and 140 mm in height. The samples, which have been investigated in this manner, include: latex dispersion, a 98%–2% latex dispersion and superplasticizer, a 90%–10% latex dispersion and superplasticizer, a 90%–10% latex dispersion and lime-saturated water, an 80%–20% latex dispersion and lime-saturated water and a series of latex dispersion–superplasticizer–lime saturated water. These samples, continually mixed for a period of 1–2 min were poured on glass plates and then cured in laboratory conditions for 7 days. The dog-bone samples were cut from these polymer plaques of 1 mm in thickness. The tests showed little or no difference in film formation for latex with and without superplasticizer but a significant decrease for latex and latex–superplasticizer systems containing lime-saturated water. The presence of a superplasticizer within the solid polymer would be expected to exert some influence on mechanical properties but appears to be of minor importance in case of low superplasticizer contents. For example, the latex cured in laboratory condition for 7 days has tensile strengths normally ranging from 3.4 to 4.5 MPa. By comparison, it may be noted that latexes made using the two above-mentioned superplasticizer concentrations gave tensile strengths ranging from 3.3 to 3.9 MPa. In the case of latex dispersions mixed with the lime-saturated water, it was found that as the percent of the lime-saturated water incorporated in the copolymer increased, the tensile strength decreased. For example, tensile strengths of the samples consisting of 90% latex dispersion and 10% lime-saturated water ranged from 1.7 to 2.1 MPa. Another group made with 80% latex dispersion and 20% lime-saturated water exhibited the lower values of tensile strength, but these were consistent. The same trend exists particularly within latex–superplasticizer systems mixed with lime-saturated water, but a broad band is required to include most of the data. The decrease in tensile strength of the samples containing lime-saturated water may be attributed primarily to the formation of salt bridges within the polymer plus the small decrease in crystalline content. This knowledge may be of great practical importance in determining the chemical stability

Table 1
Physical and chemical properties of Portland cement

Composition (%)									Specific weight (kg/m^3)	Specific surface, Blaine (m^2/kg)
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI		
20.63	5.14	2.72	63.91	1.39	2.94	0.51	0.84	1.85	3100	415

Table 2
Characteristics of methacrylic acid ester and styrene copolymer latex in dispersion state

Solid content (%)	pH value	Particle size (μm)	Minimum film forming temperature (°C)	Density (kg/m^3)	Appearance
35	8.5±1	0.17	0	1010	Milky-white aqueous dispersion

of the latex modified Portland cement pastes with and without superplasticizer against the effects of corrosive agents. However, it is more important here to consider the physical and chemical properties of portland cement and latex. These properties are given in Tables 1 and 2, respectively. In some cases, these properties may serve to indirectly assess mechanical and durability properties of the paste. However, such comparisons are not always valid and need careful consideration. Actually, strength measurements provide one of the simplest and most sensitive means of determining change in a paste as the result of the influence of various factors. In this way, an adequate knowledge about the paste characteristics can easily be obtained. On the other hand, the accuracy of the data obtained depends upon the production conditions employed in the laboratory. For this reason, considerable attention has been paid to the production of samples. The pastes of standard consistency were poured into molds of size 40×40×40 mm^3 and stored in laboratory conditions at 20±2 °C and 65% relative humidity for 1 day. The samples were unmolded at the end of this period and then cured in lime-saturated water at 20±2 °C for periods of up to 90 days. Compressive strengths were determined after curing periods of 7, 28 and 90 days. The results obtained showed the wet performance of the composites since testing was done on the saturated samples. Durability tests consist of immersing the samples in salt solutions such as 5% Na_2SO_4 and 2.5% NaCl at 20±2 °C for 62 days. The samples cured in lime saturated water for 28 days were used in these tests. The compressive strengths after 62 days of soaking in salt solutions were compared with the 90 days compressive strength of the pastes cured in lime-saturated water. The severity of attack was determined by loss of strength. Additionally, the data reported by Nagaraj et al. [5] were used to obtain mathematical models for the stress–strain behaviour of natural rubber latex modified Portland cement concretes with superplasticizer.

3. Results and discussion

3.1. Workability

The effectiveness of methacrylic acid ester–styrene copolymer latex in decreasing the water requirement of Portland cement pastes depends on the latex concentration. This dependency becomes small at very low latex concentration. From the data of Table 3, it is seen that the w/c ratio of latex modified Portland cement pastes with a latex to cement ratio of 1.75% is substantially the same as that of plain paste. The rate of reduction in water content becomes more pronounced as the latex concentration increases. For example, the addition of 2.56% latex to the Portland cement paste decreases the w/c ratio from 0.36 to 0.33. The major contribution to the drop in water requirement then must be due to an increase in the latex content. However, this hypothesis does not appear to account for most of the facts concerning the water requirements of the latex modified Portland cement pastes with latex to cement ratios of 5.25% or higher. According to this hypothesis, the water requirement of the latex modified pastes would be expected to decrease as the latex content increases. Whereas, the water content required to producing these pastes in satisfactory workability remains nearly constant. This decreasing effec-

Table 3
The effects of superplasticizer, latex and their combinations on the 28 days compressive strength of Portland cement pastes

Superplasticizer to cement ratio (%)	Latex–cement ratio (%)	Water–cement ratio	Superplasticizer concentration (%)	Latex concentration (%)	The 28 days compressive strength (MPa)
0	0	0.36	0	0	56.23
0.2	0	0.32	0.15	0	61.78
0.4	0	0.30	0.31	0	73.03
0.6	0	0.29	0.46	0	87.25
0.8	0	0.28	0.62	0	90.30
0	1.75	0.36	0	1.27	55.32
0	3.5	0.33	0	2.56	56.08
0	5.25	0.33	0	3.80	51.36
0	7	0.32	0	5.04	43.79
0.2	1.75	0.33	0.148	1.30	61.51
0.2	3.5	0.31	0.147	2.58	70.98
0.2	5.25	0.29	0.149	3.90	65.06
0.2	7	0.28	0.148	5.18	55.41

tiveness of methacrylic acid ester–styrene copolymer latex in improving workability can often be related to the viscosity increasing action of the higher concentrations of latex. In addition to this effect, there may be changes in polymer structure and properties due to polymer–paste interaction. The interplay of these factors may lead to quite complex behaviour. Consequently, it is difficult to predict the magnitude and trends of the concentration-dependent parameters. On the other hand, the water requirement of superplasticized Portland cement pastes is observed to decrease with increasing concentration of sulfonated melamine formaldehyde. The rate of reduction in water content of these pastes usually is not directly proportional to the superplasticizer concentration but has a more complex dependence on it. A decrease in w/c ratio from 0.36 to 0.32 is observed as the superplasticizer concentration is increased from 0% to 0.15%. Note that the w/c ratio range from 0.32 to 0.28 for the range of superplasticizer concentrations considered. These results confirm the fact that when the superplasticizer concentration is increased, there is always a corresponding decrease in water content. However, the use of a slightly higher concentration of superplasticizer such as 0.31% in place of 0.15% only marginally increases the workability characteristics of Portland cement pastes. The data given in Table 3 show that the w/c ratio of this paste decreases from about 0.32 to about 0.30. This abrupt change in the increase in water reduction at 0.31% superplasticizer may be a result of the saturation effect observed with these types of admixtures. This fact is confirmed by the test results obtained at higher superplasticizer concentrations.

It is quite clear from the data that there is a very marked difference between latex and superplasticizer in terms of water reduction effects. As would be expected, the latter has a much greater water reduction effect. However, the effectiveness of the former can be increased by the addition of a small amount of sulfonated melamine formaldehyde to methacrylic acid ester–styrene copolymer. The influence of latex in combination with superplasticizer on the w/c ratio of Portland cement pastes can be analysed from the data given in Table 3. The paste made with the combination of 0.148% superplasticizer and 1.30% latex has a lower w/c ratio than the paste with 1.27% latex. This result indicates that the formulation based on the superplasticizer–latex combination provides a sufficient workability. On the other hand, this formulation reduces the w/c ratio of the paste to a lesser degree than with 0.15% superplasticizer. One possible reason for the rather small difference in the w/c ratios of these pastes may be the competition of the opposing effects of increased viscosity produced by latex and flow under the dispersive action of superplasticizer. On this basis, the presence of higher amounts of latex in the formulation consisting of the superplasticizer–latex binary system would be expected to have a negative effect on the rheological properties of Portland cement pastes. However, experimental evidences clearly indicate that this is not to be the case with the w/c ratios of these pastes rarely exceeding those of pastes made with superplasticizer alone. It is interesting to note that the presence of a low superplasticizer fraction such as 0.148% in the latex–superplasticizer combination is enough to alleviate the adverse effects of increased viscosity caused by latex on the workability. This anomalous effect observed may be directly related to the change in cement concentration as it affects the water content of the mix.

3.2. Strength

The effects of superplasticizer, methacrylic acid ester–styrene copolymer latex and their combinations on the 28 days compressive strength of Portland cement pastes can be determined from the data of Table 3. It is found from these data that the magnitude of the observed effects generally increases proportionally with the concentration of superplasticizer. The 28 days compressive strength of Portland cement paste with a superplasticizer concentration of 0.15% is not quite different from that of the plain paste. However, the addition of higher amounts of superplasticizer causes a marked increase in the 28 days compressive strength of pastes. For example, the addition of 0.31% superplasticizer to Portland cement paste leads to a strength 30% higher than that of the plain paste. This difference can be as high as 60% for the Portland cement paste containing 0.62% superplasticizer. Based on the above observations, it appears that differences in strength produced by superplasticizer can adequately be accounted for on the basis of changes in the w/c ratios of pastes. In general, the 28 days compressive strengths of Portland cement pastes with superplasticizer increase in consequence of the lower w/c ratio in the mix. However, the type of admixture used plays a very significant role in determining the w/c ratio dependence of paste strength. This dependency becomes small in the case of latex modified Portland cement pastes. The introduction of latex, that is considerably looser in structure due to the lack of symmetry along the chain onto the Portland cement, makes the strength of paste more dependent on polymer concentration. This fact is confirmed by the test results obtained for the methacrylic acid ester–styrene copolymer latex modified Portland cement pastes. From the data of Table 3, latex concentrations up to approximately 1.27% are found to have little effect upon the 28 days compressive strength. This is especially true when the 28 days compressive strengths of plain and latex modified Portland cement pastes are compared. The increase in latex concentration from 1.27% to 2.56% produces only a small amount of increase in strength. This increase appears to be directly attributable to the influence of the w/c ratio. Whereas, at a high concentration of latex such as 5.04%, the 28 days compressive strength of latex modified Portland cement paste is decreased since the polymer imposes a restraint on the amount of increase in strength. These differences in mechanical behaviour are related to the softer and more amorphous structure of the polymer. A comparison between the Portland cement paste with a superplasticizer concentration of 0.15% and the latex modified Portland cement paste with a latex to cement ratio of 7% illustrates this fact. Moreover, these data obtained at a constant w/c ratio strongly suggest that the polymer to cement ratio has a much greater effect on the strength than does the w/c ratio. Generally, the 28 days compressive strength of latex modified Portland cement pastes are markedly reduced as compared to those of the superplasticized pastes. However, the strength reduction generated by higher amounts of latex is exactly counterbalanced by the addition of superplasticizer to the latex modified Portland cement pastes. The presence of about 0.148% superplasticizer in the formulation based on a combination of superplasticizer and latex leads to a lowering of the w/c ratio and thereby increases the 28 days compressive strength of the composites. The general tendency is for the Portland cement pastes made with the 0.147% superplasticizer and 2.58% latex combination to have a slightly higher compressive strength. The reason why this composite performs better, in terms of strength, than the other latex modified Portland cement pastes containing a low concentration of superplasticizer is due probably to the decrease in w/c and polymer to cement ratios, and polymer phase probably contributes relatively little to the strength loss in this case. On the other hand, probably of greater importance is the improvement in strength of Portland cement paste with a high concentration of latex. The addition of 0.148% superplasticizer to the latex modified Portland cement paste with a latex to cement ratio of 7% makes the strength of this composite equal to plain paste.

Figs. 1–3 show the effects of superplasticizer, latex and their combinations on the gain of strength with time in Portland cement pastes with different w/c ratios. Data on the development of strength of Portland cement pastes made with superplasticizer are presented in Fig. 1. It is apparent that the w/c ratio has a significant effect on the rate of gain of strength of the paste. The pastes with a low w/c ratio gain strength more rapidly than the pastes with higher w/c ratio [6]. For example, an increase in strength from about 38.50 to about 60.37 MPa is observed for the plain paste as the age of paste increases from 7 to 90 days. If the superplasticizer is used to reduce the w/c ratio of this paste from 0.36 to 0.28, the increase in strength from about 73.47 MPa at 7 days to about 91.51 MPa at 90 days is achieved. However, this effect provided by the superplasticizer is quite different from that of latex where considerably more complex behaviour is observed. The introduction of latex onto Portland cement paste decreases not only the strength but also the rate of gain of strength. Fig. 2 gives the general picture of the direction and magnitude of the property changes caused by latex. It can be seen from this figure that the trend of increase in strength from about 28 days onwards changes in consequence of water curing. The adverse effects of water curing on later strength become more pronounced at the age of 90 days. If the data presented in Fig. 2 are analysed, a value for the 90 days compressive strength of Portland cement pastes containing 5.04% latex of 33.97 MPa is obtained, this again being a typical value for the 7 days compressive strength of the same paste. The reason for this steep decrease for latex modified Portland cement pastes, as compared to the superplasticized pastes, is not obvious. But, chemical modification of the polymer incurred as the result of curing in the presence of lime-saturated water may have a drastic effect on the solubility and mechanical properties of the sample. Moreover, the latex concentrations up to about 5% and the lower degrees of polymer-

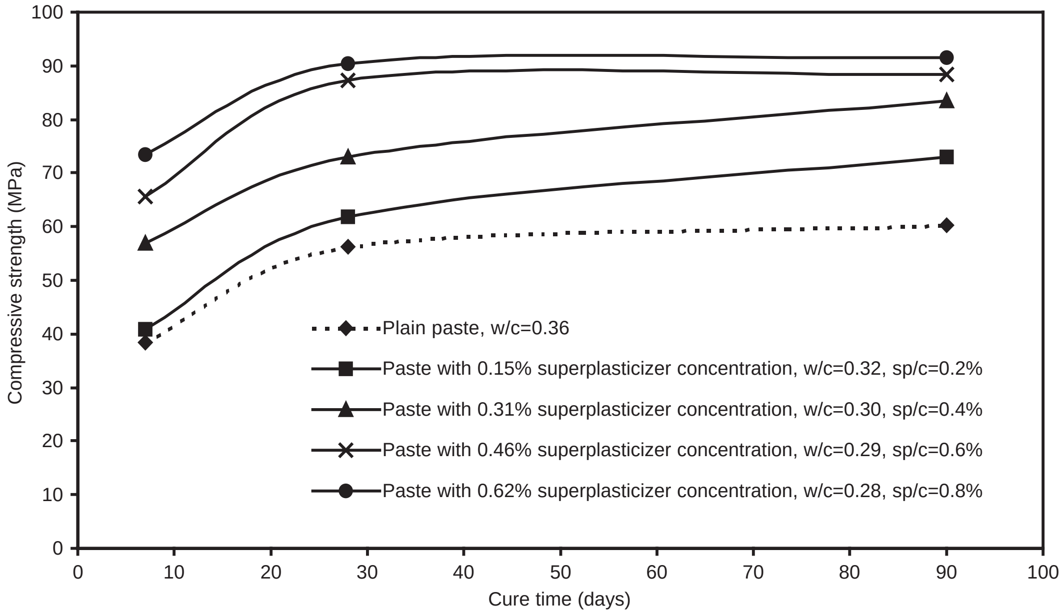

Fig. 1. The gain of strength with time in plain and superplasticized Portland cement pastes.

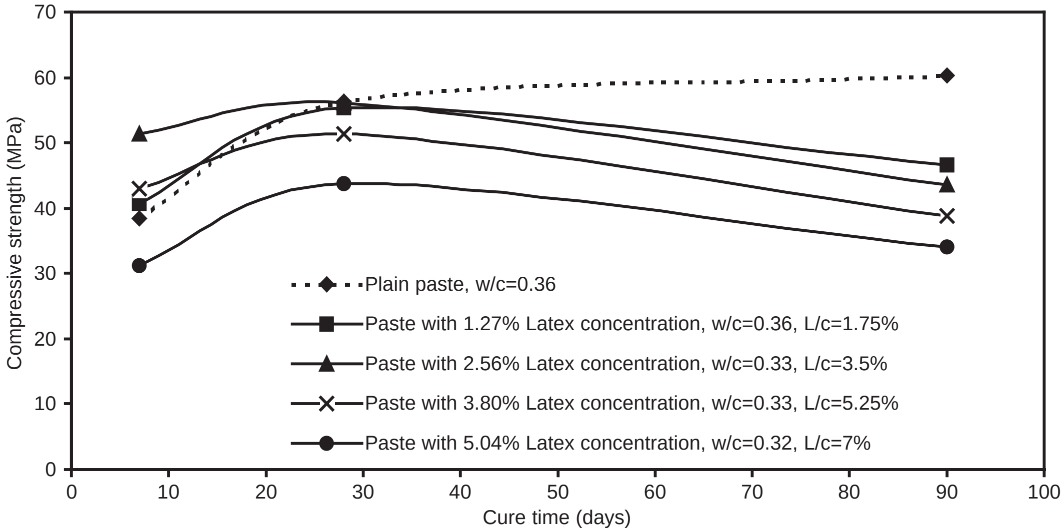

Fig. 2. The gain of strength with time in plain and latex modified Portland cement pastes.

ization obtained during curing may increase this effect. Studies [7] of moisture effects on the response of latex modified Portland cement pastes and mortars also show similar results which may occur at different ages, depending upon the nature of the polymer. The effects of water curing on the strength of latex modified Portland cement pastes with superplasticizer appear to be essentially the same as for the latex modified Portland cement pastes discussed previously. Although these pastes show a moderate increase in the early strength when cured in lime-saturated water, they show considerable decrease at the age of 90 days. The examples of this behaviour are illustrated in Fig. 3. This marked influence of latex is noteworthy and brings to mind the detrimental effect of latex in paste composition on progressive strength increase in the presence of lime-saturated water. Therefore, the long-term strength of these pastes is determined to a great extent by the latex.

3.3. Sodium chloride attack

From the result of Table 4, it can be seen that after 62 days of exposure to a 2.5% NaCl solution, the compressive strengths of Portland cement pastes with and without

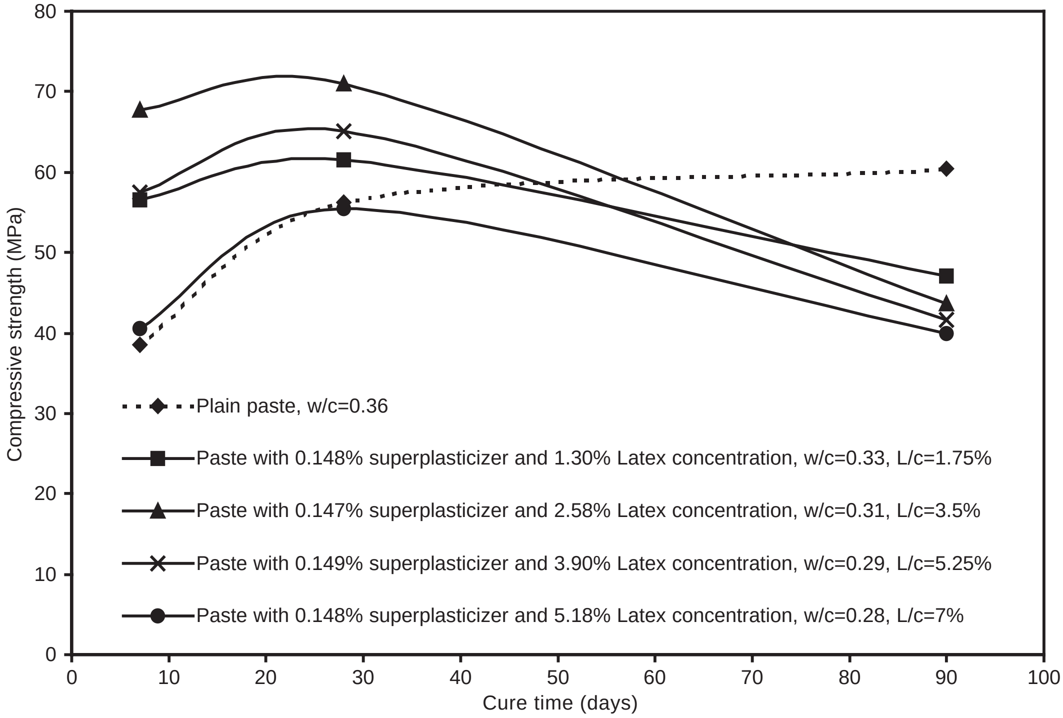

Fig. 3. The gain of strength with time in plain and latex modified Portland cement pastes with superplasticizer.

Table 4
The effects of NaCl and Na_2SO_4 solutions on the compressive strength of plain and latex modified Portland cement pastes with and without superplasticizer

Superplasticizer concentration (%)	Latex concentration (%)	Water–cement ratio	The 28 days compressive strength (MPa)	The 90 days compressive strength (MPa)	The compressive strength after 62 days of immersion in 2.5% NaCl solution (MPa)	The compressive strength after 62 days of immersion in 5% Na_2SO_4 solution (MPa)
0	0	0.36	56.23	60.37	55.46	63.47
0.15	0	0.32	61.78	72.96	67.41	77.34
0	1.27	0.36	55.32	46.51	38.71	49.69
0.148	1.30	0.33	61.51	47.05	41.52	51.43
0.147	2.58	0.31	70.98	43.66	34.09	46.72
0.148	5.18	0.28	55.41	39.93	25.12	41.86

superplasticizer exhibit either a slight increase or no significant change as compared to their 28 days compressive strengths. If these strengths are compared with those measured after 90 days of immersion in lime-saturated water, it is found that the effect of NaCl on the strengths of these pastes is not instantaneous but that the strengths continue to decrease slowly over at least 62 days of exposure to this solution. The decrease in the compressive strength of plain Portland cement paste after aging in sodium chloride solution is only about 8% of the 90 days compressive strength of the same paste. This ratio remains nearly constant for the Portland cement paste with superplasticizer. These values indicate the start of mechanical degradation and thereby serve as a criterion for aging in sodium chloride solution. This degradation is generally considered to arise as a consequence of the leaching of lime. Such an effect is usually quite high in the latex modified Portland cement pastes. This conclusion can be reached by comparing the compressive strengths of plain and latex modified Portland cement pastes after and before exposure to sodium chloride solution. Although these pastes have similar strength characteristics at the age of 28 days, their strengths are different from each other under the chloride attack. Test results after exposure to sodium chloride solution indicate that the compressive strength of latex modified Portland cement paste is about 2/3 of that of the plain Portland cement paste. The large decrease in the compressive strength of latex modified Portland cement paste may be ascribed to the plasticizing effect of sodium chloride solution absorbed by polymer. There is also some possibility of corrosion of polymer, which has a greater solubility in a chloride solution than in lime-saturated water. Leaching of lime thus appears to be an aggravating adjunct rather than the primary cause of strength reduction in the latex modified Portland cement pastes. From these considerations, it can be concluded that the degradation in latex modified Portland cement pastes will result from the combination of several factors. The same fundamentals would be expected to apply in the case of latex modified Portland cement pastes with superplasticizer. However, the residual compressive strengths are substantially lower for the composites with a high concentration of latex, which is undoubtedly one of the reasons why a lower concentration of latex is needed to achieve a comparable level of strength.

3.4. Sodium sulphate attack

The method which is used for determining the sodium chloride stability of the plain and latex modified Portland cement pastes with and without superplasticizer was applied to evaluate their stability against the effects of sodium sulphate. This method allows determination of the order of stability and of comparative stabilities of the pastes. The data given in Table 4 indicate that the compressive strengths of Portland cement pastes with and without superplasticizer continue to increase slowly for at least 62 days of exposure to a 5% Na_2SO_4 solution. Moreover, these pastes under sulphate attack show slightly higher strengths than their counterparts cured in lime-saturated water for 90 days. This difference may be due to the contribution of products of the chemical reaction (gypsum or ettringite) to the strength. The adverse effect of sulphate on strength is not observed since there is more space to be filled with reaction products. In other words, the crystallization pressure generated by the restricted growth of gypsum or ettringite crystals is not present at this stage [8]. The same trend of increase in strength due to sulphate attack is also observed for the latex modified Portland cement pastes with and without superplasticizer. In fact, it is to be expected that the reaction between the Ca^{++} ions and the carboxylate group of the polymer decreases the Ca^{++} ion concentration and thereby the risk of gypsum or ettringite formation [9–11]. However, the magnitude of this effect is dependent on the concentration of latex in the mixture. In this case, the presence of lower concentration of latex in the paste does not prevent the gypsum or ettringite to occur in the material structure. On the other hand, the latex modified Portland cement pastes with and without superplasticizer usually follow the same trends observed for their counterparts exposed to lime-saturated water for 90 days. The tendency of these pastes to fail under sulphate attack decreases as the latex concentration in the mix decreases. For example, the paste containing 0.148% superplasticizer and 1.30% latex retains appreciable strength during this period of exposure.

3.5. Stress–strain behaviour

It is well known that latex modified mortars and concretes have mechanical properties markedly different from those of plain ones. These type of mortars and concretes show a great improvement in both tensile strength and strain capacity. Due to these characteristic features of latex modified concretes, marked transition from brittle to ductile behaviour is observed. Therefore, there will be differences in the basic stress–strain characteristics of plain and latex modified concretes. The direct selection of a stress–strain relation, which is valid for large strains, does not ensure that the selected relation is compatible with a latex modified concrete. To obtain an idealised stress–strain relation for a latex modified concrete, it is necessary to start from the concept of material properties. Indeed, the selection of proper material properties is of considerable practical importance in the design of diagrams. The shape of the curve is determined primarily by the magnitudes of the parameters such as initial modulus of elasticity (E_o), peak stress (σ_m) and the corresponding strain (ε_o). On the basis of these basic parameters, various stress–strain relations for plain and latex modified concretes can be derived. In the first approximation, a stress–strain relation of the form

$$\sigma = a\varepsilon/(1+b\varepsilon)^n \tag{1}$$

can be assumed as an adequate representation of an observed relation between stress and strain for plain and latex modified concretes.

Where σ and ε denote the stress and strain, respectively. The material constants to be determined are a, b and n. The boundary conditions would help to identify all of these constants necessary to characterize the plain and latex modified Portland cement concretes.

The conditions for determining the constants a and b are:

$$\mathrm{d}\sigma/\mathrm{d}\varepsilon = 0 \quad \text{and} \quad \sigma = \sigma_m \quad \text{at} \quad \varepsilon = \varepsilon_o. \tag{2}$$

From the first of these conditions it follows that

$$b = 1/\varepsilon_o(n-1), \tag{3}$$

and from the second it obtains

$$a = (1+1/(n-1))^n\ \sigma_m/\varepsilon_o. \tag{4}$$

The first condition determines b as a function of the strain corresponding to peak load and the material parameter n. The magnitude of constant a depends on the magnitude of the ratio σ_m/ε_o and also on the number n. The value of n is determined from the condition of

$$\mathrm{d}\sigma/\mathrm{d}\varepsilon = E_o \quad \text{at} \quad \varepsilon = 0. \tag{5}$$

From this condition it finds that

$$E_o = (1+1/(n-1))^n\ \sigma_m/\varepsilon_o. \tag{6}$$

This is the same result obtained for constant a. The term in the parenthesis of this expression approaches the value 2.718 for large values of n. This value of n which makes Eq. (6) a minimum must be used in calculating E_o. On the other hand, the value of the parameter n can be calculated with sufficient accuracy if the initial modulus of elasticity of the material and the ratio σ_m/ε_o are known.

Substituting the expressions for a and b from Eqs. (3) and (4) in Eq. (1), the following equation is obtained:

$$\sigma = [(1+1/(n-1))^n\sigma_m\varepsilon/\varepsilon_o]/[1+\varepsilon/(\varepsilon_o(n-1))]^n. \tag{7}$$

The mechanical behaviour of latex modified Portland cement concretes can be characterised uniquely by this relation between stress and strain. However, this is not the only possible solution. It is possible to express the stress–strain relations in several alternative forms. The reason for this approach is that the observed stress–strain relations do not have a simple analytic form. A more general equation can be established by using a polynomial of second or higher order. Assuming that this type of equation can be used with sufficient accuracy up to the peak stress of the material, the following equation is obtained:

$$\sigma = E_o\varepsilon + (3\sigma_m - 2E_o\varepsilon_o)(\varepsilon/\varepsilon_o)^2 + (E_o\varepsilon_o - 2\sigma_m)(\varepsilon/\varepsilon_o)^3. \tag{8}$$

This equation appears to be particularly useful because of the direct physical interpretation of the parameter, E_o. Provided the assumed value of E_o is reasonably close to the exact value, a very satisfactory approximation to the true stress–strain curve both in form and in relative position can be obtained. Beyond the peak stress, the observed diagrams are of too complicated a form to be directly used in the formulation of these equations. Indeed, Eq. (7) previously derived may give exaggerated values for stresses beyond the peak stress. In order to get more satisfactory results about the post-peak behaviour of the material, Eq. (8) can be recommended. However, a better agreement can be obtained by using a more complicated model with a large number of adjustable parameters. The simplest form of this equation, which describes not only the ascending but also the descending part of the diagram, is:

$$\sigma = (a+b\varepsilon)/(1+c\varepsilon+d\varepsilon^2)^n. \tag{9}$$

The method used above for determining the constants a, b, c and d can be applied to Eq. (9). From the conditions Eqs. (2) and (5) together with the condition that σ=0 for ε=0, the following relations between the constants in Eq. (9) are found:

$$a = 0 \tag{9a}$$

Table 5
The comparison of Eq. (7) with experimental data

ε (%)	Latex–cement ratio (%)									
	0		1		2		2.5		3	
	*σ_e (MPa)	*σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)
0.0025	1.1	1.03								
0.0075	3.0	3.01								
0.0100	4.0	3.96								
0.0125	5.0	4.89								
0.0175	6.9	6.67								
0.0250	9.5	9.18								
0.0500	16.5	16.20	11	11.59	8.5	9.81	8	8.21	6	6.79
0.075	21.5	21.45								
0.1	25.5	25.24	20	19.62	17	17.01	14.5	14.24	12	11.78
0.15	29.0	29.48	25	24.92	22	22.12	18.5	18.51	15	15.32
0.2	30.5	30.62	28	28.12	25.5	25.57	21	21.39	17.5	17.71
0.25			29.5	29.75	28	27.71	23.5	23.19	19.4	19.18
0.30			30.5	30.22	29	28.82	24	24.12	20.1	19.96
0.35					29.3	29.15	24.5	24.39	20.4	20.18

*σ_e and σ_t represent the experimental and theoretical stresses, respectively.

$$b = E_o \tag{9b}$$

$$c = \left(1/\varepsilon_o\right)\left[\left(E_o\varepsilon_o/\sigma_m\right)^{(1/n)}(2 - 1/n) - 2\right] \tag{9c}$$

$$d = \left(1/\varepsilon_o^2\right)\left[1 + \left(E_o\varepsilon_o/\sigma_m\right)^{(1/n)}((1/n) - 1)\right]. \tag{9d}$$

In this analysis, the problem of calculating the value of parameter n frequently arises. This parameter is determined primarily by the non-linear least square analysis.

For the conditions of n=1 and a=0, Eq. (9) takes the form

$$\sigma = b\varepsilon/\left(1 + c\varepsilon + d\varepsilon^2\right). \tag{10}$$

In this form, the four boundary conditions are too many and the three conditions are sufficient for the complete determination of the stress–strain relation. The constants b, c and d are represented in the following forms:

$$b = E_o \tag{10a}$$

$$c = (1/\varepsilon_o)[(E_o\varepsilon_o/\sigma_m) - 2] \tag{10b}$$

$$d = 1/\varepsilon_o^2 \tag{10c}$$

Each of these equations is a mathematical formulation designed to approximately describe the observed stress–strain responses of plain and latex modified concretes over a certain restricted range of the variables involved. Experimental verification of these equations is made on the basis of data reported by Nagaraj et al. for natural rubber latex modified concretes with superplasticizer. In

Table 6
The comparison of Eq. (8) with experimental data

ε (%)	Latex–cement ratio (%)									
	0		1		2		2.5		3	
	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)
0.0025	1.1	1.02								
0.0075	3.0	2.99								
0.0100	4.0	3.95								
0.0125	5.0	4.88								
0.0175	6.9	6.67								
0.0250	9.5	9.21								
0.05	16.5	16.37	11	11.29	8.5	9.37	8	8.02	6	6.45
0.075	21.5	21.74								
0.1	25.5	25.57	20	19.48	17	16.57	14.5	14.11	12	11.44
0.15	29.0	29.60	25	25.01	22	21.87	18.5	18.53	15	15.13
0.2	30.5	30.5	28	28.38	25.5	25.52	21	21.52	17.5	17.69
0.25			29.5	30.05	28	27.79	23.5	23.34	19.4	19.31
0.30			30.5	30.5	29	28.96	24	24.25	20.1	20.16
0.35					29.3	29.3	24.5	24.5	20.4	20.4

Table 7
The comparison of Eq. (9) with experimental data

ε (%)	Latex–cement ratio (%)									
	0		1		2		2.5		3	
	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)
0.0025	1.1	1.06								
0.0075	3.0	3.09								
0.0100	4.0	4.06								
0.0125	5.0	5.01								
0.0175	6.9	6.84								
0.0250	9.5	9.38								
0.05	16.5	16.45	11	11.44	8.5	9.41	8	8.16	6	6.49
0.075	21.5	21.65								
0.1	25.5	25.36	20	19.52	17	16.55	14.5	14.19	12	11.45
0.15	29.0	29.43	25	24.94	22	21.78	18.5	18.51	15	15.10
0.2	30.5	30.5	28	28.28	25.5	25.40	21	21.43	17.5	17.65
0.25			29.5	29.99	28	27.70	23.5	23.26	19.4	19.27
0.30			30.5	30.5	29	28.93	24	24.22	20.1	20.14
0.35					29.3	29.3	24.5	24.5	20.4	20.4

Tables 5–8, the experimental data for the plain and natural rubber latex modified concretes are compared with those obtained using proposed equations. The fit of Eq. (7) with the experimental data is shown in Table 5 and it is seen that, within the range of applicability, this equation is a remarkably good representation of the experimental situation. Eq. (6) demonstrates the great importance of parameter n in determining the initial modulus of elasticity. The modulus that is usually measured in the proportional limit is often considerably lower than that predicted theoretically by using in this analytic expression a small value of n. The difference in the magnitude of E_o becomes unnoticeable only for a very large value of n (say $n \geq 1{,}000{,}000$). Thus, from this value of n, it is possible to calculate the initial modulus of elasticity of both plain and latex modified concretes. This result strongly suggests that the parameter n is not related to the type of concrete. Eq. (6) provides a value of E_o=41.4 GPa for plain concrete. In the case of latex modified concrete, the value of E_o decreases from a value of 27.6 to a value of 15.8 GPa as the latex to cement ratio increases from a value of 1% to a value of 3%. These results confirm the expected variation of E_o with latex content. Therefore, this general method for the estimation of E_o from σ_m and ε_o is very convenient and is capable of giving accurate estimates of E_o for plain and latex modified concretes. From Table 9, it may be seen that, in agreement with this model, there is a linear relationship between E_o and the latex to cement ratio for latex modified concretes. If this dependence takes a somewhat different less linear form than might have been anticipated, this may be ascribable to the degree of crystallinity of the polymer. Such an effect may partially explain increases or decreases in E_o with an increasing content of latex.

Table 8
The comparison of Eq. (10) with experimental data

ε (%)	Latex–cement ratio (%)									
	0		1		2		2.5		3	
	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)	σ_e (MPa)	σ_t (MPa)
0.0025	1.1	1.01								
0.0075	3.0	2.97								
0.0100	4.0	3.91								
0.0125	5.0	4.85								
0.0175	6.9	6.66								
0.0250	9.5	9.24								
0.05	16.5	16.52	11	11.12	8.5	9.04	8	7.91	6	6.24
0.075	21.5	21.92								
0.1	25.5	25.67	20	19.58	17	16.47	14.5	14.17	12	11.41
0.15	29.0	29.57	25	25.22	22	21.99	18.5	18.69	15	15.27
0.2	30.5	30.5	28	28.51	25.5	25.69	21	21.66	17.5	17.87
0.25			29.5	30.08	28	27.91	23.5	23.41	19.4	19.42
0.30			30.5	30.5	29	28.99	24	24.26	20.1	20.19
0.35					29.3	29.3	24.5	24.5	20.4	20.4

Table 9
Typical values of E_o, σ_m, ε_o and material constant n for plain and natural rubber latex modified concretes with superplasticizer

Type of equation	Latex–cement ratio (%)	E_o (GPa)	σ_m (MPa)	ε_o (%)	n	Correlation coefficient (r)
Eq. (6)	0	41.4	30.5	0.2	1,000,000	0.999
	1	27.6	30.5	0.3	1,000,000	0.999
	2	22.7	29.3	0.35	1,000,000	0.998
	2.5	19.0	24.5	0.35	1,000,000	0.999
	3	15.8	20.4	0.35	1,000,000	0.998
Eq. (8)	0	41.2	30.5	0.2		0.999
	1	26.0	30.5	0.3		0.999
	2	21.0	29.3	0.35		0.999
	2.5	18.1	24.5	0.35		0.999
	3	14.4	20.4	0.35		0.999
Eq. (9)	0	42.8	30.5	0.2	−3,598,242.5	0.999
	1	26.7	30.5	0.3	−3,946,249.2	0.999
	2	21.3	29.3	0.35	−1,759,294.6	0.999
	2.5	18.7	24.5	0.35	−1,624,960.5	0.999
	3	14.6	20.4	0.35	−958,962.1	0.999
Eq. (10)	0	40.5	30.5	0.2		0.999
	1	24.2	30.5	0.3		0.999
	2	19.1	29.3	0.35		0.999
	2.5	17.1	24.5	0.35		0.999
	3	13.2	20.4	0.35		0.999

A comparison of Eq. (8) with experimental data is given in Table 6. From the correlation coefficients given in Table 9, it can be concluded that there is a reasonably good fit between Eq. (8) and the data of Nagaraj et al. For this reason, Eq. (8) evidently can be applied in calculating E_o in the case of plain and latex modified concretes. However, for the actual solution of this problem, polynomial equations of higher order than Eq. (8) are useless since the physically acceptable specifications of boundary conditions in terms up to the first derivatives are enough to produce a third order polynomial equation. The results obtained from this analysis indicate that the values of E_o are consistent with those predicted by Eq. (6). Therefore, this equation can be used both as a check on the value of E_o obtained from Eq. (6) and as a relation for obtaining additional information required in defining the entire stress–strain curve. The elastic constants, determined by using these equations, emphasize the difference between the plain and latex modified concretes. However, Eq. (9) is often more suitable for describing this difference. The non-linearity of this equation produces a dependence of the stress not only on the initial modulus of elasticity but also on the parameter n. This relation is essentially a more general form of Eq. (1). However, in this case, the proper value of n cannot be determined in a manner similar to that used for Eq. (1). Moreover, the detailed dependencies of c and d constants on the parameters E_o, σ_m and ε_o are more complex than for the other equations owing to the form of this expression. Despite of these facts, Eq. (9) provides the simplest idealization for the representation of stress–strain behaviour of plain and latex modified concretes. The theoretical data obtained using this equation for plain and latex modified concretes are given in Table 7 for several values of parameter n from −3,598,242 to −958,962. Note that for these values of n, the theoretical data coincide with the experimental data. Eq. (10), which is a special case of Eq. (9), can predict the stress–strain curves of plain and latex modified concretes depending primarily on the magnitudes of E_o, σ_m and ε_o. Again, looking at the experimental data in Table 8, it can be seen that such an equation would be a very good approximation to most of the data points. The important thing to consider is that by these relatively simple equations, the mechanical behaviour of plain and latex modified concretes is predicted from a strain level of 0 to ε_o. On the other hand, there is a problem in determining the proper value of E_o . It is seen from Table 9 that the values of E_o calculated on the basis of Eqs. (6) and (8) are very close to those of Eq. (9). Whereas, Eq. (10) leads to a different value for E_o in each case. However, these calculations show that the difference between these approximations is small and that the difference in the magnitude of E_o becomes more pronounced only for plain concretes.

4. Conclusions

1. The workability of the latex modified Portland cement paste decreases with increasing latex concentration. But this depends on the w/c ratio of the mixture and can be greatly reduced by using a suitable superplasticizer. In this case, the w/c ratios range from 0.33 to 0.28. These results show progressive decrease in the water content required for obtaining sufficient workability.

2. The Portland cement pastes with and without superplasticizer show a high rate of increase in compressive strength up to 7 days. Their strengths continue to increase with the progress of hydration of cement. However, the

addition of latex to the Portland cement paste results in a decrease in compressive strength of almost all pastes, except perhaps the pastes with a low concentration of latex. Great differences exist not only in the strength values for these pastes but also in the rate of increase in strength as the latex concentration increases. The use of superplasticizer in the latex modified Portland cement pastes tends to mask the debilitating effects of a high latex concentration on the strength and the gain of strength with time. Nevertheless, curing in lime-saturated water begins to adversely affect the strengths of latex modified Portland cement pastes with and without superplasticizer from about 28 days onwards. This behaviour is exactly the reverse of that normally shown by the Portland cement pastes with and without superplasticizer. It is likely that the increased solubility of the polymer leads to a poorer, probably more porous physical structure and consequent impairment of the strength.

3. The resistance of plain and latex modified Portland cement pastes with and without superplasticizer to attack by salt solutions such as sodium chloride and sodium sulphate varies widely not only from paste to paste but in some cases within the different grades of a single paste. These salts may affect the degradation of Portland cement pastes with and without superplasticizer in several ways depending on the pH of the aqueous solution and the solubility of the corrosion products formed during their reactions with hardened pastes. The compressive strengths of these pastes are relatively little affected by 62 days of immersion in Na_2SO_4 solution as compared to those of paste cured in lime-saturated water for 90 days. However, 62 days of immersion in NaCl solution causes a decrease in the strength of these pastes. The reduction in strength due to NaCl becomes more pronounced in the latex modified Portland cement pastes with and without superplasticizer. This results from the plasticizing action of the absorbed salt solution by latex or from the partial removal of the added latex by leaching action. The magnitude of this effect is dependent on the latex concentration in the mixture. Higher concentration of latex generally increases the rate and magnitude of corrosive attack. The effect becomes insignificant as the latex concentration decreases. These results strongly suggest that the presence of latex in paste composition has a profound effect on the chemical stability of the material.

4. The stress–strain behaviour of plain and latex modified Portland cement concretes up to peak stress can be represented to a good approximation using the mathematical models proposed in this study. The general agreement between the calculated and experimental data confirms the assumption on which the calculations are based. Moreover, these relations obtained from such assumptions provide the basic material properties necessary in the design of any structural member.

References

[1] Y. Ohama, Principle of latex modification and some typical properties of latex-modified mortars and concretes, ACI Mater. J. 84 (1987) 511–518.

[2] J.A. Lavelle, Acrylic latex-modified portland cement, ACI Mater. J. 85 (1988) 41–48.

[3] J.J. Beaudoin, V.S. Ramachandran, Effect of water dispersible polymers on the properties of superplasticized cement paste, mortar and concrete, in: V.M. Malhotra (Ed.), Proceedings of Third International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI Spec. Publ., SP-119, Ottawa, Canada, 1989, pp. 221–242.

[4] Y. Ohama, K. Demura, Y. Satoh, K. Tachibana, Y. Miyazaki, Development of admixtures for highly durable concrete, in: V.M. Malhotra (Ed.), Proceedings of Third International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI Spec. Publ., SP-119, Ottawa, Canada, 1989, pp. 321–341.

[5] T.S. Nagaraj, K.T. Sundara Raja Iyengar, B. Kameswara Rao, Superplasticized natural rubber latex modified concretes, Cem. Concr. Res. 18 (1988) 138–144.

[6] A.M. Neville, Properties of Concrete, fourth and final ed., John Wiley & Sons, New York, USA, 1997.

[7] S. Chandra, Y. Ohama, Polymers in Concrete, CRC Press, Boca Raton, FL, USA, 1994.

[8] M.A. González, E.F. Irassar, Ettringite formation in low C_3A Portland cement exposed to sodium sulfate solution, Cem. Concr. Res. 27 (7) (1997) 1061–1072.

[9] J.A. Larbi, J.M.J.M. Bijen, Interaction of polymers with Portland cement during hydration: a study of the chemistry of the pore solution of polymer-modified cement systems, Cem. Concr. Res. 20 (1990) 139–147.

[10] S. Chandra, P. Flodin, Interactions of polymers and organic admixtures on Portland cement hydration, Cem. Concr. Res. 17 (1987) 875–890.

[11] S. Chandra, L. Berntsson, P. Flodin, Behaviour of calcium hydroxide with styrene-methacrylate polymer dispersion, Cem. Concr. Res. 11 (1) (1981) 125–129.