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Time-dependent mechanical properties of high-strength cements

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A high-strength cement paste based on aluminous cement with the addition of water-soluble polymer was found to have a flexural strength which increased at about 12 MPa per decade increase in strain rate over the range 10^{-6} to $10^{-2}\,\text{sec}^{-1}$. The effect of soaking in water was to markedly reduce the strength. Swelling occurred on soaking in water for both Portland and aluminous cement-based pastes but was more gradual for the latter. Wetting swelling and drying shrinkage increased with polymer content for Portland-based pastes. Creep and stress relaxation in one type of Portland cement-based paste and in aluminous cement-based paste were markedly increased by soaking, but in a second type of Portland-based paste there was little effect. These effects are attributed to the polymer content of the pastes and its distribution in the pastes.

1. Introduction

Recently it has been shown that great improvements can be achieved in the flexural strength of cement pastes by preparing them by suitable processing methods from a mixture having a low water/cement ratio with the addition of a water-soluble polymer [1–3]. It has been proposed that the increase in strength is mainly due to the removal of large pores or macro-defects in the paste [1, 2], leading to the term "macro-defect free" (high strength). This view has been the subject of dispute [4, 5].

The polymer added forms part of the microstructure of these materials, although it is believed to be cross-linked to some extent by ions from the cement [6, 7], therefore it is of interest to investigate properties in which the properties of the polymer might play a role. Time-dependent mechanical properties are an example of these and in this paper a study of creep, stress relaxation and the strain rate dependence of strength in wet and dry materials of this type is reported.

2. Experimental details

2.1. Materials

Tests were performed on samples of NIM127, kindly supplied as sheets by ICI New Science Group, Runcorn, UK, and on materials made up in our laboratory. NIM127 is a high-strength cement based on aluminous cement and polyvinyl alcohol/acetate. Cements in our laboratory were made from ordinary Portland cement with the addition of polyacrylamide or Celacol (a hydroxypropyl methyl cellulose, Aldrich Chemical Co., USA) and from an aluminous cement (Secar 71) with the addition of Gohsenol (a polyvinyl alcohol/acetate, Nippon Gohsei, Japan). The materials with the addition of water were mixed by shearing between the rolls of a twin-roll mill. In the case of the aluminous cement the polymer was mixed as a powder with the cement before adding water and mixing by hand into a crumb which was fed into the rollers. In the case of Portland cement the polymer was mixed with water to form a gel first which was placed on the rollers, and the cement powder was then added. After working in the rolls to produce a homogeneous plastic mass the cement was rolled out into sheets about 3 mm thick. The sheets were then pressed at 3 to 4 MPa for 24 h. Portland cement-based pastes were then hardened in a humid environment at room temperature (in a closed space over a water bath) while the aluminous cement-based pastes were cured at 80° C for 6 h. The composition for the aluminous cement paste in parts by weight was 7 parts polymer, 100 parts Secar 71, 12 parts water, and for the Portland-based pastes, 3 to 8 parts polymer, 100 parts cement, 15 parts water. For comparative purposes some conventional cement pastes were cast by hand into moulds and placed on a vibrating table to remove air bubbles as far as possible. At low water/cement ratio (0.2), 1% of a superplasticizer Galoryl PA340 (supplier: Orange Chemicals. Winchester, UK) was added to aid casting.

2.2. Tests

Test specimens of about 70 mm × 10 mm × the sheet thickness (typically 3 mm) were sawn out of sheets. Strength and stress relaxation tests were carried out in three-point bending on an Instron machine. Creep tests were also carried out in three-point bending on a jig which could be totally immersed in a water-bath if required. The distances between the outer loading points of the bending jigs were 40 and 60 mm, respectively. Creep deflection of the central loading point to which weights were attached was measured with a linear voltage differential transformer and continuously recorded. Measurements of changes in length of bars on wetting or

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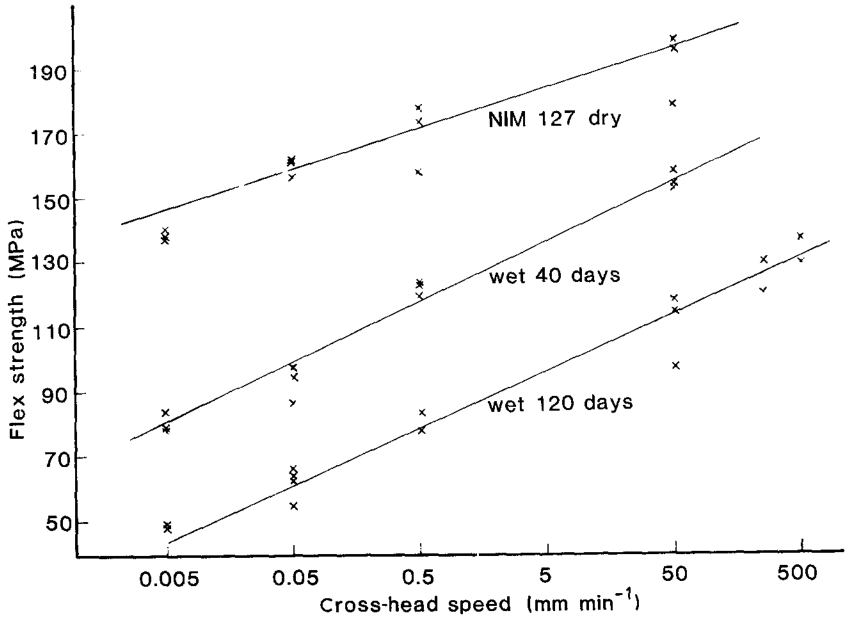

Figure 1 Dependence of strength in three-point bending of an aluminous high strength cement (NIM 127) on the cross-head speed of the Instron machine. Specimens were in as-received dry condition or soaked in water for 40 days and 120 days.

drying after hardening were made with vernier callipers.

3. Results and discussion

3.1. Strain rate dependence of the flexural strength

The relatively good reproducibility of the strength of specimens of the ICI NIM127 material made it the preferred material for the study of the effect of strain rate on strength. The results are shown in Fig. 1. The weakening of the material in water is a gradual process, as indicated by the further weakening on increasing the time of immersion from 40 days to 120 days. The wet material is overall only slightly more strain-rate sensitive than the dry material which shows a loss in strength of about 12 MPa per decade reduction in applied strain rate. A cross-head speed of 5 mm min^{-1} corresponds to an outer fibre maximum strain rate of approximately 10^{-3} sec^{-1}. The load–deflection curves showed departure from linearity, particularly evident at slow strain rates, so that the stressing rate at fracture cannot be accurately assessed.

Plain conventional concrete also shows an increase in strength as the strain rate is increased [8], and the strain rate dependence of the strength of NIM127 high-strength cement appears comparable to that of plain concrete when expressed in relative terms, i.e. an increase in strength of some 26% with maximum strain rate increasing over the range 10^{-6} to 10^{-2} sec^{-1} shown in Fig. 1 for dry NIM127 is comparable with the percentage increase in flexural strength of plain concrete over a similar range [8]. However, since high-strength cement is an order of magnitude stronger than conventional cement or concrete the strain rate dependence of its strength expressed as MPa per decade is of course much larger than that of plain concrete. Polymers generally also shown an increase in brittle strength with increasing strain rate [9]. This may be due to the growth of a flaw by viscous processes until it is of sufficient size to propagate catastrophically, slower strain rates then allowing growth to a larger size and fracture at a lower stress during the time of the test. In the case of aluminous high-strength cements, the microstructure is known to contain a polymeric matrix and very little normal hydration

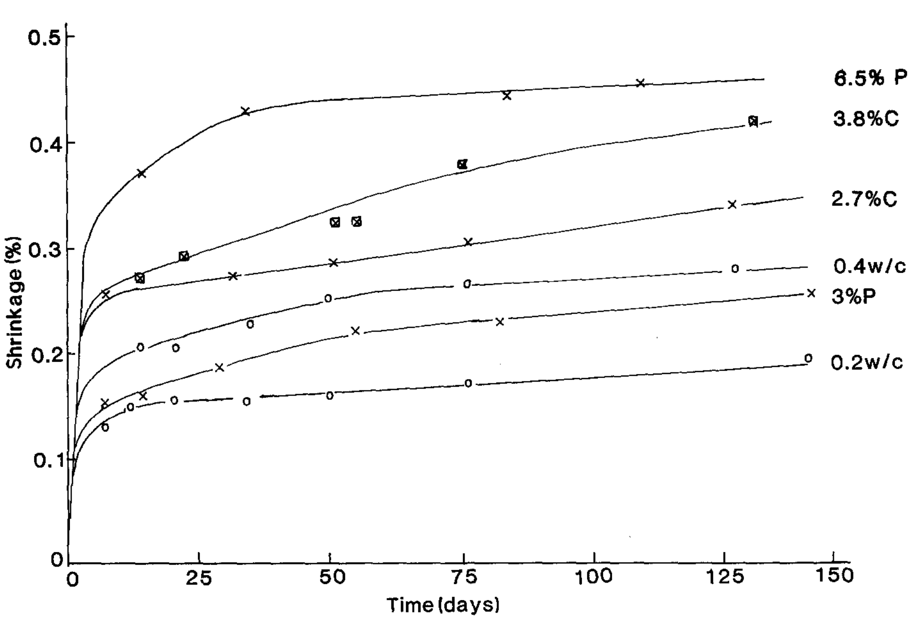

Figure 2 Drying shrinkage of various Portland-based cements after curing at high humidity. P = polyacrylamide, C = Celacol, w/c = water/cement.

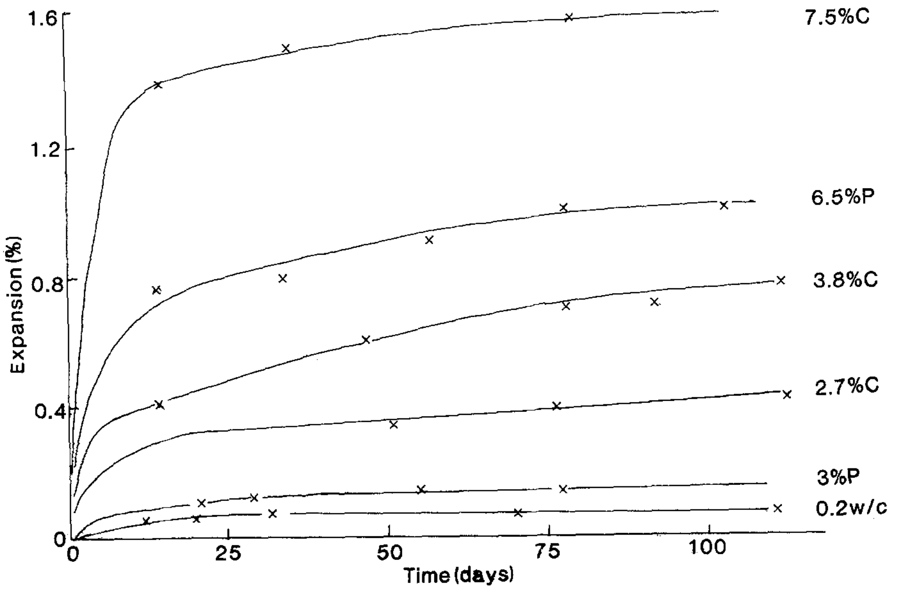

Figure 3 Expansion on wetting of various Portland-based cements. P = polyacrylamide, C = Celacol, w/c = water/cement.

product [6]. It is thus reasonable to attribute the strain rate dependence of strength to the polymeric matrix. The effect of water is then mainly to soften the matrix and allow flaw growth at lower stress, although it must also be expected in addition to produce some further hydration of the calcium aluminate to which it has access.

3.2. Swelling and shrinkage

The phenomena of creep and stress relaxation in cements and concretes are generally greatly complicated by dimensional changes accompanying changes in water content of the cement paste. Thus concrete which is drying and thus shrinking and at the same time undergoing compressive creep will undergo a dimensional change composed of drying shrinkage, together with a basic creep and an additional creep which is an interaction effect [10]. Since it is well known that polymer gels swell when taking up solvent and shrink when drying [11], it was of importance to make some measurements of swelling and shrinkage on wetting and drying high-strength cements.

The shrinkage of high-strength and conventional Portland cement pastes on drying in laboratory air after curing at high humidity for a month is shown in Fig. 2, and expansion of dried specimens on soaking is shown in Fig. 3. In general the high-strength cements show greater dimensional changes than conventional paste of 0.2 water : cement ratio, increasing with increasing polymer content.

Aluminous high-strength cements are normally produced in a dry condition so their expansion on soaking in water was measured (Fig. 4). The NIM127 expands at a much lower rate than the material produced in our laboratory, possibly due to a different heat treatment schedule during preparation. Nevertheless, both high-strength pastes show expansions in excess of that of a conventional paste of low water : cement ratio over a sufficiently long period of time.

Clearly the polymer present in the high-strength pastes we have investigated does lead to shrinkage or swelling of the paste on drying or wetting, respectively. The Portland high-strength pastes reach steady or nearly steady dimensions more rapidly than the aluminous cement high-strength pastes, presumably because of more rapid water penetration into a microstructure which is known to be more porous [2, 6].

3.3. Stress relaxation

Bending deformation has some advantage in limiting

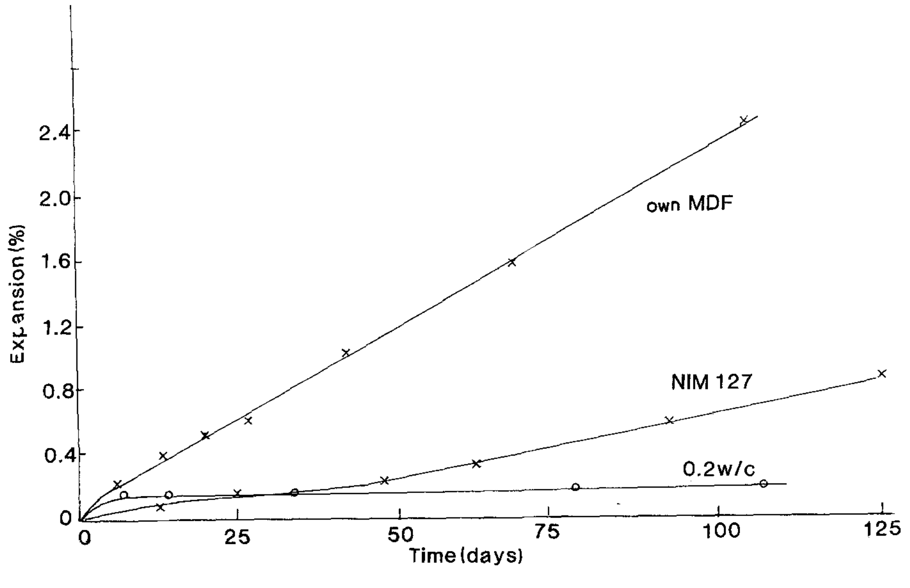

Figure 4 Expansion on wetting of aluminous cement-based pastes.

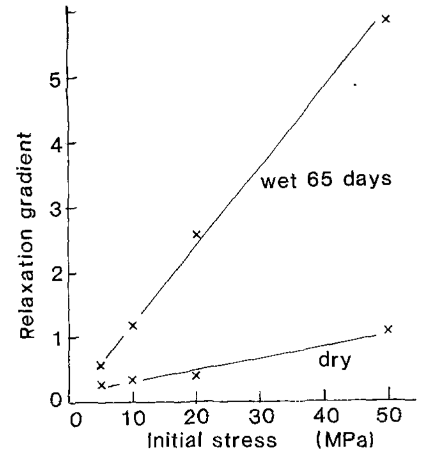

Figure 5 Stress relaxation gradient on a log (time) plot for wet and dry samples of NIM 127 aluminous cement-based high strength paste.

the effect of drying shrinkage in that uniform shrinkage does not contribute directly to bending, but it was considered in addition important to try to maintain the water content of the cement paste during stress relaxation. To this end, specimens were wrapped in cling-film.

For all specimens, linear plots could be obtained for the relaxing load against log (time) over a wide range of times (except for very short times). This result applies to a wide variety of materials, including metals and plastics [12, 13]. The gradient of the load–log (time) plot gave an indication of the rate of stress relaxation. An increase in initial stress level caused some increse in the magnitude of the gradient, so that comparisons between different specimens should be made for the same initial stress level. The effect of initial stress level and a comparison of wet and dry cement paste is shown for NIM127 in Fig. 5. The results for the aluminous high-strength paste made in our laboratory are broadly similar. Conventional cement pastes could not be tested at the higher stress levels because of their relative weakness. The effect of water/cement ratio and moisture content is shown in Fig. 6 for normal Portland cement pastes.

The pattern for Portland high-strength cements was less consistent. For dry pastes, increasing polymer content produced a slight increase in relaxation gradient for polyacrylamide pastes but a decrease for Celacol pastes, the values being generally somewhat higher than those for conventional pastes. The effect of water was markedly different for polyacrylamide pastes and Celacol pastes, as shown in Fig. 7. Much higher relaxation gradients were reached in wet Celacol pastes than in wet polyacrylamide pastes, particularly at the highest polymer contents. This is consistent with the creep results, discussed below.

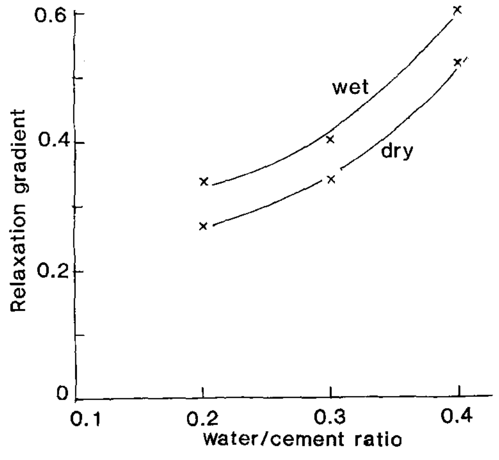

Figure 6 Stress relaxation gradients for wet and dry conventional Portland cement pastes of various water : cement ratios (initial stress = 10 MPa). Wet specimens soaked in water for periods for 6 days or more.

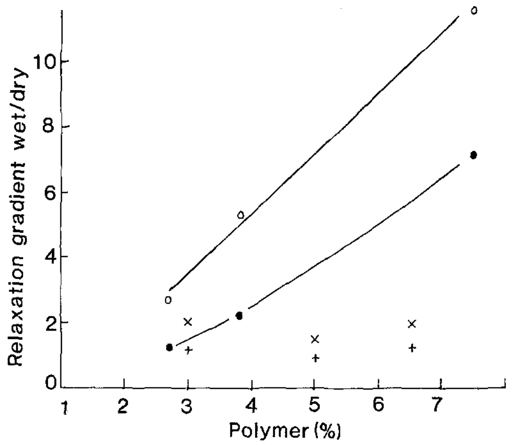

Figure 7 Ratio of stress relaxation gradients for wet and dry Portland cement-based high strength pastes. Wet specimens soaked in water for periods of 6 days or more. (+) Polyacrylamide, 10 MPa; (×) polyacrylamide, 20 MPa; (●) Celacol, 10 MPa; (○) Celacol, 20 MPa.

3.4. Creep

Creep of wet specimens was carried out under water while creep of nominally dry specimens was carried out in laboratory air. The creep deflection was normalized against the elastic deflection of the specimen at the load used. In all cases creep strains were of no more than of the order of the elastic strain and were therefore small. The creep deflection did not follow a consistent time law for all specimens, although in the majority of cases a power law for the creep deflection e at the time t was followed:

$$e = at^n$$

where a is a constant and the exponent n lay in the range 0.38 to 0.63, with the higher values of n occurring for wet cement pastes. Some specimens gave a better fit to a log t dependence and for others, particularly dry specimens, creep could not be fitted well by either law. In nominally dry specimens complications could have arisen due to a change in moisture content during the test.

Fig. 8 shows creep curves for NIM 127 pastes. Soaking for 30 days in water produced a similar creep curve but at a lower stress than for dry paste. As the soaking is continued the normalized creep rate becomes greater for the wet specimen, even at a stress which is a much lower fraction of the short-time strength. In this sense, the creep rate is affected relatively more than the short-time strength by prolonged soaking. Laboratory-made aluminous high-strength pastes showed a similar increase in creep rates when soaked for long periods.

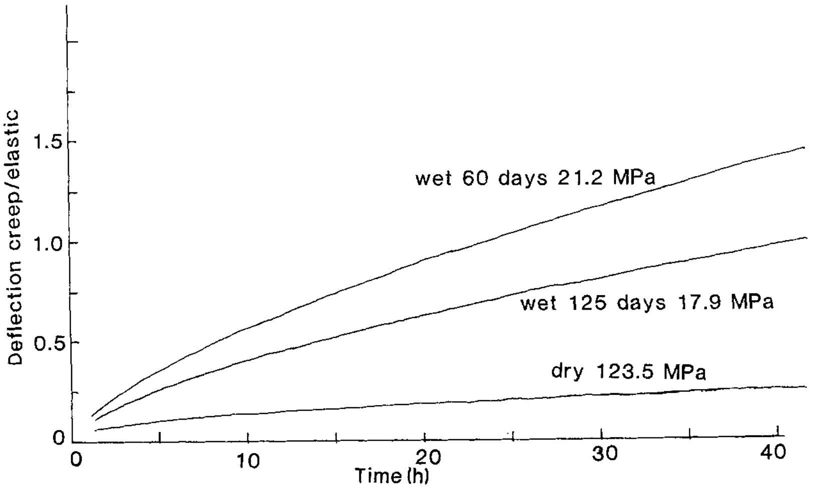

Figure 8 Creep curves for samples of NIM 127 aluminous cement-based high strength paste.

In the case of Portland high-strength pastes, 3% polyacrylamide paste and 3.8% Celacol paste both showed little creep when dry, but on soaking, the Celacol paste showed a markedly increased creep rate after 19 days and even more rapid creep after 113 days, as shown in Fig. 9, whereas the polyacrylamide paste showed little effect of soaking on creep rate even after 112 days. This distinction between polyacrylamide- and Celacol–Portland pastes is consistent with the stress relaxation results (Fig. 7).

The microstructures of aluminous high strength cement and of polyacrylamide–Portland paste has been investigated [6]. In the case of aluminous cement a continuous matrix of polymeric material appears to exist and as this softens with ingress of water, enhanced creep and stress relaxation may be expected. The microstructure of polyacrylamide–Portland paste is more complex and contains relatively more normal hydration product–hydrate gel and calcium hydroxide, often in microcrystalline form. It is possible that a continuous polymeric matrix did not exist in this case, which would account for the relatively lesser effects of soaking in water. The strength of polyacrylamide–Portland paste is however degraded by soaking, a loss in short-term strength of roughly 30% being found. It is possible that softened regions, while not being continuous, are large enough to allow the development of flaws at a lower stress when wet. The Celacol–Portland paste, whose microstructure has not been examined in detail, may have a more continuous polymeric matrix than the polyacrylamide–Portland pastes.

4. Summary and conclusions

1. An aluminous high-strength paste (NIM 127) showed a strain-rate dependence of strength which was substantial, although similar in a relative sense to that of plain concrete.

2. Prolonged soaking in water reduced the strength of the aluminous high-strength paste substantially but increased the strain rate sensitivity only slightly.

3. High-strength pastes showed greater expansions or contractions on wetting or drying, respectively, than conventional cements of low water : cement ratio, the dimensional changes increasing with the proportion of polymer.

4. Creep and stress relaxation were not excessive in dry high-strength pastes but increased very substantially on soaking in the case of aluminous pastes and Celacol–Portland paste. Polyacrylamide–Portland pastes were less affected by soaking.

5. The above results can be explained in a general and qualitative way by the presence of water-soluble polymer in high-strength cement pastes. The polymer is able to take up water and in doing so, swells and softens. Conversely the polymer can lose water, shrink and harden on drying. The softening of the polymer on wetting gives a very marked increase in creep and stress relaxation when there is sufficient polymer, and it is sufficiently well distributed to form a continuous matrix in the cement paste. The strength is reduced on prolonged wetting because of the easier growth of flaws by deformation of the softened polymer. The time factor involved is the time taken for the water to diffuse into the body of the paste; this process can be

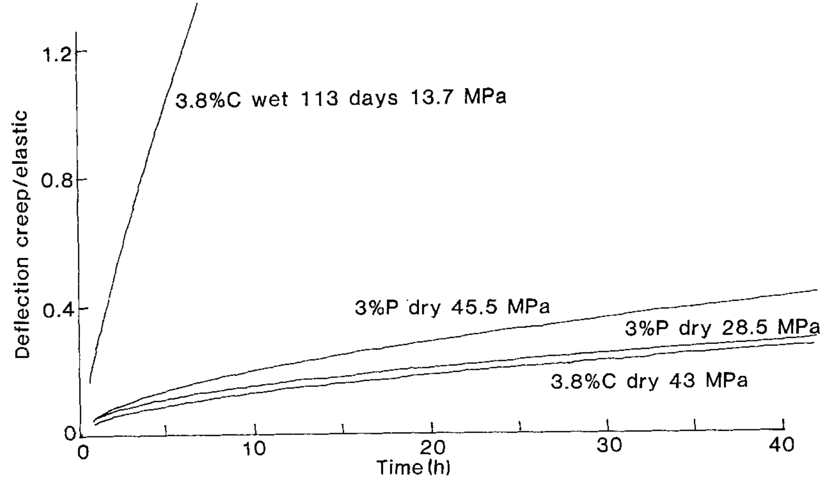

Figure 9 Creep curves for some samples of Portland cement-based high strength pastes. P = polyacrylamide, C = Celacol.

slow especially for aluminous pastes which can have very low porosity [2, 6].

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