

Improved superplasticisers for high performance concrete: the SUPERPLAST project

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1. Introduction

The performance requirements of concrete are continuously increasing and this leads to the continuous development of new improved chemical admixtures used in concrete. Superplasticisers are used for three main reasons, i) to produce highly workable concrete for easy placement, ii) to produce concrete with a low water content for higher strength and durability and iii) to produce concrete with low cementitious and water contents for better economy. SUPERPLAST was an international consortium project funded by EU Framework Programme 5 over three years, to develop high performance superplasticisers for cement-based materials. It involved 8 partners (Sika, Borregaard, Blue Circle who were replaced by Castle Cement in year 3, YKI Institute Stockholm, Ecole Supérieure de Physique et Chimie Industrielle Paris, Ecole Polytechnique Fédérale de Lausanne, Heriot-Watt University) and was completed in February 2004. The project aimed to give a fundamental understanding of the way that superplasticisers function from which new products could be developed. This paper develops a previous one [1] and describes some of the more important results.

2. Programme and procedure

Three cements – Cauldon (as reference), Hope (high C_3A) and Dunbar (low total alkali) – were used alone and in binary blends with 30% and 40% fly ash and in ternary blends with 30% fly ash and 5% silica fume - in studies of the physical and chemical behaviour of pastes, mortars and concretes. Additionally, magnesium oxide was used as a model powder in pastes. All the powders were thoroughly characterised. Four experimental polycarboxylate admixtures (PCP 1-4) and four experimental lignosulfonate admixtures (LS 1-4) were extensively characterised both in solution - using chemical analysis and molecular weight to show crosslinking, branching, side chains and backbone details - and under adsorption conditions on magnesium oxide and on the 12 cements (both plain and blended), using a variety of chemical analysis, surface characterisation, adsorption, rheology, stiffening and setting measurements. This understanding of structure - function relationships led to a conceptual model of the interaction between superplasticisers and cements.

This work was used by Sika and Borregaard to synthesise and tailor two further PCPs (PCP5-6) and one further LS (LS5), which were characterised in the same way as before. These optimised admixtures were tested in an extensive programme of concrete testing: Sika tested PCPs in concrete mixes relevant for Switzerland, Borregaard tested LSs in concrete mixes relevant for Norway, and Heriot-Watt University and Castle Cement tested both types and used exactly the same materials and mixes. A vast amount of data (including over 900 concrete mixes) was generated in the project and multivariate analysis was used to help identify the main trends.

3. Results

3.1 Adsorption and rheology

The Flatt-Bowen yield stress model [2] is a major step towards understanding superplasticiser performance. It links interparticle forces, particle concentration, maximum packing, percolation threshold, particle size and size distribution, and successfully accounts for most of the effects, making the link between the nanoscale of polymer interactions at surfaces and the macroscale of measured yield stress. An important result for SUPERPLAST is that increasing the surface layer thickness of superplasticiser on magnesium oxide from 1 nm to 3 nm substantially reduces the interparticle attractive force, leading to a reduction in yield stress.

Adsorbed layer thickness was measured on magnesium oxide using the AFM colloidal probe technique [3]. The measured layer thicknesses of the polymers PCP1-6 are presented in table 1 together with hydrodynamic radii (R_h) measured in solution by dynamic light scattering (DLS). The layer thicknesses measured are in the range 1-5 nm. There is no clear connection between the layer thickness and the adsorbed amount on MgO. However, there seems to be a trend that a longer PEG chain length gives a thicker adsorbed layer. Also a higher molecular weight (Mw) seem to give a thicker polymer layer, and this was anticipated, since there is a larger probability for

the polymer backbone to adsorb with loops when the polymer backbone is longer. Table 2 shows the same data for the LSs.

Table 1: Layer thickness from AFM colloidal probe measurements, R_h from dynamic light scattering (DLS), adsorbed amount on MgO, grafted PEG chain length and polymer Mw (at $8 < \text{pH} < 12.8$ and $0.03 < \text{ionic strength} < 0.4\text{M}$).

Result	PCP1	PCP2	PCP3	PCP4	PCP5	PCP6
Layer thickness in KCl from AFM [nm]	2	3	3-4	4-5	4	2
Layer thickness in CaSO_4 from AFM [nm]	1	4-5	3-4	4-5	2	<1
R_h in CaCl_2 from DLS [nm]	4.5	10.3	4.3	9.4	5.9	4.7
R_h in Na_2SO_4 from DLS [nm]	5	11.4	4.4	9.3		
Adsorbed amount on MgO [mg/g]	1.14	1.28	No plateau	1.01	1.45	1.99
Side chain length	average	average	long	very long	short/long	average
Polymer Mw [g/mol]	23000	112000	25000	61000	48000	32500

Table 2: Layer thickness from AFM colloidal probe measurements together with some data on the polymer characteristics.

Result	LS1	LS2	LS3	LS4	LS5
Layer thickness in KCl from AFM [nm]	3-4	1-2	1-2	2-3	2
Layer thickness in CaSO_4 from AFM [nm]	2-3	1	1	1-2	1
Mw polymer [g/mol]	84000	3000	5000	23000	16000
R_h [nm]	5.9	1.8	2.5	3.4	4.5
Adsorbed amount on MgO [mg/g]	1.1	1.85	2.5	2.1	1.4

The concept of the steric stabilising layer is sketched in Fig. 1. For the PCP polymers there seems to be a clear correlation between the side chain length and the steric stabilising layer thickness, with a longer side chain giving a thicker layer. It seems that a longer polymer backbone increases the adsorbed amount for the PCP polymers whereas longer side chains decrease it. For the LS polymers the thickest steric stabilising layer was found for the polymer with the highest Mw, and comparing with the Mw we find that this

trend fits LS1-4, with decreasing layer thickness as MW decreases. For LS polymers a high adsorbed amount does not give a thick polymer layer.

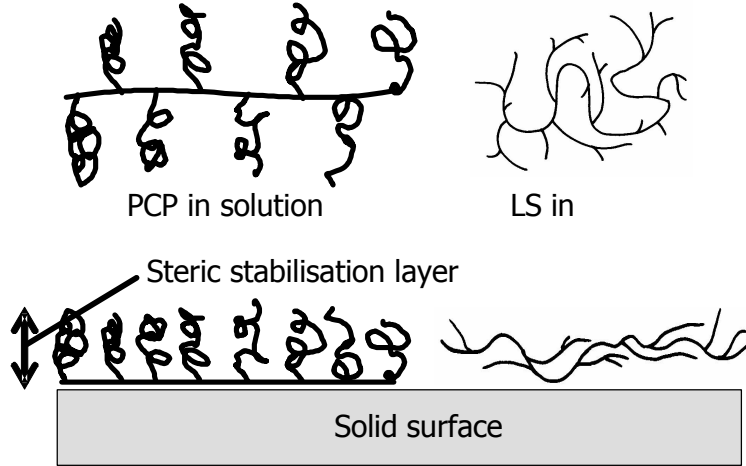


Fig. 1. Conformations of polymers in solution and when adsorbed.

The effect of adsorption on rheology is exemplified by the results of Fig. 2 and 3, showing that increasing the amount of PCP adsorbed on cement increases the flow of cement mortar. This suggests that PCPs function by steric stabilisation. The challenge is therefore to tailor polymers for optimum adsorption layer thickness and surface coverage. This was what the developed admixtures, PCP5, PCP6 and LS5, aimed to achieve.

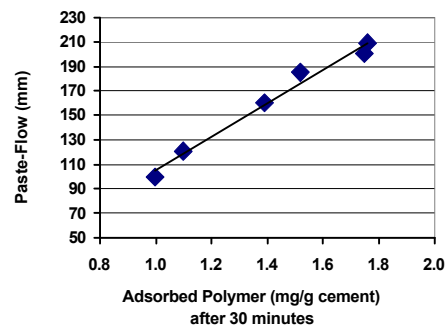
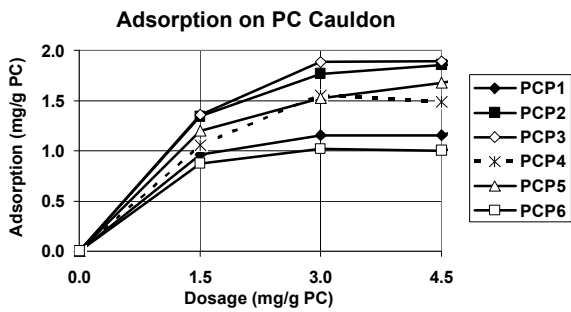


Fig. 2. Adsorption of PCPs on Cauldon cement.

Fig. 3. Effect of adsorption on mortar flow (Cauldon cement).

3.2. Performance in concrete

3.2.1. Dosages and water reduction

In both plain and blended cement mixes both PCP5 and PCP6 reduced the water content by up to 30% and LS5 reduced the water content by up to 25% (Figs. 4 and 5). Typical dosages needed were in the range 0.1-0.7% solids by weight of binder for the PCPs and 0.3-0.7% for LS5. Achieving the same water reduction with LS5 always required a higher dosage than of the PCPs. The required dosages were independent of the cements but tended to

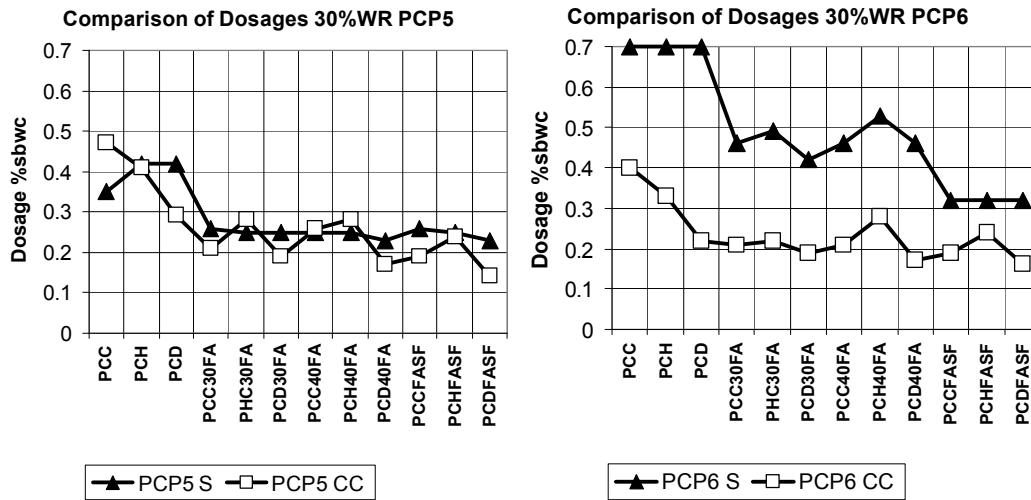


Fig. 4 Dosage of PCP5 and PCP6 for 30% water reduction with different cements, tested at Sika (S) and Castle Cement (CC). PCC = Cauldon, PCH = Hope, PCD = Dunbar, 30FA and 40FA = 30% and 40% flyash replacement, FASF = 30% flyash plus 5% silica fume.

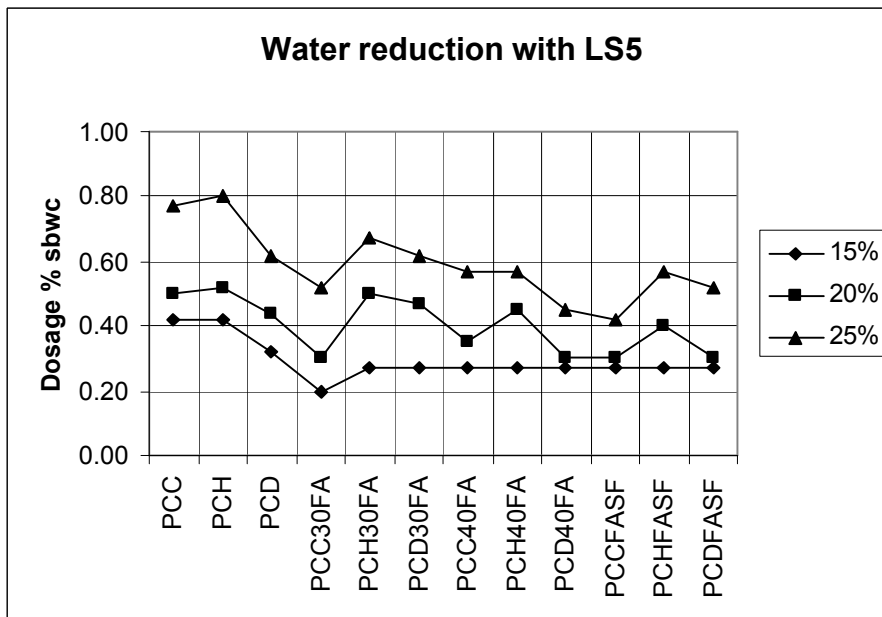


Fig. 5 Dosage of LS5 to achieve water reduction with different cements.

decrease as the degree of substitution within the blended cements increased. Thus plain Cauldon, Hope and Dunbar cements needed approximately the same dosage of PCP5 and all the blends needed the same (lower) dosage. Similarly plain cements needed the same dosage of PCP6 (higher than PCP5) and all the blends needed a lower dosage, but in the case of PCP6 there appeared to be a specific interaction with Hope cement. Sika found that

blends containing Hope cement need a higher dosage of PCP6. While confirming these trends and this Hope effect also with PCP5, Castle also found that Dunbar, both as plain cement and in blends, always required the lowest dosage of admixture. The same pattern of dosage required for water reduction with different binders is observed with LS5, but at higher dosages. There was no significant difference between the cements but increasing the fly ash content in the blended cements reduced the required dosage of lignosulfonate while the substitution of silica fume tended to bring the dosage back towards that required by the plain cements. Borregaard found that the lowest dosage of LS5 was that needed with Hope cement and 30% fly ash, which is in contrast to the Hope effect with PCP6.

3.2.2. Mixing time, addition sequence and adsorption

There is a significant difference between the dosages required for water reduction as determined in Sika's and Castle's tests (Fig. 4). Sika found that it required significantly more PCP6 and slightly more PCP5 than Castle to achieve the same water reduction. The difference was attributed to the mixing procedure used by the two partners and investigations showed that a longer mixing time gave a higher initial workability (implying a lower dosage for water reduction), less good workability retention and a shorter setting time for PCP6 and, to a lesser extent, for PCP5. This may be due to the kinetics of the adsorption process. The level of adsorption of PCP6 builds up over 60 minutes, while that of PCP5 starts much higher and remains at the same level. Thus PCP5 may be so rapidly adsorbed that a longer mixing time has comparatively little effect, while PCP6 takes longer to be adsorbed and is therefore more sensitive to mixing procedure. This effect of mixing procedure influences PCP performance and the comparatively long and energetic procedure prescribed in EN480-1 [4] and used by Castle is clearly detrimental to workability retention in PCP-containing mixes. It may be noted that it is also not representative of most industrial mixing practice, which commonly uses a short mixing time to maximise production rates. The effect of energy input during mixing was confirmed by Heriot-Watt's experiments on paste rheology. The yield stress and (to a lesser extent) plastic viscosity of a Hope cement paste containing PCP6 decreased in response to increasing shear rate (up to 100 sec^{-1}) imparted during a two minute mixing period in the rheometer. Above 100 sec^{-1} the two parameters were independent of shear rate (Fig. 6). Equally, delayed addition of SP increased the plastic viscosity of Hope cement paste sheared for two minutes at 50 sec^{-1} , and increased (LS5) or decreased (PCP5 more than PCP6) the yield stress. The shear rates experienced by the paste fraction in a concrete mixer are relatively low (probably $20\text{-}50 \text{ sec}^{-1}$) which is where rheology is most sensitive to mixing energy. Clearly, the use of standardised mixing procedures may produce conclusions which are not necessarily representative of the way admixtures perform in practical situations.

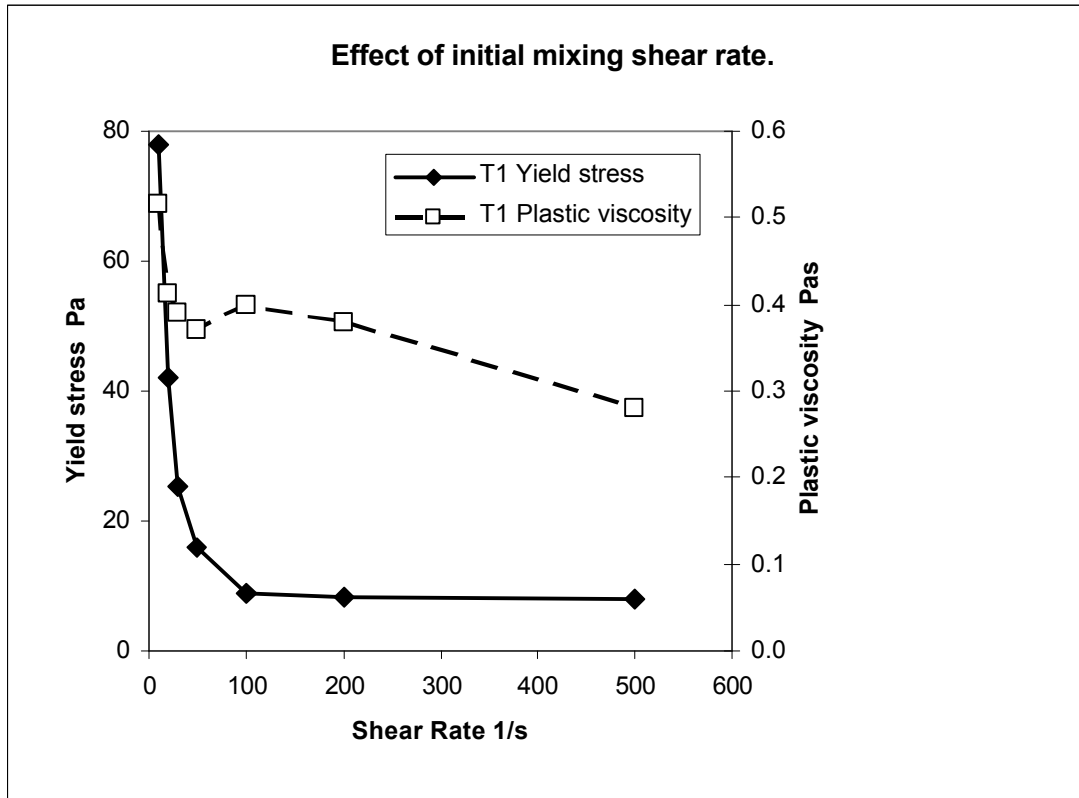


Fig. 6. Effect of energy input (rate of shear) during mixing on yield stress and plastic viscosity of a Hope cement paste of 0.375 w/c containing 0.3% PCP6.

3.2.3. Rheology and workability

Lack of space precludes a detailed discussion of rheology here. There is a direct relationship between water/binder ratio, dosage and yield stress which is accurately predictable for PCP5 and PCP6 but rather more scattered for LS5, especially with Hope cements. Rheology is more sensitive to the PCPs than to LS5 but provided the dosage is controlled with sufficient accuracy the resulting rheology with PCP is less subject to experimental scatter than with LS5. Thus while LS5 is more robust to dosage variations the rheology is actually more controllable with PCPs.

The effect of ambient temperature on workability is complex. The initial workability of concrete containing PCP was highest at 20°C and mixes at 10°C and 30°C were less workable. The initial workability of concrete containing LS5 increased as the ambient temperature rose from 10°C to 30°C.

3.2.4. Workability retention

Some differences in the observed retention of workability in PCP mixes were found by the partners and these are related to the effect of mixing time, discussed further below. Castle found that concretes with the highest water reduction typically had a slump of only 60-70% of the control after one hour,

and PCP5 and PCP6 performed worst in this respect with the 30% and 40% fly ash blends. The workability retention declined in the order Cauldon>Dunbar>Hope cements and, further, in blended cements PCP5 retained workability less well than PCP6. Fly ash reduced the flow retention of PCP5 but not of PCP6 and silica fume reduced it more for PCP5 than PCP6. In contrast, Sika found that retention increased with increasing dosage and that it was possible to achieve retention times of as much as two hours. Workability retention was better with PCP6 than with PCP5 at the same dosage. Good workability retention therefore appears to require a polymer dosage higher than a certain minimum level, which varies with the combination of cement, blend and polymer. Similarly, comparing the dosages used with adsorption curves suggests that good flow retention requires surface saturation. This explains the difference between PCP5 and PCP6 because PCP5 requires a lower dosage for water reduction and since this is below the saturation concentration it shows poor workability retention at the same starting level of workability. The difference in dosages used also explains the different workability retention observed by Castle and Sika.

In general, the objective of retaining workability at the level of 90% slump or flow after one hour was achieved at appropriate dosages. The workability retention with LS5 was longer at higher dosages and higher water/binder ratios. It was generally better than with the PCPs in all the blended cements, with the best performance shown by the 30% fly ash blends. However, retention was less good than with the PCPs in the plain cement concretes. It was again dependent on dosage and the objective of retaining workability at the level of 90% slump after one hour was not reliably achieved. The effect of ambient temperature on workability retention is complex. As noted above, the initial workability of concrete containing PCP was highest at 20°C and mixes at 10°C and 30°C were less workable. The effect is bigger for PCP6 than PCP5, but the variation was less obvious after one hour with workability generally decreasing more rapidly as temperature rose. Concrete containing LS5 showed higher workability as the ambient temperature rose from 10°C to 30°C and workability retention was best at 10°C.

Re-tempering after one hour to restore workability lost over time reduced the strength of water-reduced concretes more than that of the control concretes. This reflects the faster loss of workability in water-reduced concretes, which therefore require more water to be added to re-temper them. The effect was more significant for PCPs than for LS5, which was quite marginal, although in every case the resulting strength was still higher than the control concretes. The strength was reduced slightly more by re-tempering blended cements than plain cement concretes.

3.2.5. Setting and hydration

Both PCPs and LS5 retard the setting and hydration of all binders, and more so at higher dosages, but the effects are complex. Setting time increased with increasing water/binder ratio and with increasing fly ash content but silica

fume reduced the setting time compared to the equivalent fly ash blend. PCP6 retarded setting slightly more than PCP5 and this is reflected in the lower one-day strengths achieved with PCP6. Since PCP6 needs to be used at a slightly higher dosage this may be a simple concentration effect. LS5 dramatically increased the setting time of the plain cements but reduced the setting time of the blended cements, which were, as already noted, retarded compared to the plain cements.

Conduction calorimetry on pastes showed that the time taken to reach the top of the main peak in the rate of heat evolution increased progressively with increasing admixture concentration and that the delay was generally greater for LS5 than for PCP5 at the equivalent concentrations that would be necessary to give the same water reduction. These trends of peak height and time to reach the peak are consistent with previously published work [5]. The effects of blending with fly ash and silica fume were similar to those observed with setting time.

3.2.6. Strength development

The large water reductions generate much higher strengths than the control concretes. The strength increase when PCP5, PCP6 and LS5 are used allows the fly ash substitution to be increased from 30% to 40% and the ternary blend with silica fume to be used, in every case without detriment to the strength. Early strength development was accelerated, with concretes containing PCPs achieving significantly higher proportions of the 28 day strength at both one and seven days for all binders. The one-day strength of fly ash concretes reached nearly the same proportion of their 28-day strength as for the plain cement concretes (Fig. 7). The results show that these admixtures, with their 30% water reduction, enable a further 20% increase in 28-day strength over the level achieved with superplasticisers giving 15-20% water reduction. The greater retardation of setting with PCP6 is reflected in the one-day strengths, but the strength development caught up with those concretes containing PCP5 to the extent that most PCP6-containing concretes were actually stronger at 28 days. Compared to Borregaard's control concretes, at constant water/binder ratio the 28-day strength decreased slightly with increasing LS5 dosage. Increasing fly ash content at constant water/binder ratio reduced the 28-day strength, most noticeably with Hope cement, but this effect was offset at later ages and by the addition of silica fume. All these strength reductions at constant water/binder ratio are more than compensated by the reduction in water content. With only 15% water reduction the decrease in water/binder ratio produced a 16-20% increase in strength, and thus LS5 gave water-reduced concrete of equivalent or greater strength. Just as with PCPs the effect of LS5 was to give early strengths that are a greater proportion of the 28-day strength, but to a lesser degree. With all concretes there was a further strength increase from 28 days to 56 days and not surprisingly this was greatest with the fly ash blended cements.

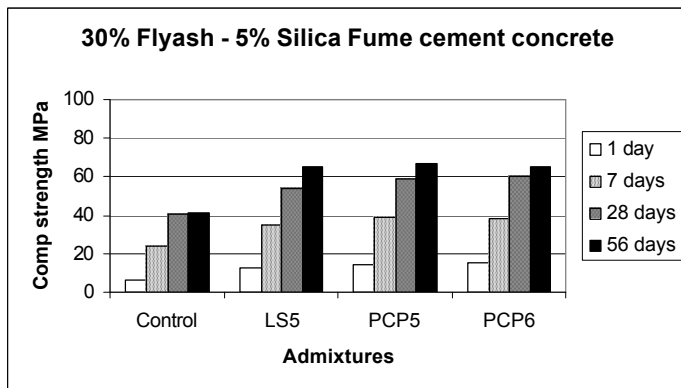
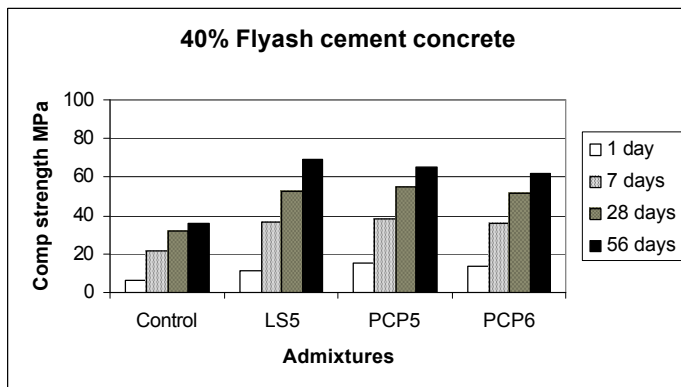
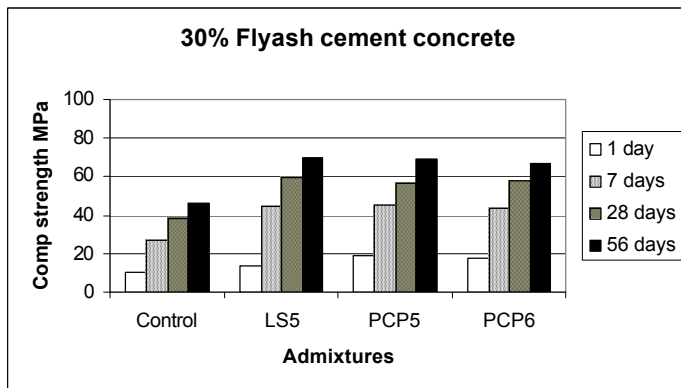
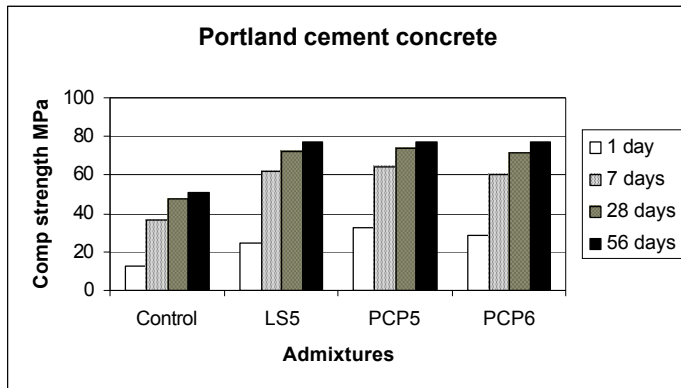


Fig. 7 Effect of admixtures on strength development of 25% water-reduced concretes, limestone aggregate 20°C cured.

3.2.7. Durability

It is too early to confirm the effects of admixtures on the durability of concrete but since durability is strongly affected by the water content of fresh concrete, the water-reductions achieved are expected to considerably improve it. Initial data shows that water penetration under pressure is much less for concretes containing PCP5 and PCP6 than for the control, with a penetration rate reduced to as little as 20%. Shrinkage is also lower as a result of the water reduction. The sulfate resistance is improved compared to the control as shown by the much lower expansion in sulphate solution. This is in line with the lower water content of the fresh concrete which decreases permeability and increases strength.

4. Implications

Reductions in the water content at the levels observed have the potential to bring about considerable improvements in the durability of concrete because lower water contents mean lower absorption and permeability, which in turn mean that the aggressive agents (sulfates in solution and water for freezing/thawing and wetting/drying) cannot gain access to the cement matrix to cause damage. The results and the new superplasticisers offer the possibility of greater use of recycled concrete, with associated environmental benefits, since aggregate obtained from recycled crushed concrete has a higher water demand than ordinary raw materials, and using these admixtures will enable water reductions.

5. Conclusions

Superplasticisers can be tailored to give higher performance by tuning the factors that control adsorption. Steric stabilisation of the binder particles as a result of the polymer molecules occupying space above the particles is important and the architecture of the polymer can optimise this adsorbed layer thickness.

Tailored polycarboxylate admixtures can reduce the water content of concrete by up to 30% and improved lignosulfonates by up to 25%, with acceptable workability retention and without retardation of strength development. The same or higher strengths are achieved with blended cements and it is possible to increase the proportion of industrial by-products, such as fly ash and silica fume, in the binder from a total of 30% up to 40% by weight.

6. Acknowledgements

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