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EFFECTS OF SUPERPLASTICIZER ON WORKABILITY AND FLEXURAL STRENGTH OF AUTOCLAVED CALCIUM SILICATES

M. Shirkavand and R. Baggott
Department of Surveying
University of Salford
Bridgewater Building, Salford M5 4WT, U.K.

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ABSTRACT

Investigations are reported into the effects of superplasticizer type and dosage on the workability of a cement-silica mix with a range of liquid/solids ratios and on the flexural strength after autoclaving. The overall objective was to achieve as high strength as possible from pourable mixes. The results showed that flexural strengths as high as 25 MPa could be achieved by using an optimum combination of superplasticizer type, dosage and liquid/solids ratio. Such mixes had excellent flow characteristics enabling direct casting without any assistance from vibration. The dosages of superplasticizer per unit weight of cement plus fine silica, were found to be similar to those for normal cement, with 2% giving optimum benefits. A critical 0.25 liquid/solids ratio was found below which strength decreased and above which the conventional dependency found with cementitious systems was observed.

Introduction

In order to achieve high strength in cementitious materials it is necessary to have low water/cement ratios whilst maintaining sufficient workability to fabricate successfully. It is not possible to obtain increased workability via increased paste to aggregate ratio without eventually compromising strength. The most successful method is to utilise superplasticizers thereby enabling as low a water/cement ratio as possible to be used for a specific workability.

Superplasticizers are now an established extension of traditional admixture usage. They were first used in the UK in 1973, although they have been in use in significant quantities in Germany since early 1972 and in Japan since the late 1960's (1). Those currently in use are based predominantly on either sulphonated melamine formaldehyde condensates or sulphonated napththalene formaldehyde condensates. Aitcin (2) explains the development leading to this situation as well as the chemical mechanisms involved in superplasticizing action.

Superplasticizers have been used very successfully with many cementitious systems, particularly to produce high performance concrete. Very little has been reported on their application in the manufacture of autoclaved cement silicas. This family encompasses a number of successful commercial products such as blocks, bricks, fibre reinforced sheets, pipes and thermal insulation materials. The science and technology associated with their manufacture was first reported by Menzel (3) and subsequently well documented by Gundlach (4)

Autoclaved cement/silica belongs to the group of cements which have some form of calcium silicate hydrate as the principle binder. This group includes calcium silicate hydrates produced from ordinary Portland cement hydrated around room temperature, ie. the binder in normal concretes, hydrate produced from reactions occurring between ordinary Portland cement and pozzolanic silicas, and finally calcium silicate hydrates produced by reacting ordinary Portland cement, ordinary Portland cement plus silica, or lime and silica, in steam at high temperatures usually in the range 160 - 200 °C.

Although the general effect of superplasticizers on the workability of cement pastes has been well documented it is not possible to identify the most effective type of superplasticizer or the optimum dosage for a particular mix except by practical trials. This is particularly the case with mixes incorporating other very fine particle size components with inherent problems of flocculation. It was suggested by Ramachandran (1) that "in many instances incorporation of more than the normally recommended dosage of superplasticizer yield further advantage, but this does not mean that excessive amount can be tolerated - beyond a particular amount the superplasticizer may produce undesirable results".

In the case of autoclaved materials comprising ordinary Portland cement and very fine silica very little work other than that of Valore (5) has been reported in the literature regarding the potential for strengthening offered by superplasticizers. The objective of the present investigation was to evaluate this potential for an inherently high strength composition with particular reference to high fluidity and flexural strength.

Experimental Investigations

Programme

A sequential approach to strength optimisation was adopted with each of six types of superplasticizer. This allowed general trends to be established as well as optimisation. An arbitrary liquid/solids ratio of 0.29 was used for the first mix and the effect of increasing superplasticizer content on workability and flexural strength was determined (liquid/solids ratio, subsequently abbreviated to LSR is used throughout ie liquid to denote either water or water plus superplasticizer and solids to denote all the powders that are reactive in the autoclave). The LSR was then reduced, the superplasticizer content adjusted to maintain or improve workability and the flexural strength of the various mixes was determined. The procedure was continued until strength started to reduce. In addition two mixes were prepared without superplasticizers at high LSR's to provide a broader measure of the effect of LSR on strength.

Specimens Preparation and Testing

The basic dry powder consisted of 60 parts cement, 30 parts BM500 silica of average particle size 3μm and 10 parts HPF5 silica of average particle size 50μm, a combination which was found to give high strength (6).

Ordinary Portland cement, manufactured by Blue Circle, was used throughout. Six commercially available superplasticizers were used in the investigation, two melamine based products, two naphthalene based products and two complex polymer systems, coded A-D, where A = Sikament FF, B = Lomar D, C = Conplast M1 , D = Sikament, E = Rheobuild and F = Cormix SP 2000.

A standard mixing procedure was used comprising dry mixing the silicas for 1 min in a small Kenwood orbital mixer, adding the combined liquid superplasticizer and water, then 3 min mixing followed by cement addition and a final 3 min mixing.

Beams were cast in steel moulds, 225x45x12mm. High fluidity mixes were poured straight into the moulds without vibration. No difference in final strength was obtained by vibrating. However if the mix was stiff, it was compacted with a steel rod in the mould.

In order to determine the workability of the cement silica paste a smaller version of the B.S flow table test for mortar was used (BS 1881:part 105:1984). In this test a PVC cylinder of 40 mm x 25 mm dia was placed in the centre of a flat transparent perspex plate under which lay paper with concentric rings for the measurement of the horizontal flow of a standard volume of paste.

Autoclave curing was carried out in a boiler heated autoclave after 24 h stand by with a cycle of 2h build up, 8h dwell time at 180°C and 3h blow down. Flexural strength was determined by three point bending over a 150mm span. Strength measurements were made on twelve replicates.

Results

Mixes without superplasticizers

The LSR of mixes without superplasticizers had to be quite high, since the addition of fine silica increased the water requirement, because of its large surface area. At 0.45 the mix showed no flow. However the paste could be easily mixed and fabricated, although only the voids near the surface could be removed even with vibration. At 0.65, the mix was flowable taking 1 to 2 seconds to extend 32 mm i.e. a very rapid flow. The flexural strength of the 0.65 mix was 6 MPa ie 27% lower than the 8.2 MPa value of the 0.45 mix, as would be expected from the higher LSR ratio.

Mixes with super-plasticizers

Type A

Figure 1 presents the results in the form of an empirical relationships between dosage of superplasticizer and flexural strength. It can be seen that over the range of LSR and dosage tested the flow was the second lowest (11mm) with 1% dosage at the highest LSR of 0.29 and at a

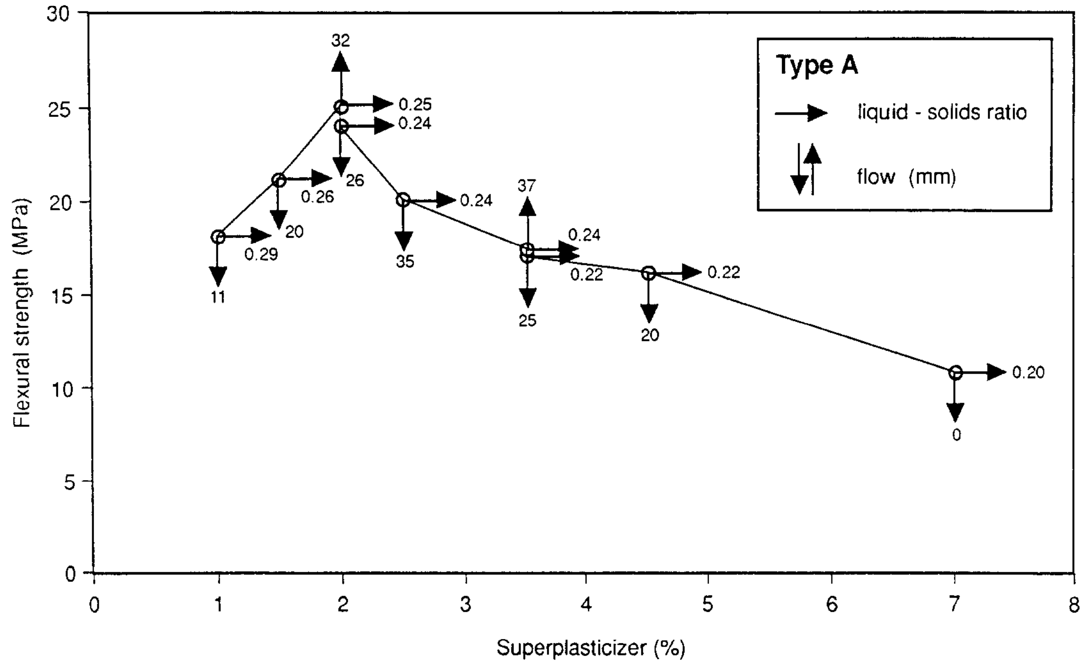

FIG 1
Relationship between flexural strength and superplasticizer content

maximum of 37mm with LSR of 0.24 and 3.5% dosage. The flexural strength obtained at 0.25 LSR was 25 MPa, which was the highest in the superplasticizer A series. The flexural strength then decreased slightly to 24 MPa at 0.24 LSR with 2% dosage and 26mm flow although this reduction in strength was indicative rather than significant.

The values of flow shown on the figure ranged from 0 to 37. Zero flow value included a range of consistencies from very stiff to completely unworkable, flows between 10 and 25 indicated consistencies ranging from thick to thin creaminess, whereas flows from 25 to 35 corresponded to increasingly runny mixes which at the higher values were of sufficient fluidity to allow easy pouring into the mould.

The superplasticizer content was then increased to 2.5% and 3.5% at 0.24 LSR. The results showed that the flow increased with increasing dosage, but the flexural strength was reduced. Furthermore the rheology of the mixture changed, in so far as the flow velocities were reduced despite the flow distance increasing producing a more 'cohesive' mixture than at 2% dosage although still appearing as runny. This resulted in an increase in air entrainment and lower flexural strength.

The LSR was then reduced to 0.22 and the dosage increased to 3.5% and 4.5% to try to achieve acceptable flow. However both the distance and velocity of flow decreased and the increased cohesiveness of these mixtures corresponded with flexural strength reductions to 17 and 16 MPa respectively. A third phenomena at these high dosages of superplasticizer and low LSR's was that the setting time was reduced, accompanied by considerably increased heat evolution indicating an

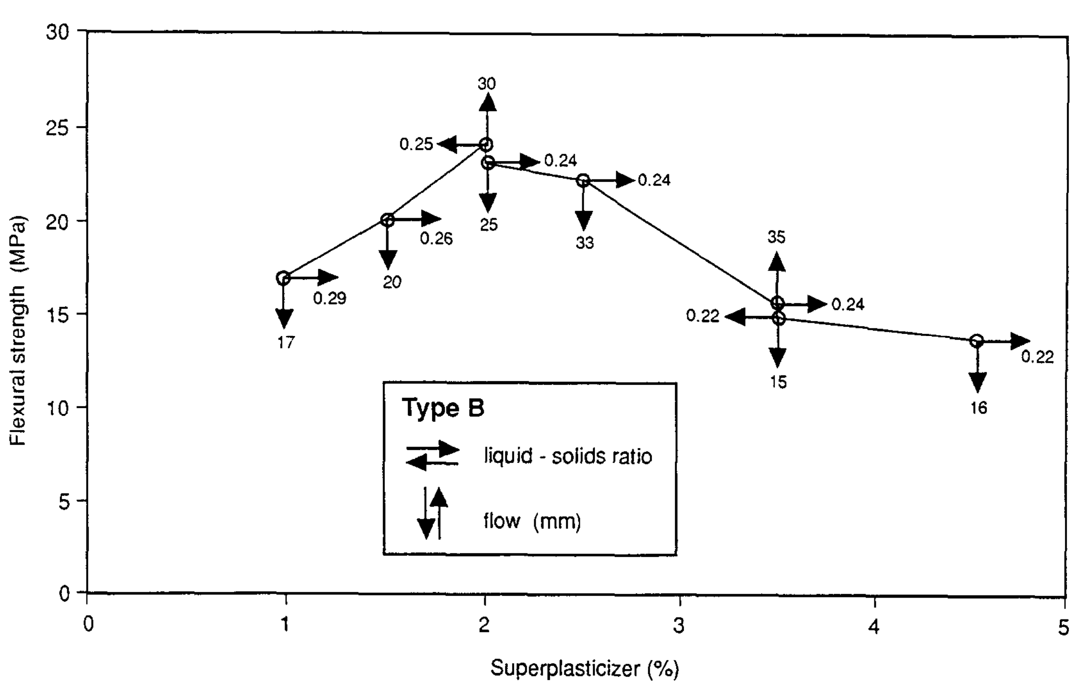

FIG 2
Relationship between flexural strength and superplasticizer content

increased rate of hydration of the cement. To confirm this trend the LSR was then further reduced to 0.20 at 5% dosage, but it was not possible to mix with the standard procedure, therefore the dosage was increased to 7% with some improvement producing a difficult to work paste with even lower flexural strength of 10.7 MPa.

Types B - F

Figure 2 illustrates the relationship between dosage of superplasticizer B and flexural strength indicating a very similar pattern to that of Figure 1. The highest flexural strength (24 MPa) was obtained with 0.25 LSR.

Figure 3 illustrates a similar overall pattern with superplasticizer C although it is slightly less effective than A or B. The highest flexural strength (22 MPa) was obtained with 0.25 LSR at 2.5% superplasticizer content.

From Figure 4 it can be seen that the highest flexural strength (20.3 MPa) was obtained with 0.24 LSR at 2% of superplasticizer D. The disadvantage with this superplasticizer was the increased air entrainment, especially at higher dosages (2.5%, 3.5% and 4.6%). This increase had an adverse effect on both the flexural strength and the surface finish of the specimens.

Superplasticizer E (Figure 5) showed a similar pattern to that of D although higher dosage rates had to be used to achieve similar workability. The maximum flexural strength (21.2 MPa) was achieved at 0.24 LSR and 3% superplasticizer.

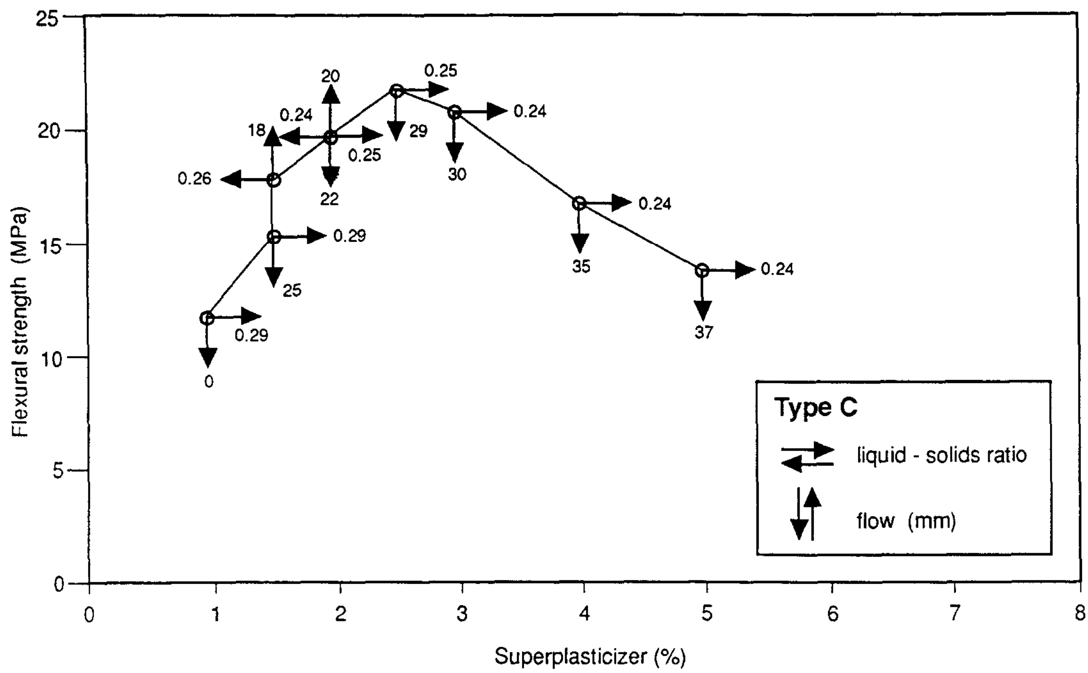

FIG 3
Relationship between flexural strength and superplasticizer content

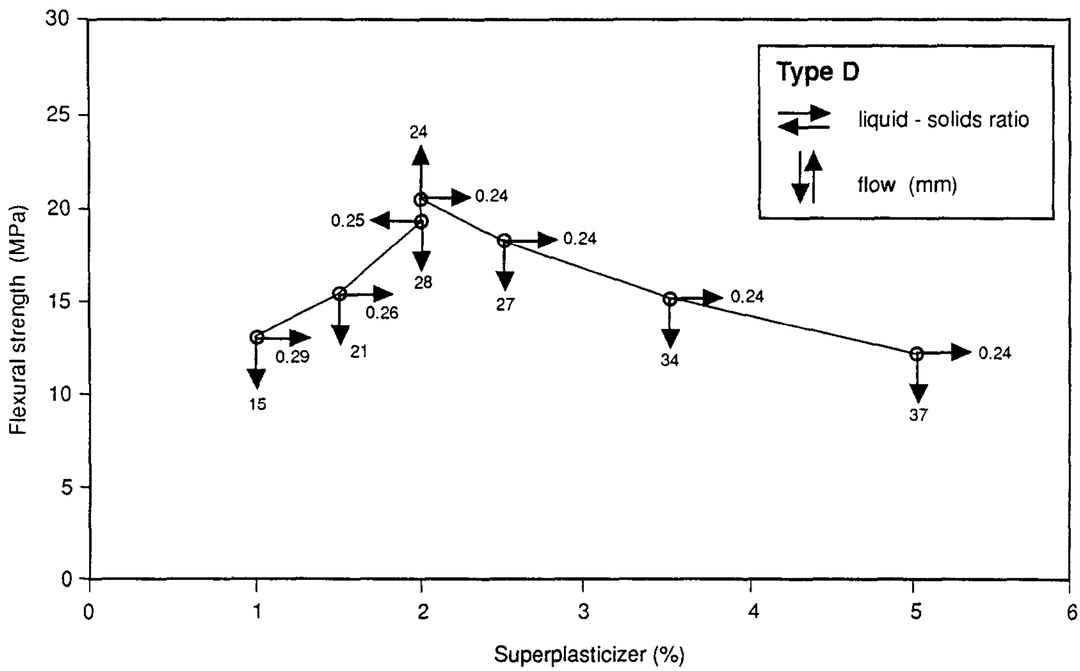

FIG 4
Relationship between flexural strength and superplasticizer content

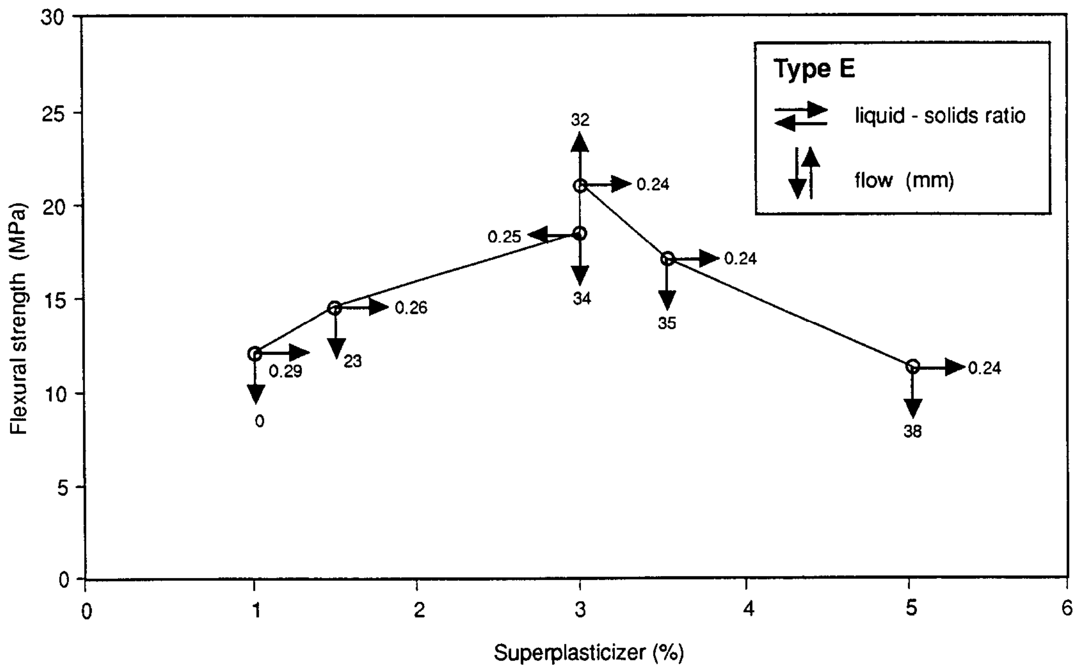

FIG 5
Relationship between flexural strength and superplasticizer content

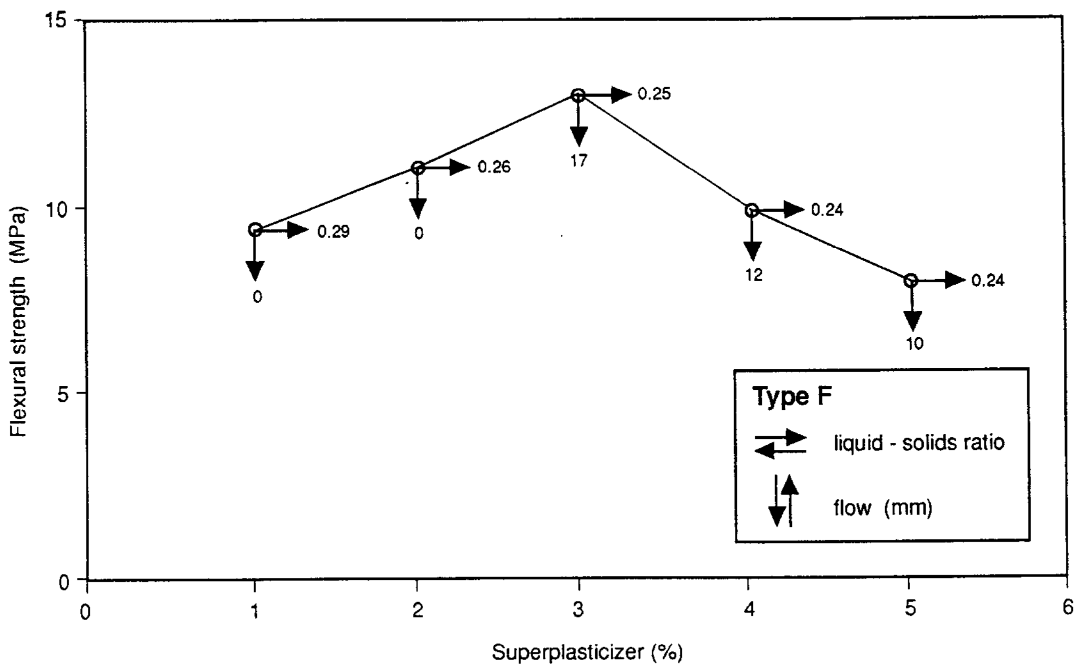

FIG 6
Relationship between flexural strength and superplasticizer content

Superplasticizer F (figure 6) was inferior in relation to strength and flow, as compared to the other five superplasticizers. The highest flexural strength obtained was 13 MPa at 0.25 LSR and 3% dosage rates. At higher dosage rate (4% and 5%) and 0.24 LSR the setting time was significantly reduced and the increased rate of hydration led to several specimens buckling in the mould.

Fracture surface

Visual examination of fracture surfaces of various specimens showed that when an LSR of 0.35 was used the size of the larger voids was in the range of 0.5 mm to 3.6 mm. Increasing the LSR reduced the size of the largest voids to around 2.2 mm. This reduction in size of voids was due to better workability obtained at higher LSR. At 0.29 LSR with 1% addition of superplasticizer type A, the size of the largest void was reduced to 1.75 mm. A reduction in LSR to 0.25 and an increase in superplasticizer A to 2 %, enabled a mix to be made with excellent flow characteristics of denser composition with maximum void sizes of 0.25 mm and reduced total number of voids. However not all the superplasticizers showed the same improvement. The superplasticizers which entrained air significantly (E and F) produced lower density mixes with larger voids. Increased air entrainment also occurred with very low LSR values and high superplasticizer dosages ie relatively stiff mixes. These mixes also contained undispersed silica distributed on what constituted planes of weakness.

Discussion

Workability

The first aspect of the result to consider is the workability levels achieved as a result of superplasticizer addition. With the present mixes it was found that at around 0.29 LSR and lower, the cement-silica mixes could only be mixed easily with the aid of superplasticizers. Addition of superplasticizers at a particular LSR improved the workability, the larger the dosage the more fluid the mix became up to a maximum level above which fluidity was reduced. As the maximum level was approached the mix rheology changed so that although the flow distance continued to increase the flow velocity started to reduce and the mix became more cohesive. These changes draw attention to other aspects of fluidity which may be involved in a particular slurry application, eg incorporating aggregate or infiltrating fibrous arrays. The parameter of interest in the present report was flow distance but the other phenomena are the subject of further investigation. At very low LSR ratios sufficient fluidity could not be provided by superplasticizer addition. The dosage level at which these changes occurred was above the upper limit of dosage imposed by other factors such as strength reductions (see later).

The performance of individual superplasticizers with regard to flow was only marginally different up to dosages of 2% , however there were significant differences in the extent of air entrainment and cohesiveness. The reasons for these differences lie in the composition of the various superplasticizers and their interaction with the particular cement and fine silicas. Aitcin (1) argues that there are no theoretical means to predict the rheological reactivity of a system making it inevitable to proceed by trial and error although there are general rules related to tricalcium aluminate content, cement fineness, water/cement ratio and coarse/fine aggregate ratio.

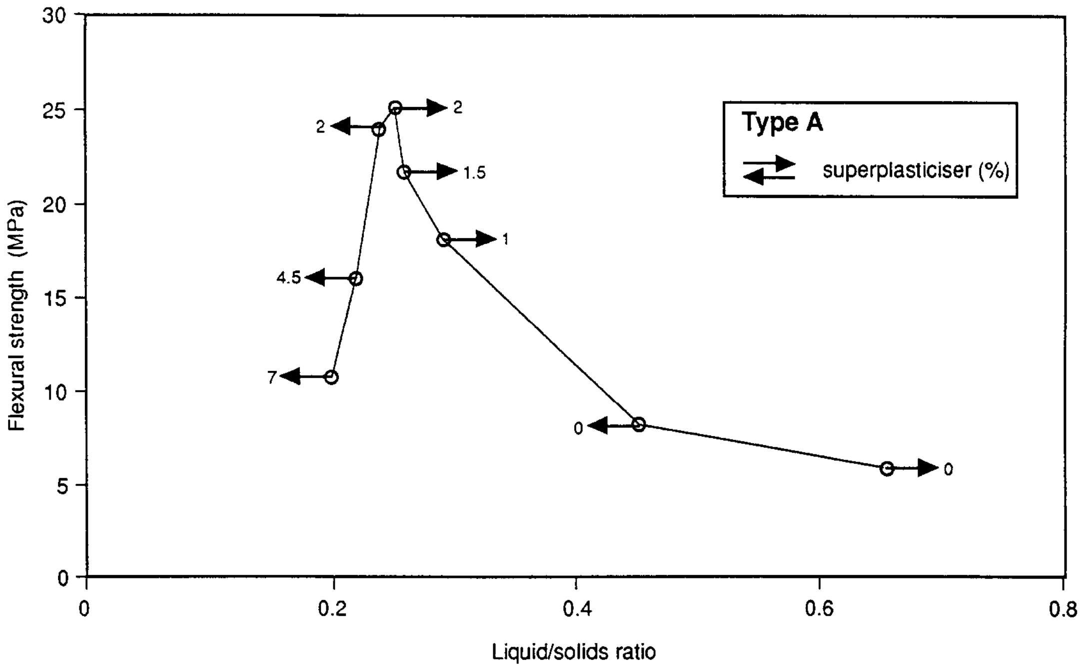

FIG 7
Relationship between flexural strength and liquid-solids ratio

Flexural strength

The next aspect of the results concerns the flexural strength values obtained and their link with the various superplasticizers. Figure 7 illustrates the relationship between flexural strength and LSR obtained with superplasticizer A. A distinct optimum in strength occured at LSR 0.25. Above this value the conventional reduction in strength with increasing LSR observed with cementitious materials generally was obtained with similar dependencies to normal concrete.

There were 208% and 323 % improvement in flexural strength at 0.25 LSR as compared to 0.45 and 0.65 LSR. Below 0.25 there was a steep reduction in strength with decreasing LSR values. A similar pattern of dependency with LSR occurred with the other five superplasticizers, in every case a distinct optimum was observed at either O.24 or 0.25 LSR. . The explanation for the decreasing strength with increasing LSR is similar to that for other cementitious systems ie increasing the water content, with the remaining components of the system remaining the same, leads to a less dense weaker structure. The explanation for the decreasing strength with decreasing LSR below the critical value in normal systems is due to entrapped air because of poor compactibility. The autoclaved cement-silica system lost strength long before this became a problem but it is thought that a related effect occured ie entrained rather than entrapped air due to the rheological changes occurring, particularly the increased cohesiveness of the wet mix. In addition to this, at the lower LSR ratios an increased heat of hydration caused internal stresses during the standby period leading in the extreme case to buckling of the specimen in the mould.

The dosages of superplasticizer to produce the optimum strength in this cement fine-silica system were not necessarily the same as the maximum dosages recommended by the various manufacturers for use with cement. Although there was a common optimum LSR to produce maximum strength for all the superplasticizers, there were considerable variations in the absolute value of the optimum strength among otherwise identical mixes containing different superplasticizers.

The high fluidity mixes at 0.25 LSR with the optimum superplasticizer content were all sufficiently fluid so that the mixture was easily poured into the moulds. At these high fluidities there was no compaction problems and the final strength for a particular LSR was determined by the size of the largest void. In the case of the most 'effective' superplasticizers complete elimination of voids above 0.5 mm was achieved whereas the less effective superplasticizers entrained larger voids. It has already been established that this type of autoclaved material behaves as a Griffiths solid (7) so the strength dependencies automatically follow because of the increased maximum defect size and the reduced surface energy.

Although a direct chemical influence of superplasticizer composition on final strength due to an interaction occurring under autoclave conditions cannot be totally ignored it is considered unlikely in view of the above evidence. It follows that both the optimum LSR strength relationship and the variability of maximum strength can be considered as indirect effects of superplasticizer type via influencing porosity.

The final aspect is the high level of flexural strength obtained, for example, values of 20 - 25 MPa, which are higher than many fibre reinforced cementitious composites. The reason for such high strength values from an extremely workable mix is the combination of autoclave curing with low LSR's and reduced maximum defect size, the latter two being possible because of superplasticizer addition.

Conclusions

The following conclusions were drawn from this investigation.

1) The incorporation of superplasticizers in mixes designed to give optimum strengthening during autoclaving enabled high fluidity to be obtained at very low liquid/solid ratios. In particular, the use of 2% superplasticizer per weight of cement plus silica in 0.25 liquid/solids ratio mixes gave fluidities comparable to that of unsuperplasticized 0.65 water/solids ratio mixes.

2) The various types of superplasticizer produced similar workability improvements but varied in their indirect influence on flexural strength. The flexural strength of the strongest of the high fluidity 0.25 liquid/solids ratio mixes was 25 MPa, nearly four times higher than the flexural strength of unsuperplasticized mixes of comparable fluidity ie 0.65 water-solids ratio.

3) The various levels of strength achieved were related to the extent to which the slurry entrained air and the size of the resulting voids in the hardened material. This was a function of the type of superplasticizer. The most effective superplasticizers minimised both the total volume and maximum size of the voids.

4) Flexural strength started to decrease significantly in mixes containing 3.5% superplasticizers dosage or more and with liquid/solids ratios below 0.24, therefore 3.5% appears to be the saturation dosage for these mixes.

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