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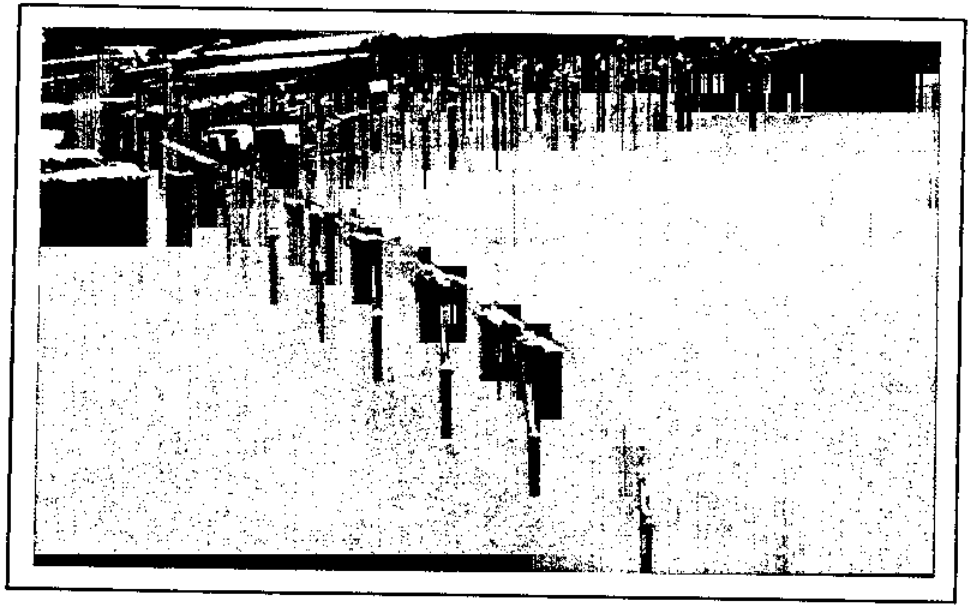

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Editor

Characterization of Cement Pastes with Silica Fume and Superplasticizer as Components of High-Performance Concretes

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Synopsis: The Marsh cone test on cement pastes containing superplasticizer and silica fume is a simple approach for obtaining a practical measure of the fluidity, which can be related to the yield shear stress of the Bingham model. Using this method, a study of the effect of temperature, water/cement ratio, silica fume type and dosage, and superplasticizer type on cement pastes with different superplasticizer dosages is presented here. The data on flow times determined by the Marsh cone indicate that the relative fluidity generally decreases with a decrease in temperature (between 5°C and 45° C), decrease in water/cement ratio, and increase in the silica fume content. The loss of fluidity that can be associated with a superplasticizer has also been quantified and is shown to vary considerably from one product to another.

The data from the Marsh cone can also be used to define the saturation dosage of a superplasticizer as that point beyond which there is no significant decrease in the flow time. Considering that it is not beneficial to the fluidity beyond this dosage, the saturation point can be taken as the maximum superplasticizer dosage to be used in concrete. For the materials studied here, the saturation dosage was generally not affected by temperature, and increased with a decrease in the water/cement ratio and increase in the silica fume content.

The practical applicability of this approach is promising for several purposes, such as the selection of superplasticizers, determining the loss of fluidity with time and for quantifying the effects of silica fume addition.

Keywords: Cement paste, superplasticizer, silica fume, fluidity, workability, rheology.

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INTRODUCTION

High strength concrete and other high performance concretes (HPC) are normally combinations of cement, aggregates, water, fine puzzolanic fillers (silica fume, fly ash, etc.) and superplasticizer. The incorporation of the latter two types of admixtures leads to a matrix that is of sufficiently fluidity in the fresh state, and is more compact and much stronger, in the hardened state, than in conventional concretes. Consequently, HPC exhibits lower permeability and higher mechanical integrity. The optimization of the matrix or the paste phase of concrete is, therefore, an important step in the design of its composition.

Since the paste phase provides flowability and cohesion, it can be considered that workability and other rheological properties of the fresh concrete depend to a large extent on the paste characteristics. Consequently, this phase, which can be considered as a synergistic combination of cement, water, silica fume (or other mineral admixtures) and superplasticizer, has to be proportioned adequately to obtain the desired workability in the concrete. The systematic and routine characterization of paste fluidity, however, requires a testing method that is simple, reliable and economical. The method used here is based on the Marsh cone, which has previously been used in the optimization of HPC (1,2). Using this approach, effects of parameters such as silica fume content, superplasticizer type, mixing sequence and time can also be analyzed, more conveniently, on pastes rather than on the concretes.

The work presented here studies the effect of superplasticizer type and dosage, water/cement ratio (w/c), silica fume type and dosage, and temperature on the fluidity of cement pastes measured with the Marsh cone. Using the data obtained, the saturation dosage of a superplasticizer, which can be considered as its maximum dosage for a given paste composition, can be defined.

Two types of cement were used in the study: CEN Class I 42.5 and 52.5 cements conforming to Spanish types I 45A and I 55A, respectively. Two different condensed silica fumes in densified form, one of them with a superplasticizer incorporated in it (denoted as R) and the other without any (denoted as E), were utilized. Five superplasticizers were studied - three naphthalene sulfonates, denoted as SD, SD1 and SR, a melamine sulfonate SM and a vinyl copolymer SS. Note that all superplasticizer dosages are defined here in terms of their solid contents. The pastes were prepared in Hobart type mixers with a capacity of 5 liters, and with two speeds of 120 rpm (high) and 60 rpm (low).

THE MARSH CONE TEST

The Marsh cone test is a simple and practical method for obtaining a relative measure of the paste fluidity. In this approach, the time taken for a specified volume of paste to flow through a cone with a small opening is measured; the longer the flow time, the lower is the fluidity. It is similar to the flow cone test used in the ASTM Standard C 939 for determining the flowability of grouts (3). The Marsh Cone has been used previously to determine the saturation dosage of the superplasticizer, and the compatibility between cement and superplasticizer (1,2). The saturation point is defined as the superplasticizer dosage beyond which the flow time does not decrease appreciably. Cement-superplasticizer combinations that do not exhibit a well-defined saturation point may indicate incompatibility. Considering the saturation point as the maximum dosage of superplasticizer for the given cement, w/c and silica fume content, the quantity required for the concrete can be chosen (4,5).

It should be noted that the Marsh cone approach has some obvious limitations (6). First, it assumes that the paste is a Newtonian fluid, which is not always true. If the paste behaves as a Bingham fluid (7,8), the Marsh cone flow times will be more closely related to the yield shear stress than to the plastic viscosity. However, this is also the case of the workability of concrete determined as the slump in the Abrams' cone (7). Secondly, the paste in the concrete could have a different rheology than that prepared independently (9), implying that final optimization should be made through tests on concrete (5).

In this study, a cone, with dimensions given in Fig. 1, and a reference volume of 800 ml of paste were used. The time taken for 200 ml of the paste to flow through the cone was measured and taken as the flow time. All tests, except those in the study of the effect of temperature, were conducted at a constant temperature of about 20°C.

To compare the results of the Marsh cone with more fundamental data from a viscometer, tests were performed simultaneously with a coaxial-cylinders HAAKE Viscositester (VT550) using an MV-DIN sensor. The paste is sheared between a fixed hollow cylinder (of 4.2 cm internal diameter) and a moving inner cylinder (with a diameter of 3.86 cm). The pastes used were composed of I 52.5 cement, superplasticizer SD1 and w/c = 0.33. They were prepared by first mixing cement with a fixed volume of water at low speed for 2 minutes, and then with the superplasticizer and rest of the water for ½ minute at low speed and 2½ minutes at high speed. Tests were conducted for different superplasticizer/cement ratios (sp/c) in the Marsh cone and the viscometer (at velocities of $N = 150$, 300 and 600 rpm). The Bingham model was applied to the data from the latter, using $\tau = \tau_0 + GN$, where τ is the measured shear stress at velocity N, τ_0 is the yield shear stress and G is proportional to the plastic viscosity. The comparison of the flow times and τ_0 values, in Fig. 2, for different sp/c show similar trends, with the saturation point occurring in both cases at about 1.5% indicating the practical usefulness of the Marsh cone results. The value of G was practically unaffected by changes in the sp/c. The trends of the Bingham model parameters are in accordance with those in the literature (7,10).

EFFECT OF TEMPERATURE ON MARSH CONE FLOW TIMES

Flow times were measured at different temperatures, using the procedure described earlier, in the Marsh cone on pastes with I 42.5 cement, w/c = 0.33 and different sp/c of superplasticizer SD1. The temperature range studied was 5°C to 45°C, and all the materials were maintained at the prescribed temperature before and during the tests in a climatic chamber. The results are shown in Figure 3. Data points are not shown for flow times greater than 200 s. It can be seen that the flow times increase with a decrease in temperature and, more interestingly, the saturation point, which occurs at about 0.75% is unaffected by the temperature. This implies that a decrease in workability due to low temperatures cannot always be compensated with an increase in the superplasticizer dosage, at least for the product studied here.

EFFECT OF WATER-CEMENT RATIO

The fluidity of the cement paste is obviously a function of the w/c and sp/c. Therefore, the superplasticizer dosage needed for a certain workability in concrete depends on the w/c of the paste. In Fig. 4a, the flow times of pastes with I 42.5 cement, superplasticizer SD, and w/c = 0.28, 0.33 & 0.40 are given. It can be observed that the flow times increase with a decrease in w/c, as expected. For practical purposes, it can be stated that the pastes with w/c = 0.40 & 0.33 do not benefit considerably from the addition of more than 0.25% & 0.5% of superplasticizer, respectively. These values can be considered as the saturation points. Considering that saturation in the paste with w/c = 0.28 occurs at sp/c = 1%, it appears that the saturation dosage increases with a decrease in w/c. The results indicate that paste fluidity increases with an increase in w/c but does not always increase with the superplasticizer dosage. The above pastes were also studied after incorporating silica fume E (as an addition of 10% by weight of cement). None of the pastes with w/c = 0.28 had flow times of less than 200 s; the others are shown in Fig. 4b. It can be seen that the superplasticizer continues to have little effect on the paste with w/c = 0.40 but the pastes with w/c = 0.33 do benefit from the addition of the superplasticizer. In the latter case, saturation occurs at about 1.5% compared with 0.5% for the paste without silica fume.

The procedure used for preparing the pastes in this series of tests, and all those hereafter, was the following: the cement, water and ⅓ of the superplasticizer were first mixed at low speed for 2 minutes; then, the silica fume was added and the paste was mixed for 4 more minutes at high speed; in the third stage, ⅓ of the superplasticizer was added and the paste was mixed for 2 more minutes at low speed; and in the last stage, the remaining ⅓ of the superplasticizer was added and the paste was mixed for 2 minutes at high speed.

EFFECT OF SILICA FUME CONTENT

As seen above, the addition of silica fume to cement paste decreases its fluidity and therefore requires the incorporation of superplasticizers. However, the superplasticizer requirement depends on the type of silica fume and its dosage (defined here in terms of the silica fume/cement ratio, sf/c). In both the cases showed in Figs. 5a and 5b, the flow times increase considerably with an increase in sf/c. However, pastes with silica fume E exhibit superplasticizer saturation at dosages that increase with an increase in sf/c, while the saturation dosages of pastes with silica fume R are not affected by the incorporation of sf/c at the dosages of 5 and 10%. As mentioned earlier, the main difference between these two silica fumes is that R is a mixture of silica fume and a dry superplasticizer, while E does not have any superplasticizer mixed with it. This suggests that no additional superplasticizer is needed for additions of 5 and 10% of silica fume R. Obviously, the incorporation of dry superplasticizer in the silica fume can partially compensate the decrease in fluidity due to its addition to the paste.

EFFECT OF SUPERPLASTICIZER TYPE

The fluidity of a paste containing a superplasticizer depends considerably on its effectiveness, which varies from one type to another. Pastes with four commercial products are compared in Fig. 6 keeping all other parameters constant. The trends are similar for the two naphthalene sulfonates SD and SR, while the melamine sulfonate SM is less efficient. The copolymer SS, which belongs to a new family of superplasticizers is much more efficient than the others, as shown by other researchers (11). However, it is also more expensive in the local market, and consequently, the choice of the superplasticizer should be based mainly on its cost-effectiveness. Moreover, the selection of superplasticizer should clearly be based on comparisons of the flow time versus superplasticizer dosage curves and the saturation points, and not on comparisons of flow times for just one superplasticizer dosage, which can be inconclusive.

Another important conclusion that can be made from Fig. 6 is the decrease in fluidity (i.e., increase in flow time) beyond a certain sp/c for superplasticizer SS. This indicates that high dosages could reduce paste fluidity, confirming the negative effect of excessive superplasticizer observed by Aïtcin et al. (12). Though the reason for this is not yet clear, it may be attributed here to the mixing procedure, which is not favorable to superplasticizers with a high water content (80%) since a large part of the mixing is done with a low water content leading to a non-homogeneous paste.

LOSS OF FLUIDITY

An important consideration in the choice of superplasticizer type, dosage and sequence of incorporation in concrete is the loss of fluidity with time (11). In order to study this aspect, the Marsh cone flow times of pastes incorporating different superplasticizers were measured during a period of 60 minutes. The superplasticizer dosages were chosen as the saturation values obtained previously. After the pastes were prepared, the mixing was continued at low speed until the flow time was measured. The results shown in Fig. 7 indicate that, as expected, all the pastes exhibit some loss in fluidity with time. However, the losses are negligible in the pastes with the naphthalene SD and the copolymer SS. The melamine SM leads to the most rapid loss in fluidity. It can be concluded that the Marsh cone test can be used to select a superplasticizer in terms of fluidity loss. Moreover, the results confirm that all superplasticizers do not have the same loss in fluidity with time.

CONCLUSIONS

The flow times, which are determined in the Marsh cone test using a simple procedure, give a satisfactory indication of the relative fluidity of the cement paste. The practical applicability of this approach is promising for several purposes, such as the selection of superplasticizers, determining the loss of fluidity with time and for quantifying the effects of silica fume addition.

The flow times obtained from the Marsh cone can be related to the yield shear stresses of the Bingham model, as with the slump of concrete. A comparative study with the Marsh cone and a viscometer yield similar trends with the two procedures.

For the materials studied here, the flow times in cement pastes (systems with superplasticizer and silica fume) generally increase (indicating a decrease in fluidity) with a decrease in temperature (in the range of 5°C to 45°C), decrease in water/cement ratio and increase in the silica fume content.

The saturation dosage of the superplasticizer can be defined as that point beyond which there is no significant decrease in the flow time. Considering that there is no benefit to the fluidity beyond this dosage, the saturation point can be taken as the maximum superplasticizer content to be used in concrete. In the systems considered here, the saturation superplasticizer dosage is generally not affected by temperature, and increases with a decrease in water/cement ratio and an increase in silica fume content (especially in those silica fumes that do not contain any superplasticizer).

The optimum dosage and the loss of fluidity that can be associated with a superplasticizer vary considerably from one product to another. However, they can be quantified for practical purposes through the Marsh cone test on pastes.

Acknowledgments

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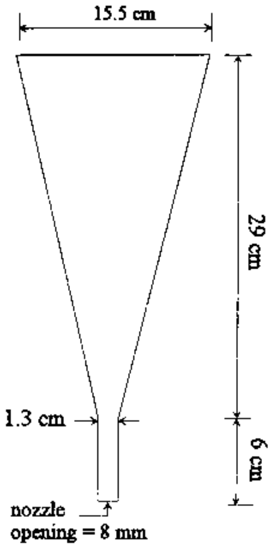

Figure 1. Marsh cone dimensions

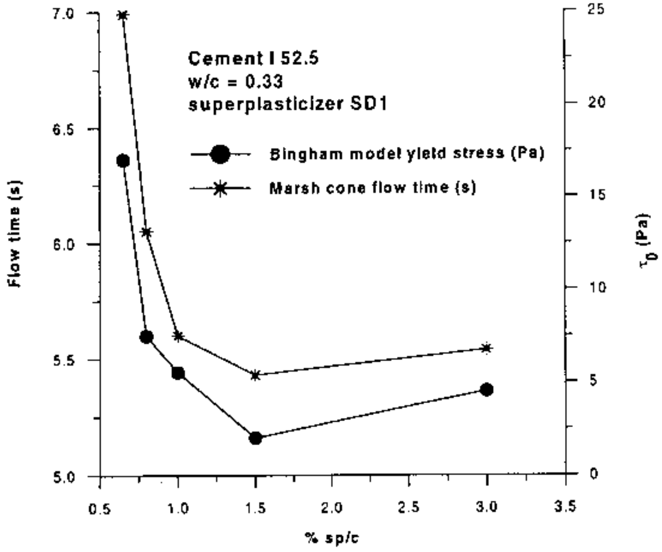

Figure 2. Comparison of Marsh cone flow times and yield shear stresses for different superplasticizer/cement ratios

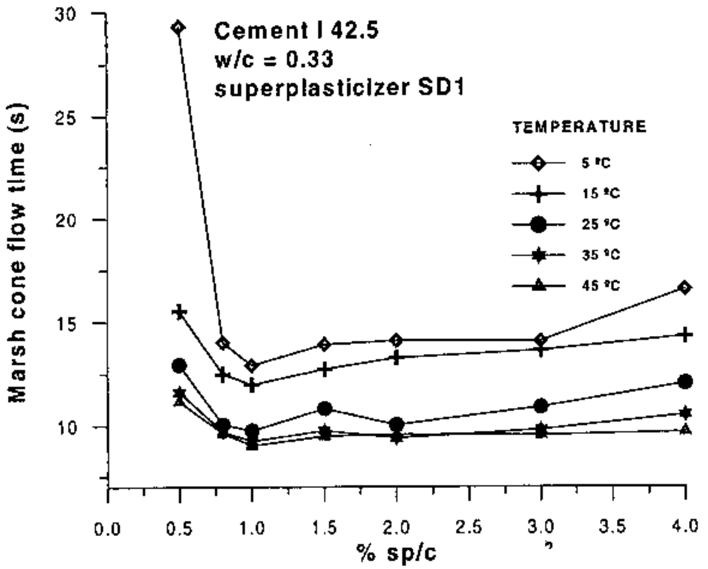

Figure 3. Effect of temperature on flow times

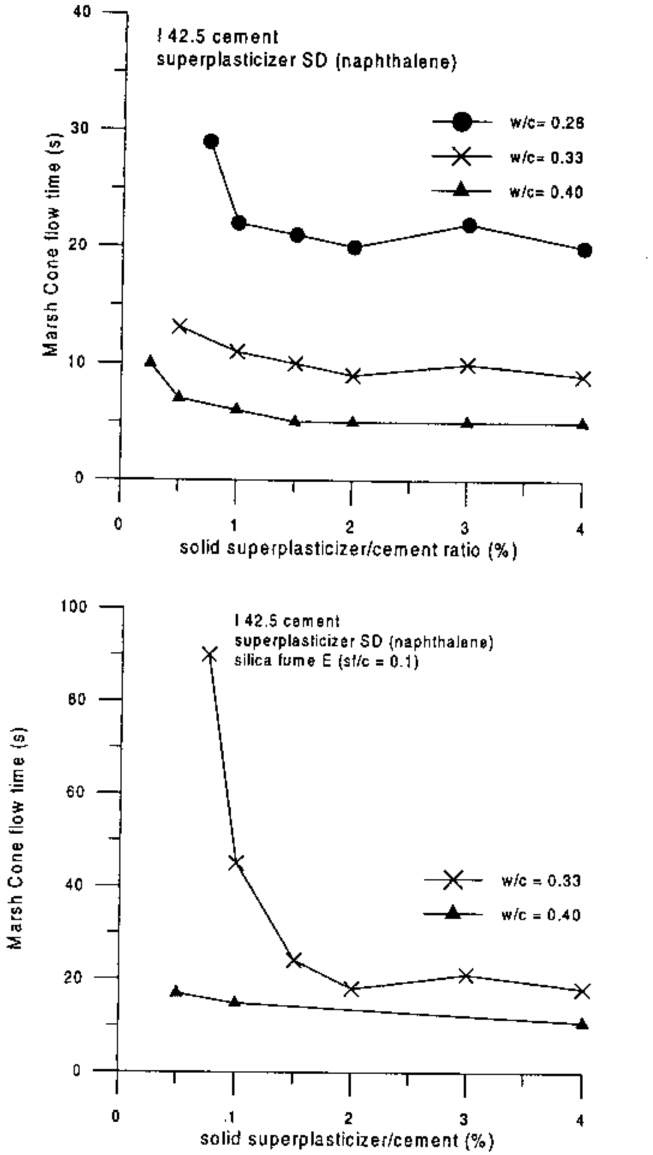

Figure 4. Influence of water/cement ratio on flow time in pastes:
(a) without, and
(b) with silica fume

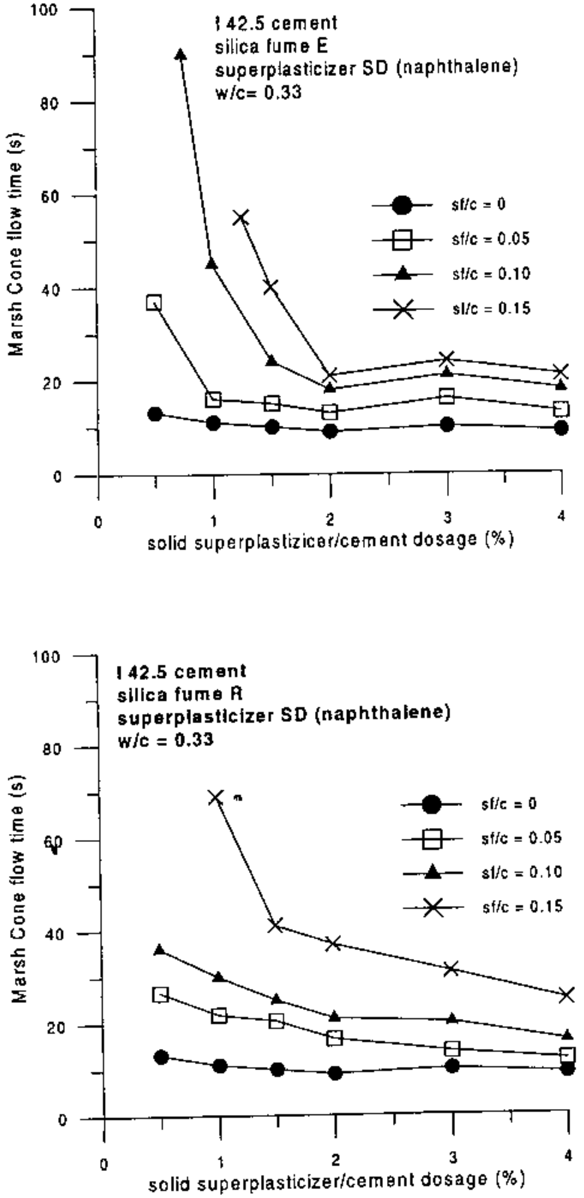

Figure 5. Influence of silica fume addition on flow time: (a) for silica fume E, (b) for silica fume R

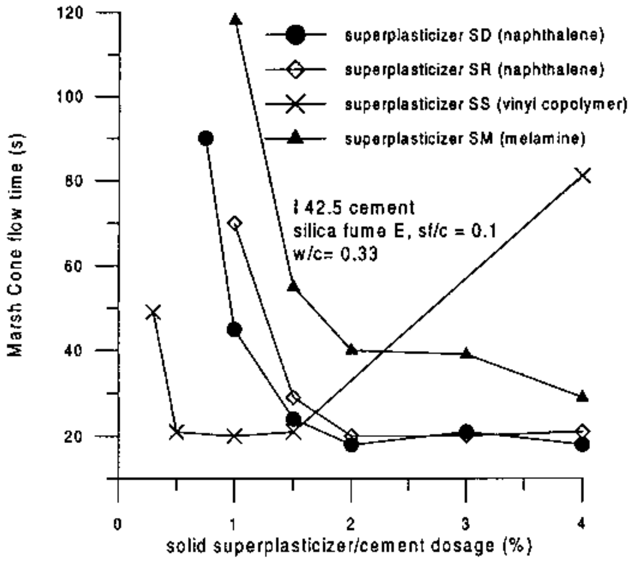

Figure 6. Influence of superplasticizer type on flow times

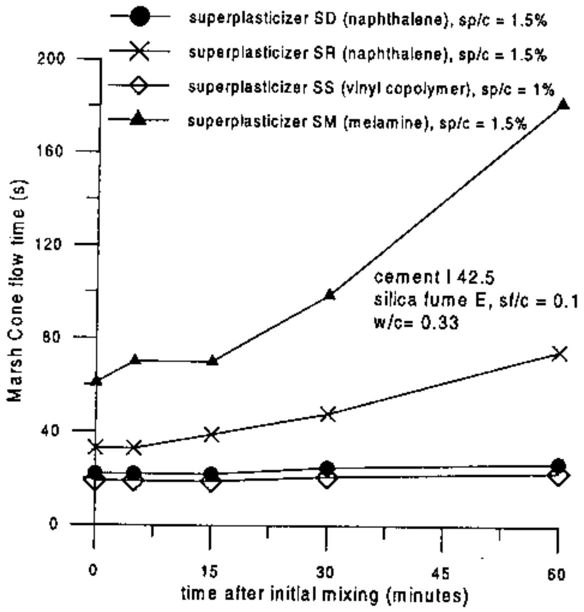

Figure 7. Loss of fluidity with time