Effects of Mixing Sequence on Mortar Consistencies When Using Water-Reducing Agents

G. M. BRUERE, Division of Applied Mineralogy, C.S.I.R.O., Chemical Research Laboratories, Melbourne, Australia

Initial percent flows and rates of loss of flow with time were measured in two series of cement mortars containing various water-reducing and set-retarding agents. In one series, the agents were added with the mix water directly to the dry cement, and in the other, the cement was premixed with water for 5 min before adding the agents. Tests for loss of flow were made following remixing of mortars.

The sequence of adding agents to mortars was shown to have significant effects on initial flows, rates of loss of flow, and the amounts of water reduction possible when using water-reducing agents.

It was found that additions of powdered calcium lignosulphonate to control mortars, several hours after mixing, increased percent flows without greatly affecting setting times. In practice late additions of powdered calcium lignosulphonate could be used to restore the slump of concrete which has started to stiffen in truck mixers. This technique should be preferable to that of adding more water to a mix.

•IT WAS observed by Bruere (2) that cement pastes made by premixing cement and water for a few minutes before adding a set-retarding agent, such as calcium lignosulphonate, had much longer setting times than equivalent pastes made by adding the mix water containing the agent directly to the dry cement. A hypothesis was proposed to explain the mixing sequence effect on the set-retarding action of calcium lignosulphonate. It was based on the observation that the mixing sequence effect was more pronounced with cements with high rather than low tricalcium aluminate contents and on the finding of Blank, Rossington and Weinland (1) that calcium lignosulphonate was much more strongly adsorbed by tricalcium aluminate than by either dicalcium or tricalcium silicate. It was considered that when calcium lignosulphonate was added with the mix water directly to dry cement it would be adsorbed strongly on tricalcium aluminate before any appreciable amount of gypsum had dissolved. This would remove a large amount of lignosulphonate from solution and seriously reduce the amount available to retard the silicate hydration reactions. However, when cement was premixed with water for a few minutes, gypsum would have ample time to dissolve and coat the tricalcium aluminate with calcium sulphoaluminate. When the lignosulphonate was subsequently added to the premixed paste, the tricalcium aluminate would be unable to adsorb it and a large amount of retarder would be available to retard the silicate hydration reactions. As a result, premixed pastes would have longer setting times than non-premixed pastes.

If this hypothesis is correct, then mixing sequence would also be expected to affect the water-reducing and slump-increasing properties of calcium lignosulphonate in concrete, since these properties depend on agent concentration.

This paper describes an investigation of the effects of mixing sequence on both initial consistencies and rates of loss of consistency of mortars containing various water-reducing and set-retarding agents.

TABLE 1

CHEMICAL ANALYSIS AND CALCULATED COMPOUND COMPOSITION OF PORTLAND CEMENT

Oxide	Percent
SiO_2	22.02
Al_2O_3	4.74
Fe_2O_3	3.14
CaO	64.00
MgO	1.20
SO_3	2.28
Total alkalies as Na_2O	1.23
Loss on ignition	1.70
Compound	**Percent**
C_3S	51
C_2S	25
C_3A	7
C_4AF	9

MATERIALS AND EXPERIMENTAL METHODS

The water-reducing and set-retarding agents used were: Calcium lignosulphonate with a low sugar content; "Daxad 15," a technical dispersing agent consisting of sodium salts of polymerized alkyl naphthalene sulphonic acids and containing 85 percent active agent (supplied by W. R. Grace Australia Pty Ltd.); citric acid; sodium gluconate and sodium mucate.

Mortars were made from an ordinary (ASTM Type 1) portland cement and a washed, rounded grain, quartz sand passing 18 BSS mesh and retained on 25 BSS mesh. Cement/aggregate ratios of ½ by weight were used. The chemical analysis and compound composition of the cement are given in Table 1.

A mechanical mixer, described in ASTM Designation C 305-58T, was used to mix mortars by the following methods:

1. The mix water containing the dissolved agent was placed in the mixer bowl; the cement and then the sand were added while mixing at slow speed. The mixer was stopped and any mortar adhering to the sides of the bowl was scraped into the bulk of the mortar. The mortar was allowed to stand for 2 min and finally it was mixed at medium speed for 1 min.
2. About 90 percent of the mix water was added to the mixer bowl and the cement was added while mixing at slow speed. The mixer was stopped and the paste was hand mixed with a spatula for about 30 sec to make it homogeneous. After the cement and water had been in contact for 5 min the paste was mixed at slow speed and the remainder of the mix water, containing the dissolved agent, was added followed by the sand. Then the mortar was mixed at medium speed for 1 min.
3. All of the mix water was added to the mixer bowl, then the cement and sand were added while mixing at slow speed. The mixer was stopped and the sides of the bowl were cleaned. The mortar was allowed to stand for 2 min and was then mixed at medium speed for 1 min. The bowl was covered and the mortar was allowed to stand for various periods of 60, 120, 180 or 240 min, when the powdered admixture was added evenly to the mortar which was then stirred at medium speed for 2 min.

Mortar batches contained 1000 g of cement and 2000 g of sand. Tests showed control mortars mixed by methods 1 and 2 had the same initial percent flows and rates of loss of flow.

Measurements of mortar consistencies were made with a standard flow table (ASTM Designation C 230-57T). Initial percent flows were measured immediately after mixing, and rates of loss of mortar consistency were determined by measuring percent at various times after mixing. In the periods between flow determinations the mortar was kept in the mixer bowl, which was covered to prevent evaporation of water, and just before each flow measurement the mortar was remixed for 30 sec at medium speed to obtain a homogeneous test sample.

Air contents of mortars were measured in a small pressure-type air-meter.

Setting times of cement pastes containing various agents, and made with equal w/c ratios, were measured according to ASTM Designation C 191-58 using an automatic recording cadograph. The pastes were mixed with an electrically driven propeller mixer at 1000 rpm in a 600 ml beaker. The propeller shaft was fitted with a stroboscope and the power supply was controlled by a Variac. This enabled the

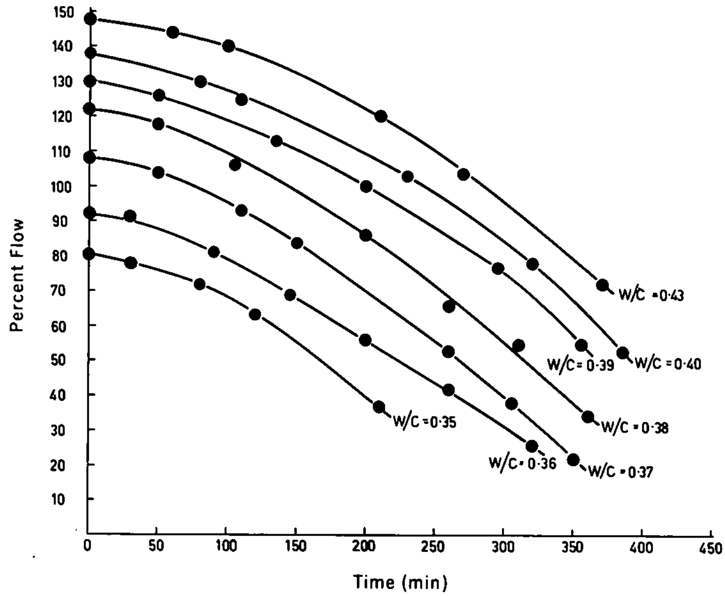

Figure 1. Flow properties of control mortars made with various water/cement ratios.

stirring speed to be kept constant, and the voltage required from the Variac to mix the pastes at constant speed was used as a measure of cement paste fluidity. The following mixing methods were used:

1. The mix water containing the dissolved agent was added to dry cement and the paste was mixed for 6 min.
2. The cement was premixed with 90 percent of the mix water for 5 min. Then the remainder of the mix water, containing the dissolved agent, was added and the paste was mixed for a further 2 min. Control pastes, containing no agent, mixed by methods 1 and 2 were shown to have equal setting times.
3. The same as method 2 except that extended premixing times of 30, 60, 120 and 240 min were used.

All tests were carried out at 20 ± 1½ C.

RESULTS AND DISCUSSION

Most of the data on rates of loss of flow of mortars were obtained at equal w/c ratios (0.36 by wt). However, the data in Figure 1 show variations of flow with time of a series of control mortars made at different w/c ratios. These data can be used to compare rates of loss of flow of mortars containing various agents, with control mortars at equal initial consistencies.

Tables 2 and 3 contain data on the effects of various agents on setting times of cement pastes and air contents of mortars, respectively.

Figures 2 to 5 show the effects of a series of water-reducing and set-retarding agents on initial flows and rates of loss of flow in two series of mortars made with equal w/c ratios, and mixed by methods 1 and 2, respectively. In the rest of this paper these two series will be referred to as non-premixed and premixed mortars.

Figures 2 and 3 show that premixed mortars containing either calcium lignosulphonate or "Daxad 15" had greater initial flows than comparable non-premixed mortars with approximately equal air contents. These effects can be related to the effects of these agents on cement paste fluidity when different mixing sequences are used. It was observed that premixed pastes containing these two agents were more fluid than equivalent non-premixed pastes. Measurements of the voltage input to the electrically driven propeller when mixing pastes at 1000 rpm showed that under equal

TABLE 2

SETTING TIMES OF CEMENT PASTES* CONTAINING VARIOUS WATER-REDUCING AND SET-RETARDING AGENTS

Agent	Concentration (% by wt of cement)	Mixing Sequence	Initial Setting Time (min)	Final Setting Time (min)
None	—	non-premixed	220	400
	—	premixed 5 min	230	410
Calcium lignosulphonate	0.25	non-premixed	390	630
		premixed 5 min	1200	1530
		premixed 30 min	510	780
		premixed 60 min	390	540
		premixed 120 min	330	450
		premixed 240 min	290	400
	0.50	non-premixed	720	960
		premixed 5 min	3180	3500
		premixed 30 min	3000	3500
		premixed 60 min	1680	2050
		premixed 120 min	720	960
		premixed 240 min	400	620
"Daxad 15"	0.25	non-premixed	230	420
		premixed 5 min	270	450
	0.50	non-premixed	280	480
		premixed 5 min	370	510
Citric acid	0.10	non-premixed	600	900
		premixed 5 min	1080	1260
		premixed 30 min	1260	1380
		premixed 60 min	900	1080
		premixed 120 min	600	840
		premixed 240 min	450	600
	0.25	non-premixed	1140	2400
		premixed 5 min	3600	4800
Sodium gluconate	0.10	non-premixed	540	900
		premixed 5 min	2340	2520
Sodium mucate	0.10	non-premixed	600	840
		premixed 5 min	2340	2520

*w/c = 0.35 by wt.

mixing conditions, equal concentrations of the two agents produced approximately equal increases in paste fluidity. However, although these two agents have similar physical effects on paste fluidity they differ significantly in their set-retarding properties. Table 2 shows that calcium lignosulphonate is a strong retarder when used at concentrations above 0.25 percent by weight of cement and is a particularly strong retarder when used under premixing conditions. "Daxad 15," on the other hand, is a weak retarder under all conditions. These considerations indicate that, with these two water-reducing agents, the predominant factor causing increased initial flows of

TABLE 3

AIR CONTENTS OF MORTARS* CONTAINING VARIOUS WATER-REDUCING AND SET-RETARDING AGENTS

Agent	Concentration (% by wt of cement)	Mixing Sequence	Air Content (% by vol)
None	—	non-premixed	6.0
	—	premixed 5 min	6.1
Calcium lignosulphonate	0.25	non-premixed	14.0
		premixed 5 min	15.8
		premixed 60 min	15.0
		premixed 120 min	14.5
		premixed 180 min	12.0
		premixed 240 min	9.0
	0.50	non-premixed	24.5
		premixed 5 min	24.0
		premixed 240 min	18.0
Calcium lignosulphonate + tributyl phosphate	0.50	premixed 5 min	4.2
		premixed 240 min	5.0
"Daxad 15"	0.25	non-premixed	12.5
		premixed 5 min	14.5
	0.50	non-premixed	12.0
		premixed 5 min	8.5

*w/c = 0.36 by wt; cement/aggregate = ½ by wt.
Note: Citric acid, sodium gluconate and sodium mucate entrained no air in mortars.

premixed compared with non-premixed mortars is the increased paste fluidity produced when the agent is used under premixing conditions rather than any effect on set-retardation caused by premixing.

Comparison of the flow data in Figures 2 and 3 with the setting data in Table 2 indicates that the rates of loss of flow of mortars can be reduced by a water-reducing agent only when the agent also has strong set-retarding properties. For example, under all conditions "Daxad 15" produced equal or increased rates of loss of flow compared with control mortars. However, calcium lignosulphonate, used at a high concentration (0.50 percent by wt of cement) and under premixing conditions so that it had strong set-retarding properties, was able to reduce rates of loss of flow of mortars significantly. In contrast to this behavior, calcium chloride, a set-accelerator, increases the rate of loss of flow greatly.

Some mortars were mixed with calcium lignosulphonate and "Daxad 15" in the presence of a small amount of tributyl phosphate to inhibit air-entrainment. Comparison of the flow properties of these mortars with those of corresponding mortars containing air showed that the presence of air had very little effect on either initial flows or rates of loss of flow. An example of the effect of air can be seen by comparing curves 5 and 7 in Figure 2. The mortars used in these tests were very workable since they were cement-rich and were made with a rounded-grain sand. Entrained air in the presence of water-reducing agents probably would have more significant effects on flow properties of lean mortars or mortars made with sharp sands than in the mortars used in these studies.

The data in Figures 4 and 5 show that the effects of mixing sequence on initial flow of mortars containing hydroxy carboxylic acids or their salts are in reverse order to the effects found in mortars containing either calcium lignosulphonate or "Daxad 15."

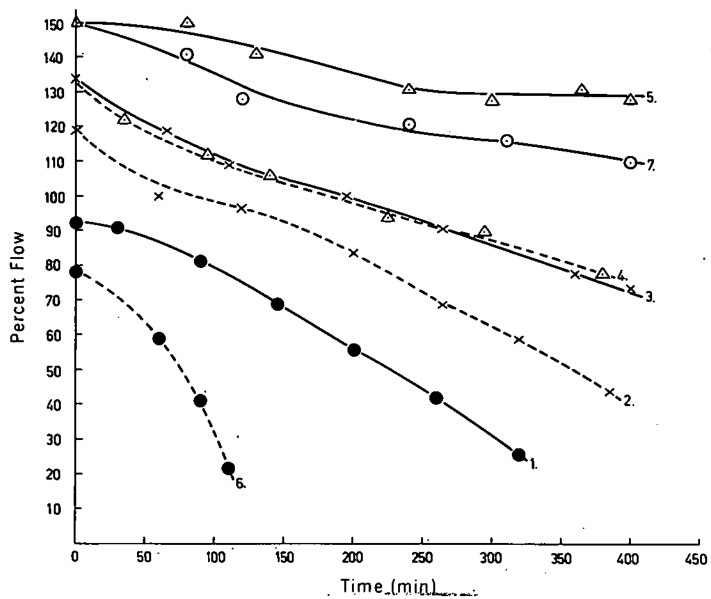

Figure 2. Flow properties of mortars containing various agents (w/c = 0.36 by wt). Agents and mixing conditions: (1) control mortar; (2) calcium lignosulphonate, 0.25 percent by wt of cement, non-premixed; (3) calcium lignosulphonate, 0.25 percent by wt of cement, premixed 5 min; (4) calcium lignosulphonate, 0.50 percent by wt of cement, non-premixed; (5) calcium lignosulphonate, 0.50 percent by wt of cement, premixed 5 min; (6) calcium chloride, 2.0 percent by wt of cement; (7) calcium lignosulphonate, 0.50 percent by wt of cement, plus tributyl phosphate, premixed 5 min.

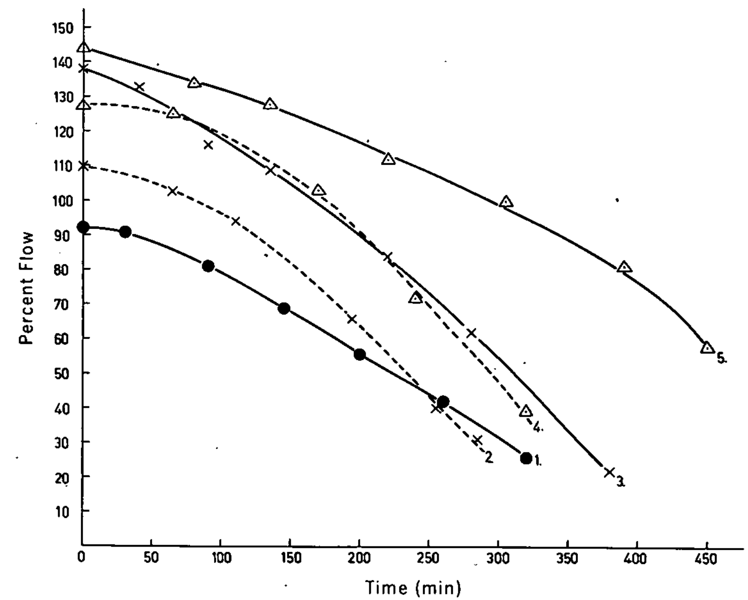

Figure 3. Flow properties of mortars containing "Daxad 15" (w/c = 0.36 by wt). Agents and mixing conditions: (1) control mortar; (2) "Daxad 15," 0.25 percent by wt of cement, non-premixed; (3) "Daxad 15," 0.25 percent by wt of cement, premixed 5 min; (4) "Daxad 15," 0.50 percent by wt of cement, non-premixed; (5) "Daxad 15," 0.50 percent by wt of cement, premixed 5 min.

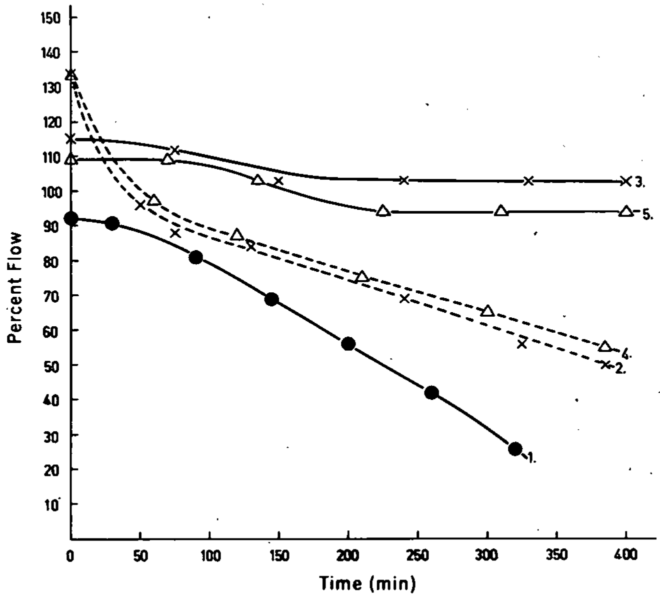

Figure 4. Flow properties of mortars containing sodium gluconate and sodium mucate (w/c = 0.36 by wt). Agents and mixing conditions: (1) control mortar; (2) sodium mucate, 0.10 percent by wt of cement, non-premixed; (3) sodium mucate, 0.10 percent by wt of cement, premixed 5 min; (4) sodium gluconate, 0.10 percent by wt of cement, non-premixed; (5) sodium gluconate, 0.10 percent by wt of cement, premixed 5 min.

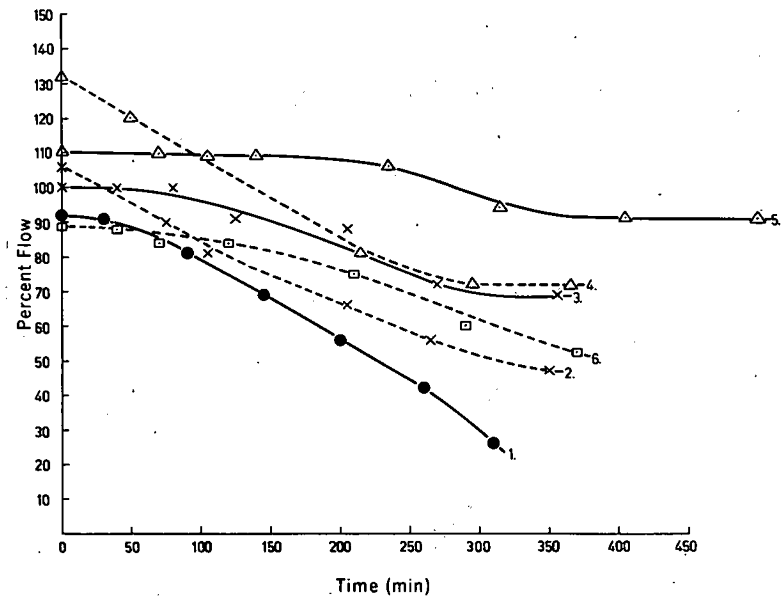

Figure 5. Flow properties of mortars containing citric acid (w/c = 0.36 by wt). Agents and mixing conditions: (1) control mortar; (2) citric acid, 0.10 percent by wt of cement, non-premixed; (3) citric acid, 0.10 percent by wt of cement, premixed 5 min; (4) citric acid, 0.25 percent by wt of cement, non-premixed; (5) citric acid, 0.25 percent by wt of cement, premixed 5 min; (6) sucrose, 0.10 percent by wt of cement, non-premixed.

Non-premixed mortars containing hydroxy carboxylic acids have greater initial flows than comparable premixed mortars. However, despite the increases in initial flows, the rates of loss of flow of non-premixed mortars containing hydroxy carboxylic acids are much greater than in control mortars for the first hour after mixing. At later stages the rate of loss of flow is constant and a little less than in control mortars. Premixed mortars containing hydroxy carboxylic acids were severely retarded and exhibited a very slow rate of flow loss. This behavior, which is similar to that observed with calcium lignosulphonate, confirms that addition of water-reducing agents can reduce rates of loss of flow of mortars only when the agents also act as strong set-retarders.

Figure 6 summarizes the flow properties of mortars made with equal initial consistencies and containing various water-reducing agents. During the first 1 to 1½ hr after mixing, the rates of loss of flow of mortars containing agents are either the same as or greater than the rate of the control mortar. However, rates of loss of flow at periods later than 1½ hr after mixing are reduced when the agent causes severe set-retardation. It can also be seen from Figure 6 that mixing sequence has significant effects on the amount of water reduction possible with the various water-reducing agents studied.

Some interesting effects on flow properties were observed when calcium lignosulphonate powder was mixed into control mortars at varying times after initial mixing (mixing method 3). Figure 7 shows that 0.25 percent calcium lignosulphonate (by wt of cement), added at 1, 2, 3 and 4 hr after mixing, instantly increases percent flows of mortars from 90 to 150, 75 to 128, 60 to 105, and 46 to 78, respectively. These late additions of calcium lignosulphonate entrain progressively less air in mortars as the delay in addition increases. Curves 2 and 3 (Fig. 7) show the increases in percent flows of mortars obtained when 0.50 percent by weight of cement of calcium lignosulphonate is added both by itself, and in conjunction with a small amount of tributyl phosphate to inhibit air-entrainment. These additions were made 4 hr after initial mixing. A comparison of curves 2 and 3 indicates that the paste fluidizing effect of calcium lignosulphonate, in the absence of entrained air, is responsible for about ⅔ of the total increase in flow produced by the agent plus 18 percent of entrained air. Curves 2 and 3 also show that entrained air has no effect on the subsequent rate of loss of flow of a mortar containing calcium lignosulphonate.

An addition of 0.10 percent (by wt of cement) of citric acid 4 hr after mixing produces a comparatively small increase in flow. However, it does reduce the rate of loss of flow for about 2½ hr (curve 4, Fig. 7).

Curves 9 and 5 (Fig. 7) show that an addition of 0.25 percent of powdered calcium lignosulphonate 4 hr after mixing increases the percent flow of a mortar by about the same amount as that obtained by adding a quantity of water equivalent to 12 percent of the original mix water.

The setting data in Table 2 show that as the time interval between initial mixing of a paste and adding powdered calcium lignosulphonate increases, setting times increase rapidly at first and then decrease. Pastes containing 0.25 percent and 0.50 percent calcium lignosulphonate added at 1 hr and 4 hr after mixing, respectively, have setting times which are not much greater than those of control pastes. Similar effects were obtained with citric acid. These effects indicate that when cement hydration reactions have progressed beyond a certain stage, additions of set-retarding agents are unable to do more than slightly retard setting times. Consequently, late additions of calcium lignosulphonate do not decrease rates of loss of flow of mortars compared with those of control mortars.

Since late additions of powdered calcium lignosulphonate increase flows of mortars without prolonging setting times unduly, it should be possible in practice to use late additions of this agent for restoring the slump of concrete which has started to stiffen in truck mixers or agitators after a long haul. Restoration of slump could be achieved with only small effects on setting times by using predetermined quantities of the powdered agent. A small amount of an agent such as tributyl phosphate could be used in conjunction with the lignosulphonate to inhibit air-entrainment. This technique of restoring workability should be preferable to that of adding more water to a mix.

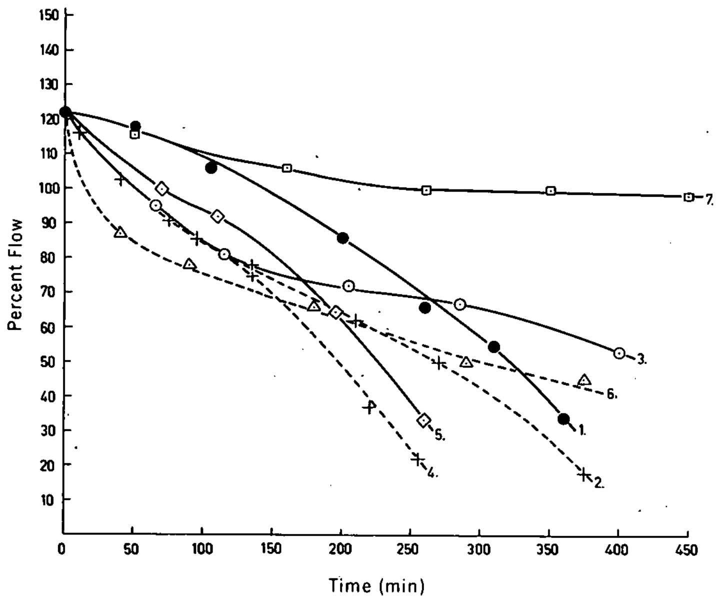

Figure 6. Flow properties of mortars containing various agents and made with equal initial percent flows. Agents, mixing conditions, water/cement ratios, and air contents: (1) control mortar, w/c = 0.38 by wt, percent air = 4.5; (2) calcium lignosulphonate, 0.25 percent by wt of cement, non-premixed, w/c = 0.34 by wt, percent air = 12.0; (3) calcium lignosulphonate, 0.25 percent by wt of cement, premixed 5 min, w/c = 0.325 by wt, percent air = 13.0; (4) "Daxad 15," 0.25 percent by wt of cement, non-premixed, w/c = 0.345 by wt, percent air = 11.5; (5) "Daxad 15," 0.25 percent by wt of cement, premixed 5 min, w/c = 0.325 by wt, percent air = 13.5; (6) sodium gluconate, 0.10 percent by wt of cement, non-premixed, w/c = 0.33 by wt, percent air = 4.6; (7) sodium gluconate, 0.10 percent by wt of cement, premixed 5 min, w/c = 0.335 by wt, percent air = 4.6.

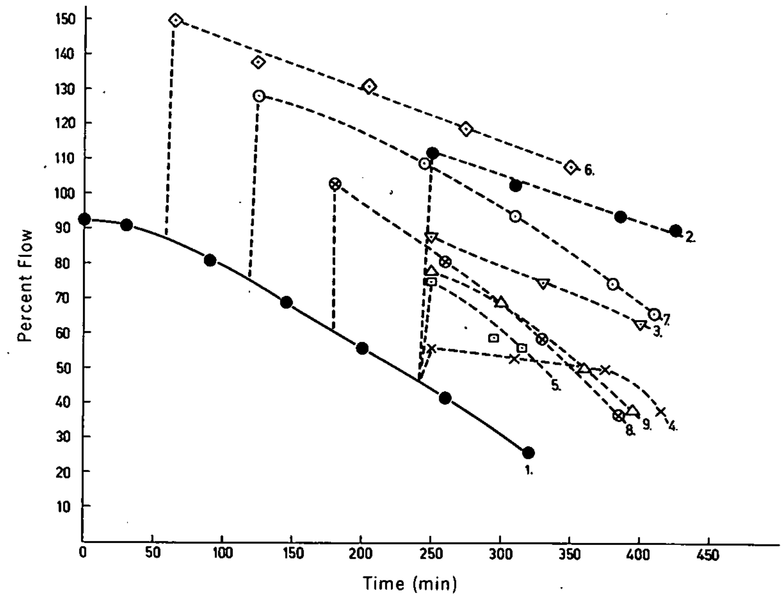

Figure 7. Flow properties of mortars containing late additions of various agents (w/c = 0.36 by wt). Agents and time of addition after initial mixing: (1) control mortar; (2) calcium lignosulphonate powder, 0.50 percent by wt of cement, added after 4 hr; (3) calcium lignosulphonate powder, 0.50 percent by wt of cement, plus tributyl phosphate, added after 4 hr; (4) citric acid powder, 0.10 percent by wt of cement, added after 4 hr; (5) extra water equivalent to 12 percent of original mix water, added after 4 hr; (6) calcium lignosulphonate powder, 0.25 percent by wt of cement, added after 1 hr; (7) calcium lignosulphonate powder, 0.25 percent by wt of cement, added after 2 hr; (8) calcium lignosulphonate powder, 0.25 percent by wt of cement, added after 3 hr; (9) calcium lignosulphonate powder, 0.25 percent by wt of cement, added after 4 hr.

CONCLUSIONS

1. The sequence of adding water-reducing and set-retarding agents to mortars has significant effects on initial flows, rates of loss of flow, and amounts of water-reduction possible with these agents.

2. Severe set-retardation is necessary for retention of flow of mortars.

3. Late additions of calcium lignosulphonate will restore the flow of mortars which have started to stiffen without prolonging setting times unduly.

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