
PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Effect of Acid Additives on the Placeability and Strength Properties of Plasticized Portland Cement Systems

N. Kh. Belous, V. D. Koshevar, and T. E. Kreer

Institute of General and Inorganic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus

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Abstract—Effect of various kinds of acids on the flowability and the flowability preservation time of plasticized cement-sand formulations and on the strength properties of the resulting materials was studied.

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In recent years, new types of superplasticizers (SP) based on modified polycarboxylates have been widely used in monolithic building. These SPs markedly diminish the water demand of portland cement systems and improve the placeability and grade strength of concretes [1, 2]. A disadvantage of some of these SPs is the short time of flowability preservation and rapid loss of placeability by building mortars and concrete mixtures. Meanwhile, obtaining formulations with a prolonged spreadable life is an important problem, which is especially pressing in construction of mass structures from monolithic concrete at remote sites and in working in summertime, when the setting and hardening of portland cement system are markedly accelerated.

To make longer the time during which the flowability of plasticized formulations is preserved, hardening retarders are introduced into the polycarboxylate plasticizer. The efficiency of these retarders is determined by the kind and content of a cement, amount of plasticizer in the systems, and order in which additives are introduced into concrete mixtures [3].

It is known that carboxylic and hydrocarboxylic acids can be used as additives that make longer the spreadable life of mortar and concrete mixtures [4]. Acids behave in portland cement systems differently by making either longer or shorter the induction period, which, in the end, reflects on the flowability preservation time of mixtures [4, 5]. To main processes occurring upon introduction of acids as hardening retarders into a nonplasticized portland cement system can be attributed their adsorption on

the surface of particles of starting cements and hydrate formations, appearance of numerous complex compounds with varied stability, and chemical interaction with calcium hydroxide, to give difficultly soluble calcium salts, and with components of the cement clinker [5, 6].

According to the data of [4], the complexation is not the main reason for the retarding action of most of organic acids because of the low stability constants of the complex systems being formed. The efficiency of organic acids in portland cement systems is occasionally quantitatively characterized by their dissociation constants, which are functions of their molecular structure [2]. However, no unambiguous conclusion about the behavior of an acid additive can be made solely on the basis of these values for a particular system, because also important are the solubility of the calcium salts being formed, amount of the additives, and mineralogical composition of a cement [2]. It is especially difficult to prognosticate the behavior of acid additives in concrete mixtures plasticized with polycarboxylate superplasticizers because of the strong influence exerted by the composition of the cement and fillers on the reproducibility of the technological properties of these mixtures [7]. Most of retarders have a competitive effect on the adsorption of a plasticizer on particles of clinker and new formations, which can impair the efficiency of these and other additives and hinder their compatibility with each other and with cements of various mineralogical compositions.

The aim of this study was to examine the possibility of using acids of various compositions as flowability

loss retarders in portland cement systems modified with polycarboxylate superplasticizers.

EXPERIMENTAL

Acids whose use in portland cement formulations has been known previously were studied. These acids contain carboxy, aromatic, and sulfo groups and groups of alcoholic hydroxyls and differ in dissociation constants [2]. In particular, citric, tartaric, succinic, sulfosalicylic, naphthalenesulfonic, maleic, and boric acids of pure grade, widely represented on the CIS market, were used. The acids were introduced into plasticized building mortars in amounts of 0.05–0.1% relative to the cement mass. As polycarboxylate superplasticizers served Stachement-2000 (Czech Republic) and Socalan HP 80 (Germany), derivatives of polyacrylic acid and a polyhydroxycarboxylic acid, respectively. The superplasticizers differ in the anionic charge density in the backbone and have limiting values of the plasticization coefficients in the given system (0.35 and 0.4, respectively) [8]. The water-to-cement (w/c) ratio in the cement-sand mixtures was varied within the range 0.27–0.3.

The experiment was performed using cement-sand mixtures at a cement : sand ratio of 1 : 1.5 and domestic cement of M500 D0 brand, manufactured by Krasnosel'stroy Open Joint-Stock Company in conformity with GOST (State Standard) 10178–85). The mineralogical composition of the cement was the following (wt %): C₃S 58.6, C₂S 18.9, C₃A 5.7, C₄AF 13.5, secondary phases 3.3. The specific surface area of the cement was 316 m² kg^{−1}, and the normal thickness coefficient, 0.248 (the coefficient was determined by the procedure recommended by GOST 310.3, and the specific surface area of the cement and finely grained filler, in conformity with GOST 310.2).

Sand of P2 brand (Krapuzhino sandpit, Logoiskii district) had a fineness modulus of 2.2, average grain density of 2650 kg m^{−3}, density in vibration-densified state of 1746 kg m^{−3}, and specific surface area of 8.9 m² kg^{−1}. The cement-sand mixture prepared in the study also contained a 0.16-mm sand fraction. Prior to being used, the sand was dried to constant weight and sieved. Before being introduced into the cement-sand mixture, the acids were fully dissolved in the mixing water. The choice of this way to introduce the acids was governed by the results of preliminary experiments, which demonstrated that addition of retarders to partly

hydrated and plasticized formulations diminishes the technological effect and impairs the strength properties of the concretes obtained.

The flowability of freshly prepared formulations and its variation with time were determined in accordance with GOST 10181–2000 immediately after the mixing and at time intervals of 30 min.

In parallel with determination of the flowability of cement-sand mixtures on a Rheotest-2 rotation viscometer, the rheological properties of control and additive-containing samples of the cement paste were examined [9]. The measurements were made at shear rate gradients of 0.5–437 s^{−1}, using a cylinder S₂ with a wedge-shaped slit angle $r/R = 0.94$. The cement paste was mixed manually for 10 min (w/c = 0.2–0.21) and then 30 ml of the paste was poured into a measuring cylinder and, in 2 min, measurements were commenced in the prescribed range of shear rates. For each value of the deformation rate D_r (s^{−1}), the created shear stress τ (Pa) and the dynamic viscosity of the resulting systems were calculated. After the maximum deformation rate was reached (437 s^{−1}), it was lowered in steps to the minimum value, which corresponded to the reverse run of rheograms. The area between the curves corresponding to the forward and reverse runs of the rheograms (hysteresis loop) characterizes the thixotropic properties of the rheological system under study. The kinetics of structuring of the cement paste was examined using each time its new portions taken from the originally prepared amount (500 ml), which was stored in a thermostat at a temperature 20°C and relative air humidity 80–90%.

The electrophoresis method with a Zetaphorometer-1Y microelectrophorometer (France) was used to determine the electrophoretic mobility of particles of cement and new formations in cement suspensions strongly diluted with distilled water (w/c = 200) without additives and in the presence of plasticizers and various acids. The Smoluchowski equation was used to calculate ζ -potentials [10].

Also, an X-ray phase analysis of the starting crystalline phases of cement and products of its hydration was made in various stages of hardening of the cement paste (DRON-4.0 diffractometer, Cu_{K α} radiation, Powder software package).

Cubic samples (7 × 7 × 7 cm) were formed from the cement-sand mixture, hardened under normal-humidity conditions (temperature 20–25°C, relative air humidity 85–95%), and strength-tested in the time interval of up

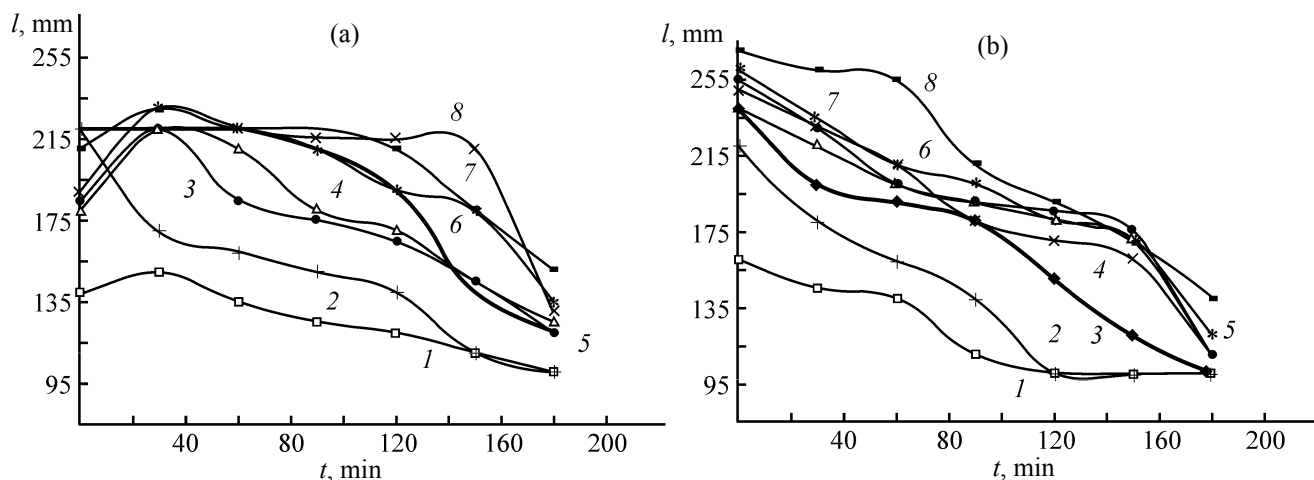


Fig. 1. Variation with time t of the flowability l of cement-sand mixtures plasticized with 0.3% (a) Stachement-2000 ($w/c = 0.3$) and (b) Socalan HP 80 ($w/c = 0.27$). (a) (5) Without retarder; with addition of 0.05% acid: (1) citric, (2) maleic, (3) tartaric, (4) sulfosalicylic, (6) naphthalenesulfonic, (7) succinic, and (8) boric. (b) (3) with addition of 0.1% acid: (1) citric, (2) maleic, (3) tartaric, (4) sulfosalicylic, (6) naphthalenesulfonic, (7) succinic, and (8) boric.

to 28 days in conformity with GOST 10180–90.

To elucidate the mechanism by which superplasticizers and acid additives affect the portland cement paste, the ζ -potentials of cement and products of its treatment with SPs and above-mentioned acids were determined. It was found that the starting cement is characterized by a low negative ζ -potential of -6.5 mV and, upon introduction of Socalan HP-80 and Stachement-2000 superplasticizers, it increases to -3.5 and -4.5 mV, respectively, i.e., changes insignificantly. This result does not contradict the data of [4], according to which, the role of the ζ -potential in the mechanism of plasticization of formulations containing polycarboxylate SPs is not too important, with a larger contribution made by the steric effect of the 2D and 3D SP molecules. Introduction of most of chelate-forming acid additives to the plasticized system and their competitive adsorption on the surface of cement particles impart to these particles an additional negative potential, equal to $-10 \dots -11$ mV for M500 D0 cement.

It was found that, for control samples of cement-sand mixtures containing a Stachement-2000 polyacrylic superplasticizer, a rather fast thinning is observed (Fig. 1a) as a result of the unhampered adsorption of SPs on particles of clinker and new formations. These samples characteristically preserve their flowability for a long time, even 120 min after the mixing, the loss of flowability does not exceed 10%.

A preliminary optimization of the content of acids with respect to their retarding effect in plasticized cement-sand systems containing Stachement-2000 demonstrated that

the threshold concentration of the acid additives introduced is 0.05% relative to the cement mass. Even at these minor amounts, the initial flowability of the mixtures decreased for many formulations relative to control samples, which is presumably due to the competitive adsorption of acids and SPs on the cement surface. With citric and maleic acids, the plasticizing effect of the superplasticizer is fully blocked (Fig. 1a), which points to incompatibility of these additives with the superplasticizer used. A characteristic feature of this system is that, in mixtures with addition of tartaric, sulfosalicylic, naphthalenesulfonic, and boric acids, their flowability exceeds, already 30 min after the mixing, that of the control samples (Fig. 1a; curves 3, 4, and 6–8). For most of the acid additives used, the dissociation constants vary within the pK range 2.8–4.2 [11]; the acids are characterized by low retarding effect: in 2.5 h after the mixing it was 3–20% (Fig. 1a). The most pronounced retarding effect was observed in this system for boric acid (pK 9.24) (Fig. 1a, curve 8): the increase in the time of flowability preservation was approximately 58% in 2.5 h after the mixing.

However, comparison of the dissociation constants of tartaric and citric acids (pK 3.04 and 3.07, respectively) and of the solubility products of the calcium salts formed in this case shows that it is impossible to make tentative conclusions about the behavior of an additive in a particular portland cement system. Probably, the retarding effect and the technological properties of the materials obtained is affected to a greater extent by the presence of a particular polycarboxylate superplasticizer.

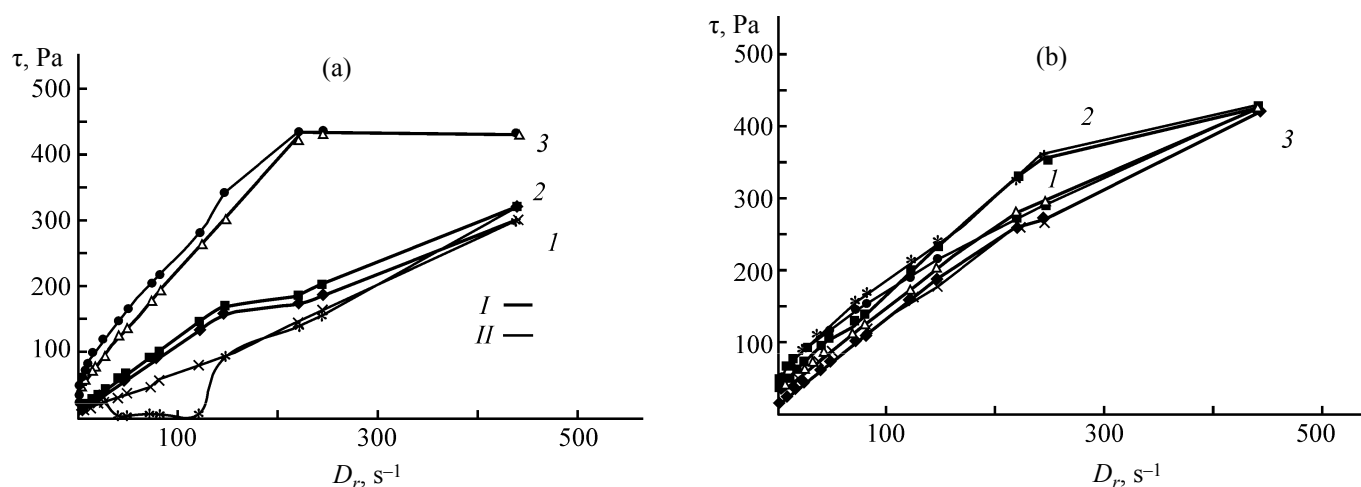


Fig. 2. Rheograms of a cement paste plasticized with Stachement-2000 (a) without a retarder and (b) with addition of 0.05% boric acid (I) 10, (2) 60, and (3) 120 min after the mixing. Run of rheograms: (I) forward and (II) reverse. (τ) Shear stress and (D_r) deformation rate.

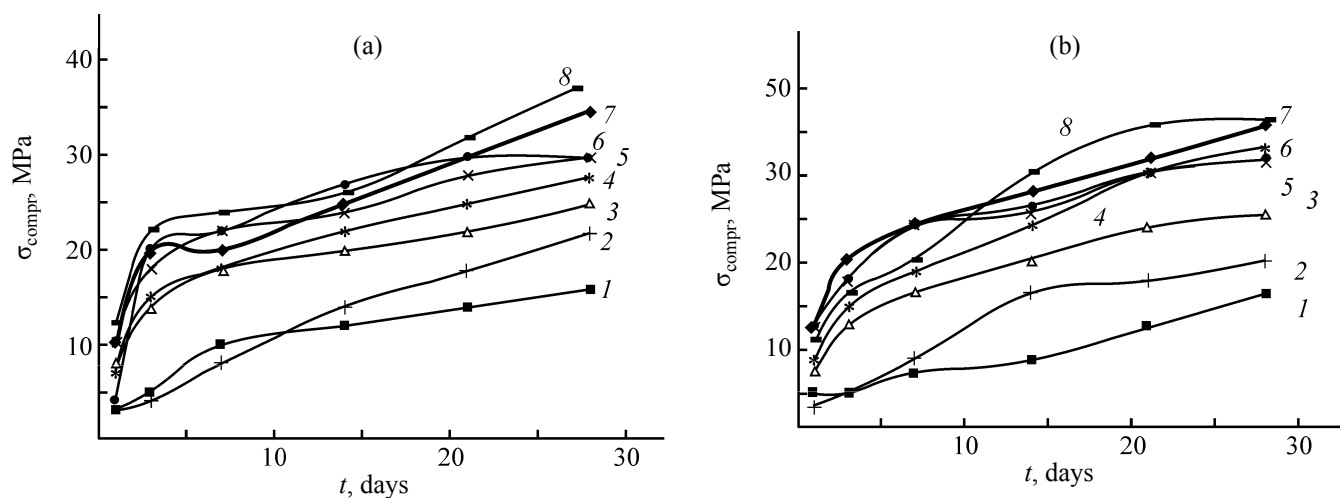


Fig. 3. Kinetic curves of the rise in the strength σ_{compr} of finely grained concretes based on M500 D0 cement and plasticized with 0.3% (a) Stachement-2000 ($w/c = 0.3$) and (b) Socalan HP 80 ($w/c = 0.27$). (t) Hardening time. (a) (7) Without retarder; with addition of 0.05% acid: (1) citric, (2) maleic, (3) tartaric, (4) succinic, (5) sulfosalicylic, (6) naphthalenesulfonic, and (8) boric. (b) (7) with addition of 0.1% acid: (1) citric, (2) maleic, (3) tartaric, (4) succinic, (5) sulfosalicylic, (6) naphthalenesulfonic, and (8) boric.

A more pronounced plasticizing effect resulting from the high activity of the additive is observed for systems containing the Socalan HP 80 superplasticizer (Fig. 1b). However, the plasticizing effect of the additive is preserved for this type of cement for only a short time: in 120 min, the loss of the initial flowability in the system is 35%. In contrast to the first system, introduction of acids is accompanied in this case by a rise in the flowability of cement-sand mixtures, compared with control samples (Fig. 1b, curves 4–8). This means that, even at a content of 0.1% relative to the cement mass, presence of acids provides an additional plasticizing effect. As also in the first case, the exception are citric and maleic acids, whose introduction reduces the plasticizing effect of the

given superplasticizer. An increase in flowability is not characteristic of the system containing the Socalan HP 80 superplasticizer, in contrast to that observed 30 min after the mixing in mixtures plasticized with Stachement-2000.

It follows from Figs. 1a and 1b that the strongest retarding effect in both polycarboxylate SPs is exhibited by the boric acid additive. Upon introduction of this acid into cement-sand mixtures plasticized with Socalan HP 80 the time of flowability preservation 2.5 after the mixing increases by approximately 50%.

Figure 2 shows rheograms of a cement paste plasticized with Stachement-2000 (Fig. 2a) and a paste

containing the SP and a boric acid additive (Fig. 2b). The rheograms of the control samples suggest that, already in 60 min after the mixing (Fig. 2a), comparatively strong coagulation-thixotropic disperse structures with a yield strength of 25 Pa are formed in the paste. As the keeping time is raised to 120 min, a strengthening of the structures was observed, with an increase in the thixotropy and in the yield strength to 50 Pa.

For the freshly prepared plasticized paste containing a boric acid additive, an increase in the deformation rate leads to a stronger rise in the shear stresses (Fig. 2b, curve 1), which points to a certain decrease in the flowability and increase in the viscosity of the paste. Further, as the keeping time is raised from 10 to 120 min, the process of structuring is substantially decelerated and the yield strength of the cement paste decreases to 15 Pa (Fig. 2b, curve 3).

On passing from higher to lower shear rates, a hysteresis is observed for all the systems under study as a result of the restoration of the preliminarily disintegrated structure of the cement paste. Comparison of full rheograms shows that the cement paste containing a boric acid additive is characterized by a narrower hysteresis loop, which indicates that the thixotropic properties of the rheological system become poorer (Fig. 2b). It should be noted that the results of the rheological studies (Figs. 2a and 2b) performed on a rotation viscometer are correlated with the earlier presented evaluation data on the flowability of cement-sand mixtures obtained using a cone (Figs. 1a, 1b).

It is known [12] that adsorption layers formed by additives can diminish the interaction energy of the cement and new formations, which results in a decrease in the strength of coagulation structures formed in early stages of hardening. It follows from the data obtained (Fig. 3a, curve 8) that use of boric acid to improve the preservation of the initial flowability in a system containing Stachement-2000 has nearly no effect on the strength parameters of hardened materials during the entire period of hardening. In contrast to these data, introduction of the same additive into mixtures plasticized with Socalan HP 80 reduces the strength in early stages of hardening of the materials (Fig. 3b, curve 8). However, later, when the effect of the additive on the hydration process becomes weaker, an abrupt rise in the strength of the structure is observed, with the strength parameters even exceeding those of the control formulations (Fig. 3b). A possible reason for the last

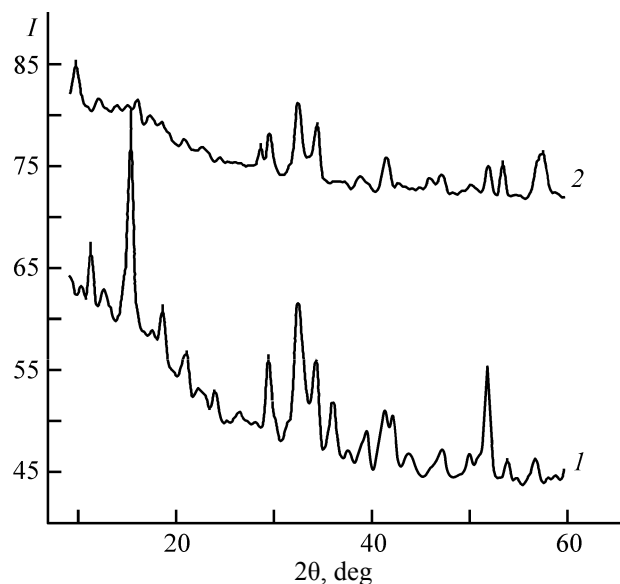


Fig. 4. X-ray diffraction patterns of a cement paste containing the Socalan superplasticizer (1) without a retarder and (2) with addition of 0.05% boric acid. Hardening time 14 days. (I) Intensity and (2θ) Bragg angle.

fact is that a denser homogeneous structure with poorly crystallized new formations is produced in slow hydration of the cement, which is confirmed by the results of an X-ray phase analysis (Fig. 4).

CONCLUSIONS

(1) The effect of addition of citric, tartaric, succinic, sulfosalicylic, naphthalenesulfonic, maleic, and boric acids on the flowability and flowability preservation time of cement-sand mixtures plasticized with polycarboxylate suspension was studied. The strongest retarding effect was observed upon introduction of boric acid into cement-sand formulations, whereas citric and maleic acids block the plasticizing effect of the polycarboxylate additives.

(2) The rheological properties of a cement paste containing polycarboxylate superplasticizers and boric acid were studied on a rotation viscometer under a mechanical shear load in the early stage of hardening. It was found that introduction of boric acid makes it possible to retard the process of formation of poorly flowable coagulation-thixotropic structures in portland cement systems.

(3) It was demonstrated that use of boric acid as a retarder of flowability loss in concretes plasticized with Stachement-2000 can improve their strength characteristics during the entire hardening period, and

in systems containing Socalan HP 80, in later stages of hardening (after 14 days).

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