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Effect of several additives and their admixtures on the physico-chemical properties of a calcium phosphate cement

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Combinations of citrate ($C_6H_5O_7^{3-}$), pyrophosphate ($P_2O_7^{4-}$) and sulfate (SO_4^{2-}) ions were used to modify the physico-chemical properties of a calcium phosphate cement (CPC) composed of β-tricalcium phosphate (β-TCP) and phosphoric acid (PA) solution. The results obtained with only one additive at a time are similar to those previously published. New facts are: the positive effect of $C_6H_5O_7^{3-}$ ions on cement failure strain and their negative effect on cement pH. The position of the setting time maximum measured at an SO_4^{2-} concentration of 0.09 M was not displaced by the addition of $C_6H_5O_7^{3-}$ and $P_2O_7^{4-}$ ions. However, the effect of SO_4^{2-} ions on the setting time was depressed by $C_6H_5O_7^{3-}$ ions. Moreover, no increase in tensile strength was observed when increasing amounts of SO_4^{2-} were added into a $C_6H_5O_7^{3-}$-containing cement. The latter results suggest a competitive effect of $C_6H_5O_7^{3-}$ and SO_4^{2-} on setting time and tensile strength. Anhydrous dicalcium phosphate (DCP; $CaHPO_4$) appeared in cement samples dried just after setting, but not in cement samples incubated for 24 h in deionized water before the drying step. It is believed that the setting reaction is stopped by the drying step, leaving a low internal pH in the sample, hence providing favorable conditions for the transformation of dicalcium phosphate dihydrate (DCPD) into DCP. Interestingly, even though $C_6H_5O_7^{3-}$ ions dramatically lowered the equilibrium pH of the cement with 5 ml of deionized water, they still prevented the occurrence of the transformation of DCPD into DCP.

1. Introduction

Calcium phosphate cements made of β-tricalcium phosphate powder [β-$Ca_3(PO_4)_2$; β-TCP] and phosphoric acid (PA) aqueous solutions have a short setting time (ST, 1–2 min) and a low tensile strength (TS, < 2 MPa) [1]. In a previous study [2], the addition of sulfate (SO_4^{2-}), citrate ($C_6H_5O_7^{3-}$) and pyrophosphate ($P_2O_7^{4-}$) ions was proposed to increase ST and TS of this cement composition. All three additives increased ST. Their effectiveness at increasing ST was in the order $P_2O_7^{4-} > C_6H_5O_7^{3-} > SO_4^{2-}$. The effect of SO_4^{2-} on ST increased up to 0.1 M. Beyond that concentration, gypsum crystals [calcium sulfate dihydrate (CSD), $CaSO_4 \cdot 2H_2O$] were believed to appear, acting as nuclei for the growth of brushite crystals [dicalcium phosphate dihydrate (DCPD), $CaHPO_4 \cdot 2H_2O$], which is the product of the setting reaction [1]

$$\beta\text{-}Ca_3(PO_4)_2 + H_3PO_4 + 6H_2O \rightarrow 3CaHPO_4 \cdot 2H_2O \quad (1)$$

The nucleation of CSD crystals accelerated the setting process and decreased the size of DCPD crystals, resulting in an increase in TS. Because (i) $P_2O_7^{4-}$ is the most effective at increasing ST, and (ii) SO_4^{2-} can simultaneously increase ST and TS, combinations of SO_4^{2-} and $P_2O_7^{4-}$ have been used to control cement properties [3, 4]. However, little work has been done to investigate interactions between these additives. Moreover, combinations of $C_6H_5O_7^{3-}$ and SO_4^{2-} or $P_2O_7^{4-}$ have not been investigated. In this study, it is thus proposed to study in more detail interactions between SO_4^{2-}, $C_6H_5O_7^{3-}$ and $P_2O_7^{4-}$ ions.

In Equation 1, PA totally reacts with β-TCP to precipitate DCPD [1]. However, humidity [5], lower pH [6, 7] and higher temperature [7, 8] can provoke decomposition of DCPD

$$CaHPO_4 \cdot 2H_2O \rightarrow CaHPO_4 + 2H_2O \quad (2)$$

This reaction was previously observed in samples prepared with an excess of PA according to Equation 1

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[1, 9]. As DCP crystals have a negative effect on TS [1, 9], cements are normally prepared with an excess of β-TCP, as in this study.

2. Materials and methods

2.1. Sample preparation

The cements were prepared by mixing thoroughly 1.5 g of dry β-TCP powder (Art. 21′218, lot 31760/1 396; Fluka, Buchs, Switzerland) with 1.2 ml of an aqueous solution containing 2.0 M H_3PO_4 (Art. 79′621, lot 332720/1 1193; Fluka), 0–0.3 M $H_3C_6H_5O_7 \cdot H_2O$ (Art. 6-0160-2; Hänseler, Herisau, Switzerland), 0–0.1 M $Na_2H_2P_2O_7$ (Art. 71501, lot 274941/1 197; Fluka), and 0–0.33 M H_2SO_4 (Art. 20-6375-3; Hänseler). The paste obtained by mixing the compounds for 30 s was filled into a syringe whose tip had been cut (12.5 mm in diameter). The setting time was then measured. A few minutes later, the samples were pushed out of the syringe, and dried in air at room temperature. Afterwards, their diametral tensile strength and weight loss were measured. At least three samples were prepared for each cement composition.

2.2. Multifactorial experimental design 2^3

To assess interaction between the SO_4^{2-}, $C_6H_5O_7^{3-}$ and $P_2O_7^{4-}$ ions, a multifactorial experimental design 2^3 was carried out. The factors and their levels were: (a) H_2SO_4 (0–0.1 M), (b) citrate ions (0–0.1 M) and (c) pyrophosphate ions (0–0.033 M)—see Table I. The samples were prepared in almost the same way as previously described. The only difference is that each sample was put into 5 ml deionized water just after being pushed out of the syringe and left there for 24 h at room temperature. Afterwards, the samples were dried in air. The pH of the incubating solution, the tensile strength, the failure strain and the weight loss of the samples were then measured and analyzed for their statistical significance [10].

2.3. Characterizations

Setting times were measured using a variation of the Vicat needle technique previously described [1]. Diametral tensile strengths [11] were measured at a strain rate of 0.5 mm min^{-1} with Adamel Lhomargy DY31 and Instron 8562 testing machines. X-ray diffraction (XRD) spectra were obtained on a Siemens Kristalloflex 805 diffractometer using CuK_α, Ni-filtered radiation, at an angular sweeping rate of 0.02° 2θ s^{-1}. The gravimetric loss of the cement samples was measured by means of a muffle furnace. The samples were calcined for 1 h at 500 °C. In these conditions, DCPD and DCP decompose according to the following reactions [12]

$$2CaHPO_4 \cdot 2H_2O \rightarrow Ca_2P_2O_7 + 5H_2O \quad (3)$$

$$2CaHPO_4 \rightarrow Ca_2P_2O_7 + H_2O \quad (4)$$

The weight losses (WL) corresponding to Equations 3 and 4 are 26.1 and 6.6% w/w, respectively. As in Equation 1 all PA reacts with β-TCP to form DCPD or DCP [1], the lower the WL, the larger the amount of DCPD transformed into DCP.

TABLE I Definition of the experiments carried out in the factorial design of experiment 2^3, where the factors are the concentration of: (a) sulfate ions (0–0.1 M), (b) citrate ions (0–0.1 M) and (c) pyrophosphate ions (0–0.033 M)

Experiment designation	Sulfate concentration [M]	Citrate concentration [M]	Pyrophosphate concentration [M]
(1)	0.0	0.0	0.000
a	0.1	0.0	0.000
b	0.0	0.1	0.000
ab	0.1	0.1	0.000
c	0.0	0.0	0.033
ac	0.1	0.0	0.033
bc	0.0	0.1	0.033
abc	0.1	0.1	0.033

3. Results

ST increases almost linearly with increasing $C_6H_5O_7^{3-}$ and $P_2O_7^{4-}$ concentrations (Fig. 1). A 15-fold increase is observed at 0.1 M $P_2O_7^{4-}$ concentration, and a ten-fold increase at 0.3 M $C_6H_5O_7^{3-}$ concentration. Up to about 0.1 M, SO_4^{2-} ions have almost the same effect as $C_6H_5O_7^{3-}$ ions. However, a further increase of the SO_4^{2-} concentration leads to a decrease in ST. At 0.3 M SO_4^{2-} concentration, ST comes back to that of the sulfate-free cement samples.

As observed for ST, TS increases with the addition of SO_4^{2-}, $C_6H_5O_7^{3-}$ and $P_2O_7^{4-}$ ions (Fig. 2). The strongest effect is observed with SO_4^{2-} ions: with more than 0.15 M SO_4^{2-} ions in the mixing liquid, TS is increased three-

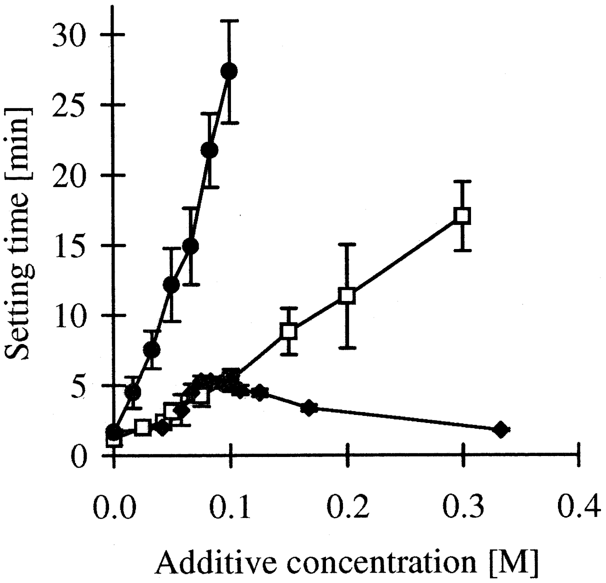

Figure 1 Effect of (□) citrate, (●) pyrophosphate and (◆) sulfate ions on the cement setting time. The cement samples were made of 1.5 β-TCP, 1.2 ml H_3PO_4 2 M and $H_3C_6H_5O_7$ w M ($0 \leq w \leq 0.3$ M), $Na_2H_2P_2O_7$ y M ($0 \leq y \leq 0.1$ M) or H_2SO_4 z M ($0 \leq z \leq 0.33$ M). The bars correspond to the 95% confidence interval of the mean.

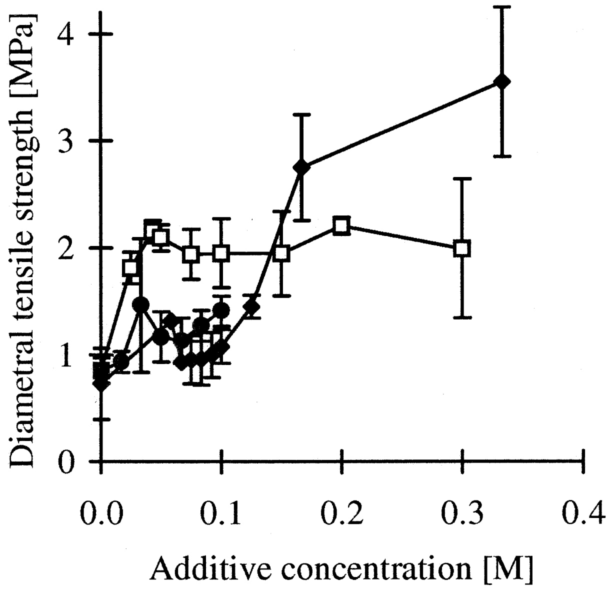

Figure 2 Effect of (□) citrate, (●) pyrophosphate and (◆) sulfate ions on the cement tensile strength. The cement samples were made of 1.5 β-TCP, 1.2 ml H_3PO_4 2 M and $H_3C_6H_5O_7$ w M ($0 \leq w \leq 0.3$ M), $Na_2H_2P_2O_7$ y M ($0 \leq y \leq 0.1$ M) or H_2SO_4 z M ($0 \leq z \leq 0.33$ M). The bars correspond to the 95% confidence interval of the mean.

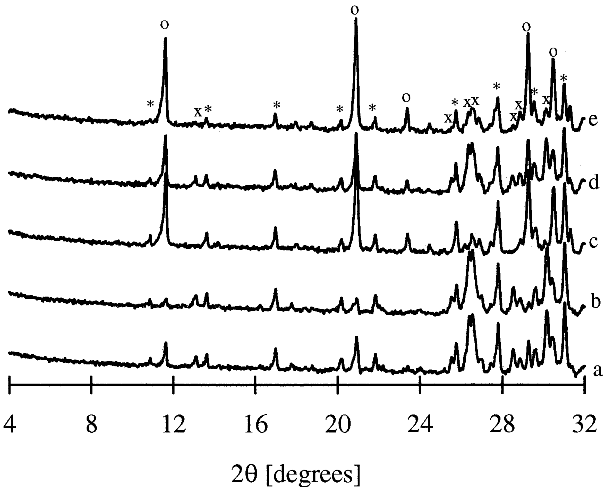

Figure 4 XRD spectra for different cement samples (a) no additives, no incubation; (b) H_2SO_4 0.1 M, no incubation; (c) $H_3C_6H_5O_7$ 0.1 M, no incubation; (d) $Na_2H_2P_2O_7$ 0.033 M, no incubation; (e) no additives, incubation in 5 ml for 24 h. The peak heights are given in (counts $s^{-1})^{1/2}$. The largest diffraction peaks of (o) DCPD, (x) DCP and (*) β-TCP (JCPDS Files No. 9-77, 9-80 and 9-169, respectively) are indicated by their corresponding symbol.

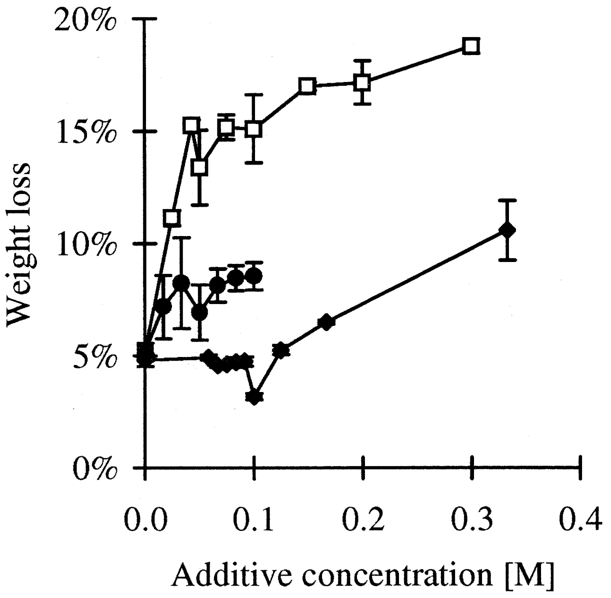

Figure 3 Effect of (□) citrate, (●) pyrophosphate and (◆) sulfate ions on the cement weight loss. The cement samples were made of 1.5 β-TCP, 1.2 ml H_3PO_4 2 M and $H_3C_6H_5O_7$ w M ($0 \leq w \leq 0.3$ M), $Na_2H_2P_2O_7$ y M ($0 \leq y \leq 0.1$ M) or H_2SO_4 z M ($0 \leq z \leq 0.33$ M). The bars correspond to the 95% confidence interval of the mean.

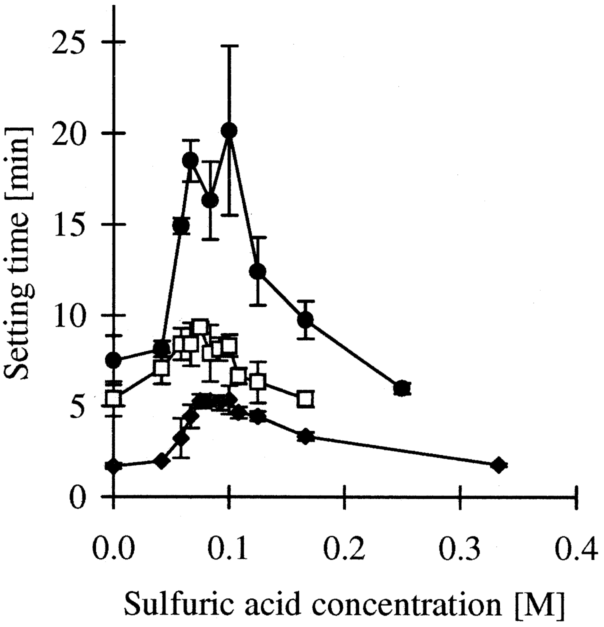

Figure 5 The effect of sulfate ions on the cement setting time. The cement samples were made of 1.5 β-TCP and 1.2 ml of a solution containing H_3PO_4 2 M, H_2SO_4 z M ($0 < z < 0.33$ M) and (◆) no other additives; (□) $H_3C_6H_5O_7$ 0.10 M; (●) $Na_2H_2P_2O_7$ 0.033 M. The bars correspond to the 95% confidence interval of the mean.

fold. The presence of $C_6H_5O_7^{3-}$ ions in the cement paste doubles TS with a concentration as low as 25 mmol. However, no further increase is observed at higher concentrations. A minor increase in strength is observed with $P_2O_7^{4-}$ ions.

In the absence of additives, the cement WL is close to 5% (Fig. 3). This value is much lower than 16.2%, the WL value that would be expected if all PA was transformed solely into DCPD. If all DCPD was transformed into DCP, WL would be close to 3.7%. This suggests that a large amount of DCP crystals are present in the cement samples as evidenced by XRD (Fig. 4). The addition of SO_4^{2-} and $P_2O_7^{4-}$ ions leads only to a small increase in WL in contrast to citrate ions, which dramatically increase it. With $C_6H_5O_7^{3-}$ concentrations as low as 0.043 M, the WL is higher than 15%. The increase in WL is correlated to an increase in the amount of DCPD crystals (Fig. 4).

$C_6H_5O_7^{3-}$ and $P_2O_7^{4-}$ additions to the cement paste do not strongly modify the effect of SO_4^{2-} ions on ST (Fig. 5): a maximum occurs at an SO_4^{2-} concentration close to 0.1 M. However, the effect of SO_4^{2-} ions is leveled off by the addition of $C_6H_5O_7^{3-}$ ions. Stronger effects are observed on TS (Fig. 6). Whereas the effect of SO_4^{2-} ions is not affected by the presence of $P_2O_7^{4-}$ ions; it is completely leveled off by $C_6H_5O_7^{3-}$ ions. SO_4^{2-} ions increase WL in the presence or absence of $C_6H_5O_7^{3-}$ or

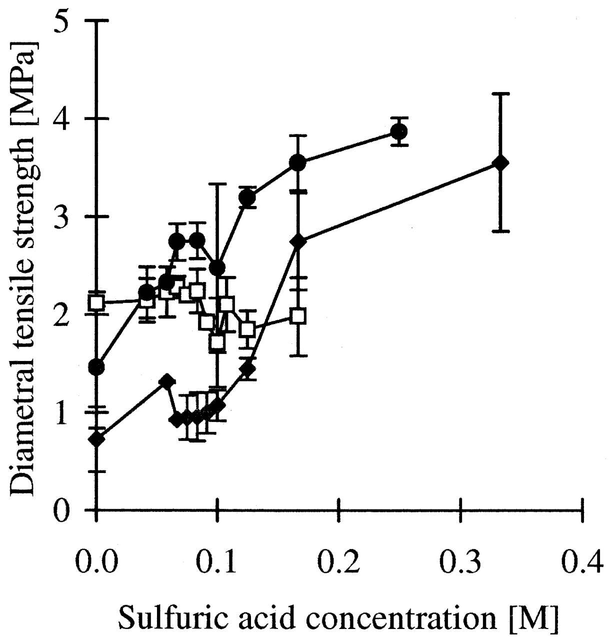

Figure 6 The effect of sulfate ions on the cement tensile strength. The cement samples were made of 1.5 β-TCP and 1.2 ml of a solution containing H_3PO_4 2 M, H_2SO_4 z M ($0 < z < 0.33$ M) and (◆) no other additives; (□) $H_3C_6H_5O_7$ 0.10 M; (●) $Na_2H_2P_2O_7$ 0.033 M. The bars correspond to the 95% confidence interval of the mean.

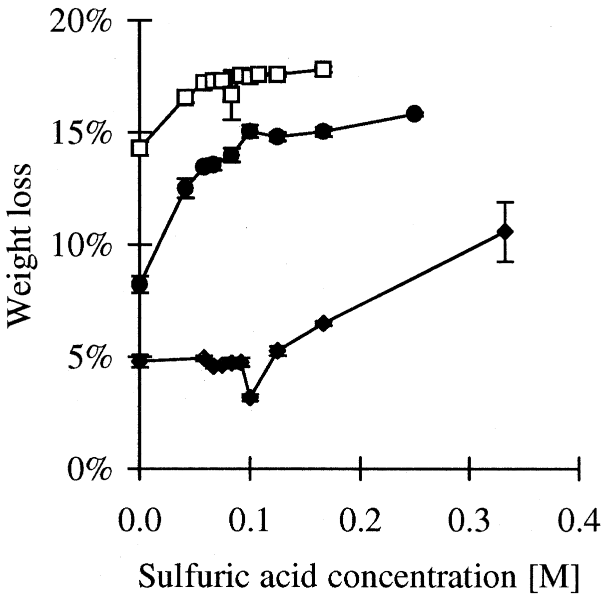

Figure 7 The effect of sulfate ions on the cement weight loss. The cement samples were made of 1.5 β-TCP and 1.2 ml of a solution containing H_3PO_4 2 M, H_2SO_4 z M ($0 < z < 0.33$ M) and (◆) no other additives; (□) $H_3C_6H_5O_7$ 0.10 M; (●) $Na_2H_2P_2O_7$ 0.033 M. The bars correspond to the 95% confidence interval of the mean.

$P_2O_7^{4-}$ ions (Fig. 7). However, WL is on average larger in the presence of additives, in particular with $C_6H_5O_7^{3-}$ ions.

3.1. Multifactorial experimental design

The multifactorial experimental design 2^3 indicates that $C_6H_5O_7^{3-}$, SO_4^{2-} and $P_2O_7^{4-}$ ions have a strong effect on cement properties (Table II, Fig. 8). The pH of the incubating solution is strongly decreased by $C_6H_5O_7^{3-}$ ions (−0.52 on average; Fig. 8a). The latter effect is strengthened by $P_2O_7^{4-}$ ions (−0.60; Table II). $P_2O_7^{4-}$ ions also interact with SO_4^{2-} ions. SO_4^{2-} ions increase the pH in the absence of $P_2O_7^{4-}$ ions (+0.02), and decrease the pH in their presence (−0.06).

The effect of all three additives on ST is cumulative (Fig. 8b), except for mixtures of $C_6H_5O_7^{3-}$ and SO_4^{2-} ions. The latter phenomenon is also observed for TS (Fig. 8c). $C_6H_5O_7^{3-}$ ions have a positive effect on TS (+0.32 MPa) in the absence of SO_4^{2-} ions, and have a negative effect (−0.06 MPa) in their presence.

The largest failure strains are five times larger than the smallest ones (Fig. 8d). These large differences are mostly due to the presence of $C_6H_5O_7^{3-}$ ions (+7.0 mm m^{-1}). The effect of $C_6H_5O_7^{3-}$ ions is larger in the absence of SO_4^{2-} ions (+8.4 mm m^{-1}) and in the presence of $P_2O_7^{4-}$ ions (+9.3 mm m^{-1}).

The WL measurements in the multifactorial experimental design are on average a lot larger than those measured before (Figs 3, 7 and 8e). They are all close to 16%, i.e. the WL expected when all PA reacts with β-TCP to form DCPD. The XRD spectra (Fig. 4) indeed show that the samples are almost DCP free. An increase in SO_4^{2-} concentration or a decrease in $C_6H_5O_7^{3-}$ concentration can provoke an increase in WL, but these effects are minor.

TABLE II Analysis of the factorial design of experiment 2^3, where the variables are the logarithm of the setting time and the tensile strength, and the factors are the concentration of: (a) sulfate ions (0–0.1 M), (b) citrate ions (0–0.1 M) and (c) pyrophosphate ions (0–0.033 M). Average values: pH, 4.33; log(setting time), 0.935 min; tensile strength, 1.65 MPa; failure strain, 16.40 mm m^{-1}; weight loss, 15.66%. The F values corresponding to a 5 and 1% error risk are 4.49 and 8.53, respectively

	pH		Log(Set. time) [min]		Tens. strength [MPa]		Failure strain [mm/m]		Weight loss [%]	
Source	Effect	F	Effect	F	Effect	F	Effect	F	Effect	F
a	−0.02	0.87[a]	0.137	94.4	0.30	22.42	−0.47	0.71[a]	0.35	16.68
b	−0.52	941.4	0.162	131	0.13	3.81[a]	6.95	155.1	−0.22	6.30
ab	−0.01	0.12[a]	−0.066	21.7	−0.19	8.96	−1.49	7.12	0.03	[a]
c	0.03	3.11[a]	0.266	353.8	0.16	6.58	3.65	42.76	−0.14	[a]
ac	−0.04	5.31	−0.013	[a]	0.03	[a]	−0.13	[a]	−0.07	[a]
bc	−0.08	23.07	−0.020	[a]	−0.02	[a]	2.35	17.67	−0.09	[a]
abc	0.02	[a]	−0.030	[a]	0.04	[a]	−0.56	[a]	−0.03	[a]

[a] Not significant at the 5% error risk.

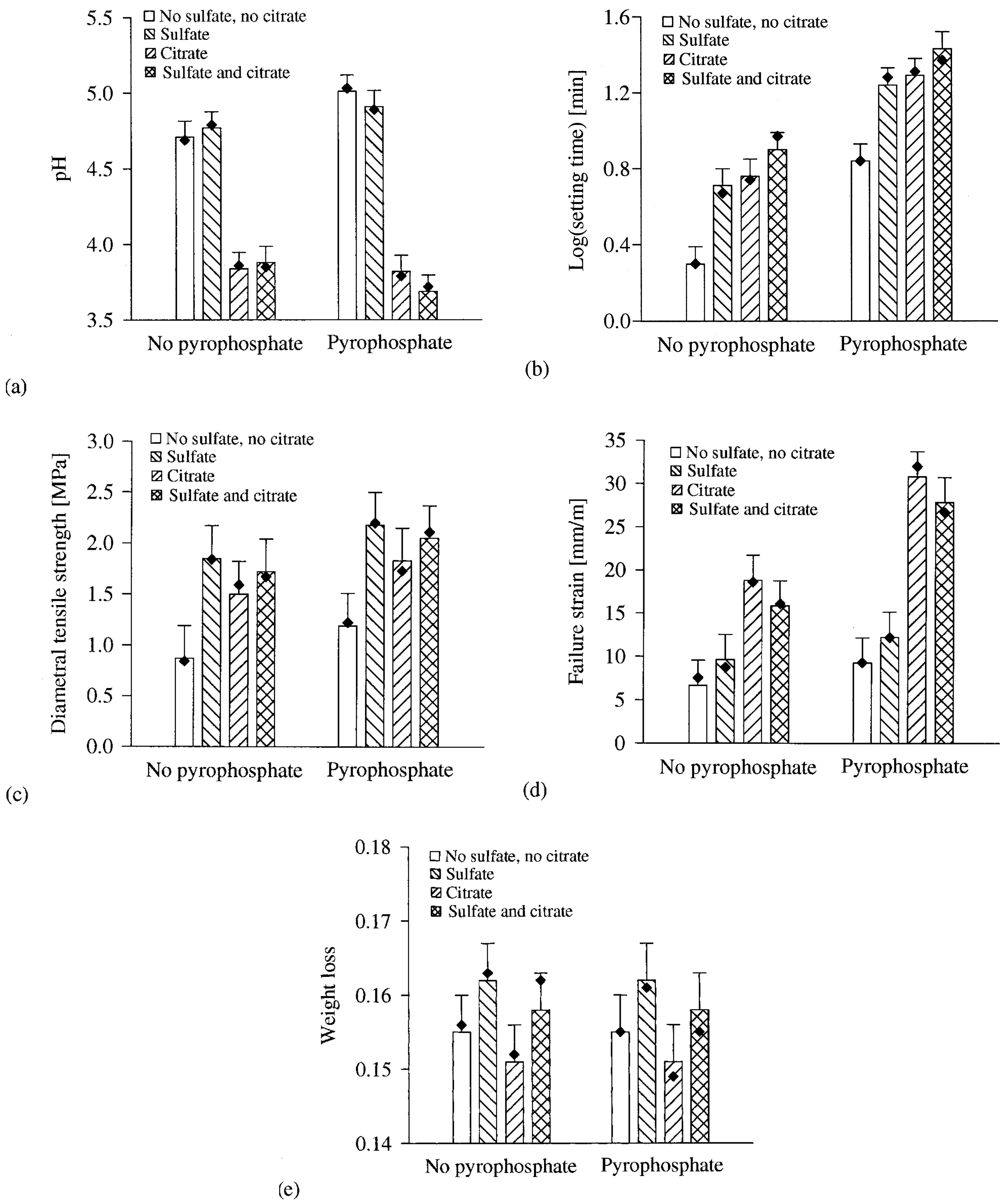

Figure 8 (a) pH, (b) setting time, (c) tensile strength, (d) failure strain and (e) weight loss results for the multifactorial experimental design 2^3. Factors: (a) sulfate ions (0–0.1 M), (b) citrate ions (0–0.1 M) and (c) pyrophosphate ions (0–0.033 M). Key: (◆) data points (average of the three replicates); (bar) adjusted values (with the statistical analysis given in Table II). The size of the error bars correspond to the 95% confidence interval on the adjusted values.

4. Discussion

The effects of SO_4^{2-}, $C_6H_5O_7^{3-}$ and $P_2O_7^{4-}$ ions are very similar to those previously described [2]. The inhibiting effect of these ions on DCPD crystal growth [3, 13, 14] promotes an increase in ST (Fig. 1). At high SO_4^{2-} concentrations (> 0.1 M), a decrease in ST is measured, probably due to the precipitation of CSD crystals that act as nuclei for DCPD crystals [2]. The extent of the effect of the additives is also similar to that previously observed. There is a three-fold increase at 0.1 M SO_4^{2-} concentration (three-fold in [2]), a three-fold increase at 0.1 M $C_6H_5O_7^{3-}$ concentration (five-fold in [2]) and a three–four-fold increase at 0.033 M $P_2O_7^{4-}$ concentration (four-fold in [2]). The slightly lower ST measured here in the presence of $C_6H_5O_7^{3-}$ ions could be due to the replacement of trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) by the more acidic citric acid. An increase in acidity is indeed known to accelerate the cement setting reaction and therefore to decrease ST [1].

The reason why SO_4^{2-} and $C_6H_5O_7^{3-}$ ions interact negatively on ST, contrary to mixtures of SO_4^{2-} and $P_2O_7^{4-}$ ions or $P_2O_7^{4-}$ and $C_6H_5O_7^{3-}$ ions is unclear (Table II, Figs 5 and 8b). However, it is interesting to observe that $C_6H_5O_7^{3-}$ ions inhibit the precipitation of gypsum [15, 16], whereas $P_2O_7^{4-}$ ions do not [17, 18]. This suggests that SO_4^{2-} and $C_6H_5O_7^{3-}$ ions inhibit DCPD crystal growth according to a similar mechanism, but different from that of $P_2O_7^{4-}$ ions.

The XRD spectra and the weight loss measurements show that large DCPD amounts are transformed into DCP during setting or drying (Figs 3, 4 and 7). In the past, DCP crystals were never observed in samples prepared with such compositions. However, the samples were always aged for 24 h in 2 ml deionized water just after setting. The samples prepared in the multifactorial experimental design 2^3 were incubated for 24 h in 5 ml deionized water following the setting reaction. A previous study done on the pH evolution of the cement during setting [9] showed that after reaching a minimum, the cement pH slowly increased to its equilibrium value. Moreover, a low pH was associated with large DCP amounts. Therefore, it is believed that the setting reaction is stopped by the drying step, leaving a low internal pH in the sample [9], hence providing favorable conditions for the transformation of DCPD into DCP. Interestingly, $C_6H_5O_7^{3-}$ ions dramatically lower the equilibrium pH of the cement with 5 ml of deionized water (Fig. 8a), but still prevents the occurrence of the transformation of DCPD into DCP (Figs 3 and 4).

The TS results are difficult to analyze due to the presence of various amounts of DCP crystals in the cement samples. As DCP crystals are known to deteriorate TS [1, 9], large differences in TS could be measured between two samples with the same initial composition. For example, the TS of samples prepared with a concentration of 0.1 M in SO_4^{2-} ions is increased two-fold by a 24-h incubation in 5 ml deionized water just after setting (Figs 2 and 8c). However, in most cases presented here, no or only minor differences are observed. The TS of cement samples prepared without additives or with a 0.033 M concentration in $P_2O_7^{4-}$ ions is the same with or without incubation (Figs 2 and 8c). Incubating the samples made with 0.1 M $C_6H_5O_7^{3-}$ slightly decreased their TS. In a previous study done with the same cement chemical composition [2], TS in the range 0.6–4 MPa were also measured. However, $C_6H_5O_7^{3-}$ and $P_2O_7^{4-}$ ions had no effect on TS. Moreover, no TS increase was measured between 0 and 0.1 M SO_4^{2-} ions. Further investigations are needed to understand these differences. The strong effect of SO_4^{2-} ions (Fig. 6) is in accordance with previously published results [2]. It was attributed to a refinement of the cement microstructure. The effect of SO_4^{2-} ions on TS is not modified by $P_2O_7^{4-}$ ions, but is leveled off by $C_6H_5O_7^{3-}$ ions (Fig. 6), suggesting again an interaction between SO_4^{2-} and $C_6H_5O_7^{3-}$ ions. Comparing Fig. 8c and d shows that SO_4^{2-} and $C_6H_5O_7^{3-}$ ions do not increase TS in the same way. As SO_4^{2-} ions do not modify the failure strain, but increase the tensile strength, SO_4^{2-} ions must increase the cement stiffness. $C_6H_5O_7^{3-}$ ions double the tensile strength, but increase almost three-fold the failure strain. Therefore, the increase in tensile strength must be mainly due to a change of the failure strain.

5. Conclusion

This study shows that all three additives and their admixtures can be used to control cement properties. Unfortunately, not all admixtures are suitable for practical applications. The most interesting additive to increase TS is the SO_4^{2-} ion used at a concentration superior to 0.15 M. However, at this concentration the effect on ST is minor. Therefore, $C_6H_5O_7^{3-}$ or $P_2O_7^{4-}$ ions should also be used. Due to their competitive interaction, mixtures of SO_4^{2-} and $C_6H_5O_7^{3-}$ ions are inappropriate. Thus, mixtures of SO_4^{2-} and $P_2O_7^{4-}$ ions appear to be the most interesting in controlling the physico-chemical properties of this CPC.

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