Effects of sodium tripolyphosphate addition on early-age physico-chemical properties of cement pastes

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Abstract

Sodium tripolyphosphate (STPP) is generally employed as a dispersing agent in ceramic processing and could be a low-cost plasticizer for cement-based materials. The aim of the present work was to evaluate the effect of STPP on the early-age behavior of cementitious matrices. Different concentrations of STPP were considered (0 g/L to 50 g/L). Rheological tests, setting time measurements, microcalorimetry and compressive strength tests were performed on Portland cement pastes with W/C ratios equal to 0.30 and 0.40. The main results showed that the effect of STPP on early-age cement paste properties was dependent on its concentration. The rheological results showed a pronounced increase of viscosity for the higher STPP dosage, immediately after the end of mixing. Microcalorimetric measurements revealed an increasing delay in early-age hydration of cement pastes as the concentration of STPP increased. This delay was also recorded on setting times for the lower STPP dosages. The effect was inverted in the case of higher STPP concentrations, for which faster setting of cement pastes was observed. In spite of the delay on the early-age hydration rate due to STPP, no significant difference was recorded between the 28 day-compressive strength values of the different mixtures investigated.

Keywords: Sodium tripolyphosphate, cement pastes, rheology, setting times, hydration, compressive strength

1. Introduction and scientific background

Sodium tripolyphosphate (STPP), Na₅P₃O₁₀, is commonly used in the making of refractory castables [1-3] and in advanced ceramic processing [4-5]. It acts as a dispersing agent of solid particles, improving the rheological properties of concentrated mineral systems (corundum mortars [1]; dry castable mixes [3]; kaolin suspensions [4-5]; plastering mortars [6]; cemented paste backfill [7]), for a relatively-low cost of production.

Typically, STPP is a white powder added to a dry mix or dispersed into mixing water. Dispersion of grains is achieved by increased electrostatic repulsion due to the presence of the adsorbed molecules on the particle surfaces (Figure 1, left side). The deflocculating agent acts to coat the positively charged particles, providing their dispersion and mutual repulsion [3]. Moreover, STPP can be used as a source of alkalinity to control the pH value of interstitial...
solution [4]. This could be beneficial for the durability of reinforced concrete. Indeed, previous papers have shown that sodium phosphate was an efficient inhibitor against steel corrosion in concrete reinforcement [8]. It slows down both the rate of dissolution processes and the rate of corrosion products formation, leading to the growth of a passive film on the metal surface, which reduces the area of active surface on steel (Figure 1, right side).

However, phosphates are also known to influence the early-age properties of cement-based systems [9]. Dissolved in the mixing water, alkaline phosphates cause an extension of the induction period, leading to a decrease of hydration rate and delay in setting times. This delay could reach several days, according to the concentration and type of phosphates (pyrophosphate, orthophosphate,…) [10-14]. Lieber [10] and Bénard et al. [13] explained this effect by an adsorption of phosphate ions at the surface of the different cement components. It can be assumed that this adsorption reduces or inhibits the dissolution of anhydrous phases and thus retards the cement hydration process. The delay caused by the presence of phosphate decreases beyond a certain concentration level. At higher concentration (> 25 g/L), Cau-dit-Coumes and Courtois [12] observed that phosphate had a positive effect on early-age hydration process: it reduced setting time, rate of heat production during cement hydration and swelling during wet curing, while workability of the mixture was improved. Bénard et al. [13] correlated heat flow evolution, phosphate speciation calculation and visco-elastic properties of early-age cement pastes containing various concentrations of orthophosphate (0 to 50 g/L). They observed that the retardation is not a monotonous function of the concentration of phosphate ions. To explain this result, they suggested the coupling of two opposite phenomena (adsorption of phosphate ions on cement particles and precipitation of a calcium-phosphate compound): at low phosphate concentration, the first phenomenon prevails, inducing a global retardation of hydration. As the ion phosphate concentration increases in the mixing solution and exceeds a limit value (25 g/L), the precipitation of calcium phosphate (hydroxylapatite) becomes predominant, leading to a decrease of hydration retardation and an early gain of stiffness of the cement pastes.

In this context, and taking into account these recent developments, a research work has been carried out to evaluate the interest in using STPP as a low-cost multi-effect admixture (set retarder, plasticizer and corrosion inhibitor) for cement-based materials. The present article focuses on the influence of STPP on the early-age properties of Portland cement pastes. Several techniques were used (isothermal calorimetry, Vicat’s needle penetration test, rheological test with Couette’s geometry, and mechanical tests) in order to quantify the influence of STPP dosage (0 to 50 g/L) on the physico-chemical, rheological and microstructural evolution of cement pastes.

![Fig. 1. Effects of STPP on cement particles dispersion (A) and on steel corrosion (B). The addition of STPP improves the dispersion of cement particles in water (A) and enables to retard the corrosion of steel rebar (B)](image-url)
2. Experimental program

2.1. Materials and mixtures

The cement used was a CEM I 52.5 N (Le Havre plant), provided by Lafarge. It contained 3.1% of gypsum and 1.5% of limestone filler. Application of Bogue’s formulas gives the following mass distribution of the main phases: 66.0% of C_3S, 8.6% of C_2S, 2.9% of C_3A and 12.4% of C_4AF.

The experimental tests were performed on cement pastes with water-to-cement (W/C) ratios equal to 0.30 and 0.40 and containing different dosages of STPP (0 to 50 g/L of the mixing water). STPP was previously dissolved in the mixing water. Cement and water were then mixed for at least 3 minutes in a 5L-mixer.

2.2. Testing procedures

For rheological tests, a controlled stress rheometer, supplied by TA Instruments, was used. The geometry chosen for this study was the co-axial one. A volume of 20 mL of cement paste was taken immediately after the end of mixing and carefully poured into the rheometer. The tests were conducted in a temperature-controlled room at 20 ± 2°C. To prevent drying during the test, the samples were kept covered.

Two types of procedures were applied to study the effect of STPP addition on the rheology of cement pastes: the tests were performed at a varying shear rate from 70 to 0 s^{-1} with a pre-shear of 10 s^{-1}, and then at a constant shear rate (20 s^{-1} and 120 s^{-1}).

The setting times were determined with an automatic Vicat’s needle apparatus at 20 ± 1°C, according to the procedure of the European standard NF EN 196-3. The samples were immersed in a thermostatic water bath to ensure a constant temperature during the tests.

The heat flow resulting from the hydration of cement pastes was measured with an isothermal microcalorimeter TAM Air at 20 ± 0.1°C. For each cement paste investigated, two 4 g-specimens were taken at the end of mixing, accurately weighed (0.01 g) and introduced into flasks. These flasks were then sealed and placed in the apparatus. The first measurement was acquired about ten minutes after the end of mixing. The results presented on the paper are average curves from two specimens for each cement paste studied.

The compressive strength of cement pastes was obtained on 4×4×16-cm^3 prismatic specimens kept in a humid chamber at 20 ± 1°C until testing. For each cement paste investigated, three specimens were tested at 3, 7 and 28 days. They were first broken into two parts with a three-point flexural system. Then, the compressive strength was determined on both parts of each specimen and the average compressive strength values provided in this article were therefore calculated from the results of 6 tests.

3. Result analysis and discussion

3.1. Rheological effects

Figures 2.a, 2.b and 2.c present the evolution of cement paste viscosity as a function of the shear rate for various STPP dosages at 7, 30 and 75 min., respectively, after the end of mixing. For all cement pastes, the viscosity decreased as the shear rate increased. This indicates a fluidification of cement pastes when the mechanical load becomes higher. The addition of STPP did not affect this rheological behavior. Indeed, the viscosity values were relatively close for the different STPP concentrations.

Figures 3.a and 3.b show the evolution of cement paste viscosity for constant shear rates of 20 s^{-1} and 120 s^{-1}, respectively. At low shear rate (Figure 3.a), we noticed an increase in viscosity for all pastes, particularly for the one containing 50 g/L of STPP. The fluctuation in the viscosity (“sawtooth” curves) may be explained by the thickening of the paste prevented by shear. In the first moments following the mixing, the paste with 50 g/L of STPP exhibited the lower viscosity. Then, a significant thickening was detected at low and high shear rates. This rapid increase was followed by a period when the viscosity showed little change. This was confirmed visually immediately after the mixing: the paste with 50 g/L of STPP ceased to flow and seemed to quickly harden.
3.2. Physico-chemical effects: setting and hydration rate

Figures 4 and 5 give the evolution of heat flow and setting rates of the different cement pastes studied, respectively. The addition of STPP caused a slowdown of hydration reactions leading to a delay in the onset of the main hydration peak. Bénard et al. explained this phenomenon by the adsorption of phosphate ions on the surface of cement grains, which may block the dissolution of the phases in mixing water [13]. Figures 4.a and 4.b show that, for both W/C ratios studied, the higher the dosage of STPP, the longer the dormant period was. There was also a decrease in intensity and an increase in width of the hydration peak as the STPP concentration increased. Vicat’s setting time results were more nuanced: for low concentrations of STPP (1 to 5 g/L), the setting of cement pastes was strongly delayed. This was consistent with the microcalorimetry results (Figure 4): the setting took place later due to a longer dormant period. The delay caused by STPP was higher for the cement paste with W/C ratio = 0.30. However, for higher concentrations (20 g/L to 50 g/L), the results of tests carried out on the W/C = 0.30-paste showed an acceleration of setting (Figure 5.a). This phenomenon seems to be in agreement with the previous observations made on the rheological behavior of the cement paste with 50 g/L of STPP. The faster stiffening of the cement pastes with higher STPP concentrations may be explained by the precipitation of calcium phosphate [13]. These crystals could facilitate the formation of solid bridges between hydrates in the mixture, enabling to reach more quickly the percolation threshold. This effect seems to be disconnected from the hydration rate of cement pastes: despite a faster setting, the hydration of pastes with a high concentration of STPP (10 to 50 g/L) was much slower than that of pastes with low STPP dosages (1 to 5 g/L). These results partially differ from those obtained by Cau-dit-Coumes and Courtois [12] and Bénard et al. [13] with orthophosphates.
3.3. Mechanical effects

Figure 6 presents the compressive strength evolution of cement pastes with different dosages of STPP. In spite of the delay of hydration due to STPP, the compressive strength of cement pastes was not significantly affected by the addition of STPP. The results obtained on cement pastes with low or high STPP concentrations were very similar to the values measured on the control paste, even at early age (3 days). This is in accordance with the results reported by Bénard, who observed that the precipitation of calcium phosphate (hydroxyapatite) did not influence the compressive strength of cement pastes [14].
4. Conclusions

This article focuses on the effects of STPP on the early-age physico-chemical properties of Portland cement pastes. The analysis of the results obtained leads to the following remarks:

- The influence of STPP on the rheology of cement paste depends on its dosage and on the shear rate. At low shear rate, an increase in viscosity was observed for all pastes, particularly for the one containing 50 g/L of STPP. At high shear rate, the viscosity of pastes decreased in time, except for the higher concentration of STPP (50 g/L), which showed a strong increase;

- The addition of STPP caused a slow-down of hydration reactions leading to a delay in the onset of the main hydration peak. As the concentration of STPP increased, the dormant period became longer and the hydration peak decreased in intensity. This phenomenon could be explained by the adsorption of phosphate ions on the surface of cement particles, which may limit the dissolution of clinker phases;

- At low STPP dosages (1 to 5 g/L), the setting of cement pastes was delayed whereas, for higher concentrations (20 g/L to 50 g/L), the experimental results showed an acceleration of setting. The faster setting of cement pastes may be due to the precipitation of calcium phosphate in the mixture. These products could participate to the formation of solid bonds between hydrates, leading to the percolation threshold of the matrix;

- The presence of STPP in mixing water did not significantly influence the evolution of the compressive strength of cement pastes between 3 and 28 days.

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