

## The effect of nitrobenzoic and aminobenzoic acids on the hydration of tricalcium silicate: a conduction calorimetric study

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### Abstract

The hydration of tricalcium silicate ( $C_3S$ ) in the presence of 0.004, 0.008 and 0.016 mol.% (with respect to 100 g of the silicate) of benzoic acid, *o*-, *m*- and *p*-nitrobenzoic and aminobenzoic acids, was followed by conduction calorimetry. Benzoic acid at 0.004 and 0.008 moles behaved as a delayed accelerator of hydration, whereas at a dosage of 0.016 moles it performed as an accelerator by decreasing the onset of the induction period and promoting the earlier appearance of the main exothermic peak. The *m*- and *p*-nitrobenzoic acids accelerated the hydration of  $C_3S$ , whereas *o*-nitrobenzoic acid acted as a retarder. Both *m*- and *p*-aminobenzoic acids retarded the hydration by delaying the appearance of the main exothermal peak. *o*-Aminobenzoic acid showed a similar effect to that of the reference at early times by not affecting the induction period and the maximum rate-of-heat peak. However, it increased slightly the amplitude of the main exothermic peak. The compounds that promoted the appearance of a heat peak at periods of 1 h or earlier exhibited an acceleration effect. In the presence of retarders this peak did not appear.

### INTRODUCTION

Admixtures are ingredients added in small amounts to a concrete batch immediately before or during mixing. They confer certain beneficial effects to concrete including enhanced frost or sulphate resistance, controlled setting and hardening, improved workability, increased strength, etc. A large number of publications and a few books have been published recently on the role and applications of admixtures [1–5]. Most published literature on admixtures is based on inorganic compounds and calcium-, sodium- and potassium-based organic compounds. There has been only meagre research activity related to pure aromatic organic compounds as admixtures [6]. In spite of the large amount of data collected on the influence of admixtures on cement, the mechanism of their action has not been completely understood. One of the main problems associated with the study of the mechanism of

hydration of cement is that it consists of many compounds that interact with the admixtures, and also amongst themselves, during hydration.

Together tricalcium silicate ( $C_3S$ ) and dicalcium silicate ( $C_2S$ ) constitute 70–80% of Portland cement. In cement nomenclature,  $C = CaO$ ,  $S = SiO_2$  and  $H = H_2O$ . In cement pastes, the hydrolysed products of the silicates predominate and influence many of the properties of cement. In view of this, many investigators have studied the influence of admixtures on the silicate components of cements before extending the studies to dual and multiple systems.

The hydration of cement and cement components is exothermic so that techniques that measure the rate of heat development as a function of time will provide valuable information on the rate of hydration of the components of cement. Conduction calorimetry is a technique that estimates both the amount of heat evolved and the instantaneous rate of heat liberation at any time. Thus, the accelerating or retarding effects of chemicals on the hydration of cement and cement components can be evaluated using conduction calorimetry.

In this work, the influence of different amounts of benzoic acid, *o*-, *m*- and *p*-nitrobenzoic acids and *o*-, *m*- and *p*-aminobenzoic acids on the hydration characteristics of  $C_3S$  was investigated by conduction calorimetry. The compounds were added in molar proportions rather than by weight percentage to permit a better understanding of the mechanism of their action. The objects of the investigation were as follows: to evaluate the effect of the additives on the rate of hydration of  $C_3S$ ; to determine the effect of the positions of the nitro or amino groups (with respect to the COOH group) on hydration; to develop an alternate accelerator to calcium chloride which is known to promote corrosion of the reinforcing steel in concrete; and to investigate the mechanism of action of these organic compounds on the hydration of  $C_3S$ .

## EXPERIMENTAL

### *Materials*

The triclinic tricalcium silicate ( $C_3S$ ), supplied by the Portland Cement Association, USA, had a Blaine surface area of  $3247 \text{ cm}^2 \text{ g}^{-1}$ . The benzoic acid, *o*-, *m*- and *p*-substituted nitrobenzoic acids, and *o*-, *m*- and *p*-substituted aminobenzoic acids were obtained from Aldrich Chemicals, USA and were used without further purification.

### *Conduction calorimetry*

The rate and amount of heat development by  $C_3S$  with and without the various additives were measured using a conduction calorimeter supplied by

the Institute of Applied Physics, Delft, The Netherlands. The calorimeter was interfaced to an Apple IIe microcomputer using a Taurus One 12-bit a/d converter and an Apple Super Serial interface card.

The benzoic acid, nitrobenzoic acid derivatives and aminobenzoic acid derivatives were added to the tricalcium silicate (0.004 moles, 0.008 moles and 0.0016 moles of acid to 100 g of  $C_3S$ ), mixed with water to yield a water to cement ratio (w/c) of 0.3 and, within a few minutes, transferred to the conduction calorimeter.

### *Solubility*

The solubilities of the additives were obtained by adding an excess of the desired additive to 15 ml of water at room temperature. The mixtures were then stirred and allowed to stand for at least 4 hours prior to decanting. The solution was evaporated and the solid residue was then dried at  $80^\circ C$ , cooled and weighed. The solubilities of the additives in lime solutions and in saturated lime solutions were obtained by measuring the relevant peak intensities using a UV spectrophotometer.

## RESULTS AND DISCUSSION

A typical conduction calorimetric curve for the hydration of  $C_3S$  is shown in Fig. 1. In the first stage, as soon as  $C_3S$  comes into contact with water, a rapid evolution of heat occurs which ceases within about 20 minutes. This is called the pre-induction period. The heat developed at this stage is attributed to the heat of wetting and the hydration of the free lime present in the silicate. In the next stage, that extends over a few hours, the reaction rate is slow and is known as the dormant or induction period. At this stage, dissolution of  $C_3S$  continues and the pH reaches a value of about 12.5. Not

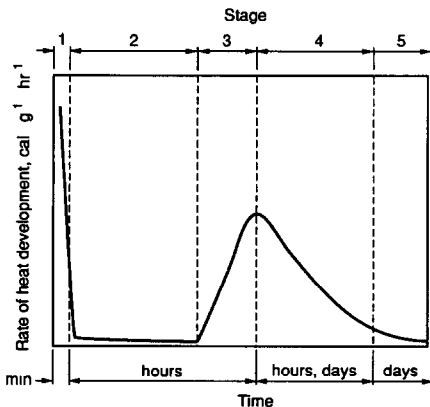


Fig 1. A typical conduction calorimetric curve of  $3CaO \cdot SiO_2$  hydrated at  $25^\circ C$ .

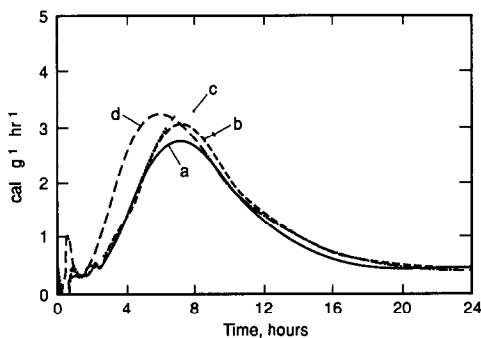


Fig. 2. Conduction calorimetric curves of  $C_3S$  hydrated in the presence of benzoic acid and its derivatives (a)  $C_3S$  ( $w/c = 0.3$ ), (b)  $C_3S$  with 0.004 moles of benzoic acid; (c)  $C_3S$  with 0.008 moles of benzoic acid; (d)  $C_3S$  with 0.016 moles of benzoic acid.

much silica goes into the solution at this stage. In the third stage, the hydration reaction proceeds actively with time, reaching a maximum value corresponding to the end of the acceleratory period. During this period, rapid crystallisation of CH and CSH occurs, followed by a rapid reaction. In the fourth stage, there is a slow deceleration of the reaction with a continuous formation of hydration products. In the fifth and final stage, the reaction is relatively slow and is diffusion-controlled. The initial heat effect, the induction period and the maximum rate-of-heat peak can be influenced by additives.

Conduction calorimetric curves of  $C_3S$  hydrated with 0, 0.004, 0.008 and 0.016 moles of benzoic acid are shown in Fig. 2. Samples containing 0.004 and 0.008 moles of benzoic acid have an induction period of 2.5–3 h and the heat peak is shifted by about 0.5 h with respect to that of the reference ( $C_3S$ ). If the integral heat developed at any time beyond 8 h is compared, it appears that a larger amount of heat is evolved by the sample in the presence of benzoic acid (Fig. 3). Benzoic acid, at a dosage of 0.004 and 0.008 moles may be termed a delayed accelerator for the hydration of  $C_3S$ . Triethanolamine has a similar effect on the hydration of  $C_3S$  [7]. At a dosage of 0.016 moles of benzoic acid, acceleration of hydration of  $C_3S$  occurs both in terms of the decrease in the onset of the induction period and the earlier appearance of the heat peak by about 1–1.5 h. At this dosage, a distinct sharp peak also develops at about 30 min.

The influence of *p*-nitrobenzoic acid on the hydration of  $C_3S$  is shown in Fig. 4. At dosages both of 0.004 and 0.008 moles, the main peak occurs 2 h earlier than that of the reference. Because of the initial exothermal heat effect, it is difficult to determine the time of termination of the induction period. At both dosages, *p*-nitrobenzoic acid develops an initial exothermal peak at about 1 h. The relative rates of hydration of  $C_3S$  can be compared by determining the amount of heat developed at different times. At 5 h, for example, the total heat developed by the reference, and by that containing

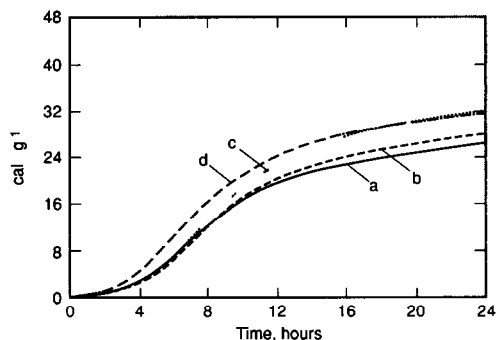


Fig 3 Integral heat development of  $C_3S$  hydrated in the presence of benzoic acid and its derivatives. (a)  $C_3S$  ( $w/c = 0.3$ ), (b)  $C_3S$  with 0.004 moles of benzoic acid; (c)  $C_3S$  with 0.008 moles of benzoic acid; (d)  $C_3S$  with 0.016 moles of benzoic acid.

0.004 and 0.008 moles of *p*-nitrobenzoic acid is 4.0, 6.2 and 9.3 cal  $g^{-1}$ , respectively. If the heat developed at 7 h (the time at which the peak effect occurs in the reference material) is compared, the sample dosed with *p*-nitrobenzoic acid (0.008 moles) produces 70% more heat than that developed by the reference. It can be concluded that *p*-nitrobenzoic acid is an accelerator of hydration of  $C_3S$ , the effect being more pronounced at higher dosages.

The conduction calorimetric curves for the hydration of  $C_3S$  containing *m*-nitrobenzoic acid are given in Fig. 5. At dosages of both 0.004 and 0.008 moles, the maximum inflection occurs between 1.5 and 2 h earlier than that for the reference. It is not easy to determine the start of the induction period for these curves because of the masking effect of the initial exotherm. There is indication that the main peak appears at earlier times as the dosage is increased. Because the total amount of heat developed by *m*-nitrobenzoic acid is higher than that of the reference at earlier times, this additive can be

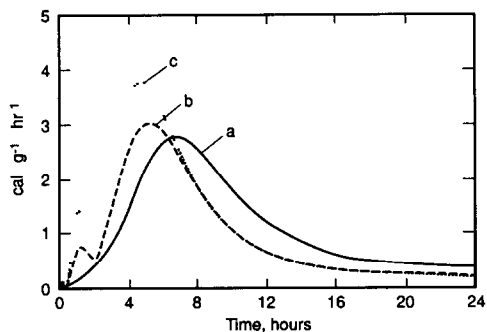


Fig 4 Influence of *p*-nitrobenzoic acid on the heat development in  $C_3S-H_2O$  mixtures (a)  $C_3S$  ( $w/c = 0.3$ ); (b)  $C_3S$  with 0.004 moles of *p*-nitrobenzoic acid; (c)  $C_3S$  with 0.008 moles of *p*-nitrobenzoic acid

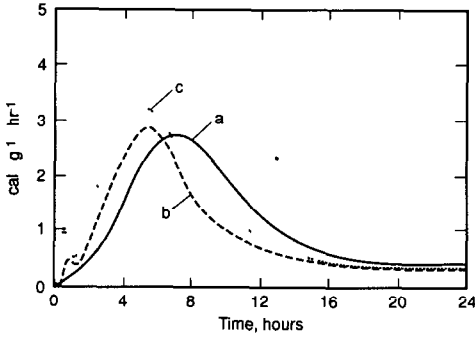


Fig 5 Conduction calorimetric curves of  $C_3S$  hydrated in the presence of *m*-nitrobenzoic acid: (a)  $C_3S$  ( $w/c = 0.3$ ), (b)  $C_3S$  with 0.004 moles of *m*-nitrobenzoic acid; (c)  $C_3S$  with 0.008 moles of *m*-nitrobenzoic acid.

considered as an accelerator. At equal molar concentrations, *p*-nitrobenzoic acid is a better accelerator than *m*-nitrobenzoic acid.

Figure 6 compares the relative effects of 0.008 molar *o*-, *m*- and *p*-nitrobenzoic acids on the hydration of  $C_3S$ . The para and meta compounds induce more intense peaks at earlier times than the reference, and are, therefore, accelerators of hydration. Benzoic acid (0.008 moles) addition results in a curve similar to that of the reference up to 5 h, but the maximum heat effect occurs later than that of the reference. However, the integral heat developed by benzoic acid addition beyond the period of 7 h is significantly higher than that of the reference and hence, benzoic acid is a *delayed accelerator*. In the presence of *o*-nitrobenzoic acid, the rate of heat development is lower up to about 7 h with respect to the reference. The inflection corresponding to the maximum rate of heat development appears about 2 h

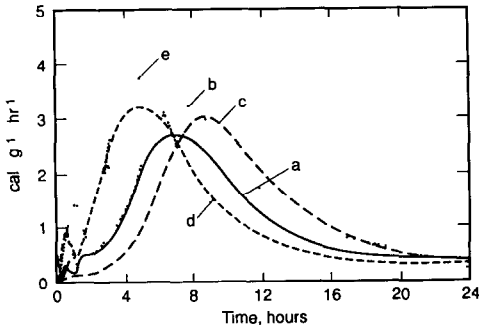


Fig 6. The relative effects of *o*-, *m*- and *p*-nitrobenzoic acids on the hydration of  $C_3S$ : (a)  $C_3S$  ( $w/c = 0.3$ ), (b)  $C_3S$  with 0.008 moles benzoic acid; (c)  $C_3S$  with 0.008 moles of *o*-nitrobenzoic acid; (d)  $C_3S$  with 0.008 moles of *m*-nitrobenzoic acid, (e)  $C_3S$  with 0.008 moles of *p*-nitrobenzoic acid

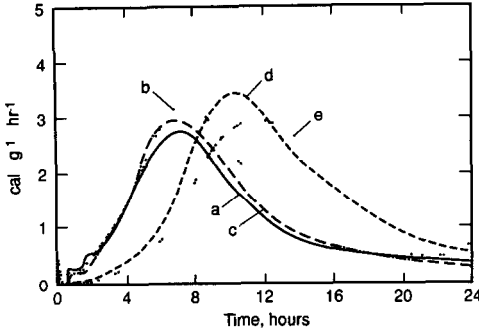


Fig 7 The influence of *o*-, *m*- and *p*-aminobenzoic acids on the hydration of  $C_3S$ . (a)  $C_3S$  ( $w/c = 0.3$ ), (b)  $C_3S$  with 0.008 moles benzoic acid; (c)  $C_3S$  with 0.008 moles of *o*-aminobenzoic acid; (d)  $C_3S$  with 0.008 moles of *m*-aminobenzoic acid, (e)  $C_3S$  with 0.008 moles of *p*-aminobenzoic acid

later relative to that produced by the reference. The induction period is also extended. This indicates that *o*-nitrobenzoic acid is a retarder.

The influence of 0.008 moles of *o*-, *m*- and *p*-aminobenzoic acids on the hydration of  $C_3S$  is different from that of the corresponding nitrobenzoic acids. The onset of the induction period, as well as the peak, is shifted to later times in the pastes containing *m*- and *p*-aminobenzoic acids (Fig. 7); and the onset of the induction periods with these additives is shifted by 2.5 and 4.5 h, respectively, with respect to the reference; the maximum intensity peak for the *p*-aminobenzoic acid occurring about 5 h later. Both *m*- and *p*-aminobenzoic acids are retarders whereas *m*- and *p*-nitrobenzoic acids are accelerators. The curve of *o*-aminobenzoic acid coincides with that of the reference and the amplitude of the main exothermal peak is marginally increased.

Several theories have been proposed to explain the accelerating or retarding action of admixtures on  $C_3S$  hydration [5]. Theories on the accelerating action are based on the following considerations: the extent of the dissolution of lime, the amount of silica dissolved, the increased permeability of the initial layer formed on the  $C_3S$ , the amount of charge and the ionic radii of the cation and anion, the existence of an adsorption complex on the surface of the hydrating  $C_3S$ , nuclei formation, changes in the adhesion properties of the surface complex, pH changes in the solution phase, catalytic effects, and the condensation of the silicate ions. By implication, the retarding effect should act negatively or not promote those phenomena that accelerate hydration. The retarding effects are generally based on the following mechanisms: the poisoning of the  $Ca(OH)_2$  and/or  $C-S-H$  nuclei, the extent of the solubility of  $Ca^{2+}$ , adsorption effects, complex formation on the hydrating  $C_3S$  surface, precipitation of the products, higher impermeability and better cohesion of the products on the surface. No single mechanism has been able to explain the accelerating or retarding effects of various admix-

tures. It is highly likely that a combination of mechanisms is operative, depending on the experimental conditions, the type and amount of admixture used and the period of hydration.

In order to determine if the solubility of the nitro and amino compounds in water has any relationship with the rate of hydration of  $C_3S$ , the solubilities of these compounds (g per 100 ml) were determined in water and saturated lime solution. Amongst the nitrobenzoic acid compounds the solubility in water was in the decreasing order: ortho (0.57%) > meta (0.24%) > para (0.02%). In terms of the integral heat developed up to 7 h (the time at which the maximum rate of heat development occurs in the reference), the para and meta compounds may be considered as accelerators and the ortho compound as a retarder. This could mean that the retardation effect is related to a higher solubility. However, benzoic acid with a solubility of only 0.004% is not as effective an accelerator as the *p*-nitro compound with a solubility of 0.022%. The solubilities of the amino compounds are in the decreasing order para (0.39%) > ortho (0.30%) > meta (0.22%). The retarding effect of these compounds is in the decreasing order para > meta > ortho. These data indicate that there is no direct relationship between the solubility and the retarding or accelerating action of the compounds studied. The solubility of the nitro compounds in lime solution was in the decreasing order: benzoic acid > meta > ortho > para; these values do not bear a direct relationship with the influence of the organic compounds on the hydration of  $C_3S$ ; similarly no relationship was obtained for the amino compounds.

A careful evaluation of the conduction calorimetric curves reveals that those with additives that produce an acceleratory effect also exhibit an exothermal inflection at about 1 h or earlier. It is also evident that the larger the intensity of the peak, the more effective the accelerating effect. Curves for  $C_3S$  with compounds that are retarders do not show this peak. The reference  $C_3S$  sample containing no additive has no early exotherm. The heat of solution or the dissolution of free lime that produces heat immediately on contact of  $C_3S$  with water was not registered because the pastes were first mixed outside for a few minutes before being placed in the isothermal calorimeter. Also, the appearance of the exotherm and its intensity are not related to the degree of solubility of the organic compounds. For example, *p*-nitrobenzoic acid with a solubility of 0.02% shows an intense peak whereas *o*-nitrobenzoic acid with a solubility as high as 0.57% fails to exhibit this peak.

It became evident that the exotherm appearing at very early periods, even at low concentrations of the additive in the aqueous phase, is indicative of an interaction between the organic compound and the hydrating surface of  $C_3S$ . The accelerating action of some of the compounds is possibly caused by the formation of a complex on the surface, promoting the formation of an unstable C-S-H primary product, with the subsequent formation of nuclei of lower or more permeable hydrosilicate. Therefore, only a small



amount of the accelerator is sufficient to influence the interactions at the surface. Studies on the accelerating action of  $\text{CaCl}_2$  have provided evidence for the existence of a surface complex formed between the chloride and the hydrating calcium silicate [8,9]. The retarding action of some of the compounds in this study seems to be related to the absence of an immediate interaction between the surface of the silicate and the retarder. It is possible that the retarders do interact on the surface, but very slowly, so that the calorimeter does not register the interactive effects. In such a case, the formation of an impermeable layer or poisoning effect may account for the retardation effect.

## CONCLUSIONS

Conduction calorimetry is a useful tool for the evaluation of the influence of organic additives on the hydration of tricalcium silicate. Even small amounts of benzoic acid, nitrobenzoic acid and aminobenzoic acid influence the rate of hydration of the silicate. The relative accelerating or retarding effects of the organic compounds depend on the added dosage, the type of groups present, such as  $-\text{NO}_2$ , or  $-\text{NH}_2$ , and on their positions with respect to the  $-\text{COOH}$  group. The *m*- and *p*-nitrobenzoic acids are accelerators of hydration whereas *o*-nitrobenzoic acid is a retarder. In general, *o*-, *m*- and *p*-aminobenzoic acids are retarders, the para form being the most effective. Benzoic acid may be termed a *delayed accelerator*. The accelerating effect is attributed to the formation of an adsorption complex between the organic compound and the C-S-H phase on the surface of the tricalcium silicate.

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