Early age hydration of cement pastes with alkaline and alkali-free accelerators for sprayed concrete

Renan P. Salvador [a,b,*], Sergio H.P. Cavalaro [a,*], Ignacio Segura [a,c], Antonio D. Figueiredo [d], Jorge Pérez [e]

[a] Department of Civil and Environmental Engineering, BarcelonaTech, Polytechnic University of Catalonia, UPC, Jordi Girona 1-3, 08034 Barcelona, Spain
[b] CAPES Foundation, Ministry of Education of Brazil, Brasília – DF 70040-020, Brazil
[c] Smart Engineering Ltd., Secretari Coloma 119, 08024 Barcelona, Spain
[d] Department of Civil Construction Engineering, Polytechnic School of University of São Paulo, Professor Almeida Prado, Trav 2, 83, 05424-970 São Paulo, Brazil
[e] Industrias Químicas del Ebro, Polígono de Malpica, D 97, 50016 Zaragoza, Spain

HIGHLIGHTS

- Early age hydration of accelerated cement pastes was evaluated.
- Kinetics and mechanisms of hydration rely on accelerator type and sulfate balance.
- A conceptual hydration model for pastes containing set accelerators is proposed.
- Results elucidate differences in mechanical strength depending on accelerator type.

ARTICLE INFO

ABSTRACT

The objective of this study is to evaluate the early age hydration mechanisms of accelerated CEM I pastes. Liquid phase analysis, conductimetry, isothermal calorimetry, in situ XRD and SEM were performed on cement pastes produced with equivalent doses of an alkaline accelerator (sodium aluminate solution) and of an alkali-free accelerator (aluminum sulfate solution). Results showed that the addition of these chemicals first changes the ionic equilibria of the medium by the consumption of Ca^{2+} and SO_4^{2-} ions from the liquid phase. The alkali-free accelerator contributes to the rapid formation of ettringite, as well as to a faster rate of alite dissolution and hydration. The aluminate accelerator leads to AFt and AFm formation, rapidly depleting gypsum and filling up the space, inhibiting further alite hydration. According to the results, variations in cement hydration mechanisms caused by accelerators with different chemical compositions are explained.

1. Introduction

Sprayed concrete is a construction technique widely used as a structural support method for tunnels and mines excavations [1]. In underground job sites, excavation is under way while the ground is transferring increasing loads to the sprayed concrete linings, making rock-fall a safety issue. In order to prevent dangerous and costly fallouts of large masses of fresh material from walls and overhead areas, sprayed concrete must present a rapid setting and a high early strength development. In addition, the matrix must have an adequate consistency to enable the build-up of layers with proper thickness [2,3]. These properties are mainly achieved by the incorporation of set accelerators.

Set accelerators comprise a range of chemicals that influence the rate of cement hydration, thereby shortening setting time and, in most cases, increasing the rate of early strength development [4]. The main classes of accelerating admixtures used in sprayed concrete are either alkaline or alkali-free. Depending on their chemical composition, different impacts on the early age hydration kinetics are observed [5,6]. Mechanical properties are also influenced, with the tendency of obtaining higher ultimate strengths when alkali-free accelerators are used [7].

Alkaline accelerators are composed mainly by sodium aluminate or sodium silicate. In the particular case of aluminate based accelerators, Na^+ and $[Al(OH)_4]^-$ ions are incorporated in the cement matrix. $[Al(OH)_4]^-$ ions react with Ca^{2+} and SO_4^{2-} ions present in the liquid phase of the cement paste, forming AFt and AFm

* Corresponding authors at: Department of Civil and Environmental Engineering, BarcelonaTech, Polytechnic University of Catalonia, UPC, Jordi Girona 1-3, 08034 Barcelona, Spain.
E-mail addresses: renan.picolo@upc.edu (R.P. Salvador), sergio.pialarissi@upc.edu (S.H.P. Cavalaro).

phases, which contribute to reduce the setting times of the matrix. Then, further C_3A hydration proceeds with limited sulfate content and C–A–H phases might also be formed [6,8]. Depending on Na^+ concentration, the formation of U-phases (sodium–calcium aluminate hydrated phases) has already been reported [9].

The main component present in alkali-free accelerators is aluminum sulfate, usually stabilized in aqueous solution by the addition of an inorganic or organic acid [10]. When this type of admixture is used in cement matrices, the mixing water is enriched with Al^{3+}, SO_4^{2-} and H^+ ions. Due to the elevated pH in the paste, Al^{3+} ions are converted into $[Al(OH)_4]^-$, which then reacts with calcium and sulfate ions present in solution. As this admixture also contributes to increase sulfate concentration in the liquid phase, ettringite is the main product formed in the matrix. Formation and growth of ettringite nanocrystals are the main processes that reduce setting times and increase the rate of strength development [11].

The most probable reactions that occur in a cement paste in the presence of $[Al(OH)_4]^-$ ions, derived from the accelerators mentioned previously, are represented by the equations shown in Table 1 [6,8]. The variation in free energy of each process was obtained from [12]. Comparing the variation in free energy of each reaction, formation of ettringite is the most thermodynamically favorable process. However, the aluminate hydrate formed is also dependent on sulfate availability. If any carbonate is present in the cement, hemicarboaluminate might also be formed.

The choice of working with a determined type of accelerator depends on the requirements of the project. Due to their high alkali content, alkaline accelerators might present some safety issues for workers and their use is limited in some countries. To overcome that problem, alkali-free admixtures have been mandatorily specified in some guidelines [13], since their alkali content is lower than 1.0% (expressed as Na_2O equivalent content). Despite that, alkaline accelerators are still used in several countries due to their more general range of application and smaller cost.

Although some works have been published about the subject [5,6,11], it is still necessary to compare the effect of each type of accelerator on the early hydration of cement by the use of more recent techniques. Moreover, the influence of early age hydration of accelerated pastes on ultimate mechanical strength has not been totally elucidated. Therefore, continued research on the subject is necessary to optimize the materials.

The main objective of this paper is to elucidate how the different chemical compositions of the two types of accelerators influence the early hydration of cement, focusing on hydration mechanisms and kinetics. The general experimental procedure consists on the evaluation of the hydration in cement pastes with and without setting accelerators. In order to achieve the proposed objective, liquid phase analysis, conductimetry, isothermal calorimetry, in situ X-ray diffraction and SEM imaging were performed. The results obtained provide the basis for the proposal of a conceptual model of hydration mechanism for each accelerator type, highlighting the main reasons for their differences in terms of performance.

2. Experimental methodology

The experimental program was performed at the Laboratory of Technology of Structures Luis Agulló at Universitat Politècnica de Catalunya (UPC) and at the Scientific and Technological Center from Universitat de Barcelona (CCIT-UB). In the following sections, materials, production processes and tests performed are described.

2.1. Materials

An ordinary type I Portland cement (CEM I 52.5R) was used in this study. Table 2 presents the cement mineralogical and chemical compositions determined by XRD-Rietveld analysis and XRF, respectively. The total sulfate content was determined by dissolving 1.00 g of cement with 10.00 g of concentrated HNO_3 (65%), according to [14]. The resulting solution was diluted in a 250 mL volumetric flask using deionized water (Mili-Q, $18\,\Omega\,s$) and analyzed by ion chromatography. The physical properties of this cement are shown in Table 3.

A superplasticizer based on a polycarboxylate solution (34% of solid content) was employed in order to emulate the condition found in most worksites. In order to prepare accelerated cement pastes, two different types of set accelerators were used. One of them is an alkaline solution based on sodium aluminate, while the other is an alkali-free composed by an aluminum sulfate solution. Their generic composition and properties, as provided by their manufacturers, are listed on Table 4.

Table 2
Mineralogical and chemical compositions of the cement.

Mineralogical composition		Chemical composition	
Compound	Content (%)	Compound	Content (%)
C_3S	58.3	LOI	2.88
C_2S	11.2	Fe_2O_3	3.26
C_3A_c	4.1	TiO_2	0.22
C_3A_o	0.6	CaO	62.62
C_4AF	13.4	K_2O^*	0.99
CaO	1.1	P_2O_5	0.10
$Ca(OH)_2$	1.7	SiO_2	19.89
$CaCO_3$	1.9	Al_2O_3	4.74
$CaSO_4\cdot2H_2O$	2.1	MgO	1.95
$CaSO_4\cdot0.5H_2O$	4.4	Na_2O^*	0.13
$K_2Ca(SO_4)_2\cdot H_2O$	1.1	SO_3	3.53
Total sum	100.2	Total sum	100.31

* The quantity of K_2O and Na_2O readily soluble, present as potassium and sodium sulfates, are 0.98% and 0.011% by cement weight, respectively. Their concentration were determined by ion chromatography from a solution extracted from a cement suspension with a/c equal to 9 (according to [15]).

Table 3
Cement properties.

Property	Result
Total heat of hydration[a] (J/g)	433.0
Molar ratio C_3A/SO_3[b]	0.39
Insoluble residue (%)	2.74
Specific surface BET (m^2/g)	2.96
d_{50} (μm)	11.4

[a] The total heat of hydration was estimated from the mineralogical composition of the cement, determined by XRD, as the relative sum of the heats of hydration of the individual phases (C_3S: 510 J/g; C_2S: 260 J/g; C_3A: 1100 J/g; C_4AF: 410 J/g) [8].
[b] Also determined from the mineralogical composition, using total C_3A and SO_3 content.

Table 1
Possible reactions of $[Al(OH)_4]^-$ in cement pastes at room temperature and their related Gibbs free energy [6,8,12].

Reactions	Equation	$\Delta_r G^0_{298}$ (kJ/mol)
$Al^{3+} + 3OH^- \rightleftharpoons Al(OH)_3 + OH^- \rightleftharpoons [Al(OH)_4]^-$	1 ($[Al(OH)_4]^-$ formation)	–
$2[Al(OH)_4]^- + 3Ca^{2+} + 4OH^- \rightleftharpoons C_3AH_6$	2 (hydrogarnet formation)	−5019.34
$2[Al(OH)_4]^- + 6Ca^{2+} + 4OH^- + 3SO_4^{2-} + 26H_2O \rightleftharpoons C_3A\cdot3CaSO_4\cdot32H_2O$	3 (ettringite formation)	−15207.02
$4[Al(OH)_4]^- + 6Ca^{2+} + 8OH^- + C_3A\cdot3CaSO_4\cdot32H_2O \rightleftharpoons 3(C_3A\cdot CaSO_4\cdot12H_2O) + 8H_2O$	4 (monosulfoaluminate formation)	−8011.78
$2[Al(OH)_4]^- + 4Ca^{2+} + 4OH^- + SO_4^{2-} + 6H_2O \rightleftharpoons C_3A\cdot CaSO_4\cdot12H_2O$	5 (monosulfoaluminate formation)	−7739.60
$2[Al(OH)_4]^- + 4Ca^{2+} + 5OH^- + 0.5CO_3^{2-} + 5.5H_2O \rightleftharpoons C_3A\cdot0.5Ca(OH)_2\cdot0.5CaCO_3\cdot11.5H_2O$	6 (hemicarboaluminate formation)	−7339.51