



# Parameters controlling early age hydration of cement pastes containing accelerators for sprayed concrete



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## ABSTRACT

The objective of this work is to parametrize the early age hydration behavior of accelerated cement pastes based on the chemical properties of cement and accelerators. Eight cements, three alkali-free and one alkaline accelerators were evaluated. Isothermal calorimetry, *in situ* XRD and SEM imaging were performed to characterize kinetics and mechanisms of hydration and the microstructure development. The reactivity of all accelerators is directly proportional to their aluminum and sulfate concentrations and to the amount and solubility of the setting regulator contained in cement. Alite hydration is enhanced if a proper  $C_3A/SO_3$  ratio (between 0.67 and 0.90) remains after accelerator addition and if limestone filler is employed, because undersulfated  $C_3A$  reactions are avoided. Combinations of compatible materials are recommended to enhance the performance of the matrix and to prevent an undesirable hydration behavior and its consequences in mechanical strength development.

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## 1. Introduction

Accelerators are commonly used in sprayed concrete applied for the stabilization of tunnel walls. These chemicals alter the kinetics and mechanisms of hydration of the cementitious material, whose effects are the reduction in setting times and the increase in the rate of mechanical strength development [1–3]. As a result, accelerators enable the build-up of concrete layers with proper thicknesses, providing an adequate support to the unstable ground and improving safety in the jobsite [4].

Several factors influence the chemical processes occurring in accelerated matrices, such as the mix design and the application method [1,5]. Galobardes [6] and Salvador et al. [7] concluded that CEM II/A-L has a better compatibility with accelerators based on aluminum sulfate than CEM I due to the addition of limestone filler. Maltese et al. [8,9] showed that the solubility of calcium sulfate used as a setting regulator in cement influences accelerator reactivity and setting times were reduced when hemihydrate was only the sulfate source.

The chemical composition of accelerators also plays an important role in hydration kinetics and mechanical strength evolution. Lootens et al. [10] and Juillard [11] demonstrated that phosphoric acid used in accelerators formulations strongly decreases the rate and extension of

alite hydration. When compared to formulations containing formic acid, final setting is retarded and compressive strength at 12 h is reduced by 50% [1]. Ultimate strength gain and modulus of elasticity are also negatively affected and reductions around 20% at 28 days have been reported [6].

Salvador et al. [12] and Xu and Stark [13] showed that accelerators based on sodium aluminate solutions rapidly deplete sulfate ions from the liquid phase. Consequently, undersulfated  $C_3A$  reactions occur, suppressing alite hydration. Compressive strengths in alkaline accelerated sprayed concrete at 12 h and 7 days are respectively 70 and 20% lower when compared to concrete produced with accelerators based on aluminum sulfate [1]. Ultimate strengths are optimized when the  $Al_2O_3/SO_4^{2-}$  ratio in alkali-free accelerators ranges between 0.38 and 0.60 [1].

Despite the relevant conclusions from former researches [6–13], variations in cement and accelerator compositions were analyzed separately and discussion of results was majorly qualitative. Therefore, a study combining the main variables affecting hydration kinetics of accelerated matrices is still necessary to parametrize the chemical interaction between cements and accelerators. Such approach would assist engineers in preliminary design studies to properly select materials without the need of numerous and extensive field spray trials, which are a common practice nowadays. This evaluation would also be an important reference to accelerator manufacturers for the development of formulations with enhanced performance with cements from different sources. Consequently, the performance of sprayed concrete could be optimized and an unpredictable hydration behavior and its consequences could be avoided.

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**Table 1**  
Abbreviations for the materials used.

Material	Type and description	Abbreviation
Clinker	Ordinary	OPC
	Sulfate-resisting	SRC
Setting regulator	Gypsum	G
	Calcium sulfate hemihydrate	H
Addition	Limestone filler	F
	Silica sand	–
Accelerator	Alkali-free, with $Al_2O_3/SO_4^{2-}$ molar ratio equal to 0.33	AF 0.33
	Alkali-free, with $Al_2O_3/SO_4^{2-}$ molar ratio equal to 0.60	AF 0.60
	Alkali-free, with $Al_2O_3/SO_4^{2-}$ molar ratio equal to 0.74	AF 0.74
	Alkaline	AK

The objective of this work is to parametrize the early age hydration behavior of accelerated cement pastes, focusing their application in sprayed concrete technology. Since sprayed concrete requires an adequate mechanical strength development until 24 h of hydration to guarantee its proper applicability, the progress of the construction work and for safety issues, the analysis conducted in this paper is restricted to ages until 24 h. The evolution of hydration and mechanical strength at later ages is the subject of the following part of this research, from which a second paper will be written [14].

An experimental program was conducted with 8 model cements produced from 2 types of clinker, different amounts and types of setting regulator and additions of limestone filler. Three alkali-free accelerators and one alkaline accelerator were formulated specifically for this study. Isothermal calorimetry, *in situ* X-ray diffraction and SEM analysis were performed to characterize the kinetics and mechanisms of hydration of accelerated pastes. By doing so, a better comprehension of how the hydration process is influenced by the chemical composition of the starting materials is achieved. Results obtained may have a significant repercussion on how to select compatible cements and accelerators to provide a proper mechanical strength development.

## 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 process and tests performed are described.

### 2.1. Nomenclature

The abbreviations for the materials used in this study are presented in Table 1 and the nomenclature of cements and pastes is described in Table 2.

### 2.2. Materials

#### 2.2.1. Cements

A total of 8 different types of cement were produced by manually homogenizing clinker, setting regulator and additions in an agate mortar for 5 min.<sup>1</sup> Their compositions are shown in Table 3 and descriptions and characterization of materials are presented subsequently.

<sup>1</sup> Four different batches of the same cement (OPC 96\_G 4) were produced by this mixing procedure and tested by isothermal calorimetry at 20 °C, using a w/c equal to 0.45. The standard deviation in the maximum value of the main hydration peak was below 0.1 mW/g cement. Therefore, this mixing procedure was considered appropriate and reproducible.

**Table 2**  
Nomenclature adopted in this paper.

Material	Nomenclature	Example
Cement	'clinker type and content'_'setting regulator type and content'_'addition'	OPC 94_G 6_F, SRC 96_G 4
Paste without accelerator	'cement type'_'REF'	OPC 98_G 2_REF
Paste with accelerator	'cement type'_'accelerator type and dosage'	OPC 96_G 4_AF 0.33 5%, OPC 96_H 3.38_F_AK 3%

**2.2.1.1. Clinkers.** Ordinary and sulfate-resisting clinkers were selected due to their different  $C_3A$  content, which plays a significant role on the overall hydration kinetics and on the evolution of alite hydration [11, 15]. Table 4 shows their mineralogical composition determined by XRD-Rietveld refinement and their chemical composition determined by XRF spectrometry. Besides, Table 5 summarizes their physical properties. Fig. 1 shows that clinkers present an analogous particle size distribution, which is important to control hydration kinetics and the rate of strength gain [16].

**2.2.1.2. Setting regulators.** Gypsum (99.5%, Sigma Aldrich) and calcium sulfate hemihydrate (99.5%, Sigma Aldrich) were selected as setting regulators. These types of calcium sulfate are commonly found in cements. Gypsum is added to clinkers before grinding and may dehydrate partially, forming hemihydrate, due to the elevated temperature reached during this process [17]. As these compounds present different solubility ( $CaSO_4 \cdot 2H_2O$ : 0.255 g/100 g  $H_2O$  at 20 °C;  $CaSO_4 \cdot 0.5H_2O$ : 0.32 g/100 g  $H_2O$  at 20 °C [18]), it is important to analyze how they affect the rate of accelerator reaction.

OPC cements were prepared with gypsum contents of 2.0, 4.0 and 6.0% to obtain total  $SO_3$  contents of 2.1, 3.0 and 4.0%, respectively. Although the standard UNE EN 197-1:2011 [19] prescribes a minimum clinker content of 95.0% in a cement type I, cement OPC 94\_G 6 (94.0% of clinker and 6.0% of gypsum) was produced for exploratory tests. Only one cement was produced with the SRC clinker, using 4.0% of gypsum to maintain the same sulfate amount as in cement OPC 96\_G 4.

Hemihydrate was added at 3.38% to produce OPC cements with the same molar amount of sulfate as 4.0% of gypsum. This difference is related to the lower water content in hemihydrate. Therefore, 0.62% of silica sand (calculated over the total mass of cement) was added with hemihydrate to maintain the same proportion of clinker and calcium sulfate.

**2.2.1.3. Additions.** Limestone filler (98%  $CaCO_3$ ,  $d_{50} = 8.3 \mu m$ ) was used at the content of 13.0% in substitution of cement to reproduce CEM II/A-L used in former studies [6,7]. Silica sand (98.5%  $SiO_2$ ,  $d_{50} = 25.5 \mu m$ ) was added to counterbalance the lower water content in calcium sulfate hemihydrate, as mentioned in the former subsection.

#### 2.2.2. Water and superplasticizer

For the preparation of cement pastes, deionized water (Milli-Q, 18  $\Omega \cdot s$ ) was employed. The superplasticizer Sikaplast T1 120, which is based on a polycarboxylate solution (34% of solid content) and recommended for sprayed concrete applications, was also used.

#### 2.2.3. Accelerators

Four accelerators were formulated specifically for this experimental program and cover the categories commonly found in practice. Their composition and characteristics are summarized in Table 6.

Alkali-free accelerators consist in aluminum sulfate solutions with additions of different amounts of aluminum hydroxide. Formic acid was used to keep the pH around 3.0 to avoid aluminum hydrolysis and the consequent precipitation of aluminum hydroxide. These formulations contain the same sulfate and formic acid contents, and the aluminum concentration was the only factor varying in their composition. Therefore,

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