Available online at www.sciencedirect.com
ScienceDirect
Cement and Concrete Research 37 (2007) 856–865
Cement and Concrete Research

A case history: Effect of moisture on the setting behaviour of a Portland cement reacting with an alkali-free accelerator

C. Maltese *, C. Pistolesi, A. Bravo, F. Cella, T. Cerulli, D. Salvioni

Mapei S.p.A., Via Cafiero, 22, 20158 Milan, Italy

Received 17 January 2005; accepted 22 February 2007

Abstract

Flash setting accelerators are a class of admixtures commonly used for sprayed concrete during tunnel excavation. They allow an immediate set of concrete which can bind to the substrate without dangerous collapses. Such a coating layer prevents the section convergence that is its tendency to squeeze. The early strength development (till 1 h) of the sprayed concrete can be connected to the final set time of cement pastes admixed with the accelerator. The lower is the final set time, the higher should be the early strength. Two main methods are used to project concrete: wet and dry. Today, for safety reasons and to obtain more homogeneous concrete layers, the wet method is becoming more diffused. This technique requires the use of liquid flash setting accelerators which are pumped to a nozzle and immediately projected onto the rock wall. In the European market, two kinds of setting accelerators are mainly available: alkali-rich and alkali-free. Recently, for several reasons, the demand of alkali-free accelerators is growing very rapidly. They are water solutions of aluminium sulphate with a total alkali metal content (expressed as equivalent of Na_2O) lower than 1%. In order to develop new and more performing accelerators, several studies are in progress to elucidate their action mechanism and the factors affecting the setting of accelerated concretes.

During an experimental study on the setting behaviour of several cement pastes reacting with an alkali-free accelerator, we found a cement showing, as time proceeded, a persistent setting time reduction. We discovered that the effect was connected to the cement exposure to the moisture. A mineralogical investigation performed on this particular cement revealed the presence of hemihydrate as setting regulator. In order to study the interaction between the alkali-free accelerator and this moist aged cement, some morphological (ESEM-FEG), crystal-chemical (XRD), physical–chemical (hydration temperature profile) and chemical (ICP) analyses on cement paste samples were carried out.

This study showed a significant setting time reduction of cement paste samples admixed with an alkali-free accelerator when they are composed of a Portland cement containing β-hemihydrate that was previously exposed to moisture. Such an effect seems to be related to the reduction of the β-hemihydrate dissolution rate.

Keywords: Accelerators; Alkali-free; β-Hemihydrate; Shotcrete; Sulphates

1. Introduction

1.1. General considerations

Since 1911, when C.E. Akelei [1] patented an equipment for spraying mixtures of cement and water, many advances were carried out in shotcrete technology. Today, two main spraying methods are available which are commonly defined as dry and wet. The former is the oldest one and arises from the Akelei's invention: cement and dry sand are conveyed by compressed air through a hose, and the water needed for hydration is introduced at the spraying nozzle. The wet process was introduced after the end of the second world war: mortar or concrete are pumped to a nozzle and pneumatically projected onto a substrate. However, due to poor/inefficient equipment, lack of know-how, and lack of experience, the quality of the first "generation" wet sprayed concrete was extremely low. Only recently, with the development of more sophisticated spraying machines (automated dosing and powerful pumps), advanced robotics and experience, wet sprayed concrete is becoming increasingly more attractive. The advantages of wet method in comparison to the dry one can be summed up as follows: 1) lower dust production;

* Corresponding author.
E-mail address: Building.lab@mapei.it (C. Maltese).

0008-8846/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2007.02.020

Table 1
Sample compositions

	Exposure time	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	K1	K2	K3	K4	K5	K6	K7	K8
Cement	No exposure	100	/	100	/	100	/	/	/	/	/	/	/	/	/	/	/	/	/
	10 min	/	/	/	/	/	100	/	/	/	/	/	/	/	/	/	/	/	/
	30 min	/	100	/	100	/	/	100	/	/	/	/	/	/	/	/	/	/	/
	2 h	/	/	/	/	/	/	/	100	/	/	/	/	/	/	/	/	/	/
	6 h	/	/	/	/	/	/	/	/	100	/	/	/	/	/	/	/	/	/
	24 h	/	/	/	/	/	/	/	/	/	100	/	/	/	/	/	/	/	/
Clinker	No exposure	/	/	/	/	/	/	/	/	/	/	97.8	97.8	/	/	97.8	97.8	/	/
	30 min	/	/	/	/	/	/	/	/	/	/	/	/	97.8	97.8	/	/	97.8	97.8
β-hemihydrate	No exposure	/	/	/	/	/	/	/	/	/	/	2.2	/	2.2	/	2.2	/	2.2	/
	30 min	/	/	/	/	/	/	/	/	/	/	/	2.2	/	2.2	/	2.2	/	2.2
Water	/	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35	35
Accelerator	/	/	/	2	2	7	7	7	7	7	7	2	2	2	2	7	7	7	7

2) higher spraying efficiency; 3) lower energy consumption; 4) better homogeneity of the concrete properties. This more efficient technology requires the use of liquid flash setting accelerators [2]. They should allow a rapid set of wet sprayed concrete thus determining a rapid concrete hardening and favouring overhead and vertical applications. The cementitious layer acts as a temporary consolidating shield, preventing dangerous falling rocks. Today, the requirement of thicker concrete layer and higher production rate, encouraged the demand for new more performing accelerators. Undoubtedly, they are the most important admixtures used in shotcrete and are mainly divided in two categories: alkali rich (composed of alkali metal hydroxides, alkali metal silicates or aluminates [2,3]) and alkali-free (which are water solutions or slurries of aluminium sulphate stabilised by inorganic or organic acids). Only recently the second type of accelerators was introduced in the market [4–6]. According to EN 934-5, a flash setting admixture can be defined as “alkali-free” when its alkali metal content (sodium and potassium), expressed as equivalent of Na_2O (% Na_2O + 0,658 × % K_2O), is lower than 1%.

1.2. Action mechanism of the alkali-free accelerators

Only few studies are available on the action mechanism of the alkali-free accelerators [7–10]. Bravo et al. [7] hypothesised that when the accelerator is added to a hydrating cement, Al^{3+} and SO_4^{2-}, coming from the admixture, could react with C_3A and Ca^{2+} to form immediately ettringite (in amorphous or crystalline state). Each mole of ettringite contains at least 32 moles of water [11]. Therefore, ettringite formation and water reduction enhance the solid/liquid ratio and the viscosity of the cementitious system thus determining a setting time shortening. The growth of ettringite crystals determines the early compressive strength development [12].

1.3. Scope

The capability of concrete to adequately bind to the substrate is related to the reaction occurring between accelerator and hydrating cement phases. In particular, the higher is the early strength between concrete and substrate, the easier and safer are the spraying applications. The early strength is generally connected to the final set time of cement pastes admixed with the accelerator [13]. The lower is the final set time, the higher should be the early strength development of the projected concrete. The reaction between accelerator and hydrating phases could be governed by several cement characteristics such as the chemical composition, the calcium sulphate phase, the particle size distribution and the ageing. The influence of these parameters was not well explored. During an experimental evaluation of the final set time of several cement paste samples reacting with an alkali-free accelerator, it was found a cement with a very slow setting, showing a significant setting time shortening as time proceeded. It was observed that the phenomenon was related to its exposure to the moisture. Furthermore, an X-ray Diffraction analysis pointed out that hemihydrate was used as setting regulator. In particular, the cement producer declared that this hemihydrate was in the β form. The study was carried out to elucidate the effect of moist ageing of this type of cement on its reaction with an alkali-free accelerator. The weathering process was simulated by exposing fresh cement samples at 20 °C and 95% R.H.

XRD patterns were collected on fresh and aged cement, to detect possible changes of crystalline phase composition. The final set time was measured on mixtures prepared with fresh and weathered cement, admixed with several dosages of the alkali-free accelerator. Setting was also determined on samples prepared with cement having different ageing times (from 10 min

Table 2
Chemical and physical characteristics of cement (analyses performed according to ENV 196/2)

CaO (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	SO_3 (%)	Cl (%)	SO_3 (%)	Free CaO (%)	Na_2O equivalent (%)	Density (kg/m^3)	Blaine specific surface area (m^2/g)
61.2	21.5	5.8	2.7	1.7	2.2	0.01	2.2	0.15	0.7	3160	400