	Raw material Mw				
	Polymethacrylic	Methoxy			
	acid	Polyethylene Glycol			
Supplier Molecular weight data	4000	750	_		
	Graft polymers				
	molar ester		calculated Mw	n number of	Mw(m) of
	per	percentage		monomer unit	monomer unit
Polymer P1	70	30	14214	46,5	305,6
Polymer P2	62	38	16938	46,5	364,2
Polymer P3	55	45	19321	46.5	415,4

Table 1. Chemical composition of the raw materials and graft polymers

Table 2. Cement analysis data sheet and Bogue calculation

Chemical analysis		Bogue calculation %		Table 3. Concrete mixing proportions	
	Average % weight analysis			1	Kgs / m3
Insoluble	0.28	C3S	56.0	Normal portland cement CEM I	340
SO3 total	3.36	C2S	14.6	Limestone	145
CO2	0.78	C3A	7.5	Fine powders (cement + limestone) 485
PF	1.83	C4AF	8.8	Sand 0/4 (mm)	820
SiO2	20.08			Aggregates 4/8 (mm)	305
AL203	4.69			Aggregates 8/12 (mm)	440
Fe2O3	2.89			Water	228
CaO	64.07			A/S	0.909
MgO	0.75			T 11 4 0 11 1 1 1 4 1 1	
Cl-	0.018			Table 4. Supplier calcite tech	nical data shi
S	0.007				
Na2O eq tot	0.83			Particale size D50 (µm)	64
Na2O eg sol	0.76			Specific area (m ² / g)	19,5
				Iso electric point	8,8 - 9
SSB (cm2 / g)	3618			Morphology	rhomboedric

Particale size D50 (µm)	64
Specific area (m ² / g)	19,5
Iso electric point	8,8 - 9
Morphology	rhomboedric

Table 5. Weight isotherm plateau data

	[polymer] mg / g of calcium carbonate			
lsotherm plateau	P1	P2	P3	
no added salt pH 12.6	9.124	9.257	7.970	
Na2SO4 50 mmole / I pH 12.6	7.857	7.060	5.536	
Na2SO4 200 mmole / I pH 12.6	4.895	1.907	0.105	
NaCl 50 mmole / I pH 12.6	_	8.074		
NaCl 136 mmole / I pH 12.6		7.402		

Table 6. Molar isotherm plateau data

	[polymer] mmole.10 ³ / g calcium carbonate			
Isotherm plateau	P1	P2	P3	
no added salt pH 12.6	0.642	0.547	0.413	
Na2SO4 50 mmole / I pH 12.6	0.553	0.417	0.287	
Na2SO4 200 mmole / I pH 12.6	0.344	0.113	0.005	
NaCi 50 mmole / i pH 12.6		0.477		
NaCl 136 mmole / I pH 12.6		0.416		







Na2SO4 concentration with polymers P1, P2, P3 and P4







Na2SO4 / NaCl ionic strength with polymer P2

<u>SP-217—14</u>

Effects of Increasing Dosages of an Alkali-Free Accelerator on the Physical and Chemical Properties of a Hydrating Cement Paste

by A. Bravo, T. Cerulli, C. Maltese, C. Pistolesi, and D. Salvioni

Synopsis:

Flash setting accelerators are commonly used for shotcrete which is basically a sprayed concrete for underground constructions. Such admixtures cause a very rapid hardening of cementitious systems thus allowing overhead and vertical applications. Two main classes of products are currently available in the market: alkali-free (non al-kaline aluminium salts) and alkali rich (sodium or potassium silicates or aluminates) accelerators. The first ones were commercially available in the last few years but only recently they have started to be appreciated by the market. The wide literature on the subject shows that the use of alkali-free accelerators gives many advantages: reduced chemical reactivity of the admixture toward human skin; less rebound, high water impermeability, increased long term compressive strength of sprayed concrete.

The action mechanism of alkali-free flash setting admixtures is still not clear; therefore, a chemical morphological analysis was carried out in order to study the effects of this new class of accelerators on the physical/chemical properties of cement pastes. XRD and temperature profile studies were performed on cement systems added with different amounts of accelerator. An ESEM study was also carried out in a time interval from a few minutes to 8 hours. Specific surface area was determined according to BET method on mortar samples mixed with the accelerator (2% and 6% by cement mass) after 24 hours and 28 days of curing. Furthermore soluble ions concentration (Al³⁺, SO₄²⁻) was also determined by ICP spectroscopy. Setting time and compressive strength were measured to compare the effects of the admixture on the mechanical properties of modified mortars with respect to its influence on the chemistry and morphology of hardening cement.

Keywords: accelerator; alkali free; ettringite; setting time

212 Bravo et al.

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INTRODUCTION

Today flash setting accelerators are commonly used to increase the stiffening rate of sprayed concrete during tunnel excavation (1,2,3,4). They are available in liquid or solid form depending on the spraying technique, which can be wet or dry (4). Such concrete admixtures are mainly divided into two categories: alkali-free and alkali rich. According to some European standards (For example the Guideline Shotcrete "Final Draft" Edited by Austrian Concrete Society, 20/02/97) a setting admixture is defined "alkali-free" when its alkali metal content, expressed as Na₂O, is lower than 1%. Normally they are water solutions or slurries of aluminium sulphate complexes. Alkaline accelerators are alkali metal hydroxides, alkali metal silicates or aluminates, with strong caustic character (5,6). In the past they were the most commonly used. Today, mainly in several European countries, alkali-free accelerators have started to be strongly required by the market. The increasing demand is due to the health risks connected with the use of strong basic substances. They cause damages on the respiratory system, burns and irritations on eyes and skin. Furthermore the incorporation of alkali metals ions into concrete could cause: long term strength reduction, increase in shrinkage and alkali-aggregate reaction. For these reasons, they affect the durability of concrete structures.

Superplasticizers and Other Chemical Admixtures in Concrete 213

Only recently some papers have been published on the working mechanism of flash setting accelerators (6,7,8) which has not been well clarified yet. This study was carried out to analyse the effects on cement hydration of different dosages of an alkali-free accelerator in order to understand a possible mechanism of action.

EXPERIMENTAL DETAILS

Raw materials

A portland cement type 1 52,5 (according to ENV 196/1) and a liquid alkalifree accelerating admixture (Dry Content:50%; Al₂O₃:16%; SO₃:17%; Density: 1,4g/cc) were used. A normalised (ENV 196/1) silica sand (0-2,5mm) was utilized for mortar preparation.

Mechanical Test

The mortars were prepared according to ENV 196/1 (Water/Cement: 0,4; Cement/Sand: 0,33; 1% by cement mass of an acrylic superplasticizer).

At the end of standardised (ENV 196/1) mixing cycle, the accelerator was added and mixed for 10 seconds. After 24 hours of curing at 20° C and 95% R.H., the samples (40x40x160mm) were demoulded and cured at 23° C and 50% R.H.. Compressive strength was determined on a size of 40x40mm of the prismatic specimens. The data are reported in Fig. 1.

Setting time measurements were carried out according to ENV 196/3 (Vicat needle method) on cement pastes without and with 2%, 4% and 6% by cement mass of accelerator (Tab. 1). The procedure is deeply explained elsewhere (3).

Morphological and Chemical-Physical Analyses

Cement pastes, mixed as described for the setting time determination, were studied as follows.

X Ray powder diffraction (XRD) pattern was analysed (Fig. 2 to 5- Philips PW 1830 diffractometer with Cu(K α) radiation) after 5 minutes, 30 minutes, 8 hours and 24 hours of cement hydration.

Temperature profile in the first 15 hours of hydration, was measured (Figs. 6,7) by a digital thermometer type Testo mod.781 inserted in a sample (0,5 kg) of cement paste. The cell containing the specimen was kept in a temperature controlled box (20°C).

214 Bravo et al.

An ESEM (Environmental Scanning Electron Microscopy-Instrument type Philips mod. XL30 ESEM FEG) study was performed from 5 minutes to 8 hours (vapour pressure of 6.0 Torr and 5°C by means of a Peltier stage- Figs. 10-15) of curing.

The specific surface area by B.E.T. method was determined on cement pastes by instrument type Coulter mod. SA3100 at 24 hours and 28 days (Fig. 8) of hydration.

Soluble ions $(Al^{3+} \text{ and } SO_4^{-2})$ concentration was measured (Fig. 9) according to the following procedure:

- 1) After 30 minutes, 3 hours and 24 hours of hydration the resulting specimen was ground;
- 2) The obtained fine powder was dipped in water (2,5 Water / Powder ratio) and mixed for 15 minutes in order to dissolve soluble ions;
- 3) ICP spectroscopy (Induced Coupled Plasma by Liberty 220 Varian Spectrometer) was employed to detect ion concentration.

RESULTS

Mechanical Test

Setting time data are presented in Table 1. Surprisingly a dosage of 2% of accelerator caused a retarding action (setting time of the reference is shorter than the sample with 2% of flash setting admixture). It was noted that higher amounts of admixture improved accelerating efficiency.

The compressive strength results are reported in Fig. 1. The accelerator slightly reduced the 24 hours mechanical strength. Such an effect was more evident at higher admixture dosages. The 28 days compressive strength of the accelerated specimens was of the same order of magnitude as that of the reference mortar.

Chemical-Physical and Morphological Analyses

The temperature profile is associated with the rate of heat liberation (9). The first peak (Fig. 6) is due to initial cement hydration and formation of hydrated sulphoaluminates. On the other hand, the second peak is related to a massive hydrated calcium silicate and portlandite precipitation (Fig. 7). This step is normally defined as "acceleratory period" and it is connected to the initial setting of the cement system.

During the initial hydration stage, an increase of temperature was observed at increasing admixture concentrations. Different amounts of hydrated sulphoaluminates, produced during the initial cement hydration, explain such effect. In fact, aluminium sulphate, contained in the accelerator, supplied a

Superplasticizers and Other Chemical Admixtures in Concrete 215

considerable amount of Al^{3+} and SO_4^{2-} in the cementitious pore solution, thus favouring sulphoaluminate formation.

The accelerator retarded the second temperature increase (≈ 4 hours with respect to 2 hours of the reference), as can be observed in Fig. 7. The increase of admixture rate determined a lowering of peak intensity and its displacement toward later times. The effect was more evident for a dosage of 6%. These experimental findings strongly suggest that the accelerator slows down C₃S hydration thus reducing early mechanical performance. As confirmed by the 24 hours compressive strengths of the accelerated mortars (Fig. 1) which are lower than the reference.

XRD performed after few minutes of hydration did not show a massive formation of crystalline phases (Fig. 2). Only a small amount of crystalline ettringite was revealed that was very similar to the reference. After 30 minutes (Fig. 3), a larger ettringite quantity was detected in cement pastes added with the accelerator. Its concentration increased at increasing dosages of admixture (Figs. 3.4.5). Although XRD is only a semi-quantitative analytical method, such hypothesis is also supported by the peaks showed in Fig. 6. As previously mentioned, according to the literature (9), these peaks are connected to the initial formation of hydrated sulphoaluminates. Figure 6 shows that increasing dosages of accelerator cause an increase of peak intensity, which means a more pronounced hydrated sulphoaluminates formation. Portlandite was clearly detected after 8 hours of hydration in the cement paste without admixture (Fig. 4). At 24 hours a possible decomposition of ettringite occurred leading to the formation of hydrated calcium monosulphoaluminate. Furthermore it seems that the accelerator caused a reduction of portlandite formation during the first day of curing (Fig. 5). The effect was more pronounced at higher admixture rates.

A small decrease of specific surface area was evident when 2% of admixture was employed (Fig. 8). A higher accelerator quantity caused an evident increase in surface area. At later curing times a general surface area reduction was noted at all dosage levels.

In Fig. 10, the ESEM micrograph of the reference paste after 5 minutes of hydration is presented. Crystals of hydrated calcium aluminates and globular masses surrounding cement grains were visible. At 2 hours and 30 minutes, which is the initial setting time, a sort of coagulation occurred and a gel like phase was clearly evident (Fig. 10). At this stage the acceleratory period already started, as observed on the temperature profile (Fig. 7), and a massive precipitation of hydrated calcium silicates was occurring. At the end of setting, 3 hours and 30 minutes, a densification of the gelatinous material was observed (Fig. 11). After 8 hours of curing, fibrous C-S-H and plates of calcium hydroxide were also visible, as confirmed by XRD pattern.