can be achieved. Nevertheless, during the change over phases of the pipe links or for rheological reasons (for example poor fluidity of sprayed concrete), a strong increase of accelerator concentration can occur which could affect hydrating cement properties.<sup>6,7</sup> Practical experiences show that extremely high accelerator dosages can negatively influence mechanical strength development of the sprayed concrete. This study was carried out in order to elucidate this phenomenon. Therefore, several cement paste samples, admixed with variable amounts of different alkali-free accelerators, were characterised for mechanical, morphological and crystal chemical properties.

### **EXPERIMENTAL DETAILS**

#### Raw materials and specimens preparation

Two portland cements, type II/A-S 42,5 R and II/A-LL 42,5 R (according to ENV 196/1; Table 1), and three liquid alkali-free accelerating admixtures (Table 2) were used.

- Cement pastes were prepared according to the following procedure:
- 1. Cement was added to water (*w*/*c*: 0.4).
- 2. The mixture was stirred by a spatula for 15 seconds to obtain a homogenous slurry.
- 3. The mixing procedure was stopped for 1 minute.
- 4. Different amounts of the liquid alkali-free accelerator (one containing an inorganic acid as aluminium ions stabilizing agent, one containing an organic acid as aluminium ions stabilizing agent and another without any stabilizing agent) were added and mixed for 10 seconds.

The resulting samples were cured at 20°C (68°F) and 50% R.H.

#### **Mechanical tests**

The accelerator performance was evaluated by measuring final setting time of the samples indicated in Tables 3 and 4 (ENV 196/3 – each result is an average of three measurements). Compressive strength was determined on cylindrical specimens [13 x 25 mm (0.5 x 1 in.)] after 1, 4, 8, and 24 hours of hydration by a compressive test machine, Controls type L1301. Typical strength versus time plots are shown in Figure 1, Cem. II/A-LL 42,5 R and alkali-free accelerator without stabilizers, and Figure 2, Cem. II/A-S 42,5 R and alkali-free accelerator without stabilizers. Mechanical strength was also measured by a digital force gauge Imada model DPS 100<sup>8</sup> when the samples were too soft to be demolded.

#### Morphological and chemical analyses

Some of the cement paste samples (Table 5), mixed as previously described, were treated with acetone in order to stop the hydration after 1, 2, 4, 8, 16, and 24 hours. These treated samples were then analyzed by X Ray Diffraction (XRD) and Thermogravimetry/Differential Scanning Calorimetry (TG/DSC), while for ESEM-FEG (Environmental Scanning Electron Microscopy – Field Emission Gun) analysis, untreated samples were used.

XRD analyses were performed with a PANalytical X'pertPro MPD diffractometer, equipped with an X'Celerator detector. All the patterns were collected working with Cu(K $\alpha$  radiation (1.54184 Å) in the 2theta range 5–80, a step size of 0.017°. These analyses were carried out with the double aim of identifying every crystalline phase, and quantifying the unhydrated cement compounds. The samples quenched with

acetone, were then heated at a temperature to eliminate all the hydrated phases, keeping the unhydrated ones intact for analysis. Data refinements according to Rietveld method<sup>9</sup> have been performed with GSAS<sup>10</sup> software using the EXPGUI graphical user interface<sup>11</sup> to obtain quantitative information. All structural models were taken from the "Inorganic Crystal Structure Database (ICSD)" (Figs. 3-6).

Water loss between 80° and 300°C (176 and 572°F) (mainly coming from hydrated sulphoaluminates<sup>12</sup>) and calcium hydroxide [300 to 500°C (572 to 932°F)<sup>13</sup>] after 5 minutes till 24 hours of curing were determined by TG/DSC (Table 6 – Netzsch model STA409 – each value being an average of two measurements).

An Environmental Scanning Electron Microscope (Philips mod. XL<sub>3</sub>o ESEM-FEG) was used to analyse the morphology of hydrating cement pastes. The special instrumental configuration of the ESEM-FEG allowed working at a low vacuum setting (6 Torr), with a 10 kV voltage, at a temperature of  $5^{\circ}C(41^{\circ}F)$ . Therefore, the sample could be analysed in the presence of significant amounts of residual water. These measurements were performed up to 24 hours of curing (Figs. 7-10).

### RESULTS

#### Mechanical test

The results reported in Tables 3 and 4 and Figures 1 and 2 show that increasing accelerator dosages shorten final setting times, increase the initial compressive strength development up to 4 hours of hydration, but reduce strengths at later curing ages (16 and 24 hours). The last effect is dramatic at very high accelerator concentrations (16-18% by cement mass), where 24 hour compressive strengths remain quite similar to the value after 16 hours.

#### Crystallographic and morphological analyses

XRD performed on the reference sample (Ref) from 1 hour to 24 hours points out ettringite and portlandite formation, respectively, after 1 and 4 hours of hydration (Fig. 3). A similar behaviour was also observed on paste series L (7% by cement mass of the alkalifree accelerator; Fig. 4) and paste series H (18% by cement mass of the alkali-free accelerator; Fig. 5) with the difference that with increasing accelerator concentrations, an increase in ettringite and a reduction of portlandite signal intensities occur.

QXRD analysis shows that  $C_3A$  is involved in the hydration reaction only within the first hour. Comparable hydration patterns were noticed between Ref and L (Fig. 6). In the contrary, 18% by cement mass of the alkali-free accelerator appears detrimental to  $C_3S$  hydration, which remains nearly unchanged at least up to 24 hours of curing.

Thermal analyses (Table 6) support XRD results: an increase of accelerator dosage promotes hydrated sulphoaluminate formation reducing the amount of portlandite.

A massive ettringite formation was clearly visible on the accelerated samples (refer to Figures 7 and 8). Quantity and crystal size seem correlated to the accelerator concentration such that increasing dosages correspond to higher amounts and larger dimensions (Fig. 7 compared to Fig. 8) of ettringite crystals. Furthermore, crystal size increase was noticed as time proceeds (Fig. 7 respect to Fig. 9). Significant morphological changes were not observed on the cement paste sample admixed with 18% by cement mass of accelerator (Fig. 8 compared to Fig. 10).

# Superplasticizers and Other Chemical Admixtures 205 DISCUSSION

This paper clearly points out that alkali free accelerators reacting with portland cement accelerate ettringite formation thus confirming previous studies.<sup>3,6,14,15,16,17</sup> Furthermore, very high accelerator concentrations are shown to strongly reduce 24 hours compressive strength development. In order to clarify this phenomenon, a short summary of the knowledge regarding setting and hardening of a "normal" Portland cement based system should be discussed.

The term "setting" means a loss of plasticity of the original paste, and its conversion to a solid material with a measurable strength normally within the first 3-5 hours of hydration. Normal set of an ordinary portland cement occurs when the apparent viscosity of the paste increases due to progressive hydration of the cement that results in a gradual increase of the existing solid/liquid ratio caused by the precipitation of the hydrates (C-S-H and Ca(OH)<sub>2</sub>;<sup>18</sup>). To produce a cement with acceptable setting characteristics, calcium sulphate as a setting regulator has to be added to the clinker. According to, for example Collepardi, calcium sulphate reacts immediately with calcium hydroxide, C<sub>3</sub>A, C<sub>4</sub>AF and water to form a thin microcrystalline layer of AFt (Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-tri) phase which slows down its hydration.<sup>19</sup> Flowability and plasticity of the cement paste are therefore preserved until normal setting. After setting, the cementitious system starts to harden which is a development of hardness and strength arising from the growth of a continuous three-dimensional network of hydrated calcium silicate phases, which can resist external stress without being broken down.<sup>20</sup>

In a previous paper, the authors, studying different accelerator classes (one containing an inorganic acid as aluminium ions stabilizing agent, one containing an organic acid as aluminium ions stabilizing agent and another without any stabilizing agent), noticed that low alkali-free accelerator dosages , 2- 3% by cement mass, hinder proper cement hydration, thus contributing to retarded setting and low mechanical strength development at early age.<sup>6</sup> On the contrary, higher quantities (4-9% by cement mass;<sup>6</sup> Tables 3 and 4 and Figs. 1 and 2) favor fast setting and proper mechanical strength development of the accelerated cementitious system. This paper shows that very high accelerator dosages (18% by cement mass) allow a very fast setting and very high initial mechanical strength increase (Figs. 1 and 2). Nevertheless, up to 24 hours of curing, a nearly complete stop of C<sub>3</sub> S hydration is evident (Figs. 1 and 2; 2 MPa after 24 hours of curing) as confirmed by XRD, TG/DSC (Fig. 5 and Table 6; low portlandite formation) and QXRD (Fig. 6; constant C<sub>3</sub> S content).

On the basis of the already mentioned setting and hardening processes of a normal portland cement and considering the results of this and previous papers,<sup>6</sup> a possible explanation of the accelerator dosage effects can be hypothesised:

1. Low accelerator amount (normally 2- 3% by cement mass) means that aluminium sulphate, contained in the admixture which supplies low amounts of Al<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> in the cementitious pore solution, can only promote the formation of small quantities of ettringite. Therefore, only a thin secondary coat of hydrated calcium sulphoaluminates can be formed on the microcrystalline layer of AFt phase (arising from the setting regulator<sup>14</sup>). This secondary coat can slow down cement hydration, and therefore be the cause of the retarded setting and low initial mechanical strength development of cementitious systems admixed with low accelerator dosages.

- 2. Medium accelerator concentrations (normally 4-9% by cement mass), which can supply higher quantities of Al<sup>3+</sup> and SO <sup>2-</sup> ions, favour immediate and extensive ettringite formation (Figs. 4 and 7 and Table 6). Fast setting of these accelerated systems can be compared to the normal set of a portland cement<sup>13</sup> with the difference that hydrated, the sulphoaluminates immediately replace the standard precipitation of C-S-H and Ca(OH)<sup>2</sup> (which occurs after 3-5 hours). This formation and the consequent increase of solid/liquid ratio cause a viscosity increment, followed by a rapid stiffening of the accelerated cementitious mass. During the first 4 hours, when C<sub>3</sub>S hydration is still at a very early stage (Fig. 6 and Table 6), mechanical strength development can arise from the growth of ettringite crystals (Figs. 7 and 9), which could form a continuous three-dimensional network of hydrated calcium sulphoaluminate phases. After 4 hours, the contribution to the strength increase arising from C-S-H formation also starts to be effective (Fig. 6 C<sub>3</sub>S reduction and Table 6 Portlandite increase).
- 3. Very high accelerator content (13-18% by cement mass) can create a very large amount of ettringite, thus promoting very fast setting and very high early mechanical strength development. Nevertheless, this layer could be so thick so as to probably hinder proper C<sub>3</sub>S hydration (Fig. 6), and therefore, the compressive strength at later curing time (when the contributions of C-S-H to the strength development becomes predominant) could be limited (Figs. 1 and 2).

The last condition is extremely dangerous for the safety and speed of tunnelling operations. In fact, if the mechanical strength of the sprayed layer does not increase rapidly, material collapses can occur.

### CONCLUSIONS

This study points out that very high alkali-free accelerator dosages can strongly hinder the strength development of concrete. This effect could arise from the thick layer of hydrated calcium sulphoaluminates formed during the first minutes of reaction between the alkali-free accelerator and hydrating cement. This layer could act as a barrier to water penetration retarding cement hydration. A mechanism to explain the different physical-mechanical effects of different accelerator dosages has been proposed.

In order to improve safety and speed up tunnelling operations, very high accelerator dosage should be avoided, optimising concrete spraying operations.

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C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Gypsum	Anhydrite	Bassanite	Portlandite	Calcite
53.6	17.0	6.1	5.6	6.9	not	3.6	1.2	6
(+/-0.2)	(+/-0.4)	(+/-0.2)	(+/-0.3)	(+/-0.2)	detected	(+/-0.2)	(+/-0.1)	(+/-0.3)
50.7	12.7	6.9	3.5	5.1	4.5	3.0	not	13.6
(+/-0.2)	(+/-0.5)	(+/-0.2)	(+/-0.2)	(+/-0.2)	(+/-0.2)	(+/-0.2)	detected	(+/-0.3)

#### Table 1—Cement compositions, %

Note: Determined by QXRD; upper line corresponds to Cem. II/A-S 42,5 R; lower line corresponds to Cem. II/A-LL 42,5 R; standard deviation is indicated between brackets.

#### Table 2—Chemical physical characteristics of the accelerators

	Inorganic acid based alkali free accelerator	Organic acid based alkali free	Accelerator without stabilizers
Solid Content (% - EN 480/8)	38.8	43.6	39.1
Main Composition (% by mass)	Al <sub>2</sub> O <sub>3</sub> : 16 SO <sub>3</sub> : 17 Inorganic Acid: 1 (0.68 M)	Al <sub>2</sub> O <sub>3</sub> : 16 SO <sub>3</sub> : 17 Carboxylic Acid: 7(2M)	Al <sub>2</sub> O <sub>3</sub> : 16 SO <sub>3</sub> : 17
Density (g/ml – ISO 758)	1.36	1.38	1.35

### Table 3-Setting times on Cem. II/A-S 42,5 R

	Accelerator dosage	Final setting time
	7	15 min 25 sec (+/-2 min)
	13	3 min 30 sec (+/-30 sec)
inorganic acid based alkali-free accelerator	16	1 min 50 sec (+/-10 sec)
	18	1 min 10 sec (+/-10 sec)
	7	18 min 15 sec (+/-2 min)
Owners a sid based alles! for a secoloristar	13	7 min 15 sec (+/-1 min)
Organic acid based alkali-free accelerator	16	4 min 35 sec (+/-1 min)
	18	2 min 30 sec (+/-30 sec)
	7	17 min 25 sec (+/-2 min)
	13	4 min 50 sec (+/-1 min)
Alkali-free accelerator without stabilizers	16	4 min 10 sec (+/-1 min)
	18	3 min 35 sec (+/-1 min)

Note: standard deviation is indicated between brackets.

	Accelerator dosage	Final setting time
	7	3 min 30 sec (+/-1 min)
	10	3 min oo sec (+/-1 min)
inorganic acid based alkali-free accelerator	13	2 min 45 sec (+/-30 sec)
	16	1 min 55 sec (+/-30 sec)
	7	6 min 10 sec (+/-1 min)
Oversis asid based alkali free assolator	10	5 min oo sec (+/-1 min)
organic acid based alkali-free accelerator	13	3 min 20 sec (+/-1 min)
	16	3 min oo sec (+/-1 min)
	7	19 min 40 sec (+/-2 min)
Alkali frag accolorator without stabilizars	10	15 min 15 sec (+/-2 min)
	13	10 min 20 sec (+/-2 min)
	16	5 min 15 sec (+/-1 min)

Table 4—Setting times on Cem. II/A-LL 42,5 R

Note: standard deviation is indicated between brackets.

### Table 5—Samples for analytical evaluation

Component	Ref	L	Н
Cement II/A-S 42,5 R (g)	100	100	100
Water/cement ratio	0.4	0.4	0.4
Acclerator, % by cement mass	0	7	18

	Time, hour	Portlandite, %	Water from hydrated sulphoaluminates, %		
Ref	1	1.9 (+/- 0.2)	2.3 (+/- 0.2)		
	2	2.0 (+/- 0.2)	2.3 (+/- 0.2)		
	4	2.7 (+/- 0.3)	2.4 (+/- 0.2)		
	8	3.8 (+/- 0.3)	/		
	16	9.1 (+/- 1.0)	/		
	24	13.0 (+/- 1.0)	/		
	1	1.6 (+/- 0.2)	9.2 (+/- 1.0)		
	2	1.6 (+/- 0.2)	9.0 (+/- 1.0)		
	4	2.0 (+/- 0.2)	9.0 (+/- 1.0)		
	8	3.7 (+/- 0.3)	/		
	16	7.9 (+/- 0.6)	/		
	24	8.7 (+/- 1.0)	/		
	1	0.9 (+/- 0.1)	14.4 (+/- 1.5)		
	2	1.2 (+/- 0.1)	15.0 (+/- 1.5)		
Н	4	1.2 (+/- 0.1)	18.7 (+/- 2.0)		
	8	1.8 (+/- 0.2)	/		
	16	3.3 (+/- 0.3)	/		
	24	3.7 (+/- 0.3)	/		

Table 6—TG/DSC Analyses



Fig. 1—Compressive strength development of cement paste samples (Cem. II/A-LL 42,5 R) accelerated with different dosages of the alkali-free accelerator without stabilizers [24 hours compressive strength of the specimens without accelerators is 12.0 MPa (1740 psi)].

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Fig. 2—Compressive strength development of cement paste samples (Cem. II/A-S 42,5 R) accelerated with different dosages of the alkali-free accelerator without stabilizers [24 hours compressive strength of the specimens without accelerators is 12.5 MPa (1810 psi)].



Fig. 3—XRD analyses of reference cement paste samples (Cem. II/A-S 42,5 R; The lower to the upper lines correspond to the XRD patterns at 1, 2, 4, 8, 16, 24 hours of hydration).



Fig. 4—XRD analyses of cement paste samples admixed with 7% of the alkali-free accelerator without stabilizers (Cem. II/A-S 42,5 R; The lower to the upper lines correspond to the XRD patterns at 1, 2, 4, 8, 16, 24 hours of hydration)

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Fig. 5—XRD analyses of cement paste samples admixed with 18% of the alkali-free accelerator without stabilizers (Cem. II/A-S 42,5 R; The lower to the upper lines correspond to the XRD patterns at 1, 2, 4, 8, 16, 24 hours of hydration)



Fig.  $6-C_3S$  amount vs. time in the three systems. (Note: Values are normalized to 100.)



Fig. 7–ESEM micrograph of L after 1 hour of hydration (unit length 1  $\mu$ m).

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