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The influence of alkali-free and alkaline shotcrete accelerators within cement systems

I. Characterization of the setting behavior

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Abstract

The influence of alkali-free and alkaline accelerators on the setting behavior of cementitious mixtures is investigated. The aluminium sulfate present in the alkali-free accelerators promotes the crystallization of ettringite prisms (2–7 μm) between the clinkers, thus connecting them in a compact mass and accelerating the setting. The very rapid setting promoted by the addition of the alkali $KAl(OH)_4$-rich admixture is mainly the result of the precipitation of CH plates and amorphous KCASSH hydrates. In this case, the crystallization of elongated ettringite rods contributes to a smaller extent to the setting. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Accelerating admixtures comprise chemicals that influence the rate of cement hydration, thereby shortening the setting time and, in some cases, increasing the rate of early strength development. Set accelerators affect both the C_3A hydration (by interfering with the C_3A–gypsum reaction) and the C_3S hydration (aiding the dissolution of lime) [1]. They mainly consist of calcium chloride, carbonate, silicate, aluminate [2], alkali metal hydroxide, and organic chemicals [1].

The alkali-free and -rich accelerators used in this work influence both the C_3S and the C_3A hydration and are employed in shotcrete for tunnel applications [4]. In this context, the accelerators of the setting become especially important when concrete (shotcrete) or mortar (gunite) are sprayed onto the tunnel walls for immediate temporary support following excavations in unstable ground [1], where a satisfactory adhesion to the substrate is required.

For the improvement of the mechanical parameters, working conditions, safety, lower environmental impact, and easier maintenance of existing tunnel facilities, alternative alkali-free admixtures were developed. These alkali-free accelerators substitute the alkali-rich aluminate and silicate admixtures used until present [3,4]. Thus, because of improved general performance summarized in Table 1, alkali-free calcium-sulfoaluminate (CSA)-based accelerating admixtures were investigated.

2. Experimental

2.1. Binding materials

Ordinary Portland cement (OPC) "Untervaz" from the Bündner Cement Industry, Untervaz Switzerland was used. Its chemical and phase composition is given in Table 2. CSA (Rockfast 450), with its typical composition (Table 2), was provided by Blue Circle Industries (UK).

2.2. Admixtures

The accelerators were supplied by SIKA (Zurich, Switzerland) and consisted of a plasticizer and four main admixtures. The plasticizer Sikatard 902 was based on a sodium carboxylate polysulfonate aqueous solution. The

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Table 1
Comparison between alkali-free and alkaline accelerators (this was modified from Huber [3])

Parameters	Alkali-free accelerators	Alkaline accelerators
Working environment	less dust, reduced chemical burns	intense dust formation, risk of chemical burns
Shotcrete–admixture leaching (Mountain water)	less leaching, same pH as normal concrete	high leaching, high pH value
Tunnel drainage	less scale deposit	scale deposit
Technological features	less rebound, increased strength, water impermeability	extremely fast setting, high rebound, strength reduction, high porosity, low structural density
Average alkali content	$< 0.2\%$	$< 25\%$
pH of the admixture	4–6	11–(>)13

alkali-free accelerating admixtures consisted of powdery CSA with the addition of powdery $Al_2(SO_4)_3 \cdot 14H_2O$ as main components (CSA–SA), and an $Al_2(SO_4)_3 \cdot 14H_2O$-based viscous solution (SA). The addition of these admixtures was given the symbol "E" when no remarkable differences in the specimens were detected. In addition, the CSA component, which was a constituent of the CSA–SA accelerating additive, was separately investigated. The alkaline accelerator (AR) consisted of a $KAl(OH)_4$ aqueous solution.

2.3. Mixing procedure

Both cement paste and mortar specimens were prepared. Mortars were obtained by mixing dry carbonate- and quartz-bearing aggregates with OPC Untervaz for 1 min. Water previously mixed with 1% plasticizer was then added and the mixture further mixed for 3 min. The accelerating admixtures were then added in amounts as depicted in Table 3 and the mixing procedure was stopped after 45 s. The mixing was performed in a Hobart pan mixer.

The total w/c ratio (including the water content of the accelerator) was held at 0.46. The mixing water temperature was held at 21 ± 1°C, and the laboratory conditions were maintained at 21 ± 1°C and 65 ± 3% relative humidity.

2.4. Investigations

SEM investigations were carried out on broken surfaces of cement pastes previously dried for 4 h at 10^{-2} Torr. After further drying at 5×10^{-2} mbar for 24 h, the samples were coated with gold and examined with a conventional JEOL JSM 840 (wolfram filament) equipped with a Tracor Microtrace TM silicon X-ray spectrometer with pulsed optical feedback preamplifier 505 and a Tracor software system. The accelerating voltage was kept at 20 kV. XRD analysis were performed after 30 min and 4 h specimens hydration on dried (10^{-2} Torr) pulverized cement pastes (63 μm) with a Seifert OED using Cu Kα ($\lambda = 1.5405$ nm) at 40 kV and 30 mA with sample rotation. The thermal analysis were performed on pulverized cement pastes after 30 min of hydration with a Mettler TGA/DTA 851e thermobalance (coupled with a Balzers Thermostar quadrupole mass spectrometer) from 30°C to 1000°C using a heating rate of 10°C/min and at a flowing dry air of 3 l/h. The evaluations were made with a STARe 5.0 Mettler Toledo software. The setting times were registered with an automatic Proceq Typ R 31 211

Table 2
Chemical and phase composition of the investigated binders

Chemical composition			Phase composition		
	Binders			Binders	
Oxides	Cement I Untervaz	CSA	Phases	Cement I Untervaz	CSA
CaO	61.7	38	C_3S	42.8	–
SiO_2	20.6	3.6	C_2S	22.9	–
Al_2O_3	4.9	47.4	C_3A	9.1	–
Fe_2O_3	2.28	1.4	C_4AF	6.9	4
SO_3	2.70	7.5	free CaO	0.72	0.3
MgO	1.90	0.3	$CaSO_4$	4.58	–
Na_2O	0.23	–	$CaCO_3$	6.65	–
K_2O	1.15	0.16	MgO	1.90	–
TiO_2	0.24	2.2	CA	–	17
P_2O_5	0.22	–	C_2AS	–	16
Mn_2O_3	0.04	–	$C_{12}A_7$	–	1
SrO	0.09	–	CT	–	4
LOI	4.04	0.3	C_4A_3S	–	58

Table 3
Accelerating admixtures and dosages

Admixture	Dosage (%)
Alkali-free accelerator (CSA–SA)	6
Alkali-free accelerator (SA)	8
Alkaline accelerator (AR)	4.5

All dosages refer to the cement weight.

penetrometer where a needle, the penetration force of which equalized the penetration resistance of the mortar, slowly penetrated the sample.

3. Results and analysis

3.1. Setting behavior

Compared to the reference unaccelerated sample (REF), the addition of the alkali-free admixtures (CSA–SA and SA) and the alkaline one (AR) strongly shorten the initial and the final setting times (Fig. 1). The CSA component separately added indicates only a slight acceleration in the setting. The alkaline admixture (AR) shows the shortest setting times.

3.2. Phases development

After 30 min of hydration, thermal analysis (Fig. 2) indicates gypsum to be present with its main peak ranging between 120°C and 140°C for all the samples, except for the sample accelerated with the alkaline admixture. In this case, an overlap with an amorphous KCAS$\bar{S}$H-like phase takes place (Section 3.3), and the crystallization of CH (peak at 440°C) can further be noted. As confirmed by XRD (Fig. 3), thermal analysis shows ettringite to be the main phase formed for the alkali-free accelerated samples (E) with its peak between 60°C and 120°C, whereas for the CSA-enriched and the unaccelerated sample (REF), its crystallization occur only to a small extent. The formation of hemi-carboaluminate AFm phases can be observed at 250°C (Fig. 2).

Compared to the unaccelerated sample (REF), the investigated admixtures influence the course of the early hydration thus accelerating the consumption of both the clinker phases, C_3A and C_3S, and increasing the ettringite formation within the first 4 h (Fig. 3), in particular, for the alkali-rich (AR) and the alkali-free (CSA–SA and SA) admixtures.

3.3. Microstructural characterization

The development of the microstructure within the first 4 h of hydration is characterized by the formation of AFt phases of different morphology and size. The accelerators promote the formation of ettringite mainly through the saturation of the pore solution with respect to aluminate and sulfate ions. Amorphous ettringite were also detected. The development of CSH remains at an initial stage and CH crystallize in different amounts mainly with a hexagonal-like form due to the large pore space available (Fig. 4).

The unaccelerated sample indicates the initial crystallization of ettringite needles (Fig. 4, REF right), foil-like CSH gel, and CH small plates. However, the structure appears loose and the clinker shapes are still recognizable. The addition of CSA promotes the formation of ettringite small prisms (< 1 μm) and a more compact structure (Fig. 4, CSA). The addition of the alkali-free accelerators (CSA–SA and SA) leads to the crystallization of large amounts of ettringite prisms (2–7 μm) between the clinkers (Fig. 4E). The ettringite often contains silicon as also reported by Lukas [5] and Fe^{3+}, which substitute for the Al^{3+} ion in the crystal lattice [6] (Fig. 5, left). The resulting structure in this case is more compact. On the other hand, the alkaline

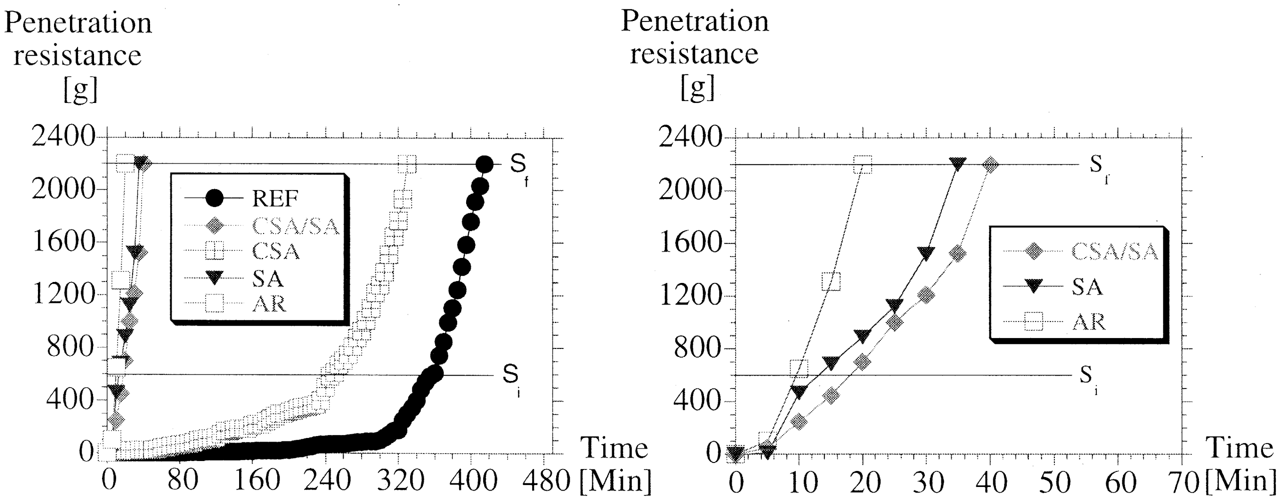

Fig. 1. Left: Penetration resistance against time. Right: Detail of the alkali-free (CSA–SA and SA) and the alkaline accelerators (AR).

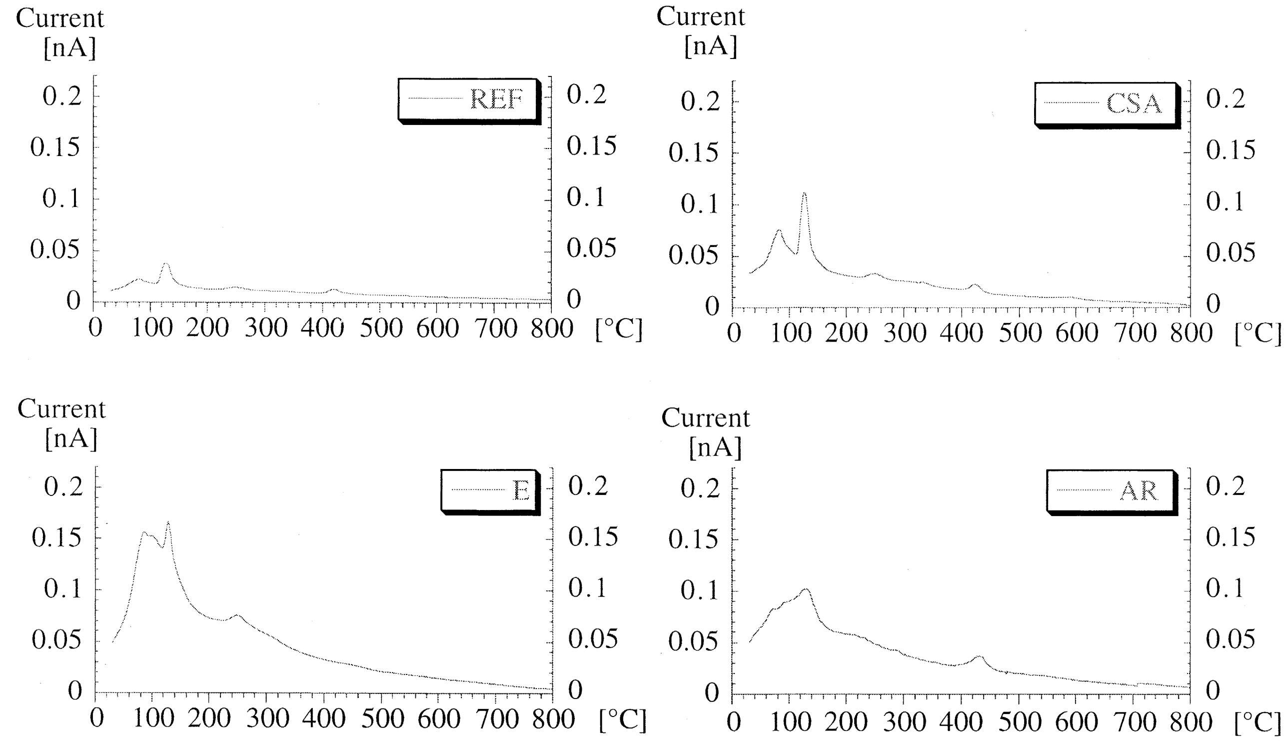

Fig. 2. DTA–H_2O liberation curves. Phases development during the first 30 min of hydration.

admixture promotes the crystallization of 3–4 μm elongated ettringite rods, amorphous KCAS$\bar{S}$H (Fig. 4, AR; Fig. 5, right), and CH plates (Fig. 4, AR).

4. Discussion

The setting of the unaccelerated sample (REF), being a normal cement, mainly follows the general fixed pattern of hydration stages suggested by Lea [1] and Taylor [2]. Its setting is completed within 6 to 7 h. Up to this stage, the microstructural investigations show an initial CSH crystallization with both foil-like and amorphous morphology and the formation of CH (2–3 μm). The CSH and the CH generally [1,2,7,8] contribute to the setting of unaccelerated samples (REF) (the small amounts of hydrates present at the contact points of neighboring clinkers appear to be sufficient for the setting). In addition, the setting of cement paste, being a mechanical process, does not directly follow the phase development at early stages, as also reported by Guo [9]. The fact that ettringites either arrange radially on the clinker surfaces or precipitate unoriented from the solution indicates that the concentration of the solution with respect to CH changes locally. Min and Mingshu [10] reported a clear relationship between CH concentration in the solution and the mechanism of ettringite formation (topochemical vs. through-solution) especially in CSA cements. Within this unaccelerated system (REF), only the ettringite crystals

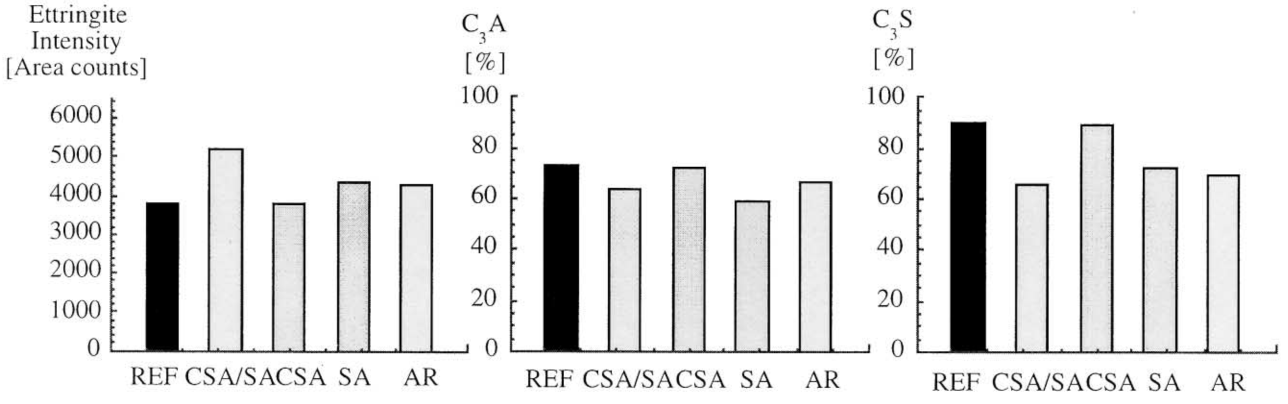

Fig. 3. XRD — the effect of admixture addition on the phase development between 30 min and 4 h of hydration.

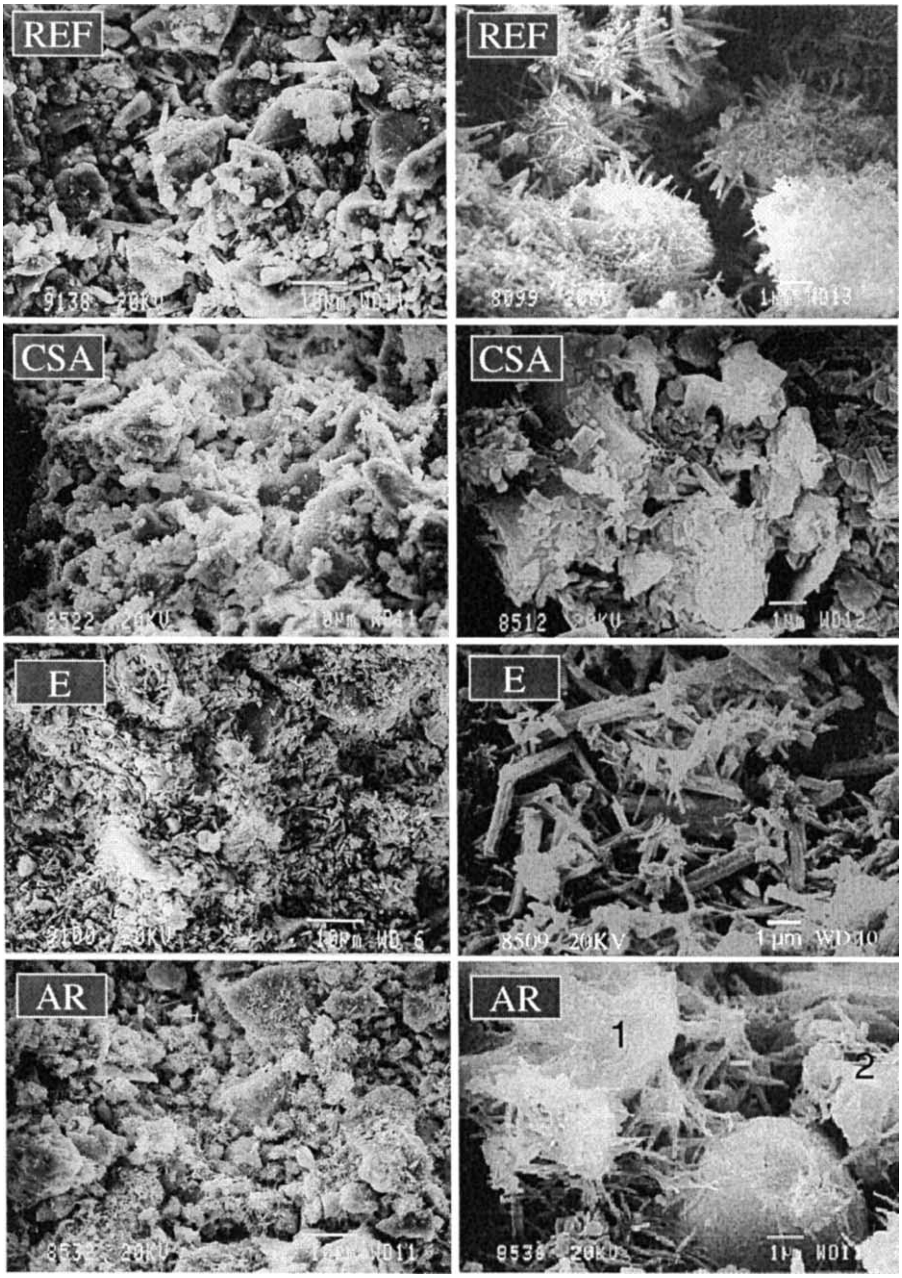

Fig. 4. Microstructure of the mixtures after 4 h. Left: General overview of the structure (magnification × 1500). Right: Details (magnification × 10,000). (1) KCASSH, (2) CH in the micrograph AR.

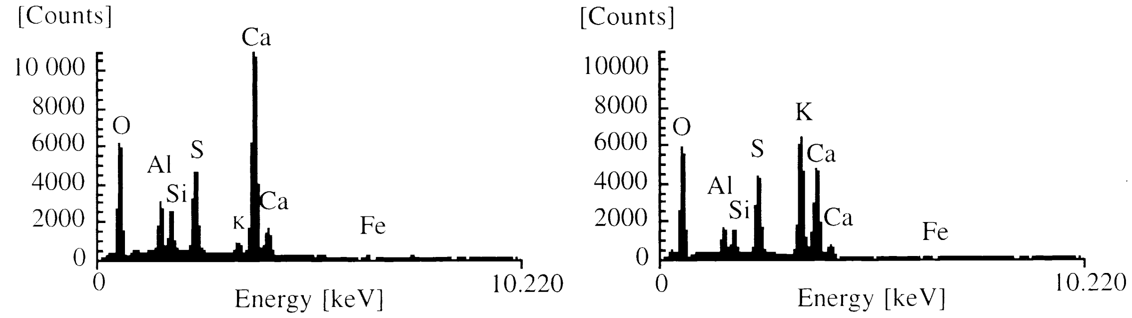

Fig. 5. EDX spectra. Left: Typical spectrum of the ettringite prisms crystallized with the addition of alkali-free accelerators (CSA–SA and SA). Right: Composition of the amorphous precipitate occurring with the alkaline accelerator (AR).

radially arranged on the clinker surfaces partially contribute in linking them and to a small extent to the setting of the sample. Nevertheless, the recrystallization of the ettringite [11], and its formation with a stubby rod morphology, are considered to be the main causes for the setting of OPC [12,13]. Ettringite needles precipitating from the solution do not appear to either partially fill the pores or to link the clinker particles to one another. This fact is mainly due to their small dimensions and amount.

The addition of CSA to the cement causes this phase to react with the formation of small prisms of ettringite on the clinker surfaces. As a consequence, more coalescence points between the clinkers are formed, thus connecting the structure. The setting time is therefore shortened (about 100 min).

The alkali-free accelerating admixtures (CSA–SA and SA) strongly accelerate the setting of the samples and change the course of the reactions especially at early stages. The influence exercised by these accelerators on the setting time has already been observed by other authors [1,9]. The CSA and the aluminium sulfate components of these accelerators promote the crystallization of ettringite prisms on the clinker surfaces at a very early stage. Within 4 h of hydration, these crystals grow and almost fill the capillary pores between the clinker grains, thus reducing the porosity. In all cases, the formation of ettringite prisms within the first 30 min is largely sufficient to set the samples. It must also be noted that gypsum is not found to contribute to the setting of the samples. In fact, the alkali-free accelerators contain a high amount of sulfates and this could be a premise for a false set [2]. Nevertheless, their aluminium content supports ettringite formation rather than gypsum. The slightly longer setting times compared to the alkali-rich admixture appear to be favorable for the shotcreting efficiency. The slightly prolonged setting of the mass allows to maintain a higher plasticity of the cementitious mass during the shotcreting process so that better adhesion onto the tunnel walls and reduced rebound is achieved. On the contrary, the very fast setting attained by using the alkali-rich admixture promotes a fast hardening of the cementitious mass, which in contact with the tunnel wall is easily rebounded.

The setting of the sample accelerated with the alkaline accelerator (AR) was due to the combined action of hydrates such as amorphous $KCAS\bar{S}H$, CH, and thin ettringite rods precipitated from the pore solution. The shortest setting times compared to the alkali-free accelerated samples (CSA–SA and SA) were due to the amorphous phase ($KCAS\bar{S}H$) and CH crystallization rather than the formation of ettringite rods. At very early stages of the hydration process (seconds to minutes), the solution concentration of unaccelerated cement systems is high in SO_4^{2-}, silicate, and saturated in Ca^{2+} ions [1]. The addition of the alkaline admixture promotes the rapid formation of $KCAS\bar{S}H$ and CH directly from the pore solution. The sulfate necessary for the formation of ettringite rod–crystals is not introduced in the system directly with the accelerator, as is the case for the alkali-free accelerated samples (CSA–SA and SA), but it derives from gypsum dissolution and it is consequently not available until later in the hydration process.

5. Conclusions

- Compared to the alkali-rich admixture, the slightly delayed setting attained with the addition of the alkali-free accelerators reduce the rebound and improve the productivity of shotcrete applications.
- The aluminium sulfate contained within the alkali-free admixtures acts as an accelerator and promotes the massive crystallization of ettringite prisms, which are responsible for the rapid setting.
- The very rapid setting obtained with the addition of the alkaline admixture can be attributed to the rapid precipitation of CH plates and amorphous KCASSH rather than to the ettringite formation.
- Both the alkali-free and alkaline accelerators promote the early hydration of C_3A and C_3S.

Acknowledgments

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References

[1] F.W. Lea, Lea's Chemistry of Cement and Concrete, P.C. Hewlett (Ed.), London, UK, 1998.
[2] H.F.W. Taylor, Cement Chemistry, second ed., Telford, London, 1997.
[3] H. Huber, Practical experiences with shotcrete containing alkali-free acceleration, Presented at Shotcrete for Underground Support VII, Telfs, Austria, 1995.
[4] D. Mai, Advanced experiences with high performance alkali-free nontoxic powder accelerator for all shotcrete systems, Presented at Sprayed Concrete Technology for the 21st Century, Edinburgh, 1996.
[5] W. Lukas, Substitution of Si in the lattice of ettringite, Cem. Concr. Res. 6 (1976) 225–234.
[6] H.H. Steinour, Chem. Rev. 40 (1947) 391.
[7] S. Chatterji, J.W. Jeffery, Studies of early stages of paste hydration of cement compounds, J. Am. Ceram. Soc. 46 (1963) 187–191.
[8] E. Breval, Cem. Concr. Res. 6 (1976) 129.
[9] C. Guo, Early-age behaviour of Portland cement paste, ACI Mater. J. 91 (1994) 13–25.
[10] D. Min, T. Mingshu, Formation and expansion of ettringite crystals, Cem. Concr. Res. 24 (1994) 119–126.
[11] E.E. Lachowski, S. Diamond, Cem. Concr. Res. 13 (1983) 177.
[12] W. Dosch, H. Keller, Presented at 6th ICCC, 1976.
[13] D.D. Double, Presented at Philos. Trans. R. Soc., New Development in Understanding the Chemistry of Cement Hydration, London, A310, 1983, 53–66.