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Alkali-free accelerators for shotcrete: A state-of-the-art review☆

Hui Xie [a,1], Xin Liu [a,1], Jiaxin Liao [b], Barbara Lothenbach [c], Frank Winnefeld [c], Xiao Liu [d], Xiangming Kong [b], Dining Li [a], Wei Wang [e], Song Mu [e], Jinxiang Hong [e], Pan Feng [a,*]

[a] State Key Laboratory of Engineering Materials for Major Infrastructure, School of Materials Science and Engineering, Southeast University, Nanjing, 211189, China
[b] Department of Civil Engineering, Tsinghua University, Beijing, 100084, China
[c] Laboratory for Concrete & Asphalt, Swiss Federal Laboratories for Materials Science and Technology (Empa), 8600, Dübendorf, Switzerland
[d] College of Materials Science and Engineering, State Key Laboratory of Materials Low-Carbon Recycling, Beijing University of Technology, Beijing, 100124, China
[e] Jiangsu Sobute New Materials Co., Ltd., Nanjing, Jiangsu, 211103, China

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ABSTRACT

Alkali-free accelerators (AFAs) are essential components in modern shotcrete, enabling rapid setting and early strength development while complying with increasingly stringent environmental and safety requirements. However, the growing complexity of AFA formulations and their interactions with cementitious systems has hindered the development of a unified understanding of their mechanisms and performance. This paper presents a comprehensive and systematic review of AFAs for shotcrete applications. The compositional design of AFAs is first summarized, highlighting their multi-component nature and the specific roles of individual constituents in accelerating setting and hardening. The effects of AFAs on cement hydration are then critically examined, with particular focus on sulfate balance in regulating aluminate reactions and the evolving understanding of silicate hydration. Subsequently, the influence of AFAs on key properties, including setting characteristics, strength development, and durability-related performance, is discussed. Compatibility issues with different cement types, supplementary cementitious materials, chemical admixtures, and environmental conditions are also evaluated. In addition, current international standards and guidelines for AFAs are compared. Overall, this review provides a structured framework for understanding AFA mechanisms and performance, offering guidance for the rational design of AFAs and their reliable application in engineering practice.

1. Introduction

Shotcrete or sprayed concrete is defined as the mortar or concrete that is projected pneumatically at high velocity onto a surface, according to ASTM C125-21a [1,2]. Due to its non-formwork construction, rapid setting and hardening, capability for applying for confined spaces, and efficient operation, it has been extensively employed in underground works, slope stabilization, pool construction, repair engineering, 3D printing, and other applications. According to the spraying process, shotcrete is classified into dry-mix and wet-mix shotcrete. In the dry-mix process, cementitious materials and aggregates are premixed and conveyed to the nozzle, where water is added before spraying; in contrast, wet-mix shotcrete involves pumping fresh concrete to the nozzle and ejecting it using compressed air [3,4]. Regardless of dry-mix or wet-mix, accelerators are among the most critical admixtures for shotcrete, playing a decisive role in early setting, hardening, and further property development [5].

Since the invention of the first cement gun by Dr. Akeley in 1907 [6], shotcrete accelerators have experienced several-generation development, as illustrated in Fig. 1. The first-generation powdered accelerator -Sigunite®- was introduced by the Swiss company Sika in 1933 [7]. It was mainly composed of basic carbonates or hydroxides, ensuring rapid setting and hardening via accelerating C_3S dissolution and hydration. Typically dosed at 2.5–6.0% of cement mass, it was primarily used in dry-mix shotcrete [8]. The severe dust generation associated with dry spraying promoted the development of wet-mix shotcrete in 1950s [3], which was accompanied with the prevalence of the second-generation of liquid alkali accelerators. Sodium silicate, as the main component of these accelerators, promotes C-S-H precipitation by accelerating C_3S hydration, thereby warranting the rapid setting and hardening [9].

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* Corresponding authors.
E-mail address: pan.feng@seu.edu.cn (P. Feng).

[1] These authors contributed equally to this work and should be considered co-first authors.

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Aluminate-based accelerators, e.g. sodium aluminate as a representative, were found to more effectively accelerate the setting and hardening of shotcrete in 1970s, by the formation of ettringite (AFt) in combination with $Al(OH)_3$ in a very short time [5,10].

The alkali bearing nature of these accelerators poses risk of alkali-aggregate reaction and low strength retention at late-age, threatening the durability of whole structure [11,12]. More importantly, the alkalinity of these accelerators poses serious health risks to construction workers [3,8]. Therefore, liquid alkali-free accelerators (AFAs) as the third-generation shotcrete accelerator have rapidly developed since the 1990s. With the main component of aluminum sulfate, AFAs promote the rapid and massive formation of AFt accelerating setting and hardening of shotcrete [5]. Owing to their effective early strength enhancement, minimal adverse impact on long-term strength, and improved safety, AFAs have taken over the major accelerator market. In 2025, the market value of AFAs for shotcrete reached approximately USD 450 million, accounting for nearly 90% of the total liquid shotcrete accelerator market, and this value is projected to grow to about USD 710 million by 2033 at a compound annual growth rate of 5.9% [13,14].

Over the last decade, a large body of research on AFAs has emerged, focusing on key macro-performances, hydration process, microstructure, durability, and application compatibility, as illustrated by the keyword co-occurrence analysis in Fig. 2. Among these topics, compressive strength and setting time, as the essential requirements for shotcrete, have become the major concerns in AFA studies. In more recent years, early strength, especially before 6 h, has been increasingly highlighted given the demands of infrastructures in highly unstable or fractured surrounding rock scenarios, water-rich conditions, low-temperature environments, etc. In order to unravel the acceleration mechanism of AFAs, hydration behavior, associated hydrates as well as microstructure have been extensively investigated using advanced experimental techniques and simulations, such as solid-state NMR and thermodynamic modelling, enabling the establishment of quantitative links between hydration behavior and macroscopic performance. In addition, durability-related topics have emerged, such as sulfate resistance, shrinkage, freeze-thaw cycles, and long-term performance, which have a strong correlation with steel fiber, mineral admixtures, and anti-freezing agent serving solutions for improving durability. The growing complexity of cementitious systems, coupled with harsher environment faced by shotcrete, has led to compatibility problems of AFAs in practical engineering applications.

Building on the abovementioned topics, the present review first summarizes the recent advancement in formulation of AFAs and discusses the existing theories regarding the effects of AFAs on hydration behaviors and hydration products to deepen our understandings on their acceleration mechanism. Moreover, the key properties of shotcrete, i.e., setting time, mechanical properties, and durability, together with the factors affecting the efficiency of AFAs (compatibility) are systematically reviewed. Standards and guidelines concerning shotcrete accelerators across different countries and organizations are further compared. This review delineates the state of the technical and emerging challenges in AFA research, offering mechanistic insights and practical guidance for improving the reliability and compatibility of shotcrete under complex service conditions.

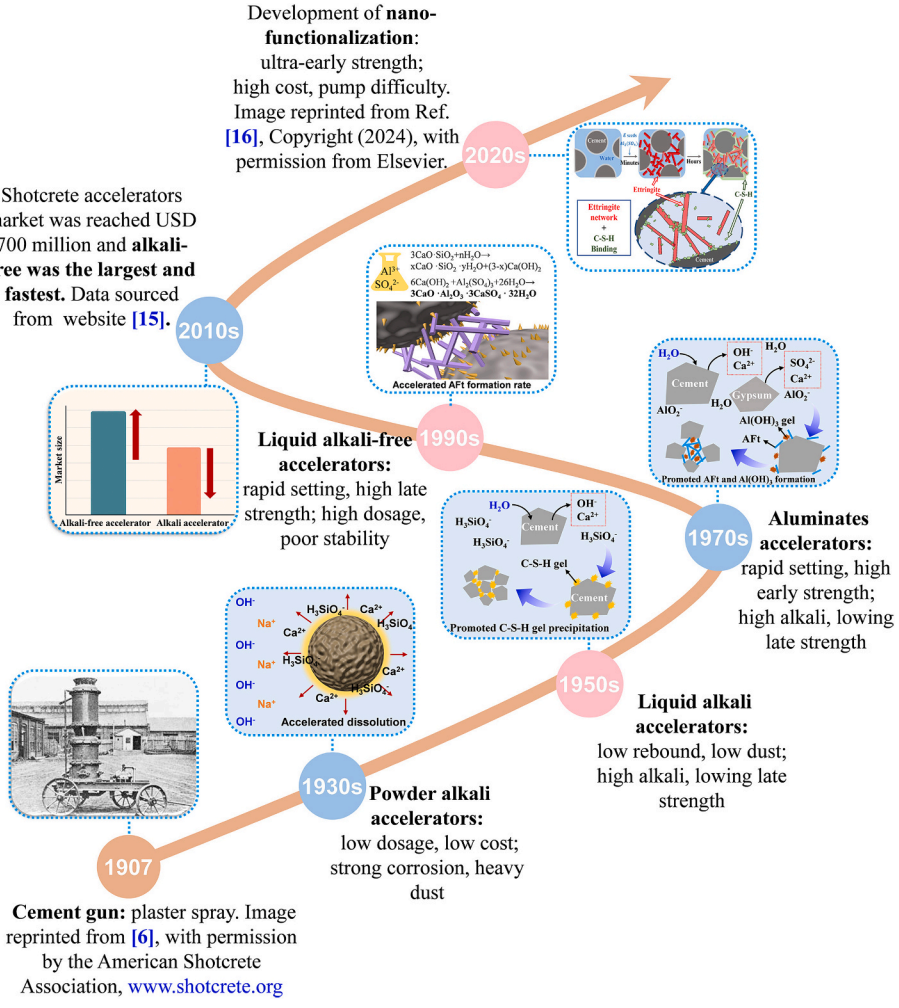

Fig. 1. The development history of shotcrete accelerators [6,15,16].

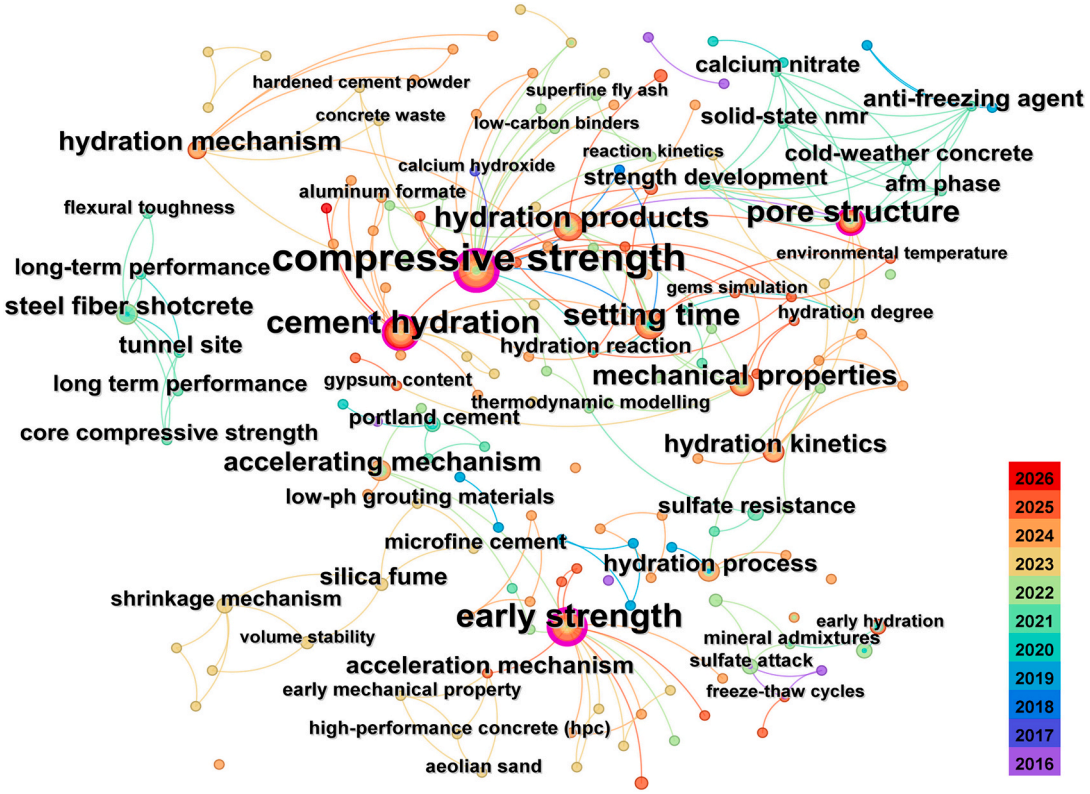

Fig. 2. CiteSpace-based keyword co-occurrence analysis of the AFA research over the last decade. Search string (Web of Science Core Collection, 2016–2026): (Topic = "alkali-free accelerator*" OR "aluminum sulfate") NOT 3D AND ("cement*" OR "mortar*" OR "concrete*" OR "shotcrete" OR "spray* concrete"). Search date: 05/01/2026.

2. Composition of alkali-free accelerators

Representative formulations of AFAs are listed in Table 1, typically exhibiting a pH range of 1.0–4.0. To improve the efficiency of AFAs, a variety of auxiliary components, such as setting and early-strength regulators, stabilizing agents, and other functional additives are incorporated alongside the primary component. These additions contribute to the overall diversity and complexity of AFA formulations.

2.1. Primary component

From Table 1, aluminum sulfate is the most extensively employed primary component in the preparation of AFAs. Alternative aluminum-containing compounds such as aluminum hydroxide [17], aluminum formate [18], and aluminum fluoride [19] are possibly used, either individually or in combination. Furthermore, synthetic or commercially available polyaluminum sulfate, typically represented by the general

Table 1
Representative composition of alkali-free accelerators.

Primary component	Setting and early-strength regulators	Stabilizing agent		Other functional additives	pH	Reference
		Organic-based	Acid			
Aluminum sulfate	Magnesium sulfate	TEA	Oxalic acid	Urea	–	[33]
Aluminum sulfate	Magnesium sulfate	TEA	Maleic acid	Amorphous Al_2O_3	–	[36]
Aluminum sulfate	Sodium fluoride	TEA	Formic acid	Polyacrylamide	–	[37]
Aluminum sulfate	Magnesium fluosilicate	DEA	Inorganic acid	Polyacrylamide	–	[32]
Aluminum sulfate	–	DEA and TEA	–	Sepiolite and glycerinum	3.1	[38]
Aluminum sulfate	Magnesium fluorosilicate	DEA	–	–	2.4	[38]
Aluminum sulfate	Magnesium sulfate	DEA	Phosphoric acid	Polyacrylamide	4.0	[23]
Aluminum sulfate	Nano silica and magnesium fluosilicate	Alkanolamine	Organic acid	Urea and 2-Amino-2-methyl-1-propanol	>2	[30]
Aluminum sulfate	Sodium fluoride	–	–	Polyacrylamide, and bentonite	–	[25]
Aluminum sulfate and aluminum hydroxide	–	–	Formic acid	–	3.0	[17]
Aluminum sulfate and aluminum hydroxide	–	–	Formic acid	–	3.0	[17]
Aluminum sulfate and aluminum formate	–	DEA	Formic acid	Commercial suspending agent and dispersing agent	2.1	[18]
Aluminum sulfate and aluminum fluoride	–	–	Hydrofluoric acid	Sodium oxalate and amide	2.5	[19]
Commercial polyaluminum sulfate	Magnesium sulfate, nano silica	DEA and ethylene glycol	Sulfuric acid	Commercial QM168C stabilizer	–	[20]
Synthetic polyaluminum	Calcium Formate and sodium fluorosilicate	TEA/ Triisopropanolamine	Oxalic acid	–	1.9	[21]

formula $\left[Al_2(OH)_n(SO_4)_{(3-n)/2}\right]$, has been reported as the viable primary ingredient, due to its higher aluminum content and lower cost compared to aluminum sulfate [20,21].

2.2. Setting and early-strength regulator

To further accelerate setting and enhance the early-age strength, magnesium salts are commonly included in the formulation of AFAs, especially magnesium sulfate and magnesium fluorosilicate, as seen in Table 1. Magnesium sulfate has been shown to effectively enhance early-age strength while slightly reducing setting time. In contrast, magnesium fluorosilicate significantly shortens setting time but can remarkably compromise early-age compressive strength [22]. The positive effects of magnesium salts can be ascribed to the promotion of C_3S hydration (Fig. 3(a)), and to the filling effect of Mg-bearing hydrates, such as MH (brucite), MgAl-hydrotalcite, M-S-H (magnesium silicate hydrates), as shown in Fig. 3(b) [22–24].

In addition, sodium fluoride has also been demonstrated to notably shorten setting time, probably due to the action of fluoride ions in enlarging the aspect ratios of AFt phases as well as promoting their formation [22]. Meanwhile, the presence of sodium fluoride leads to the formation of sodium hexafluoroaluminate, as a stabilizing agent for aluminum ions (Al^{3+}), increasing the stability of accelerators [25].

Beyond the inorganic components, alkanolamines, such as triethanolamine (TEA), and diethanolamine (DEA), are incorporated into AFAs to promote setting and hardening of cement pastes. The accelerating effect of TEA on setting time is primarily attributed to their complexation with Al^{3+} and Fe^{3+}, which promotes the dissolution of aluminate phases in cement (i.e., C_3A and C_4AF), and then facilitates the rapid formation of AFt, as shown in Fig. 3(c) [21,26,27]. In addition, it has been reported that the transformation of complexes from DEA-Al to DEA-Ca further accelerates C_3S hydration, serving as a positive factor enhancing the setting and hardening of accelerated cements [28].

It is noted that nanomaterials, such as nano-silica and ultrafine iron hydroxide [29,30], can be incorporated in AFAs to improve the early strength by providing additional nucleation sites for hydrates.

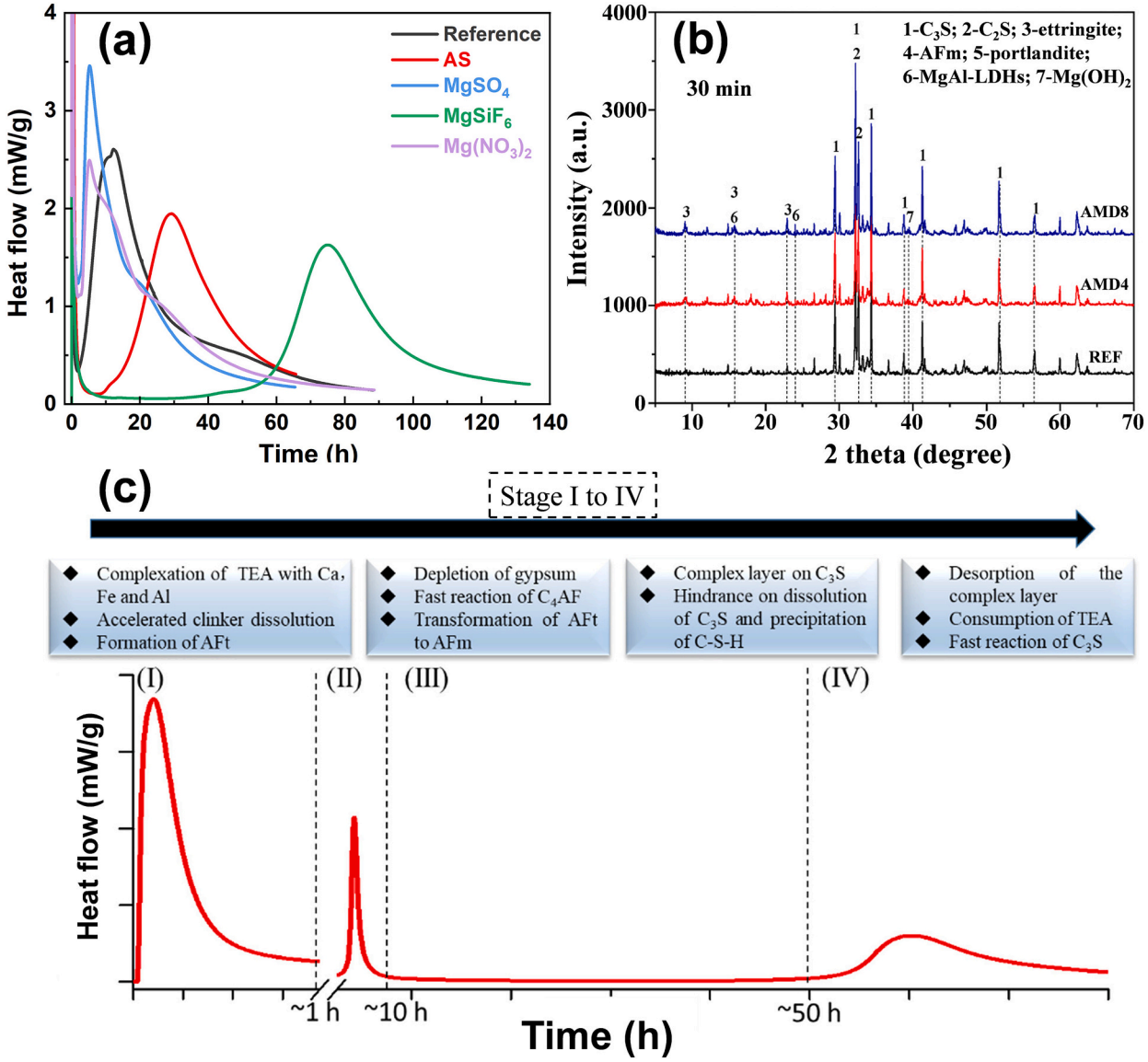

Fig. 3. Effects of magnesium salts on (a) hydration kinetics, reprinted from Ref. [22], Copyright (2025), with permission from Elsevier; and (b) hydration products, reprinted from Ref. [23], Copyright (2022), with permission from Elsevier. (c) effect of TEA on hydration behavior of cement paste, reprinted from Ref. [26], Copyright (2020), with permission from Elsevier.

2.3. Stabilizing agents

The limited solubility of aluminum sulfate (36.4 g/100 g H_2O at 20 °C) is a major constraint on the effectiveness of aluminum-based accelerators. At high aluminum concentrations, hydrolysis, polymerization and precipitation reactions occur, as displayed by Eqs. (1)–(4) [31], significantly lowering the availability of aluminum in the accelerators. Furthermore, the inclusion of setting and early-strength regulators, such as magnesium salts, often exacerbates this instability. To mitigate these issues, pH regulators and complexing agent are typically added (see Table 1).

$$Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+ \quad (1)$$

$$Al(OH)^{2+} + H_2O \rightleftharpoons Al(OH)_2{}^{+} + H^+ \quad (2)$$

$$Al(OH)_2{}^{+} + H_2O \rightleftharpoons Al(OH)_3{}^{0} + H^+ \quad (3)$$

$$mAl(OH)_3{}^{0} \rightarrow [Al(OH)_3(am)]_m \quad (4)$$

Reducing the pH of the system to below 4.0–5.0 can effectively suppress aluminum hydroxide precipitation, as hydrolysis is prevented, and can lead to the formation of polynuclear aluminum aqueous complexes as shown in Fig. 4, thereby increasing the stability of AFAs. A wide range of pH regulators - both organic and inorganic - have been used in AFA formulations, as tabulated in Table 1. These include, but are not limited to oxalic acid, maleic acid, formic acid, phosphoric acid, tartaric acid, 5-sulfosalicylic acid, sulfuric acid, and hydrofluoric acid. Moreover, alkanolamines, particularly TEA and DEA, also play roles as stabilizing agents in addition to serving as a setting and early-strength regulator. These compounds form complexes with Al^{3+} ions, increasing their concentration in accelerators [28].

2.4. Other functional additives

Beyond the components mentioned in *Sections 2.1–2.3*, a variety of other functional additives may be found in AFAs to further tailor their performance (see Table 1). For example, polyacrylamide is usually introduced into AFAs to increase the viscosity of cement pastes, and consequently reducing the rebound rate during shotcrete application [32]. Urea has been found to promote C_3S dissolution and hydration, favorable for the early strength development [33]. Bentonite serves multiple roles: it helps to reduce rebound, improves the stability of AFAs, and compensates for potential shrinkage of shotcrete [25].

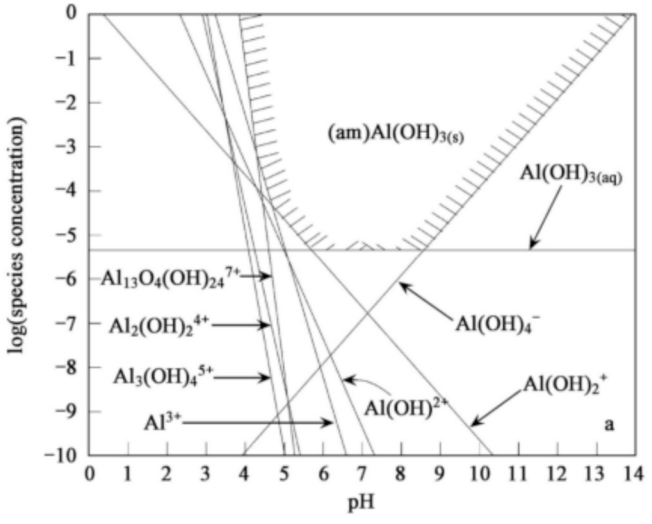

Fig. 4. Distribution of Al species as a function of solution pH, reprinted from Ref. [31], Copyright (2008), with permission from Elsevier.

In response to the global push for sustainability and carbon footprint reduction, various industrial by-products have recently been explored as alternative raw materials for AFA preparation. Examples include fluorosilicic acid waste liquid [34] and aluminum mud waste [35], both of which show promise for the sustainable development of AFA technology.

3. Hydration behavior

Portland cement hydration typically proceeds through five stages: pre-induction, induction, acceleration, deceleration, and a slow ongoing reaction period. These stages are often characterized by heat flow patterns measured via isothermal calorimetry [39], as shown in Fig. 5. The incorporation of AFAs introduces high concentrations of sulfate and aluminum in solution at early ages, significantly altering the pore solution chemistry. These changes in turn exert substantial influence on both the kinetics and thermodynamics of cement hydration across all stages. Among the hydration reactions, particular attention is given to the hydration behavior of aluminate and silicate phases, which are crucial to the early-age property of accelerated cement pastes.

3.1. Aluminate hydration

The initial aluminate hydration in Portland cements occurs within the first few minutes, during which dissolved Al^{3+} from C_3A react with calcium sulfate to form AFt (Eq. (5)), contributing in part to the distinct heat flow peak observed during the pre-induction period [40].

$$C_3A + 3Cs + 32H_2O \rightarrow C_6As_3H_{32}\ (AFt) \quad (5)$$

However, it is noteworthy that the amount of AFt generated through the aluminum hydration in Portland cement is relatively minor compared to that generated via the reaction between AFAs and calcium ions. The complexity of cement composition, coupled with the high reactivity of AFAs, presents challenges in understanding of AFAs' effects on C_3A hydration. In the presence of AFA, the formation of AFt is mainly driven by the high availability of aluminum and sulfate, which can form very rapidly if sufficient calcium is available [40]:

$$6CH + 2Al^{3+} + 3SO_4^{2-} + 26H_2O \rightarrow C_6As_3H_{32}\ (AFt) \quad (6)$$

Studies on pure C_3A systems have reported a short-term hinderance of hydration in the presence of AFA, followed by a subsequent acceleration [41,42]. The initial inhibition has been attributed by some authors to the coverage of hydrates on the C_3A surface, delaying the ion transportation [42]. More recent studies suggest that the adsorption of Ca-sulfate complexes on the surface of C_3A may provide a more plausible explanation for this retardation [43,44]. At later ages, when sulfate concentration decreases, C_3A hydration is promoted through the formation of SO_4-AFm (monosulfate), OH-AFm, and aluminum hydroxide, in contrast to the dominant formation of C_3AH_6 in the absence of AFAs [42].

In Portland cements, upon the depletion of sulfate in the pore solution, C_3A hydration restarts, marked by the secondary formation of AFt. In this stage, sulfate ions (SO_4^{2-}) are sourced from their desorption from C-S-H [45,46], which is typically reflected as a shoulder in the calorimetric heat flow curve occurring after the main hydration peak attributed to C_3S hydration. The onset of the secondary C_3A hydration is highly sensitive to the sulfate balance within the cement system. Accordingly, in Portland cement, three hydration scenarios can be identified: undersulfated, properly sulfated, and oversulfated systems [47], as depicted in Fig. 5.

Both the introduction of reactive aluminate and SO_4^{2-} by AFAs may alter the sulfate balance of cement systems and consequently affect the secondary C_3A hydration. In an undersulfated system - typically arising from cements with high C_3A content or accelerators with a high Al_2O_3/SO_4^{2-} ratio - secondary C_3A hydration precedes silicate hydration, with

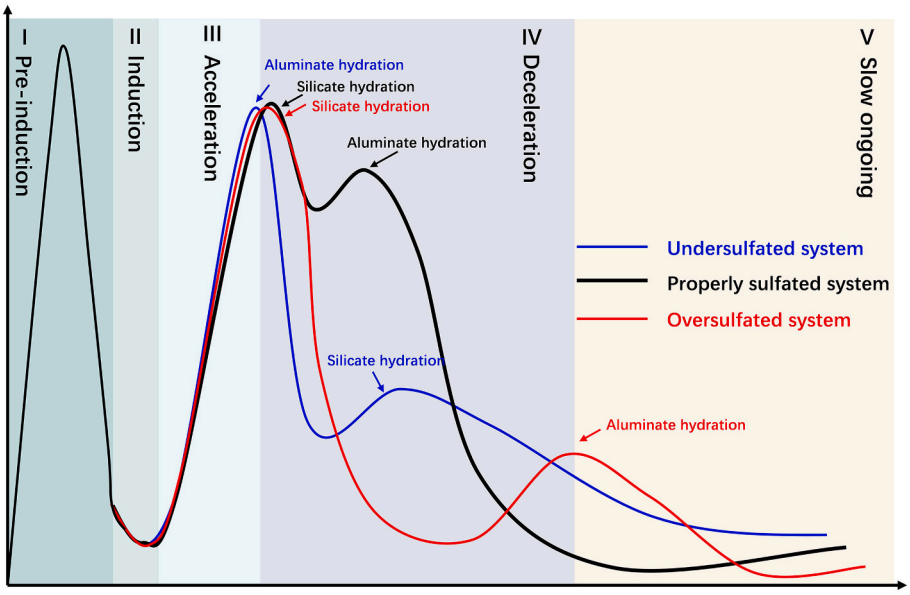

Fig. 5. Schematic hydration kinetic of accelerated cement pastes under different sulfated conditions.

monosulfate as the predominant hydrate [17]. In contrast, in a properly sulfated system, where the cement does not contribute excessive sulfate for the accelerator reaction, the secondary C_3A hydration occurs after silicate hydration, and AFt becomes the dominant phase [17]. Oversulfated systems, though rarely observed in accelerated pastes, feature strongly delayed aluminate hydration and similar hydrate assemblages to properly sulfated systems, as noted in model cement pastes [47].

The extent of sulfation in accelerated cement pastes strongly depends on the total content of aluminum and sulfate, which closely correlates with both the formulation of accelerators and cement compositions. It can be quantitatively described by the final C_3A/SO_3 ratio, proposed by Salvador et al. [17], as expressed in Eq. (7). An optimal range of 0.67–0.90 for this ratio is recommended to ensure efficient hydration without adversely affecting the induction period or the degree of hydration [17].

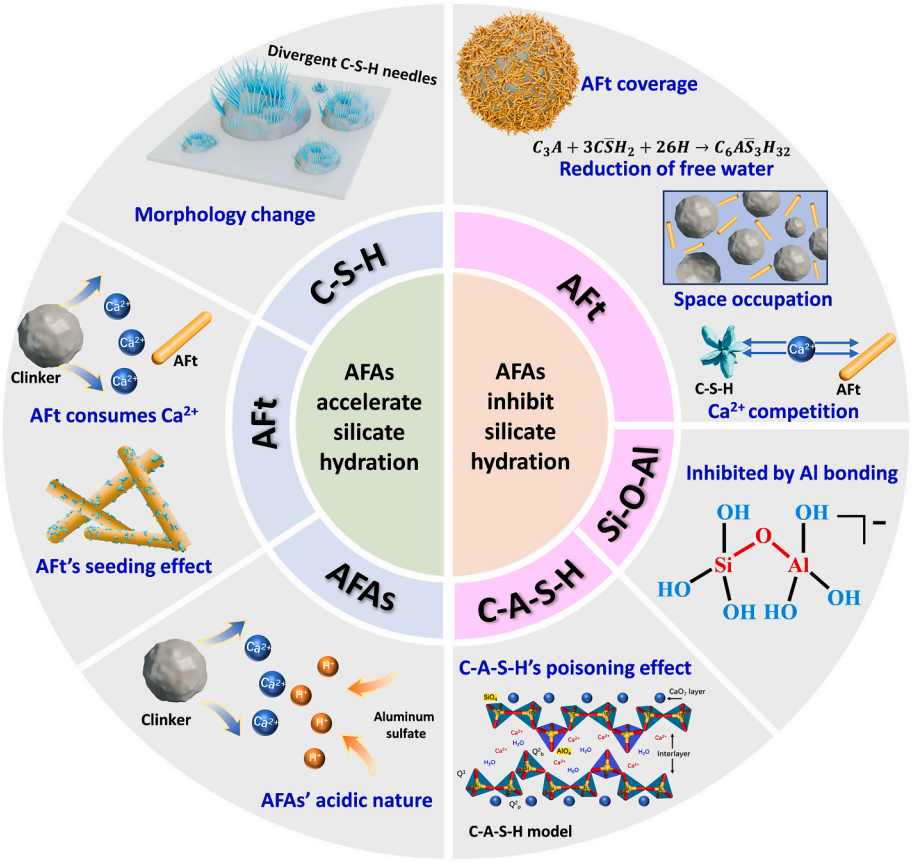

Fig. 6. Summary of mechanisms proposed to explain the effects of AFAs on silicate hydration.

where C_3A/SO_3 represent the ratio of C_3A to SO_3 in accelerated system; C_3A_{cement} represent the initial C_3A content of cement; $SO_{4cement}^{2-}$ and $SO_{4accelerator}^{2-}$ represent the sulfate contents from cement and accelerator, respectively; $SO_{4consumed\ by\ accelerator}^{2-}$ represent the sulfate content consumed by Al^{3+} from accelerator to form AFt.

3.2. Silicate hydration

There is currently no consensus regarding the effect of AFAs on silicate hydration, with various mechanisms proposed, as summarized in Fig. 6. Several studies have reported that AFAs enhance silicate hydration, primarily by promoting silicate dissolution. The progressive formation of AFt consumes large quantities of calcium ions, thereby driving the dissolution and hydration of C_3S [27,40,48,49]. In addition, the inherently acidic nature of AFAs, typically with pH values of 2–4 (see Table 1), also contributes to the enhancement of early C_3S dissolution [50,51]. However, it is worth noting that this promotion effect is transient, as the pore solution pH rapidly recovers to near-normal levels within minutes to hours [40,52].

Another explanation for the acceleration of silicate hydration involves the nucleation effect of AFt. The abundant formation of AFt at early ages has been proposed to provide nucleation sites for C-S-H growth [53]. The precipitation of C-S-H on AFt rather than directly on C_3S surfaces helps to maintain more of the reactive C_3S surface, thus promoting continued dissolution. This mechanism has gained increasing support: the extra addition of synthetic AFt seeds in accelerated cement pastes has been shown to modestly enhance silicate hydration [16], and more pronounced effects have been reported in AFt-rich cement systems [54,55].

Recent studies [56] indicate that the early-age C-S-H morphology may also play a significant role in enhancing silicate hydration. In C_3S pastes, the adsorption of SO_4^{2-} introduced from AFAs produces repulsion among C-S-H needles at early ages, resulting in more dispersed C-S-H structures, greater surface area as nucleation sites, and reducing the likelihood of inter-needle impingement, thereby enhancing silicate hydration.

Conversely, other studies report that AFAs hinder silicate hydration. In these cases, AFt is considered as detrimental due to several reasons: (1) massive formation of AFt coating C_3S surfaces hindering its dissolution [57,58], although this claim has been denied given the inability of AFt for forming a continuous and impermeable barrier layer [59]; (2) AFt formation consumes large amounts of free water, reducing its availability for C_3S hydration [58]; (3) AFt formation substantially occupies the pore space limiting room for C-S-H development [50,60]; (4) elevated Al (and sulfate) concentrations in cement pore solution inhibit C_3S dissolution by a covalent binding to surface silicate monomers [61–63]; (5) the preferred formation of AFt at early age strongly competes with C-S-H for calcium ions, lowering the amount of C-S-H formed [50]. The last mechanism was further supported by a recent study involving the delayed addition of C-S-H nanoseeds, which shifts the onset of rapid calcium consumption to a later stage, significantly enhancing the early-age compressive strength [64].

Additionally, the role of C-A-S-H, another key phase in accelerated cement pastes, has been debated. Some studies propose that C-A-S-H is unable to act as an effective nucleation site for C-S-H precipitation due to the poisoning effect of aluminum incorporation, which may delay silicate hydration [17]. However, this hypothesis lacks substantial evidence. On the contrary, synthetic C-A-S-H nanocomposites have been shown to promote silicate hydration, directly contradicting this theory [65].

3.3. Hydration products

3.3.1. AFt/AFm

AFt serves as the most crucial hydration product contributing to shortening the setting time together with enhancing the strength of AFA-accelerated cement pastes. The AFt skeleton network rapidly formed in the early age significantly enhances interparticle friction, which plays a key role in strength development [66]. As hydration proceeds and sulfate becomes depleted, AFt transforms into monosulfate in calcite free cement systems, resulting in monosulfate-dominated systems at later stages. In modern cements which generally contain some limestone, the formation hemi- and monocarbonate (CO_3-AFm) is observed, stabilizing AFt [49,67].

AFt is characterized by low interfacial energy and high supersaturation, which accounts for its rapid precipitation rate [68]. In cement pastes accelerated by aluminum sulfate, AFt has been observed to reach lengths of 0.35–0.80 μm within just 3 min, with minimal further growth thereafter [22].

The formation and morphology of AFt are highly sensitive to the chemical environment [69]. Therefore, variations in accelerator composition significantly influence both the formation kinetics and morphology of AFt. A recent study demonstrates that different magnesium salts incorporated in AFAs significantly affect AFt formation, as shown by the in-situ XRD results in Fig. 7(a) [22]. For instance, the inclusion of $MgSiF_6$ not only increases the AFt content at the early age but also raises its aspect ratio (Fig. 7(b)), promoting more effective percolation and thus accelerating setting. In addition, introducing synthetic AFt seeds into cement systems alters AFt morphology, resulting in longer and coarser crystals that facilitates both setting and strength development, as displayed in Fig. 7(c) [16]. While the influence of other AFA components on AFt formation remains underexplored, these findings suggest that fine-tuning AFA composition offers a promising route for controlling setting time and hardening behavior in shotcrete applications, deserving more attentions in future studies.

$$Final\ C_3A/SO_3\ ratio = \frac{C_3A_{cement}}{SO_4^{2-}\ cement + SO_4^{2-}\ accelerator - SO_4^{2-}\ consumed\ by\ accelerator} \quad (7)$$

3.3.2. C-S-H

C-S-H is another major strength-contributor in shotcrete, the early formation of C-S-H enhances interface cohesion strengthening the AFt network and improves the mechanical properties [66]. The effect of AFAs on C-S-H formation kinetics corresponding to silicate hydration remains debated, as discussed in *Section 3.2*. However, there is general agreement that the acidic nature of AFAs accelerates C_3S dissolution at early ages, leading to supersaturation with respect to C-S-H and promoting its nucleation [70].

In terms of the chemical composition and structure of C-S-H, it has been extensively speculated that the high aluminum concentration introduced by accelerators increased the likelihood of Al incorporation into the C-S-H structure forming C-A-S-H, as generally a higher Al uptake in C-S-H is observed in the presence of higher aluminum concentrations [71]. In fact, the statistical analyses by SEM-EDS combined with solid-state NMR in AFA-accelerated cement pastes, as shown in Fig. 8, give strong evidence on the incorporation of Al into C-S-H, with a higher Al/Si at higher dosage of aluminum sulfate [56]. Point analysis of SEM-EDS report also a reduced Ca/Si of C-S-H in accelerated cement pates, which results from the preferential formation of AFt on C_3S surfaces consuming large quantities of calcium ions [72]. This decalcification of C-S-H is believed to increase porosity and potentially compromise mechanical

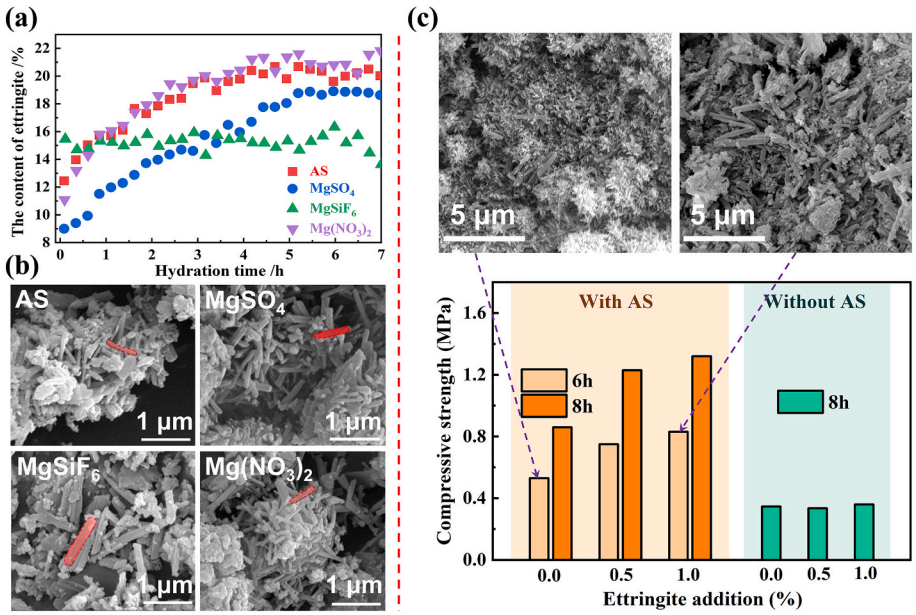

Fig. 7. Effects of different magnesium salts in AFAs on (a) the evolution of AFt content with time and (b) AFt morphologies, reprinted from Ref [22], Copyright (2025), with permission from Elsevier. (c) Effect of AFt seeds on compressive strength and AFt morphology of accelerated cementitious materials, reprinted from Ref. [16], Copyright (2024), with permission from Elsevier.

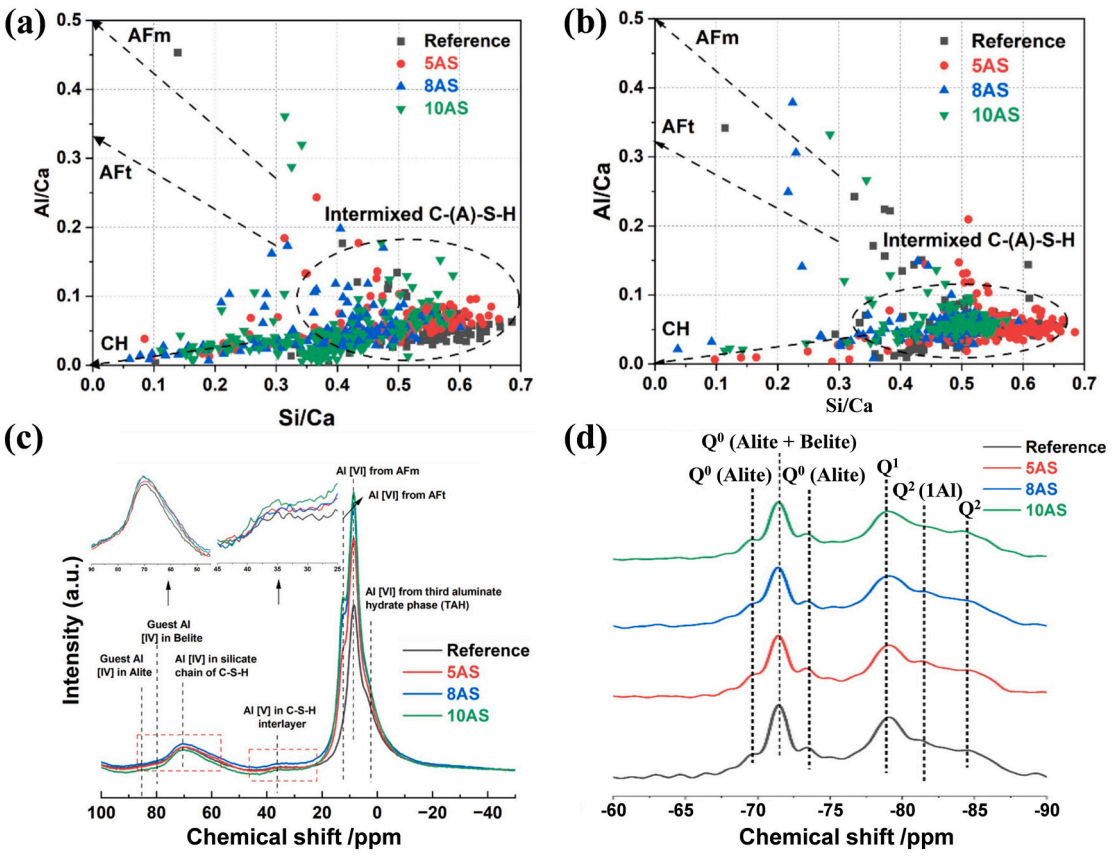

Fig. 8. 2D scatter plot of EDS analyses of inner product C-S-H examined in aluminum sulfate accelerated cement pastes hydrated for (a) 7 d and (b) 28 d; (c) ^{27}Al NMR and (d) ^{29} Si NMR spectra of cement pastes hydrated for 28 d with different dosages of aluminum sulfate, reprinted from Ref. [56], Copyright (2026), with permission from Elsevier.

properties [72].

In C_3S pastes, aluminum sulfate is observed to increase the mean chain length (MCL) of C-S-H [53], as determined by the solid-state ^{29}Si NMR. In addition, in sulfate-rich cement system, SO_4^{2-} adsorb onto C-S-H affecting the morphology of C-S-H and hydration kinetics, which is similar to effects observed in other sulfate-rich systems [73,74].

3.3.3. Calcium hydroxide (CH) and other hydrates

CH, a hydrate formed concurrently with C-S-H, is generally reduced in AFA-accelerated cement pastes due to the formation of AFt, which consumes both calcium and hydroxide ions [40,49]. Given its minimal role in early-age properties of shotcrete, studies on CH in accelerated cement pastes remains scare. One study claimed that aluminum sulfate resulted in the formation of larger and thicker CH crystals in C_3S pastes, compared to other type of accelerators [75].

Besides the primary hydration products mentioned above, minor quantities of secondary hydrates such as brucite, CaF_2, MgAl-hydrotalcite have been identified in AFA-accelerated cement pastes. Their formation is closely tied to the specific composition of AFAs used [23,38]. These secondary hydrates may act as nucleation seeds, hydration barriers, or pore-filling agents, positively or negatively altering hydration kinetics and mechanical properties of accelerated cement pastes.

4. Properties

Different performance requirements arise at various stages of the service life of shotcrete, as illustrated in Fig. 9. Prior to spraying, the rheological properties are directly related to the pumpability and shootability of the cementitious materials [76]. At this stage, however, accelerators have no influence, as they are introduced immediately before spraying. On a timescale of minutes to hours, setting behavior and bonding strength become critical prerequisites for ensuring a low rebound rate and efficient construction. From hours to days, compressive strength serves as the key parameter governing the safety of the initial support structure. Over longer periods, ranging from months to years, the toughness and durability of shotcrete are increasingly emphasized, in addition to compressive strength. AFAs exert varying degrees of influence on the properties of shotcrete across these different stages, as discussed in detail below.

4.1. Setting time

Setting time is a key parameter for evaluating the effectiveness of accelerators. A sufficiently rapid setting facilitates early load-bearing capacity and ultra-early strength development, while also enhancing adhesion and interlayer bonding of shotcrete, thereby reducing rebound and improving overall spraying quality. Upon incorporation into cement, AFAs induce a rapid consumption of mixing water accompanied by the extensive formation of an AFt network. This process accelerates the development of a percolated solid structure, ultimately leading to setting [23,77].

The Vicat needle test, as a standardized method, is widely used to determine the setting times of cement pastes. For mortar and concrete systems, modified Vicat needle and penetration resistance methods have been developed [78,79]. However, these techniques are discontinuous

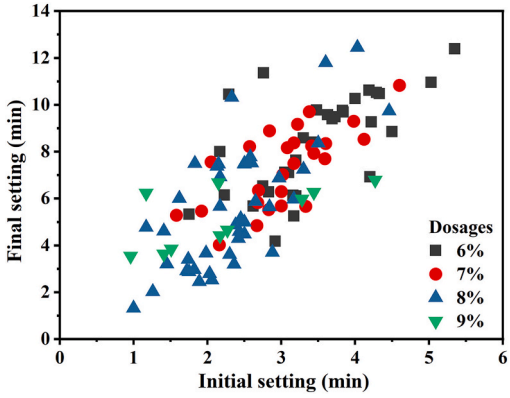

Fig. 10. Setting times of accelerated cement pastes with different AFAs dosage. Dataare compiled from [11,19–21,23,30,32,34,35,38,57,72,81–83,85,87–104].

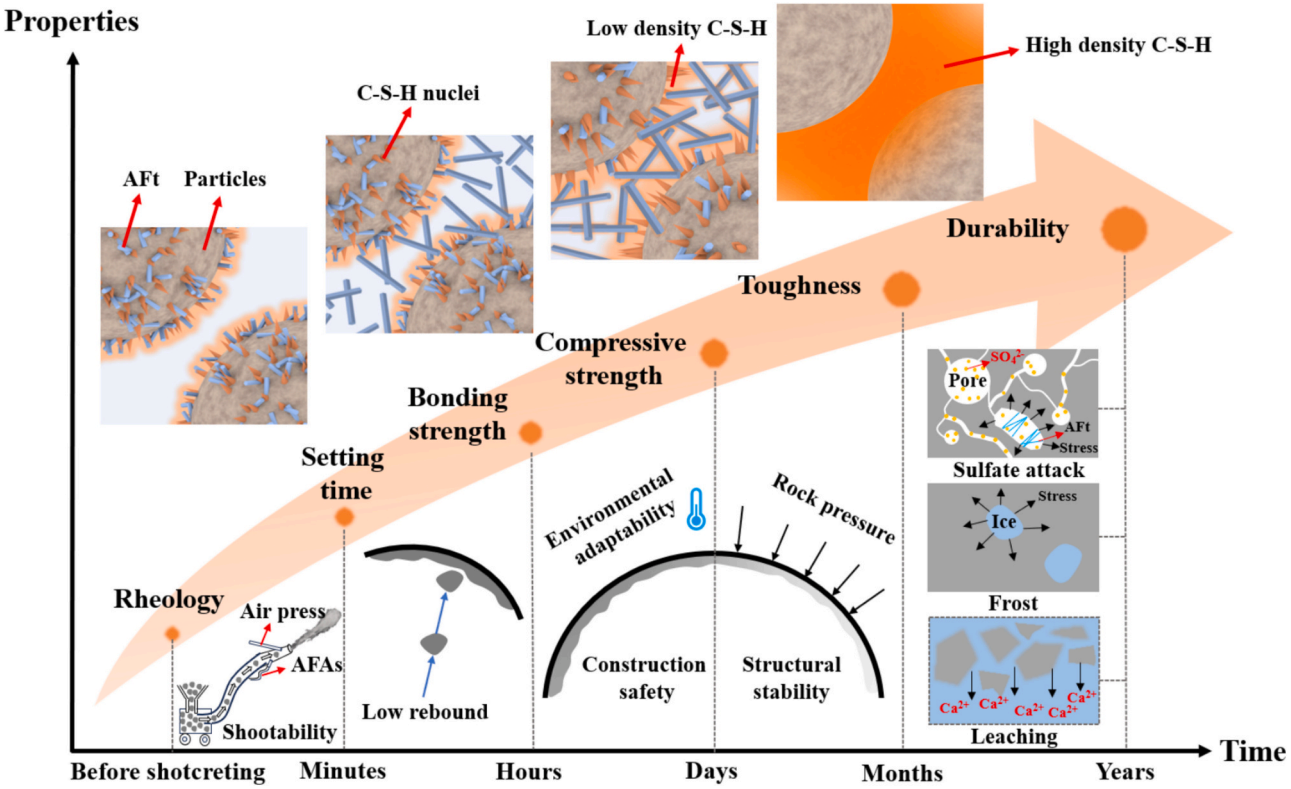

Fig. 9. Key properties required at different stages of shotcrete's service life.

and destructive, relying on empirical thresholds and lacking direct insight into the underlying chemical and microstructural evolution, which limits their robustness in practical applications [80]. As an alternative, ultrasonic measurements have been proposed as a non-destructive and continuous approach for monitoring setting behavior. This method has been demonstrated to be applicable to accelerated cement-based systems, including cement paste, mortar, and concrete [81].

Fig. 10 presents the relationship between initial and final setting times of AFA-accelerated cement pastes, as determined by the standardized Vicat needle test. Overall, a clear reduction in setting time is observed with increasing AFA dosage. Nevertheless, significant variability exists among different studies, with initial and final setting times ranging from approximately 1–5 min and 2–12 min, respectively. This pronounced scatter can be partly attributed to the short testing duration in these systems, which amplifies measurement uncertainties. In addition, the compositional flexibility of AFAs, as discussed in *Section 2*, contributes substantially to this variability. An increased availability of Al^{3+}, achieved through the incorporation of aluminum hydroxide or polyaluminum sulfate, promotes AFt formation and consequently shortens setting times even at relatively low dosage [20,23,82–85]. Furthermore, several studies have reported that the inclusion of fluorides in AFAs favors the formation of AFt with a higher aspect ratio, thereby reducing the percolation threshold and accelerating cement setting [22,86]. This effect is attributed to the incorporation of fluorides into the AFt structure, which increases the surface energy of the (001) plane and consequently alters AFt morphology [22].

It is noteworthy that certain components in AFAs may exert adverse effects on setting behavior. As key stabilizing agents, alkanolamines significantly influence setting times, with their effects strongly dependent on dosage. Previous studies [28] reported that when the diethanolamine (DEA) content was 8 wt% of the accelerator, the initial and final setting times of the cement paste were 1.7 min and 5.6 min, respectively. Increasing the DEA dosage to 12 wt% led to prolonged setting times, with corresponding values of 2.2 min and 6.2 min. A similar trend has been observed for triethanolamine (TEA), where higher dosages result in delayed setting [28]. However, the mechanisms by which varying alkanolamine dosages regulate the setting performance of AFAs remain insufficiently understood. In addition, there is no consensus regarding the role of carboxyl-containing organic acids in AFAs on the setting behavior of cement pastes. Some studies suggest that these organic acids, such as acrylic acid and copolymers of acrylic acid and *N,N*-dimethylacrylamide, can complex with calcium ions, thereby enhancing C_3A dissolution and promoting subsequent AFt formation [87,88]. In contrast, Liu et al. [89] proposed that complexes formed between carboxylic acids (e.g., tartaric acid and 5-sulfosalicylic acid) and calcium or Al^{3+} ions may adsorb onto clinker surfaces, thereby retarding hydration and prolonging the setting time.

4.2. Bonding properties

The interfacial bonding between shotcrete and the substrate plays a critical role in material utilization efficiency and overall construction quality. From a long-term perspective, it directly influences the mechanical integrity of the entire structure. Inadequate bonding not only reduces load transfer capacity but also facilitates the ingress of aggressive ions, thereby compromising durability. In practice, the rebound rate of shotcrete is widely used as an important indicator to assess the bonding performance between shotcrete and the substrate under field conditions. It is defined as the proportion of shotcrete that bounces away from the surface against which the shotcrete is being projected [105], as expressed in Eq. (8) [32,76]. Typically, acceptable rebound rates are specified as less than 15% for sidewalls and less than 25% for arch roofs [25].

$$R = \frac{m}{M} * 100\% \tag{8}$$

where R, m, and M represent rebound rate (%), the mass of rebounded shotcrete (kg), and the total mass of the concrete mixture (kg), respectively.

Accurate and complete collection of rebounded shotcrete in practice is challenging; therefore, an alternative calculation method has been proposed, as expressed by Eq. (9) [106].

$$R = \left(1 - \frac{Q_p}{Q_0}\right) * 100\% \tag{9}$$

where Q_p, and Q_0 represent placement rate (kg/s) and pumping rate (kg/s), respectively. The placement rate can be estimated with the aid of gravity sensor over a defined time interval.

As a key controlling parameter in engineering practice, the rebound rate is closely associated with shotcrete rheology, air content, apparent viscosity, spraying process, and equipment, among other factors [25,32,76,106]. For AFAs, the incorporation of polymers, serving as functional additives as discussed in *Section 2* has been shown to effectively reduce rebound. Chen et al. [107] introduced a vinyl acetate-ethylene (VAE) copolymer into AFAs, decreasing the rebound rate from 22.3% to 15.3% at the sides and from 15.2% to 10.5% at the arch. The underlying mechanism is attributed to the adsorption of polymer onto cement particles and aggregate surfaces, forming a transient network among dispersed particles. This network increases the apparent viscosity of the mixture and enhances interfacial bonding, thereby reducing rebound. In addition, the polymeric phase can absorb and dissipate impact energy, improving mixture cohesiveness and suppressing particle detachment upon impact. Beyond VAE copolymers, other organic modifiers reported in literature include hydrocarbon-grade methyl cellulose, polyacrylamide, and ethylene glycol [32,76,83]. These additives can control rebound within a range of 5%–14%, corresponding to reductions of 26%–67% compared to polymer-free systems. However, excessive incorporation of organic components may inhibit cement hydration and delay early strength development. Furthermore, potential complexation between organic modifiers and aluminum species may induce agglomeration, adversely affecting the stability and performance of AFAs [108]. These trade-offs should therefore be carefully considered in the formulation design of AFAs.

Bonding strength is another important parameter for evaluating the interfacial performance between shotcrete and the substrate. The pull-off test is commonly employed to determine bonding strength; however, the results are highly sensitive to specimen preparation, substrate conditions, curing regime, and testing age, which complicates the comparison and reproducibility of results. Consequently, studies focusing on bonding strength characterization remain limited. Bryne et al. [109] reported a 3 d bonding strength of approximately 1.5 MPa between shotcrete and hard rock under laboratory conditions, while Xie et al. [110] enhanced AFA performance by introducing a core-shell-structured tackifier, achieving increases in bonding strength of 130% at 2 h and 172% at 28 d, corresponding to values of 0.05 MPa and 1.12 MPa, respectively.

4.3. Compressive strength

Compressive strength, as one of the most crucial indicators for evaluating the effectiveness of AFAs throughout the service life of shotcrete, has therefore received considerable attention. Requirements of the compressive strength vary across different stages, including the ultra-early stage (before 8 h), early stage (1 d), and late stage ($\geq$28 d). Fig. 12 summarizes the compressive strength of mortars with varying AFA dosages at three typical ages from literatures.

4.3.1. Ultra-early stage compressive strength (before 8 h)

In recent years, the demand for ultra-early compressive strength (within 8 h) has increased significantly, driven by the expansion of infrastructure construction in increasingly challenging environments [84,90,111]. Representative projects include the Sichuan-Tibet Railway tunnel in China, where many sections are located at elevations exceeding 3000 m [112]; the Mont d'Ambin Base Tunnel (57.1 km) connecting Maurienne (France) and the Susa Valley (Italy) [113]; and the Gotthard Base Tunnel (57 km) in Switzerland, the world's longest and deepest railway tunnel [114].

Due to the immaturity of shotcrete at very early ages, particularly before 6 h, compressive strength is typically estimated indirectly using the pin penetration method specified in EN 14488-2 [115], which correlates penetration depth with strength. Based on this approach, Salvador et al. [116] reported indirect compressive strengths of AFA-accelerated mortars ranging from 1.2 to 2.8 MPa at 4 h and 4.2–13.1 MPa at 6 h, depending on the type of cement used, as shown in Fig. 11.

6 h compressive strength of mortars containing AFAs can be measured directly using a universal testing machine, and this parameter is widely adopted as a key indicator of ultra-early performance. As summarized in Fig. 12, the 6 h compressive strength of AFA-modified mortars typically ranges from 0.1 to 4.2 MPa, depending strongly on the type and dosage of AFAs. AFt, as the dominant hydrate at this stage, is considered the primary contributor to strength development [64]. Using equivalent cement paste systems, Wang et al. [66] proposed that AFt forms a load-bearing framework through interparticle interlocking and friction, while the subsequent formation of C-S-H gel reinforces the contact points within the AFt skeleton at later ages.

Various strategies have been explored to enhance ultra-early strength from the perspective of AFA formulation. In addition to aluminum sulfate, polyaluminum sulfate with high aluminum content and low bound water, serves as an alternative aluminum source in AFAs for enhancing early-strength, typical dosages ranging from 45%–57% by mass of AFAs [20,29,83]. Wang et al. [20] formulated an AFA based on polyaluminum sulfate and demonstrated that the increased availability of Al^{3+} and SO_4^{2-} ions promotes AFt formation, resulting in a 6 h compressive strength of 2.8 MPa at an AFA dosage of 9%. Similarly, Cheng et al. [84] reported that the 6 h compressive strength could reach up to 5 MPa when polyaluminum sulfate was used alone as an AFA. However, excessive use may adversely affect strength development due to the formation of expansive calcium sulfate hydrates, leading to a more porous microstructure [83].

In addition, the incorporation of $MgSO_4$ and $Mg(NO_3)_2$ into AFAs has been shown to significantly accelerate C_3S hydration, increasing the 6 h compressive strength by 48% and 72%, respectively [22]. This enhancement was also confirmed by Sun et al. [90]. Beyond accelerating C_3S hydration, the possible uptake of magnesium by AFt may enlarge its aspect ratio, favorable for their overlap and strength development [22]. Furthermore, nanomaterials such as C-S-H nano-seeds, AFt seeds, and nano-silica have proven effective in improving ultra-early strength by accelerating the formation of C-S-H or AFt phases [16,111,117]. Notably, stage-wise control strategies, such as the delayed addition of nano C-S-H seeds, have demonstrated more pronounced improvements in 6 h compressive strength [64]. Gao et al. [118] supplemented the calcium source in shotcrete by incorporating CH, thereby compensating for the excessive consumption of calcium ions caused by massive AFt formation. This promoted the formation of C-S-H and accelerated the development of ultra-early strength, leading to an increase of the 8 h compressive strength by more than 200% at the CH content of 6 wt%.

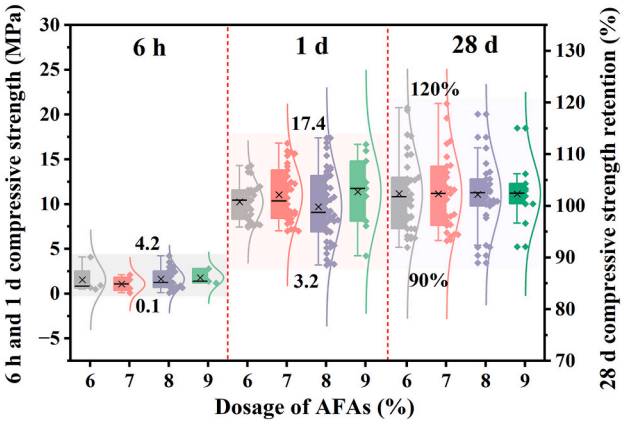

Fig. 12. A summary of compressive strengths of accelerated cement pastes with addition of different AFAs dosage at various curing stages. Data are compiled from [11,19–23,30,32,34,35,38,57,64,72,81–83,85,87–104,107,111].

4.3.2. Early-stage compressive strength (1 d)

The 1 d compressive strength is widely adopted as a key parameter for evaluating the effectiveness of accelerators, as specified in various standards [119–121] (see *Section 6*). By 1 d, the compressive strength of AFAs-modified mortar has experienced a significant increase with typical values range from 3.2 MPa to 17.4 MPa, as shown in Fig. 12.

The beneficial effects of magnesium salts observed at 6 h can extend to 1 d, owing to their sustained promotion of C_3S hydration. Additionally, $Al(NO_3)_3$ has been identified as an effective component in AFAs for enhancing the 1 d compressive strength through accelerating C_3S hydration, typically incorporated at 2%–10% by mass of the accelerator. The addition of $Al(NO_3)_3$ promotes the formation of NO_3-AFt, which refines the pore structure and improves strength, with reported 1 d compressive strength reaching up to 13.7 MPa at an AFA dosage of 6% [22–24,83,99]. It is noteworthy that the addition of these inorganic salts usually compromises the stability of accelerators. Nano-silica has emerged as a crucial early-strength agent in AFAs, with a typical dosage of 1–6% by weight of accelerators. Owing to its nucleation and pozzolanic effects, nano-silica accelerates C-S-H nucleation at early ages on the one hand and produce additional C-S-H on the other hand, both of

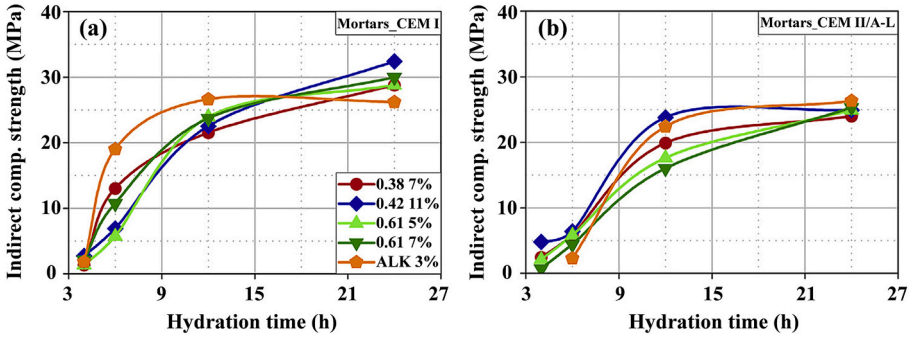

Fig. 11. Ultra-early evolution of indirect compressive strength measured by pin penetration tests for sprayed mortars with (a) CEM I and (b) CEM II/A-L, reprinted from Ref. [116], Copyright (2017), with permission from Elsevier.

which are beneficial for strength development [20,30]. An addition of 3% nano-silica in AFAs led to an increase of the 1 d compressive strength by 45% compared to the one without nano-silica [122].

Meanwhile, alkanolamines are found to be able to improve early compressive strength. The addition of 0.25% TEA to AFAs resulted in a 34% increase in the 1 d compressive strength of AFA-modified mortars compared with the TEA-free reference [28], while a combination of 2% TEA and 1% triisopropanolamine in AFA formulation increased the 1 d compressive strength by 74%, reaching 15.9 MPa [21]. The promotion effect of TEA on strength development can be attributed to two aspects: (1) its complexation with metal ions in cement, including Al^{3+} and Fe^{3+}, which enhances the dissolution of aluminate phases and their further hydration [28], and (2) the complexation of TEA with calcium ions alters the morphology of CH crystals from large and parallel-stacked lamellar shape to smaller and distorted actinomorphic one [123–125], which is believed beneficial to the early age strength development of cement mortars by improving the interfacial transition zone between hardened cement paste and aggregates [123,125]. As the TEA content in AFAs increases, the 1 d compressive strength tends to decrease due to the negative interference of aluminate reaction on silicate reaction. Moreover, when aluminum sulfate and TEA act simultaneously, this phenomenon becomes more pronounced than when TEA acts alone. Under the TEA content of 12.5% in AFAs, the 1 d compressive strength decreased by approximately 85% compared with the TEA-free AFA reference [27]. DEA has a similar effect on 1 d compressive strength as TEA [88].

It should also be noted that certain setting-regulating components may negatively impact early strength. A representative example is the incorporation of fluorides into AFAs [86], as mentioned in *Section 4.1*, which remarkably inhibits C_3S hydration and thus reduces 1 d compressive strength. As reported by Li et al. [86], the incorporation of 3% magnesium fluosilicate in AFAs decreased the 1 d compressive strength by 81% compared with fluoride-free systems. The underlying mechanism remains under debate. Some studies attribute this effect to the formation of hydration product coatings, i.e., CaF_2 and F-Ca-Al compounds, on C_3S surface, which hinder C_3S hydration [85], while others attribute the regulation of cement hydration primarily to the complexation between F^- and Al^{3+} [86]. This complexation accelerates C_3A dissolution and thus promoting AFt formation, which competes with CH formation for calcium ions depletion and consequently inhibiting C-S-H formation [86].

4.3.3. Late-stage compressive strength (≥28 d)

28 d compressive strength retention, defined as the ratio of the compressive strength of AFA-containing cements to that of a reference without AFA, is generally used to evaluate long-term mechanical performance. In contrast to shotcrete with alkaline accelerators, which typically exhibit low late strength retention [5], shotcrete with AFAs shows a higher long-term strength retention, usually greater than 90% independent on the AFA dosage, as shown in Fig. 12. In alkaline accelerator systems, the abrupt increase in pore solution pH strongly dissolves cement clinker phases, resulting in a low-polymerized and porous microstructure of C-S-H. In addition, the possible formation of sodium aluminosilicate hydrate (N-A-S-H) would lead to the creation of weak interfaces [126], contributing to significant strength loss at later ages [127]. In contrast, AFA-based systems allow for more gradual C-S-H formation in the absence of strong alkalis, leading to a more stable chemical composition and higher degree of polymerization. This results in a denser microstructure and improved long-term mechanical performance [91,100]. Nevertheless, regardless of whether alkaline or alkali-free accelerators are used, the massive formation of aluminate-containing hydrates at early age disrupts the continuity of the C-S-H gel network formed during subsequent hydration which is considered to reduce the intrinsic strength of the hardened cement paste [128].

In addition, pore structure also influences the long-term compressive strength development of AFA-accelerated mortars [128]. For systems with an alkaline accelerator, monosulfate and calcium aluminate hydrates dominate during setting, leaving a relatively large amount of capillary pores in hardened cement paste compared with the C-S-H dominated accelerator-free cement system [129]. It is detrimental to the late-age strength development. In contrast, the setting of cement paste containing AFAs is mainly governed by the interlocking of AFt crystals between cement particles, while the initial hydration of C_3S is also promoted, resulting in fewer capillary pores in hardened cement paste [27]. This could partially explain why AFAs usually lead to a higher strength retention compared with the alkaline accelerators.

4.4. Flexural strength

The enhancement of flexural strength in shotcrete is typically achieved through fiber reinforcement and polymer modification [130–133], while relatively limited attention has been paid to the specific role of AFAs. The 28 d flexural strength of shotcrete containing AFAs generally ranges from 5.2 to 6.8 MPa, which is slightly lower than that of shotcrete prepared with alkaline accelerators [100,130]. Luo et al. [134] reported that a dosage of 4% AFA increased the 1 d flexural strength of ultra-high performance concrete (UHPC) by 21%. Similarly, Zhang et al. [100] observed that AFAs enhanced the flexural strength of cement pastes at all investigated ages (i.e., 1 d, 3 d, 28 d) at an AFA dosage of 8%. The components in AFAs seem to play a role in flexural strength development of shotcrete. Liu and his coworkers' results [22] indicated that the incorporation of magnesium salts into AFAs reduced flexural strength, although the underlying mechanism remains unclear.

4.5. Durability

Shotcrete is susceptible to various durability challenges, including sulfate attack, shrinkage, freeze-thaw, permeability, calcium leaching and carbonation, which have been comprehensively reviewed in previous studies [135–137]. However, the specific role of AFAs in durability has received comparatively less attention and is summarized below.

AFAs generally leads to a lower resistance to sulfate attack of shotcrete as compared to cast concrete due to the higher porosity, higher paste volume, lower strength and thus easier ingress of water and SO_4^{2-} [138,139]. In addition, the introduction of Al^{3+} and SO_4^{2-} by AFAs promotes AFt formation and reduces local pH, leading to decalcification of C-S-H, which further compromises sulfate resistance [140–142]. The ratio of sulfate to aluminum in AFAs determines the sulfate resistance according to Kaufmann et al. [139], with higher ratios leading to less expansion of shotcrete.

AFAs tend to increase the shotcrete shrinkage due to accelerated hydration process and rapid consumption of free water [97]. Nevertheless, compared with alkaline accelerators, AFAs generally result in lower shrinkage owing to the formation of expansive AFt [95]. Whereas alkaline accelerators tend to promote the transformation of AFt to monosulfate and/or monocarbonate [143], leading to a greater shrinkage. Typically, within 90 d, the autogenous shrinkage rate of the mortar containing AFAs falls in the range of 0–800 $\times 10^{-6}$ $\mu m/m$, while alkaline accelerator modified mortars and reference ranges from 0 to 1300 $\times 10^{-6}$ $\mu m/m$ and 0–600 $\times 10^{-6}$ $\mu m/m$, respectively. On the other hand, the rapid consumption of water in AFAs-containing systems leaves less water to ice crystallization, and thereby exhibiting positive effects on the freezing resistance at the early age [144]. Additionally, the macro-pores introduced by compressed air during the shooting process also help to relieve the frost heaving pressure of pore water and thus improving the frost resistance [136].

Regarding permeability, Sakoparnig et al. [145] reported that the Cl^- ions diffusion coefficient of shotcrete containing AFAs at 75 d ranges from 1.4 $\times 10^{-12}$ m^2/s to 9.1 $\times 10^{-12}$ m^2/s, with a higher content of Al_2O_3 in AFAs promoting the formation of Friedel's salt and thereby improving chloride binding capacity and resistance to chloride ingress. However, the porous characteristics of the AFt skeleton significantly

increase the permeability of shotcrete containing AFAs [139]. The oxygen permeability coefficient of AFAs-modified concrete is 4×10^{-8} m^2/s, which is higher than that of the ordinary concrete (2×10^{-8} m^2/s) under the same molding condition [138].

Calcium leaching experiments indicate that the concentration of calcium in exposure solution without AFA reaches 150–250 mg/L after immersion for 7 days, while the sample with AFAs reduces it to 120–200 mg/L [104], suggesting the introduction of AFAs contributes to mitigate the calcium leaching. This result is probably attributed to the fact that, AFAs reduce the CH content in cement pastes with the formation of AFt/monosulfate phases possessing a lower solubility than CH and C-S-H. In terms of carbonation, which also involves calcium leaching, AFAs generally reduce carbonation resistance of shotcrete compared with cast concrete. Compared with alkaline accelerators, AFAs present a higher resistance to carbonation due to the denser microstructure than alkaline accelerators modified systems [146].

5. Compatibility of AFAs

In engineering practice, satisfactory setting and hardening performance of shotcrete cannot always be achieved, even when accelerators that strictly meet standard requirements are used. This discrepancy highlights the critical issue of accelerator compatibility. Poor compatibility may result in excessive rebound, inadequate early strength, and even structural instability, leading to material waste and potential safety risks. According to the definition of admixture compatibility in GB/T 8075–2017, Sun et al. [147] defined accelerator compatibility as the ability of a qualified accelerator, tested according to standard methods, to deliver the required performance when applied in shotcrete designed for its use, including appropriate initial and final setting times, low rebound during spraying, and adequate early and long-term compressive strength, as well as satisfactory impermeability and durability. Given the multitude of influencing factors, a unified quantitative evaluation method for compatibility has not yet been established. To address this issue, Su et al. [148] proposed a compatibility index *f(a)* incorporating contributions from setting time, compressive strength, and hydration heat characteristics, as expressed in Eq. (10).

$$f(a) = \sum_{i=1}^{5}(a_i \times 15\%) + \sum_{i=6}^{10}(a_i \times 5\%) \quad (10)$$

where a_1-a_{10} represent initial setting time (min), final setting time (min), 8 h compressive strength (MPa), 1 d compressive strength (MPa), 28 d compressive strength retention rate (%), time to the main exothermic peak (h), first exothermic peak (mW/g), second exothermic peak (mW/g), 8 h cumulative heat release (J/g), and 24 h cumulative heat release (J/g), respectively.

Using this index, the authors reported that AFAs exhibited improved compatibility with cements containing higher C_3A and C_3S. However, the applicability of this method remains to be validated, as compatibility is also strongly influenced by additional factors, such as the presence of mineral or chemical admixtures, spraying processes, and environmental conditions. These aspects are discussed in detail below.

5.1. Compatibility to cement

The compatibility between AFAs and cement is affected by factors such as the content of soluble alkalis in cement, the type of grinding aids, and cement aging. An increase in soluble alkali content in cement has been shown to promote C_3A dissolution and enhance AFt formation, thereby improving the effectiveness of the AFA [147]. This effect is primarily attributed to the increased concentration of OH^- ions in the liquid phase, thus suppressing the formation of CH [149]. However, Briendl et al. [70] suggested that, in accelerator systems, a relatively lower pH may be more favorable for the dissolution of both C_3A and C_3S.

Grinding aids commonly used in cement, such as alkanolamines, trisodium phosphate, and lignosulfonates, can significantly affect AFA compatibility. These additives dissolve during hydration and interact with clinker phases. While the role of alkanolamines has been discussed previously (see *Section 4*). Trisodium phosphate and lignosulfonates tend to adsorb on the surface of clinker, inhibiting the dissolution of C_3A and potentially weakening the effectiveness of the accelerator [150,151]. In addition, cement aging may influence compatibility. Maltese et al. [152] reported that storing fresh cement at 20 °C and 95% relative humidity for 10 min to 24 h reduced the final setting time of accelerated cement paste from 10 min to 2–4.5 min, likely due to enhanced AFt formation, although the underlying mechanism requires further clarification.

The mineral composition of cement is another critical factor. Increasing C_3A content generally promotes AFt formation and accelerates setting [153]. However, excessive C_3A may shift early hydration products from AFt to monosulfate under limited sulfate availability. The relatively loose structure of monosulfate is unfavorable for strength development, thereby reducing compatibility [154].

Furthermore, the content and type of calcium sulfate in cement also play a pivotal role in the compatibility of AFAs to cement. An appropriate increase in gypsum content can enhance sulfate availability, promoting AFA reactivity and early strength development [60]. However, excessive gypsum may retard the dissolution of C_3S via the common ion (Ca^{2+}) effect, thereby reducing strength. Wang et al. [72] reported similar findings, suggesting that insufficient gypsum promotes the formation of monosulfate rather than AFt, which exerts a more pronounced retarding effect on the hydration of C_3S; in contrast, excessive gypsum promotes the formation of AFt, which occupies space and suppresses the precipitation of C-S-H. Some studies also suggest that excessive gypsum may inhibit the dissolution and hydration of C_3A through the adsorption of introduced SO_4^{2-}, thereby delaying setting [154].

Different types of calcium sulfates are typically present in cement, including dihydrate, β-hemihydrate, and anhydrite. The presence of β-hemihydrate significantly reduces the compatibility between AFAs and cement, as evidenced by prolonged setting times, while anhydrite markedly shortens the setting time. The differences in setting behavior are mainly attributed to the different solubilities of calcium sulfates, which in turn affect the kinetics of AFt formation. In the system with the highest solubility (β-hemihydrate), the hydration products are mainly rounded and small masses, primarily composed of AFt or gypsum formed by the rapid rehydration of β-hemihydrate. In contrast, the least soluble anhydrite leads to the formation of fine needle-like AFt. These differences in hydration products result in distinctly different setting behaviors [155].

In addition to setting behavior, the calcium sulfate type also influences compressive strength of cement systems containing AFAs. Li et al. [156] investigated the effects of sulfate type on the setting time and compressive strength of a pure clinker system, as shown in Fig. 13. The results indicate that different types of calcium sulfate prolong the setting time of accelerated clinker paste to some extent, with hemihydrate showing the most pronounced retarding effect. Meanwhile, the incorporation of different sulfates significantly enhances the compressive strength at all curing ages, especially at 1 d. Among them, anhydrite exhibits the most significant improvement in early compressive strength, followed by hemihydrate, while dihydrate shows the least effect. For late ages (7 d and 28 d), these differences become less significant. The enhancement associated with anhydrite is attributed to its low solubility, which moderates early calcium release, promotes C_3S dissolution, and facilitates the formation of C-S-H.

The combined influence of C_3A and calcium sulfate contents in cement on compatibility can be interpreted in terms of the sulfate balance of the system. This balance can be quantitatively characterized by the final C_3A/SO_3 ratio (see *Section 3.1*), as proposed by Salvador et al. [17]. Based on cement hydration kinetics, they suggested that an optimal final C_3A/SO_3 ratio in the range of 0.67 to 0.9 in CEM I pastes ensures comparable hydration behavior in systems containing AFAs.

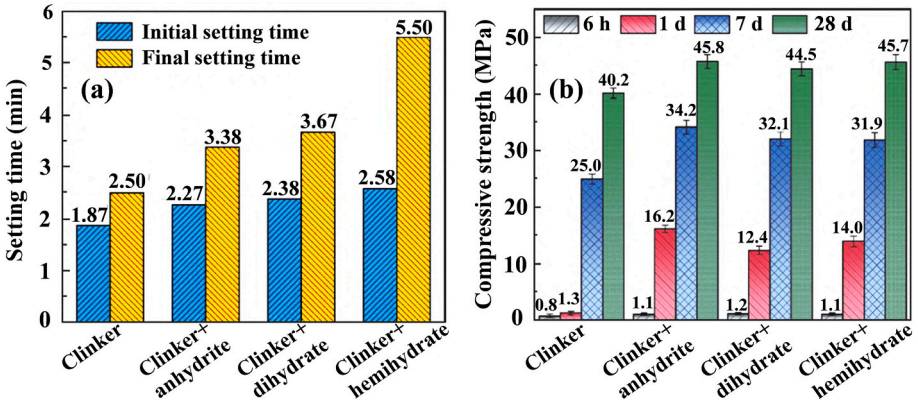

Fig. 13. Influences of different sulfate types on (a) setting time of clinker pastes and (b) compressive strength of mortars, reprinted from Ref. [156], Copyright (2025), with permission from authors and the copyright holder.

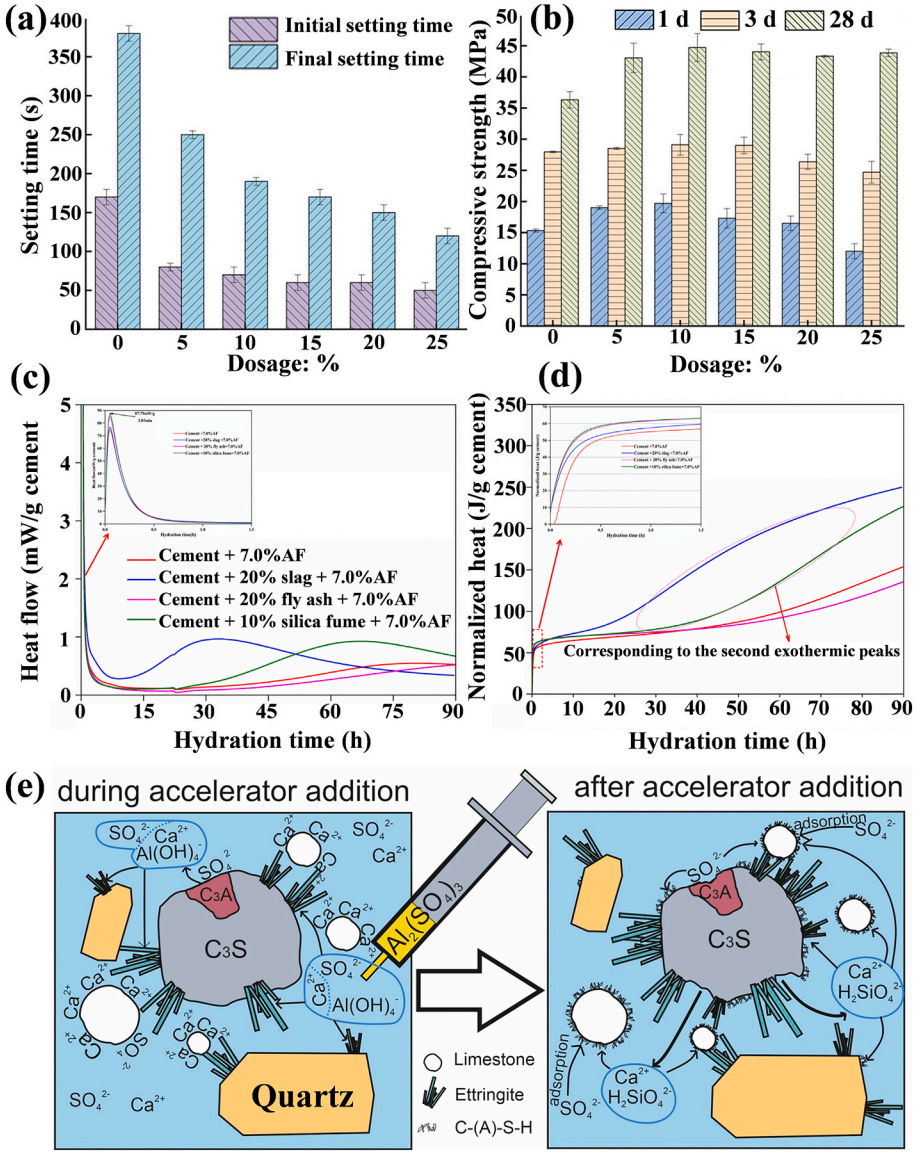

Fig. 14. Effects of different mineral admixtures on the performance of accelerated cement paste: (a) and (b) effects of silica fume on setting time and compressive strength, reprinted from Ref. [159], Copyright (2024), with permission from ICE Publishing; (c) and (d) effects of mineral admixtures on the hydration kinetics of accelerated cement paste, reprinted from Ref. [164], Copyright (2021), with permission from Elsevier; (d) strengthening mechanism of limestone in shotcrete, reprinted from Ref. [70], Copyright (2020), with permission from Elsevier.

5.2. Compatibility to mineral additions

Mineral additions, such as silica fume, fly ash, blastfurnace slag and limestone, are often incorporated into shotcrete to enhance performance and reduce cost [157,158]. However, their use may also introduce compatibility issues with AFAs. Silica fume exhibits good compatibility with AFAs. As shown in Fig. 14(a) and (b), at a constant AFA dosage, replacing 20% of cement with silica fume shortened the initial and final setting times of the paste by 66% and 61%, respectively, compared with the reference. At a 10% replacement level, the 1 d and 28 d compressive strengths increased by 28% and 23%, respectively. These improvements are primarily attributed to the nucleation and pozzolanic effects of silica fume [159]. In addition, when used together with AFAs, the high specific surface area of silica fume effectively increased the viscosity of shotcrete, thereby reducing rebound [160]. However, excessive silica fume (e.g., approximately 9% of cement mass) led to excessive water consumption, reducing the degree of hydration and resulting in a more porous structure and increased rebound [161]. In terms of durability, the incorporation of silica fume helped to improve the sulfate resistance of shotcrete [162], but increased the risk of shrinkage cracking [163].

Fly ash, another widely used supplementary cementitious material rich in silicon components, exhibits more complex and sometimes contradictory interactions with AFAs. Wang et al. [20] reported that fly ash significantly prolonged setting time and suppressed strength development at high replacement levels (10%–25%). Similarly, Yang et al. [164] observed that while fly ash may promote setting, it reduced early compressive strength, likely due to a dilution effect. In contrast, Shantanu et al. [165] suggested that fly can ash acts as an active sites for AFt nucleation, accelerating the interlocking of AFt among particles. Under compression, these interlocked structures can provide yield stress, thereby improving the strength of AFA accelerated cement-based materials.

The effect of blastfurnace slag on the performance of AFAs also remains subject to debate. Zhou et al. [159] found that a slag promoted early AFt formation due to its fine particle size, thereby shortening initial setting time when used together with AFAs. However, the dilution of clinker phases reduced early heat release, slightly prolonged final setting time, and decreased early compressive strength. At late ages, with the continuous generation of CH, the reactivity of the glass phase of the slag gradually increased, leading to a 25% improvement in 28 d compressive strength. In contrast, Yang et al. [164] reported that slag significantly shortened both initial and final setting times (by more than 50%) and promoted C_3S hydration (see Fig. 14(c) and (d)). These inconsistencies are likely attributable to variations in slag composition, particularly the chemistry of the glass phase and its reactivity.

When combined with AFAs, limestone can accelerate hydration and improve early compressive strength due to the additional nucleation sites for C-(A)-S-H provided by limestone. In addition, Galan et al. [70,166] attributed this partially to the slight dissolution of $CaCO_3$ releasing small amounts of calcium, which contributes to the formation of calcium-bearing product, favorable for setting and hardening of shotcrete, as illustrated in Fig. 14(e). Lothenbach et al. [67] highlighted that the presence of hemi- and/or monocarbonate in $CaCO_3$-rich system stabilizes AFt, which may also account for the improved early strength.

5.3. Compatibility to other chemical admixtures

In addition to accelerators, shotcrete often incorporates other chemical admixtures depending on practical requirements. For instance, polycarboxylate superplasticizer (PCE) are used to maintain workability during transportation, viscosity enhancer agents are added to improve cohesiveness and reduce rebound, and air-entraining agents are introduced to improve frost resistance. These admixtures are generally polymer-based and are used over a wide dosage range. Relative to the mass of cement, the dosages of PCE are typically 0.1%–1%, viscosity enhancer agents about 0.5‰-0.7‰, and air-entraining agents can be as low as 0.05‰ [102,165,167–169]. Their simultaneous use with AFAs may introduce additional compatibility challenges.

In general, although PCEs improve the workability of fresh mixtures prior to spraying, they tend to retard the setting of AFA-containing systems, with the retarding effect becoming more pronounced at higher dosages [36]. Sun et al. [167] reported that PCE molecules adsorb onto cement particle surfaces, generating steric hindrance that inhibits rapid interlocking of AFt, thereby prolonging the initial setting time. However, this dispersion effect increases the contact area among cement particles, water, and AFAs, which may accelerate hydration and shorten the final setting time. At higher dosages (e.g., $\geq$0.2%), complexation between carboxyl groups and calcium ions delays the formation of CH and C-S-H, extending the induction period and significantly suppressing early strength development. In addition, Winnefeld et al. [170] reported that PCE can alter the growth location of AFt in ordinary Portland cement systems, shifting it from clinker surfaces to interstitial spaces; however, whether this mechanism applies to accelerated systems and how it affects performance remains unclear. In practical engineering applications, increasing the dosage of AFAs is usually adopted to address poor compatibility between AFAs and PCE [171].

Although viscosity enhancing agents effectively increase the cohesiveness of shotcrete, a too high viscosity may entrain additional air during spraying, leading to the formation of macropores that reduce matrix compactness. Moreover, the presence of ether groups in viscosity enhancing agents can bind with calcium ions on cement particle surfaces, forming an isolation layer between cement and water, which significantly retards cement hydration and suppresses strength development [168]. Similarly, air-entraining agents improve freeze-thaw resistance by introducing a stable system of fine air bubbles, but the increased air content inevitably reduces mechanical strength [169].

5.4. Compatibility to spraying process

Most research work on AFAs-cement systems is conducted under laboratory conditions using cast specimens, which differ significantly from the spray application used in practice. Parameters such as spraying velocity, pressure, distance, layer thickness, timing of accelerator addition, and nozzle geometry all influence key properties of shotcrete, including rebound, cracking, setting and hardening, thereby affecting the compatibility of AFAs to shotcrete [172–175].

Spraying pressure has a notable effect on rebound. Chen et al. [176] reported that reducing pressure increased the effective spray area and decreased rebound associated with high material concentration in the central impact zone. Sakoparnig et al. [177] showed that pulsation of shotcrete and accelerator flow at the nozzle can induce pressure fluctuations, leading to heterogeneous mixing and the formation of ettringite-rich and weakly hydrated zones, which may compromise mechanical performance and durability. Spraying distance is another critical parameter. Su et al. [178] studied effects of spraying distance on the rebound rate of shotcrete with three aggregates sizes. They reported that the optimal rebound rate for the system with an aggregate size of 5–11 mm was achieved at a spraying distance of 0.9 m, whereas for aggregate sizes of 11–17 mm and 17–25 mm, the optimum occurred at a spraying distance of 1.0 m. Moreover, the thickness of the sprayed layer affects the risk of shrinkage cracking. Due to simultaneous water loss at the exposed surface and the bonding interface, a thinner initial sprayed layer generally leads to faster cracking and failure [179,180].

In addition, during practical construction, the timing of accelerator addition, i.e., the interval between mixing raw materials with water and accelerator addition, can vary significantly. Increasing time interval was found to exaggerate the retarding effect of gypsum on C_3A [167]. As a result, insufficient dissolution of C_3A limits calcium ion availability for AFt formation, reducing AFA effectiveness. For example, delaying AFA addition by 60 min increased the initial and final setting times from 2.7 and 4.8 min to 17 and 61 min, respectively, while reducing 28

d compressive strength by 25%. However, contrasting results have been reported. Pott et al. [181] suggested that delayed addition of AFA can lead to increased AFt formation and improved 1 d compressive strength by over 20%. This effect was attributed to the removal of early hydration products from C_3A surfaces during secondary mixing, providing additional nucleation sites for AFt. These conflicting findings indicate that the influence of delayed addition remains insufficiently understood.

Nozzle geometry also plays a key role in shotcrete performance. A smaller nozzle diameter increases spraying velocity and improves shotcrete compaction, thereby enhancing flexural strength. For instance, increasing the nozzle diameter from 15 mm to 25 mm reduced flexural strength by approximately 30%, with a slight decrease in compressive strength. Shorter nozzles reduce frictional losses and increase compaction due to the shorter travel distance, resulting in improved mechanical performance. Replacing a 200 mm nozzle with a 100 mm nozzle increased the flexural strength of shotcrete by 20% [182]. Furthermore, multi-channel airflow designs improve the dispersion of AFAs and promote more homogeneous mixing with the concrete [183].

5.5. Compatibility to environmental conditions

Shotcrete is often applied under challenging environmental conditions, including low temperatures, high rock temperatures, and water seepage or gushing, which impact the AFAs' compatibility by affecting the early setting and hardening, bonding with surrounding rock, and long-term durability. Xu et al. [184,185] reported that lower temperature significantly suppresses the hydration of C_3A and C_3S, prolonging the setting time of AFA-accelerated cement systems, and delaying early strength development. Compared with 20 °C, the setting time of the accelerated cement paste was prolonged by up to 100% at 5 °C, and the 1 d compressive strength decreased by up to 75%. Lu et al. [186] further suggested that lower temperatures inhibit the hydrolysis of Al^{3+} in AFAs to form $[Al(OH)_4]^-$, thereby suppressing AFt formation and diminishing the effectiveness of AFAs.

To evaluate such effects, the concept of temperature compatibility has been proposed to describe the ability of AFAs to maintain performance under varying thermal conditions [187,188]. Zhang et al. [189] showed that temperatures below 10 °C significantly reduced this compatibility, primarily due to suppressed surface hydration rates and the development of thermal gradients between inner and outer layers, which can accelerate cracking and weaken structural performance.

Various strategies have been proposed to improve the low-temperature compatibility of AFA. For instance, with 7% AFA, the additional incorporation of 1.5% calcium bromide ($CaBr_2$) or 1.5% calcium nitrate ($Ca(NO_3)_2$) increased the 1 d compressive strength of mortar at 5 °C by 540% and 480%, respectively [185]. These salts react with C_3A to form fine needle-like new phases, i.e., Br-AFm and NO_3-AFm (see Fig. 15), which act synergistically with AFt promoted by AFAs to enhance setting and early strength.

Nanoparticles, such as nano C-S-H seeds, also provide an effective approach by accelerating the hydration of C_3S at low temperature. Their addition increased the 1 d compressive strength of AFA-modified mortar at 5 °C by 273% [184]. In addition, the incorporation of gypsum and silica promote the hydration of C_3S in AFA-containing cementitious materials at low temperature; at a dosage of 10%, the 6 h compressive strength of AFA-modified mortar cured at 5 °C was increased by more than 300% [190]. Blending calcium sulfoaluminate cement with ordinary Portland cement has also been reported to exhibit similar strengthening effects [186]. Moreover, by reducing water to cement ratio and combined with heating mixing water and aggregates, the 28 d compressive strengths of shotcrete at 0 °C can be increased by 40% [189].

Shotcrete may be exposed to elevated temperatures in deep underground constructions, geothermal regions, and tunnels with high geothermal gradients, where high rock temperatures significantly influence both early-age behavior and long-term performance. At early ages, elevated temperatures accelerate cement hydration, leading to substantial increases in 1 d compressive and flexural strengths by approximately 170% and 143%, respectively, compared with standard curing conditions. However, the temperature gradient between the surrounding rock and the shotcrete surface induces significant thermal stresses. Moreover, the distribution of hydration products becomes non-uniform, with AFt content increasing from the inner to the outer layers and its morphology evolving from fine to coarse crystals, resulting in heterogeneous pore structures. Consequently, the 28 d compressive and flexural strengths decreased by 31% and 47%, respectively, relative to standard curing [191,192].

In addition, shotcrete is frequently applied in water-rich environments, such as karst regions, where the performance of AFAs can be severely compromised. The presence of water weakens the interfacial bonding between shotcrete and the substrate, leading to increased rebound rates during application. Furthermore, such environments adversely affect durability, particularly by accelerating calcium leaching, one of the most critical degradation mechanisms, which ultimately threatens the long-term service life of the structure [104].

6. Global standards and guidelines

To guide the application of shotcrete, various standards and guidelines have been released by worldwide organizations, including the International Organization for Standardization (ISO), American Concrete Institute (ACI), American Society for Testing and Materials (ASTM), European Committee for Standardization (CEN), Japan Society of Civil Engineers (JSCE), National Standards of the People's Republic of China (GB). These documents mainly address material sampling, testing methodologies, and application procedures. However, only limited attention has been given specifically to accelerators for shotcrete.

For instance, in ASTM standards, accelerators for shotcrete are typically expected to comply with Type C (accelerating) or Type E (water-reducing and accelerating) requirements as defined in C494/C494M – 24 *Standard Specification for Chemical Admixtures for Concrete* [193]. However, no distinct provisions are made for accelerators for shotcrete. Similarly, the *Recommended Practice for Shotcreting in Australia (2nd version)* [194] refers to compliance with Australia standard AS 1478 *Chemical Admixtures for Concrete, Mortar and Grout* [195], without tailored guidance for accelerator applications either.

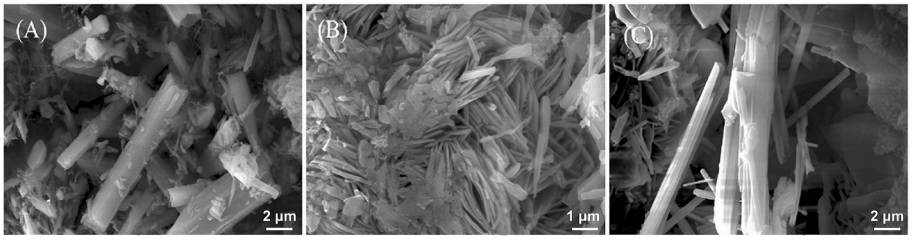

Fig. 15. Morphologies of hydration products in AFA-C_3A and inorganic salts modified AFA-C_3A systems: (a) AFt phase, (b) Br-AFm phase, and (c) NO_3-AFm phase, reprinted from Ref. [185], Copyright (2023), with permission from Elsevier.

Given the distinct chemical composition, physical properties, and performance expectations of shotcrete accelerator compared to conventional concrete accelerators, specialized specifications are necessary. To date, a few standards provide detailed technical requirements for shotcrete accelerators, including:

- China: GB/T 35159-2017 *Flash Setting Admixture for Shotcrete* [121].
- Europe: EN 934-5: 2007 *Admixtures for Concrete, Mortar and Grout – Part 5: Admixtures for Sprayed Concrete-Definitions, Requirements, Conformity, Marking and Labelling* [196]
- Japan: JSCE-D 102-2005 *Specification for Set Accelerating Agent for Sprayed Concrete (Mortar)(Draft)* [119]
- South Korea: KSF 2782: 2007 *Set Accelerating Agent for Shotcrete* [120]

The comparative summary of these standards is presented in Table 2. Key performance indicators for shotcrete accelerators, particularly setting time and compressive strength, especially at early ages, are emphasized across all standards. For setting time, the European standard allows the widest range, while the Chinese, Japanese, and Korean standards specify more consistent limits. As for compressive strength, the early age compressive strength, at 12 h and 1 d for example, are especially highlighted. Notably, the Chinese enterprise standard Q/CR 807-2020 *Liquid Alkali-Free Flash Setting Admixture for Shotcrete of Tunnels* [197] mandates a minimum compressive strength of 1 MPa at 6 h, underscoring the growing demand for rapid strength development, especially for major infrastructures. Standard test methods such as the Vicat and Gillmore needle tests are commonly employed to determine setting time.

Furthermore, GB/T 35159-2017 and EN 934-5 provide more comprehensive specifications for physical properties, including pH, density, chloride content, sodium equivalent (Na_{eq}) content, and recommended dosage ranges. The Chinese standard particularly highlights the importance of AFA stability, given its critical role during on-site application.

Considering the global diversity of AFA formulations, there is a clear need for the development of a more unified, comprehensive international specification. Such a standard would help harmonize construction quality, enhance compatibility across products and regions, and promote the healthy development of the global shotcrete market.

7. Conclusions and perspectives

7.1. Conclusions

This paper presents a comprehensive and systematic review of the current research progress on alkali-free accelerators (AFAs) for shotcrete, with particular emphasis on their composition, effects on hydration kinetics and hydration products, early- and long-term performance, as well as compatibility issues. In addition, global standards and technical guidelines related to AFAs are critically summarized and compared. This review establishes an integrated framework that links material composition, hydration mechanisms, and macroscopic performance of AFAs in shotcrete systems. It provides both scientific insights and practical guidance for optimizing accelerator formulations, understanding shotcrete performance evolution, and improving material selection and application strategies in engineering practice. The main conclusions are as follows:

- AFAs exhibit high diversity and tunability where an aluminum-containing compound serves as the core component, supplemented by setting and early-strength regulators, stabilizing agents, and other functional additives, with these multi-component synergy enabling rapid setting and early strength development of shotcrete. It is

Table 2
Comparisons of global standards from different countries.

Properties	GB/T 35159-2017	EN 934-5	JSCE-D 102-2005	KSF 2782: 2007
Setting time	Initial setting time≤ 5 min; Final setting time ≤ 12 min	Initial setting time≤ 10 min; Final setting time ≤ 60 min	Initial setting time≤ 5 min; Final setting time ≤ 15 min	Initial setting time≤ 5 min; Final setting time ≤ 15 min
Compressive strength	At 1 d: Compressive strength ≥ 7 MPa At 28 days: Compressive strength of test mix ≥ 90% compressive strength of control mix At 90 days: Compressive strength of test mix ≥ compressive strength of test mix at 28 days	At 28 days: Compressive strength of test mix ≥ 90% compressive strength of control mix At 90 days: Compressive strength of test mix ≥ compressive strength of test mix at 28 days	At 12 h: Compressive strength >1 MPa At 1 d: Compressive strength >9 MPa At 28 d: Compressive strength of test mix >75% compressive strength of control mix	At 1 d: Compressive ≥ 9 MPa At 28 d: Compressive strength of test mix ≥ 75% compressive strength of control mix
Physical properties	• pH ≥ 2.0. • Density D (manufacture's stated value): D ± 0.03 (D > 1.1); D ± 0.02 (D ≤ 1.1). • Solid content S (manufacture's stated value): 0.95S–1.05S (S > 25%); 0.90S–1.10S (S≤25). • Stability≤5 mL. • Chloride content≤0.1%. • Na_2O_{eq} ≤ 1.0%.	• Homogeneity: • Color: • Effective component: • Density D (manufacture's stated value): D ± 0.03 (D > 1.1); D ± 0.02 (D ≤ 1.1). • Solid content S (manufacture's stated value): 0.95S–1.05S (S≥20%); 0.90S–1.10S (S<20). • Chloride content≤ 0.1% or not above the manufacturer's stated value. • pH: manufacture's stated value ±1 or within manufacture's stated range. • Na_2O_{eq} ≤ 1.0% by mass of mixture • Corrosion behavior: no corrosion promotion effects on steel embedded in concrete.	Not available	Not available
Dosage	6–9% by mass of cement	≤ 12% by mass of cement	Not available	Refer to manufacturer's stated value

noteworthy that certain components may exert dual effects; for instance, fluorides accelerate setting but at the expense of early strength, while stabilizing agent such as alkanolamines may inhibit hydration at high dosages. Therefore, a clear understanding of the individual and synergistic contributions of each component to shotcrete performance is essential for optimizing accelerator formulations.

- AFAs significantly change the solution chemistry of cements by introducing large amounts of aluminum and sulfate, thereby altering the reaction processes of aluminate and silicate phases. The hydration of aluminates is closely related to the sulfate content in the system and can be categorized into undersulfated, properly sulfated, and oversulfated scenarios. Both undersulfated and oversulfated lead to inappropriate cement hydration and thus unsatisfied setting and strength development. The effect of AFAs on silicate hydration remains controversial, with both promoting and inhibiting mechanisms proposed. The main hydration products of AFA-accelerated cementitious materials typically include AFt, AFm, C-S-H and CH, among which AFt and C-S-H dominate different stages of setting and strength development. The chemical composition and microstructure of these products are strongly influenced by the composition of AFAs.
- Setting time and early compressive strength are the two most critical parameters when evaluating the efficiency of AFAs. There are significant variations reported across studies for these two parameters, largely due to differences in AFA composition. In addition, AFAs also affect flexural strength, interfacial bonding strength, long-term strength development, and durability of shotcrete. However, studies on these aspects are still limited with some mechanisms remained unclear.
- The compatibility of AFAs with cement systems and environmental conditions remains a major challenge in shotcrete applications. It is influenced not only by cement composition, mineral and chemical admixtures, but also by spraying processes and service environments. Variations in these parameters can significantly alter the hydration pathways and microstructure development, thereby affecting the performance of AFAs. A proper match among cement composition, accelerator formulation, and application conditions is essential to minimize compatibility issues.
- There are significant differences in performance requirements for shotcrete accelerators among different countries and organizations, and a unified evaluation framework is lacking. Differences in test methods and evaluation criteria may limit the comparability of results, posing challenges for the reliable assessment and broader global application of AFAs.

7.2. Perspectives

Significant progress has been made in past years in understanding the performance of AFAs for shotcrete. Building upon these advances, future research is expected to further promote the development of AFA, with particular emphasis on the following aspects.

- Development of next generation high-performance and low-carbon AFA formulations

A deeper understanding of the interactions between AFAs and cementitious systems is essential for next-generation accelerator design. Future research should focus on decoupling the mechanisms by which accelerator components influence cement hydration kinetics, hydrate nucleation processes, and microstructure development, and on establishing quantitative relationships between accelerator composition and resulting macroscopic properties. Particular attention should be given to clarifying the intrinsic trade-off between setting and ultra-early strength development, which remains a critical challenge in current formulations. In parallel, the incorporation of industrial by-products and other low-carbon raw materials into accelerator formulations should be further explored, which would not only promote the utilization of industrial solid wastes but also contribute to reducing the carbon footprint of shotcrete.

- Quantitative evaluation of AFA compatibility to different systems

At present, the lack of robust quantitative methods for assessing AFA compatibility with different cementitious systems remains a major limitation for both research and practical applications. Future efforts should therefore focus on unraveling the effects of key factors, including cement type, mix design, environmental conditions, mineral admixtures, spraying parameters, on the critical properties of shotcrete, such as setting behavior, mechanical strength development, permeability resistance, and long-term durability. It will be possible to develop reliable quantitative frameworks for compatibility evaluation and significantly improve accelerator selection and performance prediction in engineering practice.

- Global standardization and unified evaluation frameworks for AFAs

Despite their widespread application, significant discrepancies exist among national and regional standards regarding the technical specifications, testing methods, and evaluation criteria for AFAs. These inconsistencies may hinder the consistent evaluation and application of accelerator products. Establishing unified international standards would facilitate technology transfer, ensure consistent product quality, and promote the global development of shotcrete technology. Future efforts should focus on harmonizing technical requirements and testing procedures across different regions to improve the practicality and reliability of the standards throughout the entire production-application chain of AFAs.

- Integration of artificial intelligence into AFA design and optimization.

The integration of artificial intelligence into AFA formulation design represents a promising emerging direction. Establishing comprehensive databases linking accelerator compositions with the performance of shotcrete throughout its service life could provide the foundation for data-driven material design. Based on such datasets, machine-learning-based optimization algorithms may enable the rapid identification of optimal AFA formulations tailored to specific construction conditions and performance requirements. Such approaches have the potential to significantly accelerate the development of next-generation accelerators and improve the efficiency and precision of formulation design.

CRediT authorship contribution statement

Hui Xie: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis. **Xin Liu:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis. **Jiaxin Liao:** Writing – review & editing, Investigation. **Barbara Lothenbach:** Writing – review & editing. **Frank Winnefeld:** Writing – review & editing. **Xiao Liu:** Writing – review & editing. **Xiangming Kong:** Writing – review & editing. **Dining Li:** Writing – original draft. **Wei Wang:** Writing – review & editing. **Song Mu:** Writing – review & editing. **Jinxiang Hong:** Writing – review & editing. **Pan Feng:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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