Recent progress and technical challenges in using calcium sulfoaluminate (CSA) cement

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Abstract

Calcium sulfoaluminate (CSA) cement can be used as a replacement for Portland cement to reduce CO_2 emissions. However, the performance of CSA cement remains unknown with regard to its hydration mechanism, mechanical and long-term performance. Therefore, it would be beneficial to consolidate the literature on CSA cement to facilitate its use in the construction industry. To this end, recent progress and technical challenges of using CSA cement are discussed in this paper. We begin with the introduction of the different types of CSA cement and the manufacturing process. This is followed by a detailed discussion on the hydration mechanisms and phase assemblage, mechanical performance, and long-term durability of CSA cement. Finally, the applications of CSA cement are discussed.

Keywords: Calcium sulfoaluminate cement, production, hydration, mechanical properties, transport properties, durability.

1. Introduction

Concrete has ruled the construction sector for more than one century with the production rate rising from 1.5 billion tons in 2000 to over 3 billion tons in 2012 and over 6 billion tons in 2022 [1, 2]. The consumption of concrete is estimated to amount to over 18 billion tons annually by 2050 [3]. As the most important component of concrete, cement has established its indispensable role, among which, Portland cement is one of the most widely used types. Increasing global demand for concrete drives the production of Portland cement to rise by a factor of 25 since 1950 [4, 5]. However, cement production is responsible for roughly 5-8% of CO_2 emissions in the world today and a further increase in CO_2 emissions is anticipated due to the rising global population and urbanization rate [6, 7].

Consequently, it is urgently needed to find a solution to reduce CO_2 emissions in the cement sector. Four levels of solutions have been identified in the "Cement Technology Roadmap" proposed by the World Business Council for Sustainable Development (WBCSD) and International Energy Agency (IEA), including thermal and electric efficiency, alternative fuels, clinker substitution, and carbon capture and storage [5]. However, improving energy efficiency can only partly contribute to the objective of reducing CO_2 [8]. Using alternative fuels has a limited impact on CO_2 emissions from cement kilns [9]. For carbon capture and storage, the current technologies such as the post-combustion technology and oxyfuel technology that can be used do not allow a wide scope of applications due to extremely high overall cost [8]. Among these strategies, clinker substitution is pointed out as the most promising approach for the cement industry [10, 11]. In this scenario, one technological measure is the use of supplementary cementitious materials (SCM) such as granulated blast furnace slag, fly ash, limestone powder, calcined clay, and other by-products [12]. However, the supply of supplementary cementitious materials with adequate quality, particularly blast furnace slag and fly ash, is rather limited as compared to cement production [10]. That is to say, merely relying on the contribution of supplementary cementitious materials may not be able to completely meet the requirements of further CO_2 reduction.

Another strategy is to use alternative binders. Four classes of low-carbon alternatives have been listed by Gartner and Sui [13], including reactive belite-rich Portland cement (RBPC) clinkers, carbonatable calcium silicate clinkers (CCSC), magnesium oxides derived from magnesium silicates (MOMS) and belite-ye'elimite-ferrite (BYF) clinkers. Although the scope of alternative binders is broader, these four classes of alternatives are more likely to be commercialized in near future. The limitation of RBPC clinkers includes a relatively slow hardening process and limited reduction of carbon emissions (normally less than 10% below those for Portland cement) [14]. CCSC is a kind of 'carbonatable' clinker and can only get hardened by reaction with CO_2. The reduction of CO_2 by using this kind of material is 30-40% upon production at this moment and is expected to reach 70% if a circular CO_2 economy develops in the future [13]. However, relatively pure CO_2 is required in the curing chamber, which would limit the practical application. Although MOMS even has the potential to make concrete with a negative carbon footprint, it is currently difficult to develop an energy-efficient industrial manufacturing process [15, 16]. Among these, BYF cement also refers to one specific type of calcium sulfoaluminate (CSA) cement, which can be used as a replacement for Portland cement without any technological modification in the cement industry [17].

According to a calculation performed by Aranda and Torre [18], the CO_2 emissions from both the materials production and operational processes are lower for CSA cement when compared to that of Portland cement. For the former, the production per ton of Portland cement would release 0.54 tons of CO_2, while the manufacturing per ton of CSA cement would merely release 0.27 tons of CO_2, which is estimated according to the stoichiometry of chemical reactions. For the latter, in comparison to the clinkerization process of Portland cement where 1450 ℃ is normally required, the operation temperature can be reduced to 1250 ℃ for CSA cement [19]. Such a temperature difference would also contribute to a reduction of up to 0.04 tons of CO_2 per ton of CSA cement production. Furthermore, up to 0.02 tons of CO_2 emissions can be further reduced in the grinding of CSA cement compared to Portland cement.

The benefits of using CSA cement are not limited to low carbon emissions and energy savings, CSA cement also has promising engineering properties for different applications. For example, the fast setting and hardening of CSA cement makes it suitable for urgent repairing, ceiling, and soil stabilization [20, 21]. In some other cases, the retardation of CSA cement is needed for achieving a longer setting time, while the hydration mechanism in the presence of retarders remains unknown to some extent [22]. In addition, CSA cement can also be used for shrinkage compensation and self-leveling in the presence of swelling components [23]. However, the expansion mechanism of CSA cement has not been well understood. Furthermore, problems may occur when using CSA cement for reinforced concrete, where reinforcement can be corroded due to a low pH value of CSA cement after hydration [24].

Therefore, it would be beneficial to consolidate the literature on CSA cement to facilitate its use in the construction industry. For this purpose, recent progress and technical challenges of using CSA cement are discussed in this paper. We first introduce different types of CSA cement and the manufacturing process including the clinkerization process and the hydrothermal-calcination process. We then discuss the hydration of CSA cement including the effect of sulfate content, setting characteristics, the effect of retarders, CSA-based blended cement, and thermodynamic modeling. Following this, the mechanical properties, transport properties, and durability of CSA cement are reviewed. Finally, we also discuss the use of CSA cement in various applications such as urgent repair works, waste stabilization, and 3D concrete printing.

2. Types and production

2.1. Different types of CSA cement

From a broad viewpoint, the nomenclature, CSA represents a series of cement containing sulfate and aluminate phases. These materials can be classified into different categories according to the main crystalline phases ye'elimite and belite, as listed in Table 1. In addition, the percentage of phases in different types of CSA cements is roughly indicated in Fig. 1. The term CSA cement represents those cements that contain ye'elimite as the main phase and the ye'elimite content can amount between 50% to 80% [18]. Other phases such as belite, ferrite (C_4AF), and anhydrite ($C\overline{S}$) may also be included in the clinker. However, it should be noted that such a type of CSA cement is quite expensive due to the high price of raw materials such as bauxite [24, 25].

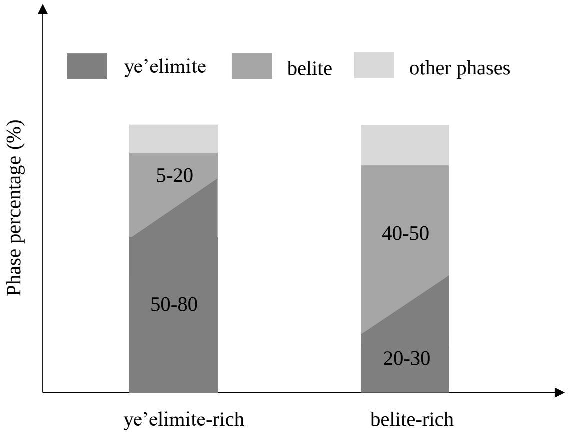


Fig. 1 Percentage of phases in ye'elimite-rich and belite-rich CSA cement [18, 24, 26, 27].

The term belite-rich calcium sulfoaluminate (BCSA) cement is used to describe the one with belite as the main phase [28]. Different from CSA cement with a high content of ye'elimite, BCSA cement has a much lower content of ye'elimite ranging from 20-30%, while belite accounts for about 40-50% of the weight. Such a lower content of ye'elimite in BCSA as compared to CSA cement is beneficial for reducing the clinker production cost due to the high cost of raw materials. As shown in Fig. 2, according to the estimation, only low ye'elimite CSA formulations would be economically competitive with Portland cement at around USD 60 per ton [7]. The most common among the BCSA type is the iron-rich BCSA cement, which is also known as belite calcium sulfoaluminate ferrite (BCSAF) cement. It has a lower aluminum demand and hence, a greater potential to replace Portland cement [29]. As compared to CSA cement with high contents of alumina (30-40%) and sulfur trioxide (8-14%), the alumina and sulfur trioxide contents in BCSAF cement range between 14-17% and 3.5-4.5%, respectively [18]. Aluminum-rich BCSA is the second category of the BCSA type. It is also called aluminum-rich calcium sulfoaluminate (BCSAA) cement, and can be used to further improve the early-age mechanical strength due to the presence of mayenite ($C_{12}A_7$) and calcium monoaluminate (CA), a known shotcrete accelerator [27, 30, 31].

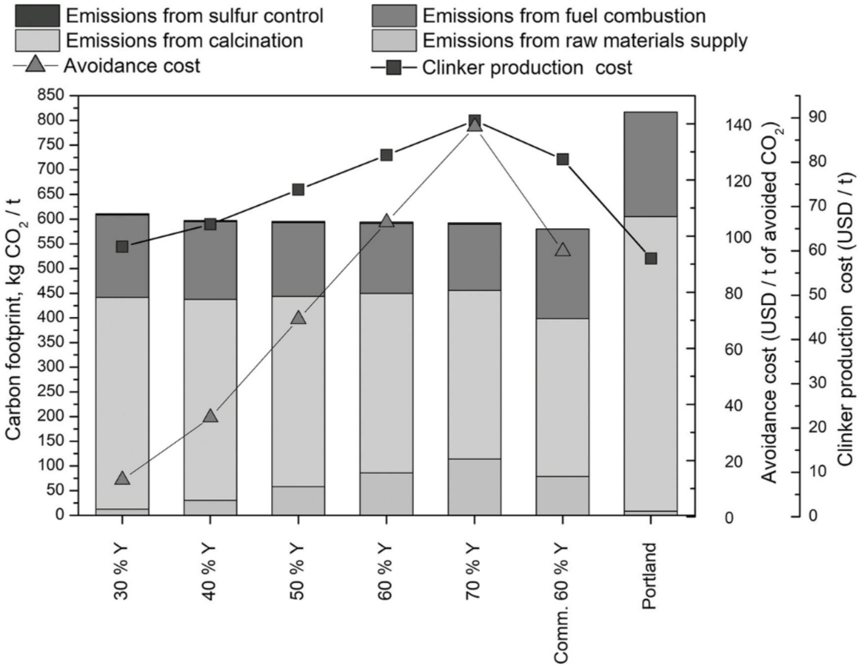


Fig. 2 Avoidance cost, associated emissions and clinker production costs as a function of the ye'elimite content, and compared to commercial CSA and Portland cement clinker production (adapted from [7]).

In addition, the term alite calcium sulfoaluminate (ACSA) cement is used for the type with ye'elimite as the main phase and alite (C_3S) as the second major phase. Other phases may be present such as belite. However, it should be noted that the existence of alite and ye'elimite in the same system is challenging as ye'elimite is not stable anymore at the higher processing temperature of alite [18, 24].

Table 1 Different types of calcium sulfoaluminate (CSA) cement.

Type	Main phase	Other phases
Calcium sulfoaluminate cement	$C_4A_3\overline{S}$	C_2S, C_4AF, $C\overline{S}$, …
Iron-rich belite calcium sulfoaluminate cement	C_2S	$C_4A_3\overline{S}$, C_4AF, …
Aluminum-rich belite calcium sulfoaluminate cement	C_2S	$C_4A_3\overline{S}$, $C_{12}A_7$, CA, …
Alite calcium sulfoaluminate cement	$C_4A_3\overline{S}$	C_3S, C_2S, …

2.2. Production of CSA cement

2.2.1. Clinkerization process

Clinkerization is the most commonly used production process for CSA cement, where a high temperature is always needed for the diffusion of solid atoms and molecules. Different types of raw materials can be used for production, depending on the final product. For pure ye'elimite, pure reagents such as calcite, alumina, and calcium sulfate compounds (gypsum, bassanite, and anhydrite) can be used. For commercial utilization in industry, bauxite, natural gypsum, and limestone are commonly adopted. For the estimation of the mineralogical phases, modified Bogue equations can be used [32]. In case that silica is contained in raw materials, belite phases would form and BCSA cement is produced. Furthermore, alite phases are preferred as compared to the belite phase in a combination with ye'elimite in terms of its steel corrosion resistance and very high early strength requirement. However, the process to produce BCSA is rather complicated as alite and ye'elimite have different temperature requirements for clinker formation [33]. As stated above, ye'elimite requires a temperature lower than 1300℃, while a suitable temperature for alite is higher than 1300℃. Two-cycle firing can be a solution to obtain both phases, where alite and ye'elimite are produced in the first cycle (1450 ℃) and the second cycle (1250 ℃), respectively [34]. However, it should be noted that the second firing cycle would result in a negative impact on CO_2 emissions.

As mentioned, the use of CSA cement is restricted due to the high cost of alumina-bearing raw materials (e.g. bauxite). Using industrial wastes is beneficial to reduce the cost of CSA. Furthermore, the environmental benefit of using CSA cement is improved as cement becomes an effective repository for waste materials that would otherwise be landfilled. Several successful trials have been made to produce BCSA cement, where waste materials including marble sludge, fly ash, aluminum anodizing sludge, and flue gas desulfurization sludge for their high lime, alumina, and sulfur trioxide contents were used [35-39]. Other types of waste materials such as metallurgical industry residues can be used to produce BCSAF cement where ferrite is an indispensable part [32, 40].

A quantitative environmental impact assessment of CSA clinker was made including the aspects of mining/waste utilization, energy consumption, and waste emissions [41]. A comparison was made between the CSA clinker preparation by using industrial solid waste and by using conventional raw materials. Results show that the total environmental burden can reduce by 39% by using industrial solid waste as compared to the conventional process. More details can be found in Fig. 3 where the contributions of each CSA clinker production process to the environmental burden are listed.

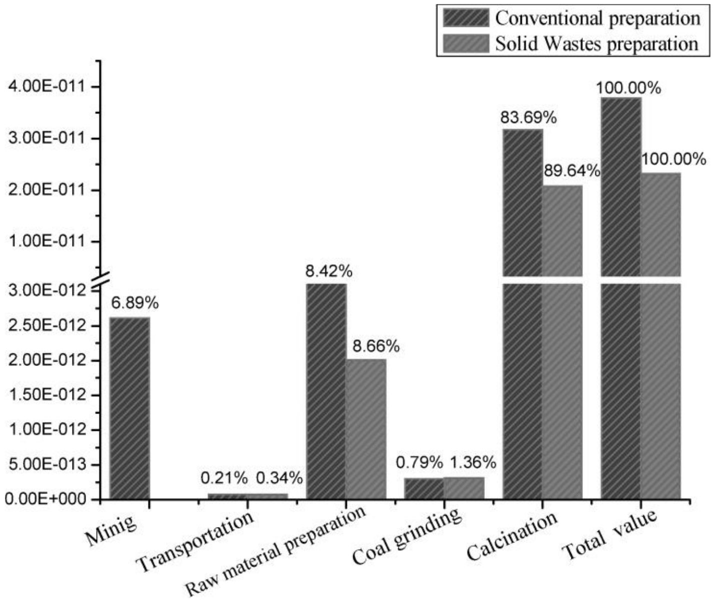


Fig. 3 Each CSA clinker production step contributes to the environmental burden (taken from [41]).

2.2.2. Hydrothermal-calcination process

Compared to the clinkerization process, the hydrothermal-calcination process requires a lower temperature and less energy [39, 42]. Some other advantages include finer particle sizes, higher surface area, and more homogeneous morphology [43]. However, a two-step process, i.e. the hydrothermal process and the calcination process, is required, which makes the production process more complicated. The hydrothermal synthesis consists of two reaction steps including dissolution and precipitation, where the precipitates can be further transformed to the final clinker product after calcination [24]. This method was first used for the synthesis of the highly reactive belite phase [42, 44], while limited exploration was done on CSA cement.

Rungchet et al. [45] used the hydrothermal-calcination method to produce BCSA cement by using waste materials including fly ash, aluminum-rich sludge, and flue gas desulfurization gypsum. The hydrothermal process was carried out using an autoclave at 130℃. Afterwards, the hydrothermal products were placed in an electric furnace at temperatures of 1050℃ for the second stage of calcination. After calcination, ye'elimite and β-belite phases can be obtained, while the quantities of these phases varied according to different treatments (see Fig. 4). Results show that the highest content of ye'elimite but lowest content of β-belite can be obtained by using water under hydrothermal treatment. In addition, the calcination product anhydrite indicates an incomplete combination of calcium, aluminum and sulfate to form ye'elimite. When being treated with 1 M sodium hydroxide, both ye'elimite and β-belite are formed completely without the formation of anhydrite.

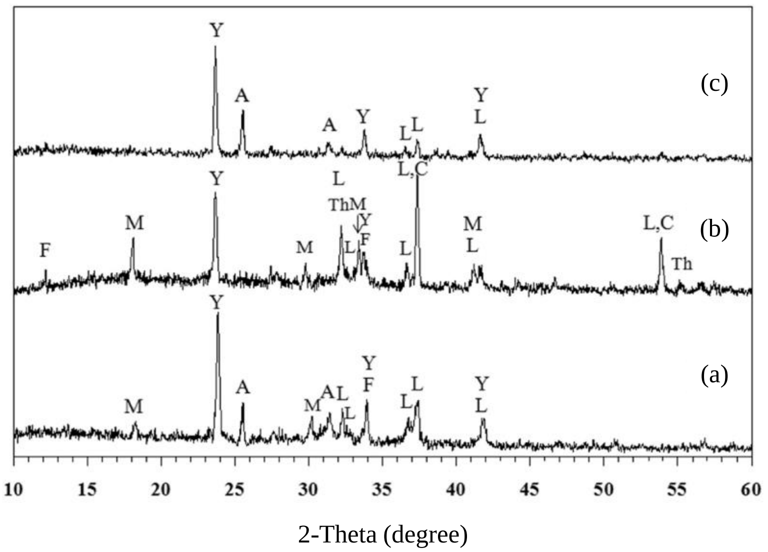


Fig. 4 XRD pattern of calcination products at 1050℃ from hydrothermal products (a) under water and hydrothermal treatment, (b) under 1 M sodium hydroxide and hydrothermal treatment, and (c) under water without hydrothermal treatment. Y (ye’elimite), L (lartnite), A (anhydrate), M (mayenite), Th (thenardite), F (brownmillerite), and C (lime) (taken from [45]).

3. Hydration characteristics

3.1. Basics

One of the major differences between Portland cement and CSA cement is the very fast rate of hydration associated with CSA cement. The majority of the hydration heat evolution occurs between 2 and 12 h of hydration [46]. The main hydration products are crystalline ettringite, monosulfoaluminate, and amorphous alumina hydroxide (AH_3) [47]. During the hydration process of CSA cement, three main events take place: (i) dissolution of crystalline anhydrous phases, (ii) appearance of new phases such as crystalline ettringite, and amorphous gels such as alumina hydroxide hydrate, and (iii) consumption of free water. The following equations summarize the hydration reactions.

$$C_4A_3\bar{S}+18H \rightarrow C_3A.C\bar{S}.12H+2AH_3 \tag{1}$$

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \rightarrow C_3A.3C\bar{S}.32H + 2AH_3 \tag{2}$$

Also, various hydration products such as C-S-H phases, strätlingite, monocarboaluminate, gibbsite, or hydrogarnet may precipitate depending on the minor phases present in the CSA cement [46, 48-50].

3.2. Effect of sulfate content

The hydration of CSA cement depends on several factors such as the amount and reactivity of the calcium sulfate and other minor phases [51, 52]. Eqs. (2), (3), and (4) show the reaction of the ye'elimite phase with different calcium sulfate sources (gypsum, bassanite, and anhydrite) in the aqueous medium. The reaction yields ettringite phases and amorphous alumina hydroxide. In the beginning, there is enough calcium sulfate present and therefore, the major hydration product would be ettringite once the sulfate is depleted and there is enough free water available, monosulfoaluminate is also formed. Also, bassanite can react with water to form gypsum, according to Eq. (5).

$$C_4A_3\bar{S} + 2C\bar{S}H_{0.5} + 37H \rightarrow C_3A.3C\bar{S}.32H + 2AH_3 \quad (3)$$

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \rightarrow C_3A.3C\bar{S}.32H + 2AH_3 \quad (4)$$

$$C\bar{S}H_{0.5} + 1.5H \rightarrow C\bar{S}H_2 \quad (5)$$

The amount of calcium sulfate in the system plays a major role in the final hydrate assemblage. From Eqs. (3), (4), and (5), it can be seen that the main crystalline hydration product is ettringite or monosulfoaluminate together with amorphous alumina hydroxide. The ratio between calcium sulfate and ye'elimite (also known as the molar ratio) is the decisive factor in the precipitation of either ettringite or monosulfoaluminate in the final product [52-55]. In addition, the amount of ettringite is affected by the reactivity of calcium sulfate (solubility and dissolution rate) at early ages [56]. Winnefeld et al. [57] studied the rate of hydration of CSA clinker blended with gypsum and anhydride at a constant molar ratio (see Fig. 5). The rate of hydration for the blend with CSA clinker and anhydrite was the lowest due to the slow dissolution of the anhydrite and resulting undersupply of calcium and sulfate ions [47, 57]. On the other hand, the dissolution of gypsum and basanite is much faster and therefore results in a quite fast hydration rate [52]. Telesca et al. [58] studied the hydrate assemblage and morphology of the hydrates of CSA cement with different gypsum contents. Fig. 6 shows the SEM images taken at two different hydration ages. Authors observed that the ettringite particles are shaped as prismatic crystals with a hexagonal cross-section with sizes varying to a significant extent in addition to the typical needle-like shape. From Fig. 6, it can be seen that there exist quite large ettringite crystals (0.6–1.0 µm wide, up to about 10 µm long) together with grains of CSA clinker and gypsum particles are also visible.

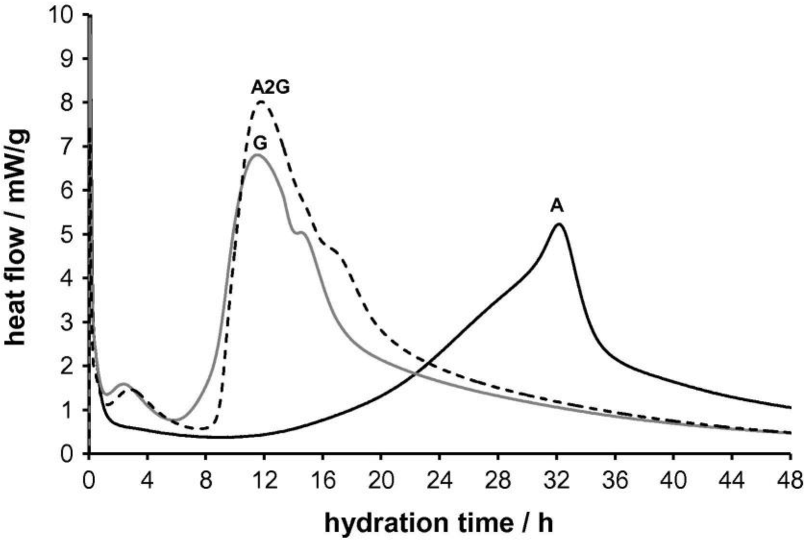


Fig. 5 Rate of heat release measured for CSA clinker blended with G (gypsum), A (anhydrite), and A2G (the combination of gypsum and anhydrite) (taken from [57]).

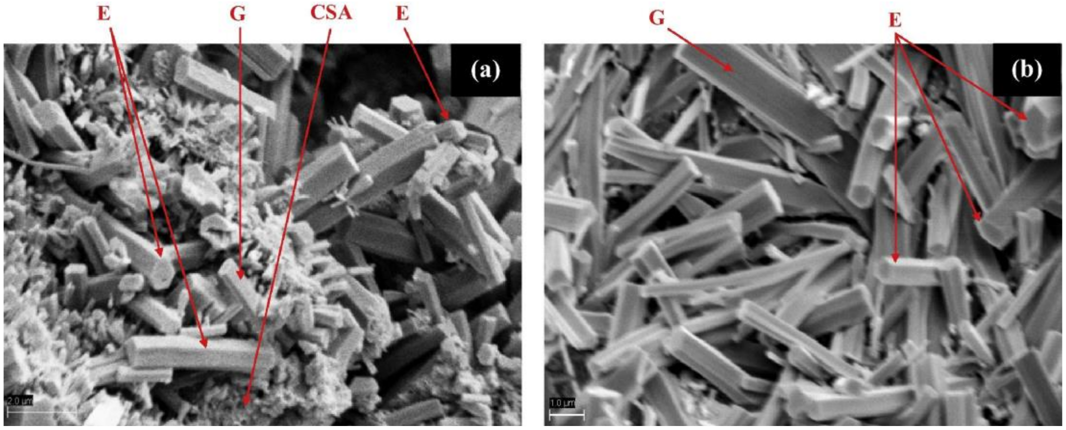


Fig. 6 SEM images of CSA cement in the presence of sulfate sources cured at (a) 6 hours and (b) 24 h, E (ettringite), G (gypsum) (taken from [58]).

As mentioned earlier in section 2.1, typically, belite-rich CSA cement contains very high amounts of belite and a lower amount of ye'elimite. Studies have shown that the type and content of sulfate plays a major role in the hydration of such systems as well [53, 59, 60]. One of the important findings is that the high amount of sulfate could retard the dissolution of α-belite and ferrite phases. Therefore, high sulfate content could increase the rate of early-age hydration and retard the hydration at later ages [50]. In a recent study, Mrak et al. [55] investigated the hydration kinetics and phase assemblage of BCSA cement prepared at different molar ratios. Authors postulated that with an increase in molar ratio, the dissolution of belite and ferrite phases will reduce, resulting in slower later-age hydration. Also, at a lower molar ratio, a higher amount of strätlingite is formed as there is less ettringite precipitation and more alumina available. Therefore, the content and type of sulfate source is very crucial in determining the rate of hydration and final phase assemblage in such systems [54, 61, 62].

Finally, it is worth mentioning the hydration characteristics of CSA cement in the presence of sulfate and alkalis. A handful of studies reported that in the presence of sulfate sources (either gypsum or anhydrite) the hydration gets accelerated as the alkali content in the pore solution increases, however, resulting hydrates have lower mechanical strength. Authors argue that at high alkali content, instead of ettringite, lower strength U phase is formed. This phase is a kind of calcium sulfoaluminate hydrate morphologically similar to calcium monosulfoaluminate (but with sodium in the structure) [63-65].

3.3. Setting characteristics and effects of retarders

Compared to Portland cement, CSA cement hydrates much faster and there is no induction period [46]. This is due to the high reaction rate of the ye'elimite phase in the presence of water and calcium sulfate. As mentioned before, in the presence of a calcium sulfate source, the reaction of ye'elimite is enhanced, in contrast to the Portland cement hydration [47, 51]. Therefore, generally for practical applications, the use of retarders is recommended [22, 66].

Several types of retarders were used to control the hydration of CSA cement. Organic acids like citric acid and tartaric acid, sugars such as sodium gluconate, and inorganic compounds like borax are generally used to retard the hydration of CSA cement [22, 67-73]. The studies reported that retarders either suppress the precipitation of the ettringite by reducing the dissolution of the ye'elimite or bind the calcium ions and thereby reduce the reaction rate. Contrastingly, in the presence of borax, a poorly crystalline phase called ulexite is formed which covers the ye'elimite surface and prevents further nucleation and growth of ettringite [66, 74, 75].

The rheological behavior of CSA cement is not much studied; mainly due to the very fast-setting behavior. However, a handful of studies focused on the rheological behavior of CSA cements with retarders. Recent studies reported that the plastic viscosity of CSA cement is significantly higher in comparison with Portland cement at the same water-to-cement ratio. This could be due to significantly different surface interactions, particle shape, and surface texture of CSA cement compared to Portland cement [22, 76-78]. In a recent study, Mohan et al. [22] investigated the pumping behavior of CSA cement-based mixtures. The authors observed higher pumping pressure loss for CSA cement-based mixtures compared to Portland cement-based mixtures and associated this with the significantly high plastic viscosity of the CSA mixture. However, CSA-limestone blends could reduce the plastic viscosity and thereby the pumping pressure.

3.4. CSA-based blended cement

Blending cement may enhance performance and allow the achievement of new properties. As stated, due to the high price of alumina-bearing raw materials, the cost of CSA cement is relatively high. Therefore, the combination of CSA cement and other materials is rather economic, which is more attractive to the industry [79].

Blends of CSA cement and Portland cement are commonly used. However, it is important to understand the physico-chemical properties of CSA/ Portland cement blends for use in concrete structures. It was found that the addition of CSA cement has an ignorable effect on the hydration of alite, but controls the dissolution and hydration of the alumina phase [80]. Researchers have studied ternary systems containing CSA cement, Portland cement, and anhydrite [81, 82]. The thermodynamic calculations indicated that the setting of the blended system is mainly controlled by the formation of ettringite from the hydration of ye'elimite, while Portland cement contributed to the strength by forming C-S-H from the hydration of alite at later ages. Furthermore, the addition of anhydrite would retard the early hydration of aluminate, while it reacts with ye'elimite to form more ettringite. Studies focusing on the hydration behavior of CSA/Portland cement blends at different replacement levels revealed that the hydration rate and phase assemblage is sensitive towards the ye'elimite content, free lime, and sulfate content. Higher ye'elimite content suppresses the Portland cement hydration and thus the hydration rate would be much higher. On the other hand, if the ye’elimite content is relatively lower, the alite from Portland cement hydrates initially and ye'elimite hydration occurs in the presence of lime [80, 83].

While calcium carbonate in the form of calcite has been widely used as an additive in Portland cement [84], only a few works have been carried out to study the hydration of CSA cement in the presence of calcium carbonate. The addition of calcium carbonate or its polymorphs could be beneficial either by proving nucleation sites for hydration or by forming carboaluminate phases. The carboaluminate phases could help in proving higher mechanical strength due to their stabilizing effect on ettringite [22, 85-87]. Martin et al. [87] found that the presence of calcium carbonate would accelerate the hydration of CSA cement due to an increase in nucleating sites. In addition, the chemical reaction between calcium carbonate and ye’elimite would result in the formation of monocarboaluminate, ettringite, and amorphous alumina hydroxide phases. In the case that calcium sulfate is consumed, hemicarboaluminate would form instead of monocarboaluminate [24].

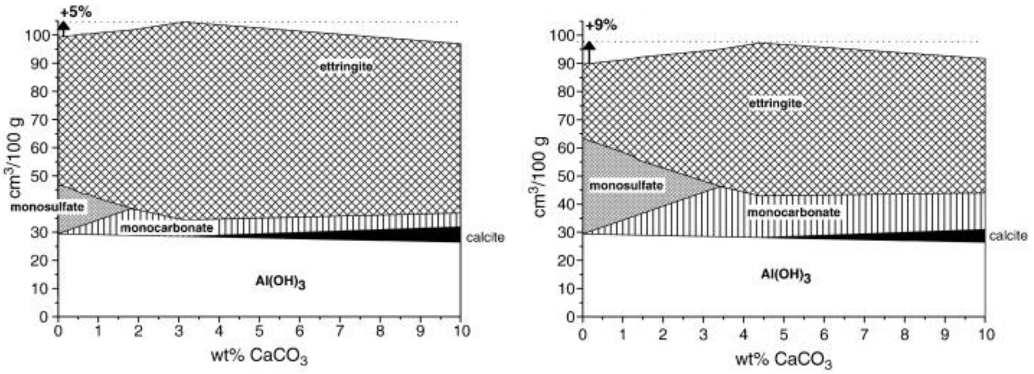
The hydration of CSA cement blended with industrial by-products such as blast furnace slag and fly ash was also investigated mainly in search of more sustainable concrete mixtures [73, 88-91]. Results indicated the main hydration products are identified as ettringite, monosulfate, alumina hydroxide, and strätlingite. The presence of blast furnace slag in CSA cement contributes to the formation of more strätlingite, while the formation of ettringite and monosulfate is reduced. Studies exploring the influence of fly ash on the hydration of CSA cement reported that the presence of fly ash enhanced the reaction of belite, resulting in more C-S-H precipitation, an increase in strätlingite, and also destabilization of monosulfate [87, 92]. Fly ash dissolution is generally slower in CSA-fly ash blends compared to Portland cement. This is due to the lack of portlandite and the low pH of the pore solution [88, 93, 94]. However, calcium ions from the C-S-H phase could take part in the pozzolanic reaction and transform into C-S-H with a lower Ca/Si ratio [95]. Also, the destabilization of monosulfate phase may cause reduced chloride binding capacity as will be explained later in section 5.2 of this paper.

3.5. Thermodynamic modeling

Thermodynamic modeling of cementitious systems can enable understanding the phase assemblage with respect to the rate of hydration and therefore, efficient development of alternate binder systems with low-CO_2 footprint. Currently, there are several powerful geochemical modeling tools (e.g. PHREEQC [96], EQ3/6 [97], CHESS [98], GEMS [99, 100], etc.) to compute the equilibrium phase assemblage and speciation in a complex system from its total bulk elemental composition and its physical state (i.e. pressure and temperature), with reasonable accuracy [99, 101]. Though the thermodynamic modeling of Portland cement-based systems is well studied, studies focusing on CSA cement-based materials are not many and therefore, the database is also not complete [102, 103].

One of the main assumptions in the thermodynamic modeling of cementitious systems is that the pore solution and the hydrates are in a thermodynamic equilibrium state or a metastable equilibrium [104, 105]. However, often, depending on the timeframe and temperature of the hydration reaction, choices need to be made with regard to the suppression or consideration of certain phases in the system, as this has a significant influence on the final hydrate assemblage. For instance, in the case of CSA cement systems, precipitation of amorphous alumina hydroxide is reported instead of a more stable gibbsite phase. In the early stages of hydration (minutes to hours), mainly amorphous alumina hydroxide with very high solubility is precipitated in the system. As time progresses, the solubility of the alumina hydroxide phase reduces, and, microcrystalline alumina hydroxide forms. Finally, after a timeframe of months to years, gibbsite forms. The precipitation of amorphous alumina hydroxide is responsible for the initial formation of the calcium aluminate phase, while the formation of less soluble microcrystalline alumina hydroxide stabilizes monosulfoaluminate [106, 107].

Thermodynamic modeling can be useful for several applications. One such important application is the prediction of the amount of ettringite and thereby the crystallization pressure on expansion characteristics. This can be achieved by coupling thermodynamic and transport modeling and using the input from the pore solution data. Such analysis can be useful in the case of CSA cements as the primary hydration product from CSA cement hydration is ettringite [108, 109]. Furthermore, this will enable the optimization of the mixture avoiding excessive volumetric changes leading to cracking. Another application is the hydrate assemblage determination in blended CSA cement. For instance, the addition of limestone powder has beneficial effects on CSA cement due to its high alumina content. Thermodynamic modeling studies have shown that the amount of sulfate in terms of the ratio of sulfate to alumina phase plays an important role in such blended systems. A relatively high sulfate to alumina ratio could precipitate higher amounts of ettringite and less monosulfate and monocarbonate as shown in Fig. 7 [110]. Another application can be in the field of clinker production. Thermodynamic-based clinker equilibrium calculations can be helpful in determining the temperature and pressure conditions where clinker phases (especially ye'elimite) become stable [111-114].



(a) 80% ye'elimite – 20% anhydrate

(b) 90% ye'elimite – 10% anhydrate

Fig. 7 Volume change calculations obtained from thermodynamic modeling as a function of limestone powder (a) 80 wt.% ye'elimite and 20% anhydrite, (b) 90 wt.% ye'elimite and 10% anhydrite (taken from [110]).

4. Mechanical properties

Compared to Portland cement with the same water-to-cement ratio, CSA cement shows high early-age mechanical strength due to the rapid formation of ettringite from the hydration of the ye'elimite phase [49, 115-117]. However, the retarders which are often used in CSA systems to increase its setting time have been found to decrease the early-age strength development. For instance, Vahid et al. [118] evaluated the compressive strength of CSA cement containing tartaric acid as a set controller. The addition of tartaric acid (0.22‰ or 0.44‰ by the mass of CSA cement) delayed the formation of ettringite which significantly lowered the 1-day compressive strength of the CSA mixture compared to a Portland cement mixture with the same water-to-cement ratio. On the other hand, the compressive strength at 28 and 56 days of the CSA cement-based mixture was higher than that of the Portland cement-based mixture as the effect of the retarder diminished at later ages. A similar study compared the early-age compressive strength (1 and 7 days) of CSA cement-based mixtures with and without gluconate and borax (dosage of 0.1 % of the binder) as retarders (see

Fig. 8) [22]. The addition of gluconate significantly lowered the early-age strength development. On the other hand, when borax was used as the retarder, similar compressive strength to that of pure CSA was observed. In the case of retarders like gluconate, the retardation arises from the hindrance caused by ettringite formation as it binds with calcium ions on its surface [68, 119]. However, in the case of borax, the retardation effect has been attributed to the formation of the metastable phase ulexite, whose stability depends on the amount of sulfates in the pore solution. Once the sulfates in the pore solution are consumed, there is renewed formation of ettringite at a rapid rate which enhances the strength development [75, 120].

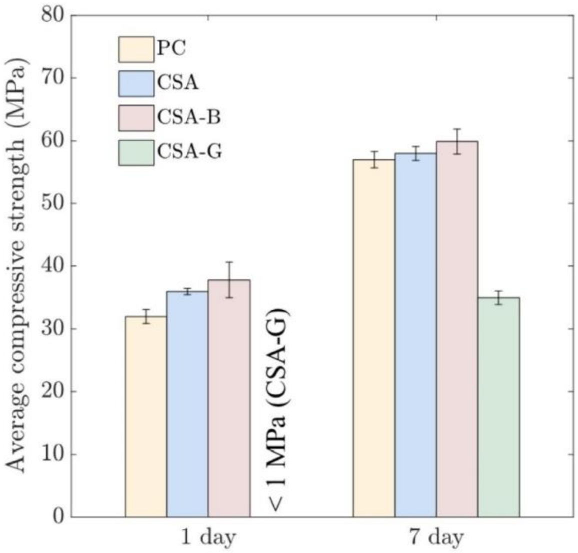


Fig. 8 Effect of gluconate (CSA-G mixture) and borax (CSA-B mixture) retarders on the early-age strength development of CSA cement in comparison with a Portland cement mixture having the same water-to-cement ratio (PC mixture) (taken from [22]).

The strength development of CSA cement is also strongly influenced by the type and amount of sulfate used. For instance, an increase in the amount of anhydrite in the range of 20 to 30 % in CSA cement has been found to increase the 7-day and beyond compressive strength values (see Fig. 9). This can be attributed to the higher ratio of ettringite to monosulfoaluminate in the hydrated CSA system with the increase in the amount of anhydrite [121]. The strength development is also influenced by the type of sulfate (gypsum, bassanite, and anhydrite as discussed in the previous section) being used. For instance, replacing the sulfate type with gypsum instead of anhydrite has been found to accelerate both the early-age and later-age compressive strength since gypsum accelerates the ye'elimite hydration more effectively as compared to anhydrite [57].

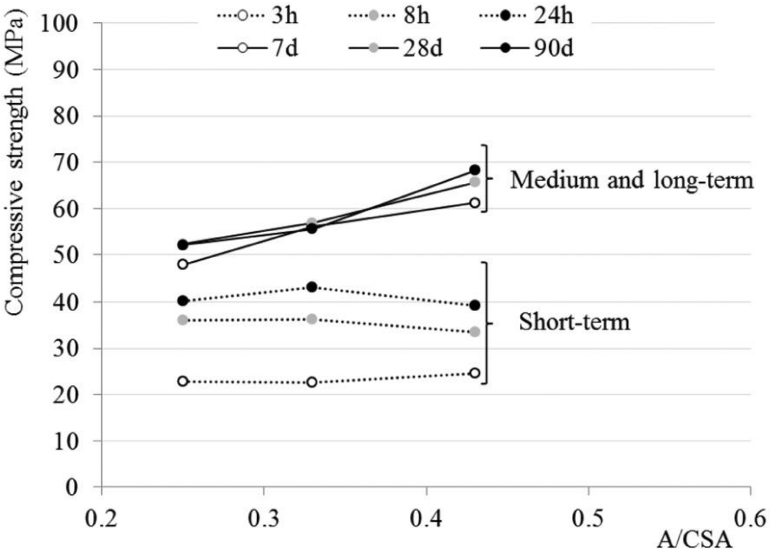


Fig. 9 Effect of anhydrite (A) addition on compressive strength development of CSA cement (taken from [121]).

It is also worth mentioning the compressive strength development of Portland cement-CSA cement-anhydrite ternary systems. The amount of anhydrite content and the ratio of Portland cement to CSA cement is the most important factor that influences strength development [81, 122]. A higher proportion of anhydrite content has been found to improve both early-age and later-age compressive strength. On the other hand, for a fixed CSA/anhydrite content, an increase in the Portland cement content was found to decrease the 7-day compressive strength while a similar compressive strength was obtained at the later age (100 days), irrespective of the Portland cement content. The initial strength development is primarily due to the hydration of ye'elimite present in the CSA cement. However, as mentioned in the previous section, beyond 7 days, the alite in the Portland cement begins to react and contribute to the strength development [81].

5. Long-term performance

In the following section, we review the transport properties of the CSA cement. The water absorption, oxygen permeability, carbonation, and chloride diffusion characteristics of CSA cement will be discussed in this section. Following this, in section 5.2, we present a review of the durability of CSA cement against common deterioration issues such as embedded steel corrosion, sulfate attack, alkali silicate reaction, and physical attacks such as freeze-thaw and salt scaling.

5.1. Transport properties

The transport properties of cementitious systems are closely linked with the characteristics of their pore network. Compared to Portland cement, studies have shown CSA cement systems have a refined and densified microstructure. If the belite content is not very high, the hydrated paste will mostly be dominated by ettringite crystals which form more rapidly within the first 7 days. The belite reacts more slowly and results in the formation of the C-S-H gel. Ettringite crystals have been found to grow in the empty spaces between the C-S-H matrices thus leading to a very refined microstructure [123]. Recent mercury intrusion porosimetry (MIP) studies have revealed that compared to a Portland cement-based system with a similar water-to-cement ratio, the cumulative pore volume in the BCSA cement system is similar or even slightly higher, however, the threshold pore diameter is much lower due to the pore refinement [124, 125]. Apart from the pore volume and size, tortuosity is an important parameter that affects the transport of ions through cementitious systems. A higher tortuosity has been linked with lower transport properties [126]. Recently, Mohan et al. [125] computed the tortuosity of a BCSA cement-limestone system by using the corrugated pore structure model [127] and compared it with a Portland cement-slag system having the same water-to-cement ratio. The CSA-based system was found to have a much higher tortuosity which may be attributed to its more refined pore network. In the same study, the authors also evaluated the geometric complexity of the pores by measuring the surface fractal dimension [128, 129]. Although the macro-fractal dimension was similar for CSA and Portland cement-based mixtures, the micro-fractal dimension was found to be significantly higher for CSA mixtures thus indicating a more complex pore network in the micro-pore region.

Hargis et al. [130] examined the transport properties such as the oxygen permeability and water absorption for CSA mixtures. The CSA mixtures showed reduced water absorption and oxygen permeability as compared to a Portland cement mixture with the same water-to-cement ratio. Additionally, they found that water absorption decreased with a decrease in the water-to-cement ratio, but the changes in the anhydrite content of CSA cement did not alter the water absorption.

CSA cement has been found to show a lower carbonation resistance compared to Portland cement. The carbonation resistance is also found to strongly depend on the water-to-cement ratio and the anhydrite content. As with Portland cement systems, a decrease in the water-to-cement ratio increases the carbonation resistance. An increase in the anhydrite content will result in a dilution of CSA clinker and thus lower the CO_2 binding capacity. Despite this, the carbonation resistance decreases with an increase in the anhydrite content which can be attributed to the increased ye'elimite hydration kinetics at higher anhydrite content [130]. Monosulfoaluminate present in the hydrated CSA system acts as a carbonation buffer and destabilizes monocarbonate. However, with further progress of carbonation, the monocarbonate decomposes leading to the reduction in pore solution pH [131].

Compared to Portland cement with the same water-to-cement ratio and the same age, CSA cement shows a higher chloride diffusion coefficient. This may be due to the lower chloride binding capacity of CSA cement [132]. Similar to the carbonation resistance, the resistance against chloride diffusion is strongly dependent on the anhydrite content of the CSA cement. A higher amount of anhydrite increases the ettringite content instead of monosulfoaluminate in the hydrated CSA system. Ettringite has a lower chloride binding capability as compared to monosulfoaluminate, thus causing a faster chloride diffusion [133-135].

To summarize, CSA cement has a densified microstructure with better pore refinement as compared to Portland cement which leads to lower water absorption and oxygen permeability. However, CSA cement has a lower carbonation resistance and higher chloride diffusion due to its lower binding capacity as compared to Portland cement. Further, the above discussions show the transport properties are strongly dependent on factors such as the type and amount of sulfate and the water-to-cement ratio of the CSA cement. The chloride binding capacity, for instance, can be significantly improved by lowering the anhydrite content in the CSA cement. Due consideration must be given to these factors while designing cementitious mixtures using CSA cement for ensuring its long-term performance.

5.2. Durability

One of the major durability issues in reinforced concrete is embedded steel corrosion. Compared to Portland cement with the same water-to-cement ratio, CSA cement has lower resistance to both carbon dioxide and chloride ion ingress. Additionally, the pH of the pore solution in CSA cement is lower than that of Portland cement, thus increasing the susceptibility to embedded steel corrosion [93, 132]. Despite this, a recent study indicates that the alkalinity of the pore solution is still high enough to ensure the passivation of the embedded steel [136]. Carbonated CSA concrete showed a reduced corrosion rate compared to Portland cement and Portland cement-limestone concrete counterparts, which can be attributed to its lower electrical conductivity arising from its densified microstructure. The susceptibility of concrete made with CSA cement to chloride-induced steel corrosion was studied by Kalogridis et al. [137]. When exposed to tap water, the CSA cement provided adequate protection against steel corrosion after 12 months of exposure. However, when immersed in a 3.5 % sodium chloride solution, a higher corrosion rate was observed for CSA cement compared to Portland cement. In the CSA mixture, the concentration of chloride ions in the pore solution was found to progressively increase and this combined with other factors such as the low hydroxyl ion concertation of the pore solution, ultimately led to the depassivation of embedded reinforcing steel. On the other hand, Glasser and Zhang [49] who examined the reinforcement steel in CSA concrete in service for 14 years and exposed it to an intertidal zone, observed high corrosion protection for the steel embedded in the concrete. These contradictions in results may be due to the difference in the composition of the CSA cement. While the former study used a CSA cement with lower ye’elimite content (around 20 % by mass only as compared to over 50 % used in most BCSA cement), the exact composition of the CSA field concrete used in the latter study was unknown. This indicates the need for more research examining the effect of CSA cement composition, particularly the ye’elimite, belite, and anhydrite content on embedded steel corrosion.

As indicated earlier, in a CSA cement with a sufficient amount of anhydrite, the microstructure will be dominated by ettringite in place of monosulfoaluminate. This provides an advantage against certain durability issues such as sulfate attack since ettringite does not react with external sulfates, in comparison to monosulfoaluminate. Further, hydrated CSA cement contains less calcium hydroxide, another phase that is susceptible to sulfate attack. Due to these factors, many studies have shown CSA cement to be more resistant against external sulfate attack as compared to

Portland cement [138-141]. Nevertheless, CSA cement has been found to be susceptible to magnesium sulfate attack due to the decomposition of ettringite by magnesium ions [142]. CSA cement has also been observed to show higher resistance against other forms of chemical deterioration such as alkali-aggregate reaction which can be attributed to its low pH and lower alkali content, in addition to the more densified microstructure thus reducing the water availability for the alkali-aggregate reaction [143]. Recently, Damion et al. [144] showed that CSA cement has a lower resistance to sulfuric acid attack, while another study [145] reports contradictory findings of improved resistance in comparison to Portland cement. Such contradiction again may be due to the difference in composition of CSA and points to the need for further research in these areas.

There are very limited studies that evaluate the resistance of CSA cement against various physical attacks. In a study that examined the freeze-thaw damage of a CSA cement with low ye'elimite content, higher resistance to freeze-thaw damage was observed in comparison to Portland cement. However, there are seldom studies focusing on the freeze-thaw resistance of the more typically used high ye'elimite CSA cement which has a more refined pore size distribution. Edward [146] evaluated the salt scaling resistance of CSA mixtures in both laboratory and field conditions. Although laboratory concrete showed good salt scaling resistance, the field concrete showed poor resistance to salt scaling. This was primarily attributed to the rapid loss of workability in CSA cement resulting in improper compaction and finishing of the field CSA concrete, and the resultant poor quality of the concrete surface. CSA cement has also been found to show higher physical salt crystallization damage in comparison to Portland cement [147, 148] which may be due to the higher crystallization pressure arising from its more refined microstructure [149, 150].

To summarize, the limited studies and the conflicting observations on important durability issues such as embedded steel corrosion necessitate the need for further research in these areas. In comparison to Portland cement, the lack of monosulfoaluminate and reduced calcium hydroxide content in the hydrated CSA cement provides a higher resistance against durability problems such as external sulfate attack. More studies are also required in understanding other durability issues such as acid attacks and various physical-based deteriorations of CSA mixtures.

6. Applications

There are a handful of applications for using CSA cement based on the above-mentioned properties such as concrete with high early-age strength, self-leveling screed, self-leveling topping mortar, glass-fiber-reinforced composites, etc. [151]. In this section, we mainly discuss three rather innovative utilizations, including concrete repair, waste stabilization, and 3D concrete printing.

6.1. Concrete repair

Concrete repair often requires the repair materials to set and get hardened fast, especially in some urgent cases such as repairing a bridge or runways of an airport [152-155]. CSA cement has been considered a suitable repairing material because of its fast setting, dense structure, and shrinkage resistance. As stated, the main mineralogical phase of CSA cement, ye'elimite, would contribute to the rapid formation of ettringite, and consequently lead to high strength at early ages [82]. Therefore, CSA cement is utilized as rapid set cement, as well as a shrinkage reducer. However, the shrinkage-resistance property of CSA cement also relates to the presence of lime. As shown in Eqs. (2) and (6), each unit of ye'elimite can produce three moles of ettringite in the presence of lime, while merely one mole of ettringite is formed in the absence of lime.

$$\mathrm{C_4A_3\overline{S} + 8C\overline{S}H_2 + 6CH + 74H \rightarrow 3C_3A.3C\overline{S}.32H} \tag{6}$$

In presence of lime, according to Eq. (6), blending CSA cement and Portland cement would further enhance the expansion as portlandite can be released by alite hydration from Portland cement. Ye'elimite is combined with gypsum and portlandite to yield ettringite.

In addition, the curing condition also plays a significant role to limit shrinkage. The shrinkage of concrete with a CSA cement-to-lime ratio of 10:1 was measured. Results showed that the sample expanded more when cured under water, while the measured shrinkage was less when cured by covering with a plastic sheet [156]. In practice, reducing the content of lime is beneficial to lower the expansion to zero, which is desirable for repairing.

6.2. Waste stabilization

Another application of CSA cement is to stabilize waste. Usually, Portland cement blended with slag or fly ash is used for the encapsulation of intermediate-level or low-level radioactive wastes. However, reactive metals contained in the waste may react due to the high alkalinity of cement. Being a type of cement with lower alkalinity, CSA cement has been tested as an encapsulation binder for radioactive wastes [157]. For example, the low alkalinity of hydrated CSA cement allows the precipitation of radionuclides as hydroxides such as strontium hydroxide [158].

In addition, the relatively short setting time of CSA cement is also beneficial for the encapsulation of radioactive wastes [157]. In contrast to Portland cement, the hydration rate of CSA cement is not retarded by heavy metals [159]. Another advantage of CSA cement over Portland cement is the lower bleed as large quantities of water are consumed for the formation of ettringite [160]. The lower internal humidity also helps to inhibit further corrosion and limits radiolytic gas generation.

6.3. 3D concrete printing

3D concrete printing is a new construction method with a high degree of automation [161-163] in which elements are constructed through the subsequent deposition of extruded layers. For most 3D printed concrete, Portland cement is the primary binder accounting for about 15-45% of the total mix proportion, which is higher than that of conventional mold-cast concrete [164, 165]. Such a high proportion of cement would result in more CO_2 emissions. Alternatively, CSA cement can be used for more sustainable 3D concrete printing. In this case, a retarder is also added to prolong the open time of the CSA cement-based mixture [22].

Using a high content of binder and the absence of formwork would lead to high shrinkage (plastic, dry, and chemical shrinkage) [164, 166, 167]. Several studies have proposed using additives such as shrinkage-reducing admixtures, fibers, superabsorbent polymers, or coarse aggregates as mitigating strategies [167-169]. CSA cement has the potential to fully overcome this drawback because of the characteristic of shrinkage resistance [170, 171].

Another challenge is to control the stiffening process as there are conflicting requirements during the pumping and deposition phase. Previous studies have proven that relying on merely the thixotropic structural build-up of the material itself may not be sufficient for a high construction rate [172, 173]. Instead, a two-stage mixing method has been proposed based on CSA cement, i.e. retarding the reaction at the initial stage and speeding up the structural build-up rate after extrusion [66], as schematically shown in Fig. 10. A borated CSA cement mixture is intermixed by using a static mixer with a mixture of limestone and calcium hydroxide right before extrusion. Both mixtures have a long open time. After being mixed, the presence of calcium hydroxide would increase the pH of the CSA cement mixture and destroy the retardation effect achieved by using borax. However, the mechanical integrity of the printed element is low due to the presence of weak striation regions [174-176]. Although the reaction between CSA cement and calcium carbonate would occur, the improvement in mechanical integrity is still limited as ions still need to migrate between two striations [174]. Another challenge is the compatibility as the shrinkage/expansion behavior is different between these two mixtures, which further introduces inner stresses and cracks.

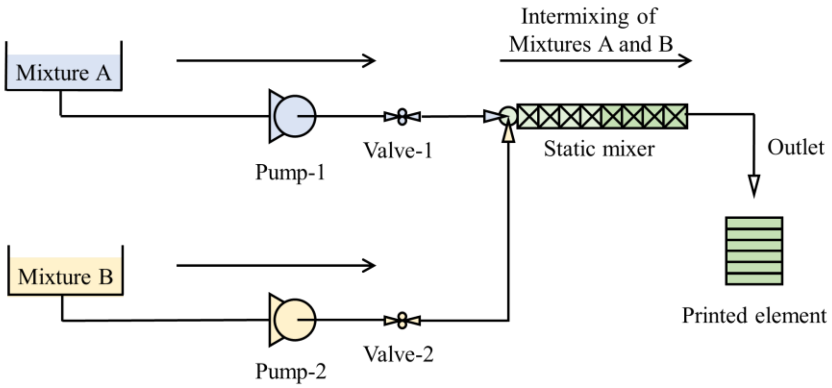


Fig. 10 Schematic view of the inline mixing process, where mixture A is a borated CSA cement-based mixture and mixture B is a limestone powder-based mixture (taken from [66]).

7. Conclusions and perspectives

The use of calcium sulfoaluminate (CSA) cement is beneficial for reducing CO_2 emissions. Based on the discussions, the following conclusions and research needs are pointed out:

(1) The use of CSA cement is restricted due to the high cost of alumina-bearing raw materials. One solution is to use belite-rich CSA cement or CSA-blended cement which is rather economical as compared to Portland cement. There have been a few successful laboratory trials to manufacture CSA from sludge materials. This can help in lowering its production cost and further contribute to making CSA more environmentally friendly. The feasibility of such methods for large-scale production needs to be explored through further research.

(2) The hydration and the final hydrate assemblage of CSA cement depends on the amount and reactivity of the calcium sulfate and other minor phases. The higher sulfate content can increase the rate of early-age hydration due to the formation of ettringite, which is in contrast to the Portland cement hydration. To control the fast hydration of CSA cement, retarders are generally used including different types of organic acids, sugars, and inorganic compounds. The hydration can be predicted using thermodynamic modeling, for which the database is not complete, especially for those CSA cements with the addition of retarders.

(3) Mechanical strength of the CSA cement-based mixture is strongly influenced by the type and amount of retarders used. In addition, the strength development also depends on the sulfate phase, which can be further attributed to the different ratios of ettringite to monosulfoaluminate in the hydrated system.

(4) Although CSA cement has a densified microstructure with better pore refinement in comparison to Portland cement, it has a lower carbonation resistance and higher chloride diffusion due to the reduced binding capacity. There are only limited studies and also conflicting observations on durability issues such as embedded steel corrosion, thus pointing out the need for more research in this area.

(5) CSA cement has been used for applications such as repair, waste stabilization, and 3D concrete printing. For such applications, shrinkage/expansion behavior plays an important role, which is closely related to hydration and phase assemblage. An important challenge is to regulate the hydration and stiffening process of CSA cement to meet the different rheological requirements depending on the type of application.

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