

Mini-review:

Durability of calcium sulfoaluminate cement concrete*

Bowen TAN¹, Monday U. OKORONKWO², Aditya KUMAR³, Hongyan MA^{†‡1}

¹*Department of Civil, Architectural and Environmental Engineering, Missouri University of Science and Technology, Rolla, MO 65401, USA*

²*Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, MO 65401, USA*

³*Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65401, USA*

[†]E-mail: mahon@mst.edu

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Abstract: Calcium sulfoaluminate cement (CSAC), first developed in China in the 1970s, has received significant attention because of its expansive (or shrinkage-compensating) and rapid-hardening characteristics, low energy-intensity, and low carbon emissions. The production and hydration of CSAC (containing ye'elinite, belite, calcium sulfate, and minors) have been extensively studied, but aspects of its durability are not well understood. Due to its composition and intrinsic characteristics, CSAC concrete is expected to have better performance than Portland cement (PC) concrete in several aspects, including shrinkage and cracking due to restrained shrinkage, freeze-thaw damage, alkali-silica reaction, and sulfate attack. However, there is a lack of consensus among researchers regarding transport properties, resistance to carbonation, and steel corrosion protectiveness of CSAC concrete, all of which are expected to be tied to the chemical composition of CSAC and attributes of the service environments. For example, CASC concrete has poorer resistance to carbonation and chloride penetration compared with its PC counterpart, yet some studies have suggested that it protects steel rebar well from corrosion when exposed to a marine tidal zone, because of a strong self-desiccation effect. This paper presents a succinct review of studies of the durability of CSAC concrete. We suggest that more such studies should be conducted to examine the long-term performance of the material in different service environments. Special emphasis should be given to carbonation and steel rebar corrosion, so as to reveal the underlying deterioration mechanisms and establish means to improve the performance of CSAC concrete against such degradation processes.

Key words: Calcium sulfoaluminate cement (CSAC); Durability; Carbonation; Chloride; Steel corrosion

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1 Introduction

Concrete is the most used man-made material, with multiple tonnes consumed annually for every person on earth (Gagg, 2014). Portland cement (PC) is the most commonly used binder for concrete. The production of PC clinker—which includes calcination of limestone and processing of raw materials at high-temperature (≈ 1500 °C)—emits over 7% of the

worldwide anthropogenic greenhouse gas emissions. Simply put, production of each tonne of PC results in emission of >800 kg of CO₂ (Damtoft et al., 2008; Gartner, 2014). Researchers have been working to identify ways to reduce the CO₂ emissions associated with the production and use of PC. According to the United Nations Environment Program Sustainable Building and Climate Initiative (UNEP-SBCI), there are three approaches which can improve the eco-efficiency of PC: improving cement efficiency; increasing the use of supplementary cementitious materials (SCMs); developing sustainable alternative cements (or non-Portland cements) (UN Environment et al., 2018). One of the most reliable, low-carbon emission alternative cements is calcium sulfoaluminate

[‡] Corresponding author

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ORCID: Bowen TAN, <https://orcid.org/0000-0003-1054-1719>; Hongyan MA, <https://orcid.org/0000-0003-3674-3845>

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cement (CSAC). CSAC normally consists of a dominant cementing phase of ye'elmitite (C_4A_3S) (cement chemistry notations used in this paper are as follows: $A=Al_2O_3$, $C=CaO$, $F=Fe_2O_3$, $H=H_2O$, $S=SiO_2$, $S=SO_3$) and several minor phases (e.g. belite and gypsum). The production of CSAC requires a calcination temperature of 1250 °C, which is 200 °C lower than that of PC. Furthermore, CSAC requires a much lower grinding energy than PC due to its lower fracture energy (Aranda and de la Torre, 2013). Typical raw materials for production of CSAC are limestone, calcium sulfate, and aluminum-rich minerals or industrial by-products. Alite (the dominant phase in PC clinker) releases around 1.80 g CO₂/mL of the cementing phase, whereas ye'elmitite releases only 0.56 g CO₂/mL (Gartner, 2014). However, production of an eco-efficient cement is not merely about reducing CO₂ emissions and energy consumption during manufacturing. The cement must also result in durable concrete (either plain or reinforced by steel rebar), otherwise the environmental benefits gained in cement production will be counteracted by a shorter service life (Hargis et al., 2017). In spite of its importance, there have been few studies on the durability of CSAC concrete compared to those on PC concrete. So far, most research on CSAC has focused on the production and hydration of the cement (Aranda and de la Torre, 2013), which will not be reviewed here. In this paper, we present a brief overview of the state-of-the-art of important durability-related aspects of CSAC concrete. Note that the high-temperature stability and fire hazard resistance of CSAC concrete were out of scope of this work. Ettringite, as a dominant phase in CSAC concrete, has a hexagonal prismatic crystal shape, with columns of aluminum-oxygen octahedra linked by calcium and hydroxide ions as well as sulfate and water molecules on the outer surface of the columns (Aranda and de la Torre, 2013). The water molecules between the columns can be lost at around 100 °C, leading to structural decomposition. However, concrete is rarely exposed to such high temperatures in regular service environments. We conclude our review by summarizing future research needs regarding the durability of CSAC concrete based on a discussion of general deterioration concerns.

2 Durability of CSAC concrete

2.1 Pore structure and general transport properties

The major hydration product of CSAC is ettringite, a crystalline compound that forms as a result of hydration of ye'elmitite. When the belite content of CSAC is not high, the formation of C-S-H gel in the resulting paste is limited. Therefore, in such CSAC pastes, the hydrate assemblage is dominated by crystals, and the pore network comprises a limited volume of gel pores and small capillary pores (<10 nm). This has been confirmed by Mercury intrusion porosimetry (MIP) results in the literature (Hargis et al., 2017) compared a CSAC paste to a PC paste of the same water-to-cement ratio *w/c* (i.e. 0.4) and similar porosity (11.4% vs 12.1%). They found that the CSAC paste had a finer overall pore structure indicated by the threshold pore diameter, although it contained more pores bigger than 100 nm owing to the packing of large crystalline hydrate grains. As a result, the water absorption capacity (4.30% vs 7.42%) and O₂ diffusion coefficient (1.39×10^{-8} m²/s vs 3.95×10^{-8} m²/s) of the CSAC paste were both lower than those of the reference PC paste. Guo et al. (2014) reported similar results. Nevertheless, in the context of chloride ingress, it was reported that the chloride diffusion coefficient of CSAC (a high sulfate type) concrete was higher than that of PC concrete under the same exposure conditions (Quillin, 2001). However, note that chloride ingress depends on the binding capacity of the cement, in addition to the pore structure. In CSAC pastes, monosulfoaluminate (which forms as a result of phase transformation of ettringite, after the exhaustion of sulfate in the system) is able to bind chloride to form Friedel's salt (Paul et al., 2015), while ettringite cannot. Therefore, a CSAC paste over-dosed with calcium sulfate shows poor chloride penetration resistance and steel rebar protectiveness (Kalogridis et al., 2000). The hydrate assemblage in a CSAC system can be manipulated by changing the gypsum-to-ye'elmitite ratio. Through such manipulations, the chloride binding capacity, and thus the chloride penetration resistance of CSAC concrete, can be enhanced (Jen et al., 2017). Zhao et al. (2014)'s results confirmed this by showing that gypsum-deficient CSAC concretes have lower chloride diffusion coefficients than equivalent PC concretes prepared using the same mixture proportions.

2.2 Shrinkage and cracking potential

The volumetric stability of CSAC binder is directly linked to the relative amount of ettringite in the hydration product phase assemblage, which is controlled by the chemistry of the CSAC clinker (Chen et al., 2012). Thus, by altering the clinker composition and calcium sulfate content, CSAC concrete (or pastes/mortars) can be produced with the desired dimension stability—shrinkage compensating or expansive (self-stressing) attributes (Beretka et al., 1996; Guo et al., 2014; Hargis et al., 2017). Contrary to the notion that self-desiccation in CSAC may lead to higher autogenous shrinkage, recent research has shown comparable autogenous shrinkage for CSAC and PC (Sirtoli et al., 2019), and for both cement types the effect can be mitigated using similar methods (e.g. use of an appropriate *w/c* and internal curing) (Quezada et al., 2018). Therefore, shrinkage and the associated potential for cracking are not expected to be a problem for CSAC concrete, provided that the material is proportioned on the basis of performance requirements.

2.3 Freeze-thaw damage

In general, researchers agree that CSAC concrete performs better than PC concrete with the same *w/c* in freeze-thaw environments, as measured by the relative dynamic modulus, weight loss, and surface scaling (Guo et al., 2014; de Bruyn et al., 2017; Moffatt and Thomas, 2018). The high freeze-thaw damage resistance of CSAC concrete has been attributed to its lower porosity and the inclusion of more coarse pores (de Bruyn et al., 2017). In addition, the strong self-desiccation effect of CSAC hydration can lead to a relatively low degree of saturation in the microstructure (Glasser and Zhang, 2001), which could also contribute to the high freeze-thaw damage resistance of concrete (Li et al., 2012). Moffatt and Thomas (2018) reported that a CSAC concrete showed worse in-field scaling resistance than a reference PC concrete. However, the poor performance of the CSAC concrete was attributed to field manipulation (e.g. placement, compaction, and curing) rather than its materials design.

2.4 Sulfate attack

It has been theorized that CSAC is more resistant

to chemical sulfate attack than PC due to the absence of C_3A and the limited amount of CH in the hydrate phase assemblage (Winnefeld and Lothenbach, 2010; Aranda and de la Torre, 2013). The dominant hydration product in CSAC paste, ettringite, does not react with sulfate and, therefore, does not induce expansion. Thus, typical CSAC pastes exhibit excellent resistance to external sulfate attack (Quillin, 2001; Guo et al., 2014). When insufficient calcium sulfate is blended with CSA clinker, for example, for the purpose of promoting formation of monosulfoaluminate which binds chloride ions, the material may be susceptible to expansion and cracking due to the formation of ettringite following external sulfate attack (Jen et al., 2017). Sulfate ions may also diffuse and react with calcium ions, precipitating gypsum. Gypsum precipitation in such a manner, however, requires unhydrated $\text{ye}'\text{elite}$ and water to form an expansive product (Aranda and de la Torre, 2013). Even if unhydrated $\text{ye}'\text{elite}$ is available, water can be the limiting reactant in most cases due to the strong self-desiccation of CSAC concrete (Glasser and Zhang, 2001). When MgSO_4 is the sulfate source, it can even react with ettringite in an alkaline aqueous environment, leading to the formation of gypsum, alumina gel, and magnesium hydroxide, resulting in layer-by-layer spalling of CSAC concrete (Liu et al., 2016). Another rare form of sulfate deterioration of CSAC concrete may be induced by thaumasite formation at low temperatures. However, this is possible only if the material is exposed to carbonate ions (Rahman and Bassuoni, 2014). The potential of thaumasite formation in CSAC concrete has not been assessed. Although CSAC could be chemically more stable in a sulfate environment, its resistance to physical sulfate attack (e.g. recrystallization when subjected to wet-dry cycles in sulfate solutions) is not necessarily better than that of PC (Liu et al., 2014; Zhang et al., 2017). This is because resistance against physical sulfate attack is dictated by the pore structure rather than the chemical composition.

2.5 Alkali-silica reaction

There have been very few studies of the alkali-silica reaction (ASR) characteristics of CSAC concrete. However, most researchers agree that CSAC is less prone to ASR than PC (Zhang et al., 1999; Juenger et al., 2011). A recent accelerated ASR study

of mortar specimens containing reactive aggregates (Kleib et al., 2018) showed that expansion is seven times lower in CSAC than in PC. The observed high resistance of CSAC to ASR compared to PC is attributable to: (a) the lower alkalinity of the CSAC pore solution, and consequently a lower amount of hydroxyl ions available to attack the siliceous network to cause the dissolution of the aggregate (Lindgård et al., 2012); (b) the lower amount of $\text{Ca}(\text{OH})_2$ in CSAC leading to less Ca^{2+} being available in the pore solution to facilitate the precipitation of expansive ASR gels (Wang and Gillott, 1991); (c) the higher amount of aluminum in CSAC: at 28 d of hydration, the aluminum concentration in the pore solution of PC paste is about 0.133 mmol/L (le Saout et al., 2013) compared to 26 mmol/L for CSAC (Winnefeld and Lothenbach, 2010) which is two orders of magnitude higher. Several studies have shown that a high content of aluminous species in cement mitigates ASR in concrete. The aluminum ions are either absorbed onto the silica surface thereby limiting the dissolution of the amorphous silica of the aggregate (Chappex and Scrivener, 2012), or cause the formation of a C-A-S-H phase which improves the alkali binding capacity of the paste (Hong and Glasser, 2002). Although the above theoretical insights offer some explanation for the observed resistance of CSAC to ASR, further studies are needed to fully understand the mechanism of ASR mitigation in CSAC-based concretes.

2.6 Carbonation

Studies have found that carbonation of CSAC-based materials can lead to a decline in ettringite content and loss of compressive strength (Sherman et al., 1995). X-ray diffraction (XRD) and thermal gravimetric (TG) results showed that, following the breakdown of ettringite, the contents of calcium carbonate, gypsum, and aluminium hydroxide gel increase (Sherman et al., 1995; Mechling et al., 2014). Zhou and Glasser (2000) confirmed these results using synthetic ettringite subjected to a moist CO_2 -rich atmosphere. They also reported that under specific conditions hemihydrate could form, and subsequently recrystallize to form an alumina-ferric oxide-monosulfate phase. The overall impact of carbonation on a CSAC system depends on various factors including the w/c (Beretka et al., 1996; Zhang

et al., 2009; Mechling et al., 2014), type (i.e. gypsum, hemihydrate, or anhydrite) and amount of CaSO_4 blended in the cement (Brien et al., 2013; Hargis et al., 2017), type and amount of SCMs (Zhang et al., 2009; Ioannou et al., 2014, 2015), and the exposure condition (i.e. atmospheric or elevated concentration) (Quillin, 2001). There is a lack of consensus among researchers regarding the rate of carbonation. Some reported that CSAC-based materials tend to carbonate much faster than their PC counterpart with similar 28-d strength and equivalent cement content, or identical w/c (Quillin, 2001; Ioannou et al., 2015; Moffatt, 2016; Hargis et al., 2017; Carsana et al., 2018; Moffatt and Thomas, 2018). Conversely, some researchers found that CSAC and PC have a similar rate of carbonation (Glasser and Zhang, 2001; Zhang and Glasser, 2005; Guo et al., 2014). A few studies found that, in terms of resistance against carbonation, CSAC can perform better than PC (with unspecified composition but similar 28-d strength) (Duan et al., 2013; Geng et al., 2014). Table 1 summarizes these inconsistent findings. The contradictions in past studies reveal the knowledge-gaps that still exist in the context of the carbonation of CSAC systems. Further studies are thus needed to reveal: (a) the effects of carbonation on CSAC phases other than ettringite; (b) the effect of carbonation on the microstructure and physical properties of CSAC-based materials; (c) the roles of SCMs and other additives in enhancing the carbonation resistance of CSAC.

2.7 Steel corrosion

It is well-known that steel reinforcement in concrete can be corroded when exposed to moisture and oxygen, which can be facilitated by a low pH of the pore solution induced by carbonation and/or the presence of chloride ions. Similar to PC, CSAC is able to establish a high enough pore solution pH to passivate steel reinforcement (Andac and Glasser, 1999; Winnefeld and Lothenbach, 2010). However, a considerable amount of chloride ions (derived from fuel and raw materials) may be present in CSAC's pore solution (Andac and Glasser, 1999), which may amplify the risk of steel corrosion. Furthermore, improperly proportioned CSAC may have a high carbonation rate (Ioannou et al., 2015; Hargis et al., 2017) and chloride diffusion coefficient (Kalogridis et al., 2000; Quillin, 2001). These factors could

Table 1 Comparison of the carbonation resistance of CSAC- and PC-based concrete

CSAC composition	Experimental condition	Result	Reference
$\text{C}_4\text{A}_3\text{S}:\text{C}_5\text{S}_2\text{S}:\text{C}=1:1:0.5$, synthesized from calcination of three different mixtures of fly ash (FA), blast furnace slag (BS), and clay (CL)	Mortar specimens: 25-mm cubes, using $w/s=0.5$ for composition FA, and $w/s=0.4$ for compositions BS and CL. Specimens were demolded after 4 h, cured at 23 °C and 100% relative humidity (RH) for 28 d; then placed in a constant temperature room (21 °C, 67% RH) for 6 months to 1 year for atmospheric carbonation. For accelerated carbonation, only the FA samples with $w/s=0.4$ were used, placed in a carbonation chamber (4% CO_2) for 1, 2, 7 or 28 d after curing, and tested for compressive strength and density. XRD was employed for characterization	Atmospheric carbonation: strength decreased after 180 d and 365 d carbonation; retained after 365 d. XRD indicated that specimens were further carbonated slightly after 365 d; Accelerated carbonation: specimens were carbonated gradually with time; after 28 d, most ettringite was carbonated (from 47.9% to 18.5%), and 67% of strength was retained. Density was not changed	Sherman et al., 1995
Two types of commercial rapid hardening cements, i.e. calcium sulfoaluminate cement (CSAC) and calcium ferroaluminate cement (CFAC)	Concrete specimens, two replicates of 200 mm×75 mm×75 mm prisms ($w/c=0.563$), cured for 24 h, stored in water at 20 °C for 2 d, placed indoors (at 20 °C and 65% RH) and in sheltered and unsheltered locations outdoors. Samples for accelerated carbonation test were stored in nitrogen cabinet for up to 28 d before exposure to a CO_2 enriched atmosphere with 4.3% CO_2 , at 20 °C and 65% RH. Carbonation depths were determined using phenolphthalein indicator. PC samples of the same mix design were prepared for comparing the accelerated carbonation	Carbonation rate: $\text{PC} < \text{CFAC} < \text{CSAC}$. CSAC concrete tends to carbonate more rapidly than CFAC and PC concretes under accelerated conditions, the carbonation depth for PC samples is less than 3 mm and is more than 25 mm at 60 d. After 180 d, the outer layer of the indoors (non-accelerated) CSAC samples contained significantly more calcite than did the uncarbonated center	Quillin, 2001
CSAC: 40% C_2S , 27% $\text{C}_4\text{A}_3\text{S}$, 11% C_5S , 3% C_3A , 3% C_4AF , 3% $\text{CSH}_{0.5}$, 2% C_3A , and 2% calcite	Concrete specimens: 300 mm diameter×100 mm cylinders, $w/c=0.35$; cured by burlap and plastic at room temperature for 24 h, demolded, placed in a chamber at (22 ± 2) °C, 4% CO_2 , 100% RH for 14 d. 75 mm×75 mm×280 mm prisms were cast, placed in a standard atmospheric carbonation chamber ((22 ± 2) °C, 65% RH, 0.04% CO_2) for testing carbonation under non-accelerated conditions. PC specimens with $w/c=0.4$ were prepared for comparison	The compressive strength of CSAC specimens was higher than that of PC ones. CSAC specimens under accelerated carbonation showed a 15%, 50%, and 66% decrease in compressive, flexural, and tensile strength, respectively. Porosity increased after carbonation. The carbonation rate of the CSAC system was much faster than that of the PC system	Moffat, 2016
A European commercial binary CSAC with 54.9% $\text{C}_4\text{A}_3\text{S}$, 20.9% CaSO_4 , 16.6% C_2S , and 4.7% C_4AF	Mortar specimens: three sets of CSAC mortar prisms (40 mm×40 mm×160 mm) with $w/c=0.45$, 0.58, and 0.78; the mortar of $w/c=0.45$ was made when the components were cooled at 10 °C; cured under 20 °C and 95% RH, demolded after 4 h; stored in water at 20 °C for 27–28 d, then placed in a carbonation room at 20 °C and 65% RH. PC samples with $w/c=0.5$ were prepared for comparison	Compressive strength: 0.78 mortar (lost 36% after 7 d) < 0.58 mortar (quasi constant) < 0.45 mortar (increasing). Carbonation depth at 7 d: 0.78 > 0.58 > 0.45 > PC. All CSAC samples showed lower volume stability in a carbon saturated environment, which rose with the rise of w/c . The carbonation kinetics of CSAC was faster than that of PC	Mechling et al., 2014
55% CSAC, 30% CaSO_4 , and 15% FA (GAF15)	Concrete specimens: $w/c=0.35$, 0.50, and 0.65, 300 mm×75 mm×75 mm prisms; initially conditioned for 14 d, then water cured at 20 °C for 28 d. Carbonation chamber was set to 20 °C, 65% RH, and the concentration of CO_2 was 4%. PC samples with $w/c=0.5$ were prepared for comparison	The resistance to carbonation reduced with the increase of w/c for both GAF15 and PC specimens. The strength loss and carbonation depth of GAF15 were higher than those of PC	Ioannou et al., 2015

To be continued

Table 1

CSAC composition	Experimental condition	Result	Reference
A commercial CSAC produced in Italy, with 78% CSA clinker (52% $\text{C}_4\text{A}_3\text{S}$, 20% C_2S , and minor phases) and 22% anhydrate	Concrete specimens: 100 mm-cubes, $w/c=0.55$; CSAC was used individually or mixed with PC and Portland-limestone cement. Specimens were cured for 7 d, then exposed under accelerated (4%) and atmosphere carbonation (0.04%) environments at RH=65%. In another case, specimens cured for 28 d were exposed for 70 d in an accelerated carbonation environment	CSAC specimens showed slightly higher carbonation depth both in accelerated and natural environments	Carsana et al., 2018
A commercial CSAC produced in China (normal strength); and an iron-rich CSAC (high strength)	Concrete specimens were acquired from service. Normal strength samples: mixed in the cold winter of 1982 with hot mix water, w/c was 0.55–0.60, 1% NaNO_2 added; sample core drilled in 1997, the core was stored until 2001. High strength samples: $w/c=0.30$, centrifuge cast in 1993, kept outdoors until 1998. XRD, SEM, and infrared spectroscopy were used for characterization	The carbonation depth of CSAC concrete made at high w/c ratio was comparable to that of a PC concrete of equivalent quality. There was still ettringite near the surface area after 16-year exposure. Resistance to carbonation was improved by decreasing w/c	Zhang and Glasser, 2005
CSAC obtained from municipal solid waste incineration (MSWI: 29.71% CaCO_3 , 14.23% CaSO_4 , 24.92% Al_2O_3 – $\text{C}_4\text{A}_3\text{S}+\text{C}_2\text{S}$, added with 5% of CaSO_4 ; two sets of commercial CSAC rapid hardening cement: Cem I (CSAC), Cem II (PC)	Mortar specimens, 40 mm×40 mm×160 mm, $w/c/s=0.5/1.0/3.0$, mix and cured for 28 d; then heated under 60 °C for 48 h; two opposite surfaces were exposed to the carbonation chamber for testing, while the other surfaces were sealed with paraffin (MHURD, 2009)	Initial carbonation depths of two sets of CSAC samples were lower than those of Cem II (PC) samples, and the growth rates were higher. The resistance of carbonation of Cem I samples was better than that of MSWI and Cem II samples at 28 d of carbonation	Guo et al., 2014
Mineral composition of CSAC was not provided. Oxide composition: CaO : 45.25%; Al_2O_3 : 28.93%; SO_3 : 11.88%; SiO_2 : 7.96%; Fe_2O_3 : 3.71%; and minors	Concrete specimens: 100 mm×100 mm×400 mm; water:cement:fly ash:sand:gravel: superplasticizer=205:250:250:714:986:2.5 ($w/b=0.41$). Preconditioning: curing under 90% RH and (20±3) °C for 26 d, followed by drying at 60 °C for 48 h. Carbonation: CO_2 concentration=(20±3)%, under (70±5)% RH and (20±3) °C, for 14–56 d. PC concrete specimens with the same mix proportion (with comparable and slightly higher strength at 28 d and 84 d, respectively) were prepared for comparison	Carbonation depth of CSAC concrete was distinctly smaller than that of PC concrete; layered double hydroxides could capture CO_2 thus improving the carbonation resistance of concrete	Duan et al., 2013

significantly affect the ability of CSAC to maintain the passivation of steel. Moffatt and Thomas (2018) compared the steel corrosion resistance of a high-belite CSAC with that of PC. Although the CSAC concrete had a lower w/c (0.35 vs 0.40) and higher cement content (530 kg/m³ vs 450 kg/m³), and achieved higher 28-d compressive strength (67 MPa vs 56 MPa), it performed worse than PC concrete in protecting steel from corrosion. This deficiency was tied to the transport properties of the CSAC concrete, represented by faster carbonation and chloride penetration. In contrast, Carsana et al. (2018) investigated a CSAC concrete and a PC concrete with identical

mixture proportions ($w/c=0.55$, cement content is 327 kg/m³), and found that CSAC provided better steel protectiveness than PC even after carbonation. In their work, the CSAC concrete carbonated faster, but its 28-d strength (75 MPa vs 64 MPa) and electrical resistivity (under both sealed and water-saturated conditions) were higher than those of the reference PC concrete. Furthermore, investigation of 14-year old field concrete has shown that CSAC can protect steel reinforcement quite well, even when it is located in a severe service environment (such as a seawater intertidal zone) and even though its carbonation is not slower than that of PC concrete (Glasser

and Zhang, 2001). The excellent steel corrosion resistance of CSAC concrete was attributed to its strong self-desiccation enabled by the rapid hydration of CSAC, which leads to fast consumption of water and establishment of a dry internal micro-environment, which is very difficult to re-saturate. Results from previous studies relevant to the steel corrosion resistance of CSAC concrete are summarized in Table 2. Results from the various studies appear to be contradictory. These contradictions imply that further studies in this field are needed: (a) to reveal the mechanisms (physical, chemical, and/or electrochemical) of steel corrosion, and its mitigation,

in CSAC concrete; (b) to elucidate the effects of the chemical composition of CSAC and mixture design of CSAC concrete so as to maximize the steel protectiveness of CSAC.

3 Summary and future research

Due to its intrinsic characteristics, CSAC concrete has been shown to perform better than its PC counterpart in several aspects, including rapid early-age strength development, low shrinkage and cracking potential, and resistance to freeze-thaw damage,

Table 2 STL test conditions for the aluminium and the aluminium honeycomb panel

CSAC composition	Experimental condition	Result	Reference
CSA(1)-C ₂ S: 27% C ₄ A ₃ S, 40% C ₂ S, 11% C ₃ S, 3% C ₃ H _{0.5} ; CSA(2)-PC: 30% CSA (37% C ₄ A ₃ S, 6% C ₂ S, 22% C ₃ S, 3% C ₃ H _{0.5}) +70% PC	Reinforced concrete specimens: $w/c=0.35$, cement content 530 kg/m ³ ; 280 mm×115 mm×150 mm prisms consisting of two layers of black steel. Preconditioning: cured at 100% RH for 14 d, followed by exposure to lab air for 14 d; a plastic dam was placed on the top and all other surfaces were coated with a two-part waterproof epoxy. Accelerated corrosion (ASTM, 2013): The dammed area was subjected to repeated 4-week cycles consisting of 2-week ponding in 30 g/L NaCl solution and 2-week drying. PC concrete ($w/c=0.4$, cement content 450 kg/m ³) was prepared as reference; the 28 d compressive strengths of the CSA(1)-C ₂ S, CSA(2)-PC, and PC concretes were 67, 56, and 56 MPa, respectively	The CSA(1)-C ₂ S system started to show severe corrosion after 2 cycles, and stabilized after 4 cycles. The other systems showed low or intermediate corrosion after 30 cycles. Linear polarization resistance data matched the corrosion. The CSA(1)-C ₂ S system half-cell potential was >5 times more negative than that of the other two systems, while the corrosion current density was 3 times higher	Moffatt and Thomas, 2018
CSA(1)-C ₂ S: 27% C ₄ A ₃ S, 40% C ₂ S, 11% C ₃ S, 3% C ₃ H _{0.5} ; CSA(2)-PC: 30% CSA (37% C ₄ A ₃ S, 6% C ₂ S, 22% C ₃ S, 3% C ₃ H _{0.5}) +70% PC	Reinforced concrete specimens: $w/c=0.55$, cement content 327 kg/m ³ , 150 mm×150 mm×530 mm prisms with two rebars (11.3 mm diameter)—a standard carbon steel bar placed 50 mm below the top surface and a 316 stainless bar above the bottom surface. Preconditioning: cured in wet burlap for 24 h, then demolded and placed under wet burlap for 28 d. Exposure: marine environment at the high tide level. Evaluations: linear polarization with three-electrode cell; cored specimens for slice-by-slice (1 mm) chloride content analysis. PC concrete ($w/c=0.4$, cement content 450 kg/m ³) was prepared as reference	After 3 years, the CSA(1)-C ₂ S system had the lowest surface chloride concentration of 0.18%, but the highest chloride concentration of 0.11% at the position of the rebar (threshold=0.05%). The other systems showed far greater surface concentrations (0.5%–0.7%), but the threshold concentration penetrated only 20–30 mm. The steel was corroded more severely in the CSA(1)-C ₂ S system	Moffatt and Thomas, 2018
A commercial CSAC produced in Italy, with 78% CSA clinker (52% C ₄ A ₃ S, 20% C ₂ S, and minor phases) and 22% anhydrate	Reinforced concrete specimens: $w/c=0.35$, cement content 530 kg/m, 70 mm diameter×110 mm cylinders with ribbed steel bar (16 mm diameter, sand blasted). Preconditioning: moist cured for 7 d. Exposure conditions: cycles at 20 °C or 40 °C, 80% or 95% RH, and 48 h water immersion; a series of specimens were put in the cycles after accelerated carbonation (4% CO ₂ , 65% RH). PC and limestone PC concrete specimens were prepared with the same mix proportions	The steel was initially passive in the CSAC concrete; CSAC tended to have a higher carbonation rate than the references, but a lower corrosion rate than limestone PC concrete (higher than PC concrete). Blending PC into CSAC can help improve its resistance to carbonation and corrosion	Carsana et al., 2018
A commercial CSAC from China	Centrifuge cast fine aggregate steel reinforced concrete ($w/c\approx0.25$) pipe made in 1978, put in service (tidal zone, twice daily immersion by sea water) for 14 years. No comparison with PC	The steel mesh from the section close to low tide with a 7–8 mm concrete cover was uncorroded after 14 years	Zhang and Glasser, 2005

sulfate attack, and alkali-silica reaction. However, mixed findings have been reported in some areas. For example, CSAC is more prone to carbonation and chloride ingress than PC, and both processes are expected to lower the pore solution pH and facilitate the corrosion of steel rebar. However, some researchers have reported the protection of steel rebar by CSAC and attributed it to the effects of self-desiccation of the CSAC paste. Owing to the small number of studies available, especially on the long-term durability of CSAC, the role of the transport properties and the chemistry of CSAC with respect to the protection of steel rebar in CSAC concrete is not fully understood. In summary, more studies on the durability of CSAC concrete, including both lab-based studies and field exposure tests, are needed to clarify the long-term performance of this material in various service environments. Emphasis should be given to a comprehensive examination of CSAC's resistance against carbonation and steel rebar corrosion because of the susceptibility of ettringite to carbonation and the relatively low pH of CSAC concrete (Fig. 1). The mechanisms underlying deterioration need to be understood so they can be mitigated to improve the performance of CSAC concrete.

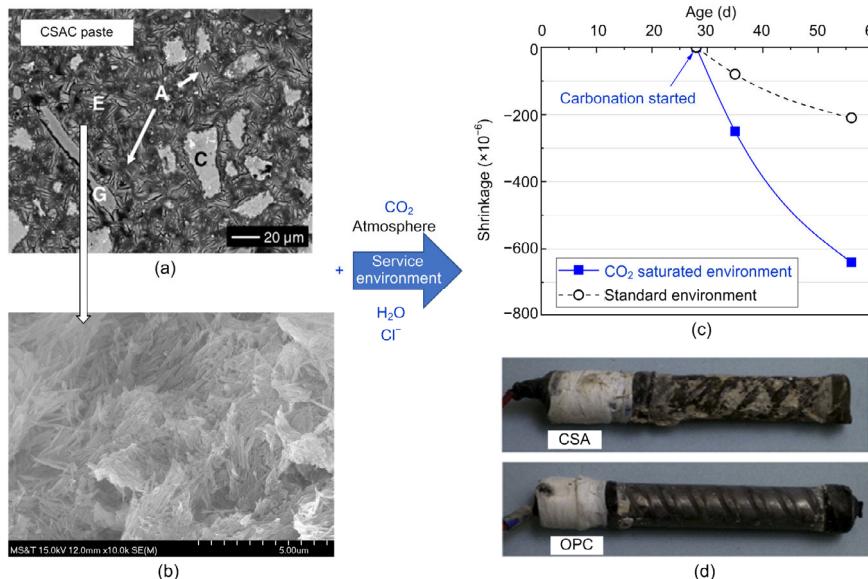


Fig. 1 Carbonation and steel corrosion in CSAC concrete

(a) SEM image of CSA paste hydrated for 16 h (C=CSA clinker, G=gypsum, E=ettringite, A=aluminum hydroxide). Reprinted from (Winnefeld and Lothenbach, 2010), Copyright 2010, with permission from Elsevier; (b) SEM image of ettringite; (c) Dimensional stability of CSAC mortar over time (after a 28-d curing period) in the standardized environment and in a carbon dioxide saturated environment, $w/c=0.78$, plotted using data in (Mechling et al., 2014); (d) Examples of steel bars extracted from CSAC and PC concrete specimens after 1 year exposure, showing different extents of corrosion. Reprinted from (Carsana et al., 2018), Copyright 2018, with permission from Elsevier

Contributors

Bowen TAN: data collection and writing the original draft; Monday U. OKORONKWO: methodology and writing the original draft; Aditya KUMAR: conceptualization, reviewing and editing; Hongyan MA: conceptualization, supervision, reviewing, and editing.

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Conflict of interest

Bowen TAN, Monday U. OKORONKWO, Aditya KUMAR, and Hongyan MA declare that they have no conflict of interest.

References

- Andac M, Glasser FP, 1999. Pore solution composition of calcium sulfoaluminate cement. *Advances in Cement Research*, 11(1):23-26.
<https://doi.org/10.1680/adcr.1999.11.1.23>
- Aranda MAG, de la Torre AG, 2013. Sulfoaluminate cement. In: Pacheco-Torgal F, Jalali S, Labrincha L, et al. (Eds.), *Eco-efficient Concrete: a Volume in Woodhead Publishing Series in Civil and Structural Engineering*. Woodhead Publishing, Oxford, UK, p.488-522.

- https://doi.org/10.1533/9780857098993.4.488
- ASTM (American Society for Testing Material), 2013. Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments, ASTM G109-07. ASTM, USA.
- Beretka J, Marroccoli M, Sherman N, et al., 1996. The influence of C_4A_3S content and WS ratio on the performance of calcium sulfoaluminate-based cements. *Cement and Concrete Research*, 26(11):1673-1681.
https://doi.org/10.1016/S0008-8846(96)00164-0
- Brien JV, Henke KR, Mahboub KC, 2013. Observations of peak strength behavior in CSA cement mortar. *Journal of Green Building*, 8(3):97-115.
https://doi.org/10.3992/jgb.8.3.97
- Carsana M, Canonico F, Bertolini L, 2018. Corrosion resistance of steel embedded in sulfoaluminate-based binders. *Cement and Concrete Composites*, 88:211-219.
https://doi.org/10.1016/j.cemconcomp.2018.01.014
- Chappex T, Scrivener KL, 2012. The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction. *Cement and Concrete Research*, 42(12):1645-1649.
https://doi.org/10.1016/j.cemconres.2012.09.009
- Chen IA, Hargis CW, Juenger MCG, 2012. Understanding expansion in calcium sulfoaluminate-belite cements. *Cement and Concrete Research*, 42(1):51-60.
https://doi.org/10.1016/j.cemconres.2011.07.010
- Damtoft JS, Lukasik J, Herfort D, et al., 2008. Sustainable development and climate change initiatives. *Cement and Concrete Research*, 38(2):115-127.
https://doi.org/10.1016/j.cemconres.2007.09.008
- de Bruyn K, Bescher E, Ramseyer C, et al., 2017. Pore structure of calcium sulfoaluminate paste and durability of concrete in freeze-thaw environment. *International Journal of Concrete Structures and Materials*, 11(1): 59-68.
https://doi.org/10.1007/s40069-016-0174-3
- Duan P, Chen W, Ma JT, et al., 2013. Influence of layered double hydroxides on microstructure and carbonation resistance of sulfoaluminate cement concrete. *Construction and Building Materials*, 48:601-609.
https://doi.org/10.1016/j.conbuildmat.2013.07.049
- Environment UN, Scrivener KL, John JM, et al., 2018. Eco-efficient cements: potential economically viable solutions for a low- CO_2 cement-based materials industry. *Cement and Concrete Research*, 114:2-26.
https://doi.org/10.1016/j.cemconres.2018.03.015
- Gagg CR, 2014. Cement and concrete as an engineering material: an historic appraisal and case study analysis. *Engineering Failure Analysis*, 40:114-140.
https://doi.org/10.1016/j.engfailanal.2014.02.004
- Gartner E, 2014. Industrially interesting approaches to “low- CO_2 ” cements. *Cement and Concrete Research*, 34(9):1489-1498.
https://doi.org/10.1016/j.cemconres.2004.01.021
- Geng HN, Duan P, Chen W, et al., 2014. Carbonation of sulfoaluminate cement with layered double hydroxides. *Journal of Wuhan University of Technology (Materials Science Edition)*, 29(1):97-101.
https://doi.org/10.1007/s11595-014-0874-y
- Glasser FP, Zhang L, 2001. High-performance cement matrices based on calcium sulfoaluminate-belite compositions. *Cement and Concrete Research*, 31(12):1881-1886.
https://doi.org/10.1016/S0008-8846(01)00649-4
- Guo XL, Shi HS, Hu WP, et al., 2014. Durability and microstructure of CSA cement-based materials from MSWI fly ash. *Cement and Concrete Composites*, 46:26-31.
https://doi.org/10.1016/j.cemconcomp.2013.10.015
- Hargis CW, Lothenbach B, Müller CJ, et al., 2017. Carbonation of calcium sulfoaluminate mortars. *Cement and Concrete Composites*, 80:123-134.
https://doi.org/10.1016/j.cemconcomp.2017.03.003
- Hong SY, Glasser FP, 2002. Alkali sorption by C-S-H and C-A-S-H gels: part II. Role of alumina. *Cement and Concrete Research*, 32(7):1101-1111.
https://doi.org/10.1016/S0008-8846(02)00753-6
- Ioannou S, Reig L, Paine K, et al., 2014. Properties of a ternary calcium sulfoaluminate-calcium sulfate-fly ash cement. *Cement and Concrete Research*, 56:75-83.
https://doi.org/10.1016/j.cemconres.2013.09.015
- Ioannou S, Paine K, Reig L, et al., 2015. Performance characteristics of concrete based on a ternary calcium sulfoaluminate-anhydrite-fly ash cement. *Cement and Concrete Composites*, 55:196-204.
https://doi.org/10.1016/j.cemconcomp.2014.08.009
- Jen G, Stompinis N, Jones R, 2017. Chloride ingress in a belite-calcium sulfoaluminate cement matrix. *Cement and Concrete Research*, 98:130-135.
https://doi.org/10.1016/j.cemconres.2017.02.013
- Juenger MCG, Winnefeld F, Provis JL, et al., 2011. Advances in alternative cementitious binders. *Cement and Concrete Research*, 41(12):1232-1243.
https://doi.org/10.1016/j.cemconres.2010.11.012
- Kalogridis D, Kostoglouidis GC, Ftikos C, et al., 2000. A quantitative study of the influence of non-expansive sulfoaluminate cement on the corrosion of steel reinforcement. *Cement and Concrete Research*, 30(11):1731-1740.
https://doi.org/10.1016/S0008-8846(00)00277-5
- Kleib J, Aouad G, Louis G, et al., 2018. The use of calcium sulfoaluminate cement to mitigate the alkali silica reaction in mortars. *Construction and Building Materials*, 184: 295-303.
https://doi.org/10.1016/j.conbuildmat.2018.06.215
- le Saoût G, Lothenbach B, Hori A, et al., 2013. Hydration of Portland cement with additions of calcium sulfoaluminates. *Cement and Concrete Research*, 43:81-94.
https://doi.org/10.1016/j.cemconres.2012.10.011
- Li WT, Pour-Ghaz M, Castro J, et al., 2012. Water absorption and critical degree of saturation relating to freeze-thaw damage in concrete pavement joints. *Journal of Materials*

- in *Civil Engineering*, 24(3):299-307.
[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000383](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000383)
- Lindgård J, Andiç-Çakir Ö, Fernandes I, et al., 2012. Alkali-silica reactions (ASR): literature review on parameters influencing laboratory performance testing. *Cement and Concrete Research*, 42(2):223-243.
<https://doi.org/10.1016/j.cemconres.2011.10.004>
- Liu ZQ, Deng DH, de Schutter G, 2014. Does concrete suffer sulfate salt weathering? *Construction and Building Materials*, 66:692-701.
<https://doi.org/10.1016/j.conbuildmat.2014.06.011>
- Liu ZQ, Li XN, Deng DH, et al., 2016. The damage of calcium sulfoaluminate cement paste partially immersed in $MgSO_4$ solution. *Materials and Structures*, 49(1-2):719-727.
<https://doi.org/10.1617/s11527-015-0532-7>
- Mechling JM, Lecomte A, Roux A, et al., 2014. Sulfoaluminate cement behaviours in carbon dioxide, warm and moist environments. *Advances in Cement Research*, 26(1):52-61.
<https://doi.org/10.1680/adcr.12.00070>
- MHURD (Ministry of Housing and Urban-Rural Development of the People's Republic of China), 2009. Standard for Test Methods of Long-term Performance and Durability of Ordinary Concrete, GB/T50082. China Architecture & Building Press, Beijing, China (in Chinese).
- Moffatt EG, 2016. Durability of Rapid-set (Ettringite-based) Binders. PhD Thesis, University of New Brunswick, Canada.
- Moffatt EG, Thomas MDA, 2018. Durability of rapid-strength concrete produced with ettringite-based binders. *ACI Materials Journal*, 115:105-115.
- Paul G, Boccaleri E, Buzzi L, et al., 2015. Friedel's salt formation in sulfoaluminate cements: a combined XRD and ^{27}Al MAS NMR study. *Cement and Concrete Research*, 67:93-102.
<https://doi.org/10.1016/j.cemconres.2014.08.004>
- Quezada I, Thomas R, Maguire M, 2018. Internal curing to mitigate cracking in rapid set repair media. *Advances in Civil Engineering Materials*, 7(4):660-671.
<https://doi.org/10.1520/ACEM20170140>
- Quillin K, 2001. Performance of belite-sulfoaluminate cements. *Cement and Concrete Research*, 31(9):1341-1349.
[https://doi.org/10.1016/S0008-8846\(01\)00543-9](https://doi.org/10.1016/S0008-8846(01)00543-9)
- Rahman MM, Bassuoni MT, 2014. Thaumasite sulfate attack on concrete: mechanisms, influential factors and mitigation. *Construction and Building Materials*, 73:652-662.
<https://doi.org/10.1016/j.conbuildmat.2014.09.034>
- Sherman N, Beretka J, Santoro L, et al., 1995. Long-term behaviour of hydraulic binders based on calcium sulfoaluminate and calcium sulfosilicate. *Cement and Concrete Research*, 25(1):113-126.
[https://doi.org/10.1016/0008-8846\(94\)00119-J](https://doi.org/10.1016/0008-8846(94)00119-J)
- Sirtoli D, Wyrzykowski M, Riva P, et al., 2019. Shrinkage and creep of high-performance concrete based on calcium sulfoaluminate cement. *Cement and Concrete Compo-*
- sites*, 98:61-73.
<https://doi.org/10.1016/j.cemconcomp.2019.02.006>
- Wang H, Gillott JE, 1991. Mechanism of alkali-silica reaction and the significance of calcium hydroxide. *Cement and Concrete Research*, 21(4):647-654.
[https://doi.org/10.1016/0008-8846\(91\)90115-X](https://doi.org/10.1016/0008-8846(91)90115-X)
- Winnefeld F, Lothenbach B, 2010. Hydration of calcium sulfoaluminate cements-experimental findings and thermodynamic modelling. *Cement and Concrete Research*, 40(8):1239-1247.
<https://doi.org/10.1016/j.cemconres.2009.08.014>
- Zhang DC, Xu DY, Cheng X, et al., 2009. Carbonation resistance of sulfoaluminate cement-based high performance concrete. *Journal of Wuhan University of Technology (Materials Science Edition)*, 24(4):663-666.
<https://doi.org/10.1007/s11595-009-4663-y>
- Zhang L, Glasser FP, 2005. Investigation of the microstructure and carbonation of CSA-based concretes removed from service. *Cement and Concrete Research*, 35(12):2252-2260.
<https://doi.org/10.1016/j.cemconres.2004.08.007>
- Zhang L, Su MZ, Wang YM, 1999. Development of the use of sulfo- and ferroaluminate cements in China. *Advances in Cement Research*, 11(1):15-21.
<https://doi.org/10.1680/adcr.1999.11.1.15>
- Zhang WM, Gong S, Kang B, 2017. Surface corrosion and microstructure degradation of calcium sulfoaluminate cement subjected to wet-dry cycles in sulfate solution. *Advances in Materials Science and Engineering*, 2017:1464619.
<https://doi.org/10.1155/2017/1464619>
- Zhao J, Cai GC, Gao DY, et al., 2014. Influences of freeze-thaw cycle and curing time on chloride ion penetration resistance of sulfoaluminate cement concrete. *Construction and Building Materials*, 53:305-311.
<https://doi.org/10.1016/j.conbuildmat.2013.11.110>
- Zhou Q, Glasser FP, 2000. Kinetics and mechanism of the carbonation of ettringite. *Advances in Cement Research*, 12(3):131-136.
<https://doi.org/10.1680/adcr.2000.12.3.131>

中文摘要

题 目：硫铝酸钙水泥混凝土的耐久性问题

概 要：由于组分特征的不同，硫铝酸钙水泥混凝土在一些方面天然优于硅酸盐水泥，如收缩和收缩裂缝控制及对冻融破坏、碱骨料反应和硫酸盐侵蚀的抵抗作用。然而，学界在硫铝酸盐水泥混凝土的传输性能、抗碳化性能及钢筋腐蚀防护性能等方面尚未达成一致意见。这些分歧皆归因于硫铝酸钙水泥化学组分及服役环境条件的变异性。一些研究发现，有的硫铝酸钙水泥混凝土虽然抵抗碳化和氯离子侵蚀的能力不如硅酸盐混凝土，但强

烈的内部自干燥使其可以在海洋潮汐环境中很好地保护混凝土结构中的钢筋。

关键词：硫铝酸钙水泥；耐久性；碳化；氯离子；钢筋锈蚀

Introducing new Editorial Board Member:



Dr. Hongyan MA is an assistant professor of Civil Engineering in Missouri University of Science and Technology (Missouri S&T), USA. He received his PhD in Civil Engineering from the Hong Kong University of Science and Technology (HKUST), China in 2013, Master of Engineering

in Structural Engineering from Shenzhen University, China in 2008, Bachelor of Engineering in Inorganic Non-metallic Materials Engineering and Bachelor in Law from Chongqing University, China in 2005. Before joining Missouri S&T in October 2015, he worked as a Post-doctoral Fellow in HKUST for two and a half years. Dr. MA's current research interests include next-generation cements, functional materials, biotechnology in construction, smart systems for testing and evaluation, hydration kinetics of cementitious materials, multi-scale characterization and modeling of concrete properties, and concrete deterioration and damage mitigation. Dr. MA has published over 80 refereed papers. These publications have received over 2000 citations, with an *h*-index of 26. He is an editorial board member of three journals, and an active reviewer for 40 prestigious journals. Dr. MA is also an active member of American Concrete Institute (ACI) and American Society of Civil Engineers (ASCE). He is a member of ACI Committees 122, 236, 242, and 546E, and an ASCE ExCEEd Fellow. Since joining Missouri S&T, Dr. MA has received the Joseph H. Senne Jr. Academy of Civil Engineers Scholarly Achievement Award, 2019 College of Engineering and Computing Dean's Scholar, and 2019 Faculty Research Award of Missouri S&T.