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Belitic calcium sulphoaluminate (BCSA) cements and the current durability standards: What are we testing?

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ABSTRACT

The service life of concrete is often estimated using parameters attained from durability tests, as corrosion in concrete under natural exposure typically takes several decades. Standardised tests, such as several of those outlined in EN 12390, are performed on specimens after 28 days of curing using conditions designed to accelerate natural effects. These tests were originally created for Portland cements (PCs), which at 28 days will have their major phases mostly hydrated, and thus have a durability representative of their lifespan. However, these tests can underestimate the potential of binder systems that chemically evolve beyond 28 days, such as belitic calcium sulphoaluminate (BCSA) cements, which are often reported to underperform under these procedures. BCSAs at 28 days curing would only fully consider the hydration of ye’elimite, which reacts rapidly, whereas belite typically starts to react much later. The hydration products of belite can contribute to the further filling of pores, lowering the porosity in the binder matrix and improving durability. Therefore, this study aims to review (i) the hydration of binders across time, specifically BCSA cements, (ii) reported durability results at these times, and (iii) assess how representative any results are of a hydrated binder. Furthermore, we aim to recommend alterations to testing that result in more representative data, such as incorporating ‘equivalent hydration’ into testing regimes.

KEYWORDS: *Belitic calcium sulphoaluminate cement, durability testing, standards, testing methods*

Introduction

Calcium sulphoaluminate (CSA) cements have ye’elimite ($C_4A_3\bar{S}$) as the primary reacting phase, alongside other phases such as belite (C_2S), ferrite (C_4AF) and gypsum ($C\bar{S}H_2$). High belite CSA binders, known as BCSA, do not have a fixed composition, but generally have 50-60% belite and 20-30% ye’elimite (Bescher et al., 2019), where the major variable is ferrite and gypsum content. Due to inconsistencies across literature, the following terminology will be used: US BCSA cement as ‘BCSA(US)’; series 3 cement as ‘BCSA(F)’; and lower belite CSA systems as ‘(B)CSA’. The main hydration products of BCSAs are ettringite ($C_6A\bar{S}_3H_{32}$, AFt), monosulphate ($C_4A\bar{S}H_{12}$, AFm), amorphous aluminium hydroxide (AH_3), and strätlingite (C_2ASH_8). BCSA cements will set rapidly and achieve greater early strengths than PCs, where the AFt formation from ye’elimite hydration produces expansive stresses that can help prevent shrinkage through equivalent expansion, resulting in a ‘volumetrically neutral’ cement. BCSAs also act as a low-CO₂ binder, with reductions in the required clinkering temperature and the binder releasing less CO₂ during hydration. A major obstacle within the current implementation of BCSA cements into the UK and Europe is the perceived subpar performance under durability tests, such as EN 12390-10,11. However, these tests are often conducted under accelerated environments to obtain results in a reasonable time. These standards were created based upon the hydration factor of PCs, which achieve a high level of hydration at 28 days. Slower hydrating phases, such as belite or fly-ash, will therefore have insufficient time to hydrate properly when the tests are conducted. As corrosion initiation can take decades, using accelerated tests on binders that would have otherwise achieved close to complete hydration can lead to unrealistic results.

Binder phases and their hydration products

Alite (C_3S) is the major component of many traditional cements. C_3S is reactive at early ages; findings by Cuesta et al., (2021) show an alite paste at 28 days to reach 80% reaction. Aluminate (C_3A) will rapidly produce ettringite; often responsible for ‘flash-setting’ in concretes and fully hydrating within 28 days. Belite is typically used in small quantities for long term strength, as C_2S only starts to show significant hydration at ~3 months (Bescher et al., 2019). At 28 days only ~20% of the belite phase will have hydrated but at 3 months curing this will be ~48% (Cuberos et al., 2010). Within aluminium rich environments, belite

will preferentially react to form strätlingite (Table.1), yet in environments depleted in AH_3 there will be preferential production of C-S-H and portlandite. For Ye’elimite, XRD analysis of a BCSA(US) determined hydration to be almost complete after 10 hours of setting (Bescher et al., 2019). SEM analysis by Song et al., (2015) suggests the initial reaction of ye’elimite immediately after adding water produces AFt, AFm, AH_3 and hydrogarnet, with small globules of hydrogarnet surrounded by AH_3 (Table.1). After this, the ye’elimite is expected to either produce AFt or AFm, depending on the gypsum content. Ferrite tested in a BCSA(F) by Glasser and Zhang, (2001) was revealed to be mostly inert even after 10 years, with a very slow reaction with water. A typical PC has the major components of ~50-65% wt.% alite, ~10-25 wt.% belite, ~5-10% aluminate, and ~5-10% ferrite, with varying amounts of gypsum, meaning that Portland cements will often have reached ~70-80+% of total feasible hydration, if ferrite is considered inert. For BCSA(US), as the gypsum will have mostly hydrated with the ye’elimite, it is expected that at 28 days curing the binder will have a total hydration degree of ~47-57%. At 3 months of curing, the hydration would account for almost 75% of a BCSA(US), which bridges the gap between PC.

Table.1 The most common hydration reactions of each of the major phases mentioned within this study.

Phase	Typical Hydration Equations	Reference
Alite	$C_3S + 5.3H \rightarrow C-S-H + 1.3CH$	Bishnoi and Scrivener, 2009
Aluminate	$C_3A + 3\bar{C}\bar{S}H_2 + 32H \rightarrow C_6\bar{A}\bar{S}H_{32}$	Zheng et al., 2021
Belite	$C_2S + AH_3 + 5H \rightarrow C_2ASH_8$	Cuberos et al., 2010
	$C_2S + 43H \rightarrow C-S-H + 0.3CH$	Cuberos et al., 2010
Ye’elimite	$4C_4A_3\bar{S} + 80H \rightarrow C_6\bar{A}\bar{S}H_{32} + C_4\bar{A}\bar{S}H_{12} + 2C_3AH_6 + 8AH_3$	Song et al., 2015
	$C_4A_3\bar{S} + 2\bar{C}\bar{S}H_2 + 34H \rightarrow C_6\bar{A}\bar{S}_3H_{32} + 2AH_3$	Cuberos et al., 2010
	$C_4A_3\bar{S} + 18H \rightarrow C_4\bar{A}\bar{S}H_{12} + 2AH_3$	Song et al., 2015
Ferrite	$C_4AF + 16H \rightarrow 2C_2(A_{0.5}F_{0.5})H_8$	Cuberos et al., 2010

Durability of different binder systems

Alongside carbonation and Cl ingress tests, service life of a concrete can be estimated from deterioration depth and dissolved calcium content from acid attack. The microstructurally changed zone (i.e. where the concrete has been damage by acid attack) mostly matches with the maximum chloride content, meaning where porosity has been increased the concrete is most vulnerable to further degradation (Fjendbo et al., 2022). The stabilities of the different hydration phases across pH can be seen in Table.2.

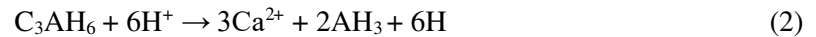
Table.2 adapted from Damion and Chaunsali, (2022), showing the lowest pH before destabilisation.

Phase	pH stability	Reference
Portlandite	12.4 – 12.6	De Windt and Badreddine, 2007
Monosulphate	11.6	Gabrisová et al., 1991
Ettringite	11	McCarthy et al., 1992
Hydrogarnet	10	Gabrisová et al., 1991
C-S-H	8.8	Baston et al., 2012
Calcite	4.5 – 6	Khaitan et al., 2009
AH_3	3 – 4	Allahverdi and Škvára, 2000
Ferric phases	1.5 - 2	Allahverdi and Škvára, 2000

Within PCs, portlandite will act to preserve other hydration products, although once fully dissolved the C-S-H phases will begin decalcification. As C-S-H gel is the major pore-filling component in most cements, any complete decalcification will lead to large increases in the porosity. Portlandite is a well-known buffer of acids, achieved through the raising the pH of systems. A study by Afroughsabet et al., (2021) recorded a pH for PC as 13, while CSA was only 9-10. This buffering ability can be seen in Eq.1, where CH will dissolve to neutralise two ions of H^+ . This does however mean that CH is exceptionally vulnerable to acid attack with an open system or low enough pH, leading to rapid dissolution and increases in porosity, and then to further attack within the binder (Damion and Chaunsali, 2022; Scrivener et al., 1999).



When hydrogarnet dissolves (Eq.2) it can reprecipitate as AH_3 , which is stable to significantly lower pH values of 3-4 (Table 2). This reprecipitation means infill of AH_3 in outer layers, reducing pore space in the degraded sections of the cement, and reducing the effects of further ingress (Scrivener et al., 1999). The produced AH_3 can also act to further buffer a solution (Eq.3) leading to reasoning that these hydrates in CSA-based binders could provide a greater buffering potential to a CH based binder (Dyer, 2017).



A carbonation test after 28 days curing by Afroughsabet et al., (2021) of reinforcement revealed almost no tarnish to the PC steel fibres, whereas the CSA had significant oxidation. Similarly, a study by Alapati et al., (2022) concluded that of the binders tested at 28 days, CSA performed the worst, and a test by Damion and Chaunsali, (2022) showed that in H_2SO_4 , PC binders outperform (B)CSA, where PC lost 4% area and CSA 12.4%. A pH 1.5-2 H_2SO_4 test by Damion et al., (2022) had similar results, with PC outperforming the tested (B)CSA. However, after 14 years in the intertidal zone a tested BCSA(F) showed no corrosion of the embedded steel, implying little Cl ingress (Glasser and Zhang, 2001). The carbonation of BCSA(F) in field tests are also comparable to PCs, even with ettringites reported weakness to carbonation (Afroughsabet et al., 2021), and a study by Dyer, (2017) demonstrates CSAs situationally outperforming PC, with a better core strength retention after acid attack testing. A (B)CSA tested by Chi et al., (2021) also showed promise for resistance to sulphide and chloride attack, as well as carbonation. In a pH 2-3 citric acid test (B)CSA outlasted PC by 50%, seemingly due to a severe vulnerability of portlandite to citric acid, and the higher pH leading to extended preservation of AH_3 (Damion et al., 2022). A study by Cuesta et al., (2021) had a PC and a belite cement (BC) tested at 3 months, with the BC outperforming or matching the performance of PC for the three durability tests of 5% $MgCl_2$ solution, 3% Na_2SO_4 solution and 3x ion seawater. This indicates that with a high enough belite content, and time for significant hydration, a BCSA could produce comparable results to a PC. The belite rich BCSA compositions appear to be more durable than any tested low-belite variations, with the reportedly most resistant being the high belite, high ferrite BCSA(F), which are comparable to PCs. This may be due to a reduction in AFt and/or greater pH stability of included phases such as ferrite, Table.2, or the testing environments allowing for increased hydration. There are several ways in which we could improve the total hydration of binders to meet that seen by tested PCs, such as extended curing periods, accelerated curing methods, and seeding and/or activation of cements. The most definite (albeit slow) way of testing a representative binder would be to introduce 'equivalent hydration' into testing procedures, instead of a set 28 days of curing. This could be achieved through including an earlier step in the standards to test (or model) hydration of alternative binders, and then test at 70-80% total hydration. This may have some issues with binders that use inert components, such as BCSA(F) however, but this can be mitigated by using an equation such as "hydrated product % / hydrated product % after 5 years", where if the value is ≥ 0.7 the binder can be considered representative of its in-service performance. Accelerated curing at 40°C has been shown to produce a similar strength development past 7 days curing that would usually take beyond 28 days in a BCSA (Borštnar et al., 2020). Higher temperature curing has however been shown to decrease average ettringite crystal size, perhaps through slight thermal decomposition, and produce a system with a higher porosity, due to lack of time for C-S-H infill before hydration (Borštnar et al., 2020), so may not provide a representative binder. Certain minor elements such as Na, K, S and B have been shown to stabilise high-T polymorphs of C_2S , although how this affects the hydration of the cements is not adequately understood (Cuberos et al., 2010), (Cuesta et al., 2021). Using 2wt% Borax to activate belite within a BCSA similar in composition to BCSA(F) by Cuberos et al., (2010) resulted in the formation of 54wt% α'_H-C_2S , completely replacing the $\beta-C_2S$. The 0wt% borax sample recorded C_2S reaction of 20, 48 % at 1, 3 months and the 2.0 wt% borax sample recorded 49, 62% reaction at 1, 3 months. However, a later study by Álvarez-Pinazo et al., (2013) using the same compositions of BCSA and borax reported at 28 days curing $\beta-C_2S$ having 47% hydration and α'_H-C_2S having 27% hydration. This leads to an unknown in how activation truly effects the hydration belite.

Conclusions

At 28 days a typical PC will reach $\geq 70-80\%$ total hydration, while a BCSA will be closer to 50%. When given 3 months to cure, a BCSA will have closer to 70-80% total hydration. If a BCSA is given enough

time to hydrate, then the reduction in porosity should produce a binder with much greater performances in testing procedures. This can be achieved by testing binders on a 'equivalent hydration' as opposed to a set 28-day curing time, though implementing an earlier step to test or model hydration of alternative binders, and test when they reach hydration representative of their in-service performance. Using 40°C curing conditions may also provide a more realistic test at 28 days of curing.

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