CALCIUM SULPHOALUMINATE CEMENTS (CSA) FOR SUSTAINABLE SHOTCRETING – PRE-STUDY

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Kalciumsulfoaluminatcement (CSA) för hållbar sprutbetong - förstudie

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PREFACE

The ongoing climate change has forced concrete industry to actively seek ways to reduce its carbon dioxide footprint. Concrete as the most used construction material is mostly based on Portland cement, which is known for its high emissions. Also, the shotcreting technology in Sweden only uses Portland cement.

The aim of this pre-study was to investigate the possibility to partially replace Portland cement with Calcium Sulfoaluminate cement. This replacement should primarily reduce the carbon dioxide footprint and at the same time improve concrete properties, specifically from the shotcreting perspective, i.e., shorter setting, faster strength development and lower shrinkage. The pre-study was divided into two main parts, i.e., a literature review along with some laboratory tests.

The project was performed at Luleå University of Technology in the research subject of Building Materials, the project leader was Andrzej Ćwirzeń, while laboratory tests were performed by PhD students Ankit Kothari and Thanyarat Buasiri. The project was done in close cooperation with Tommy Ellison from BESAB and Hans Hedlund from Skanska. The reference group included Staffan Carlstrom (Swerock), Giedrius Zirgulis (Rise), Patrik Vidstrand (BeFo), Per Tengborg (BeFo), Lisa Hernqvist (TRV), Stefan Sandelin (Cementa), Jonas Magnusson (NCC) and Lars Wikstrom (LKAB).

It is our belief that this pre-study is a first step towards significant reductions in the carbon dioxide footprint produced in the rock engineering industry. The research was co-financed by BeFo, SBUF and LTU.

Stockholm

Patrik Vidstrand

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FÖRORD

De pågående klimatförändringarna har tvingat betongindustrin att aktivt söka nya sätt att minska sitt koldioxidavtryck. Betong, som det mest använda byggmaterialet, är till största delen baserad på Portlandcement, som är känt för sina höga utsläpp. Även sprutbetongtekniken i Sverige använder endast Portlandcement.

Huvudsyftet med denna förstudie var att undersöka möjligheten att delvis ersätta Portlandcement med kalciumsulfoaluminatcement. Denna ersättning ska i första hand minska koldioxidavtrycket och ska samtidigt förbättra betongegenskaper specifikt ur sprutbetongperspektivet, det vill säga kortare härdning, snabbare hållfasthetsutveckling och lägre krympning. Förstudien var uppdelad i två huvuddelar, en litteraturgenomgång och några laboratorietester.

Projektet utfördes vid Luleå tekniska universitet inom forskningsämnet Byggmaterial, projektledare var Andrzej Ćwirzeń, medan laboratorietester utfördes av doktoranderna Ankit Kothari och Thanyarat Buasiri. Projektet har gjorts i nära samarbete med Tommy Ellison från BESAB och Hans Hedlund från Skanska. I referensgruppen ingick Staffan Carlström (Swerock), Giedrius Zirgulis (Rise), Patrik Vidstrand (BeFo), Per Tengborg (BeFo), Lisa Hernqvist (TRV), Stefan Sandelin (Cementa) Jonas Magnusson (NCC) och Lars Wikström (LKAB).

Det är vår tro att förstudien är ett första steg mot en signifikant minskning av bergindustrins koldioxidbelastning. Forskningsarbetet samfinansierades av BeFo, SBUF och LTU.

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SUMMARY

The shotcrete was invented over 100 years ago and it is commonly used to repair concrete structures and for securing a rock mass in tunnels and mines. Material requirements are significantly tougher in comparison with cast insitu or precast concrete. Shotcrete is exposed to severe conditions from the very moment when it is placed on the rock surface with a high impact speed, rebound, a limited possibility for effective curing, required fast strength development, low shrinkage, etc. Other factors also include vibration from ongoing nearby blasting, natural movement of mass rock, vibrations from machines, running of natural water or pressure changes due to passing vehicles. The shotcrete used in Sweden is based on Portland cement, which despite several advantages is also known for its very high CO_2 footprint, (700-900 kg of CO_2/ton of the produced cement). This in combination with a typically high binder content >450 kg/m^3 results in a generally negative environmental impact. Furthermore, the high amount of cement combined with chemical accelerators result often in a high shrinkage leading to cracking and eventually to problems with durability and safety. Regular concretes can contain large amounts of secondary cementitious materials (SCM) to reduce the CO_2 footprint. Unfortunately, the maximum SCM amount for shotcrete is reduced in Sweden and in other countries to just 6% due to the slower strength development, durability problems and low robustness.

The solution proposed in this pre-study was to replace Portland cement partly or fully with calcium sulphoaluminate (CSA) and Belitic Calcium Sulphoaluminate (BCSA) cements. Both cements are not new products, and their manufacturing process is very similar to Portland cement. The project aimed to evaluate the concept and to collect data required for preparation of a full PhD research project proposal. It was a close cooperation between Luleå University and Technology, BESAB and Skanska.

The obtained results, including literature review and performed laboratory test, confirmed that in comparison with regular Portland cement both CSA and BCSA have lower CO_2 footprint, rapid hardening, and significantly lower shrinkage, require a shorter curing time, and provide a better durability in certain exposures. Both cements appeared as very promising materials for concrete used in shotcreting.

Keywords: CSA cement, ecology, CO_2 emission, shotcrete

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SAMMANFATTNING

Sprutbetong uppfanns för över 100 år sedan och det används ofta för att reparera betongkonstruktioner och för att säkra en bergmassa i tunnlar och gruvor. Materialkraven är betydligt tuffare jämfört med gjuten insitu eller prefabricerad betong. Sprutbetong utsätts för svåra förhållanden från det ögonblick då den placeras på bergytan med hög slaghastighet, bakslag, en begränsad möjlighet till effektiv härdning, nödvändig snabb hållfasthetsutveckling, låg krympning etcetera. Andra faktorer inkluderar också vibrationer från pågående närliggande blästring, naturlig rörelse av mässtan, vibrationer från maskiner, körning av naturligt vatten eller tryckförändringar på grund av passerande fordon. Sprutbetong som används i Sverige är baserad på Portlandcement, som trots flera fördelar också är känd för sitt mycket höga CO_2-fotavtryck, (700–900 kg CO_2/ton av det producerade cementet). Detta i kombination med ett typiskt högt bindemedelsinnehåll >450 kg/m3 resulterar i en generellt negativ miljöpåverkan. Dessutom resulterar den höga mängden cement i kombination med kemiska acceleratorer ofta i en hög krympning som leder till sprickbildning och så småningom till problem med hållbarhet och säkerhet. Vanliga betonger kan innehålla stora mängder sekundära cementeringsmaterial (SCM) för att minska CO_2-fotavtrycket. Tyvärr reduceras den maximala SCM-mängden för sprutbetong i Sverige och i andra länder till bara 6% på grund av långsammare styrkeutveckling, hållbarhetsproblem och låg robusthet.

Den lösning som föreslogs i denna förstudie var att ersätta Portlandcement helt eller helt med kalciumsulfaluminat (CSA) och belitic Calcium Sulphoaluminate (BCSA) cement. Båda cementen är inte nya produkter, och deras tillverkningsprocess är mycket lik Portlandcement. Projektet syftade till att utvärdera konceptet och samla in data som krävs för att utarbeta ett fullständigt doktorandprojektförslag. Det var ett nära samarbete mellan Luleå universitet och teknik, BESAB och Skanska.

De erhållna resultaten, inklusive litteraturgranskning och utfört laboratorietest, bekräftade att i jämförelse med vanlig Portlandcement både CSA och BCSA har lägre CO_2 fotavtryck, snabb härdning och betydligt lägre krympning, kräver en kortare härdningstid och ger en bättre hållbarhet i vissa exponeringar. Båda cementen framstå som mycket lovande material för betong som används i shotcreting.

Nyckelord: CSA cement, ekologi, CO_2-utsläpp, sprutbetong

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1   INTRODUCTION

Shotcrete, (sprayed concrete), was invented over 100 years ago in 1907 with a patent issued in 1911 in the USA. The method is based on spraying mortars or concretes using air pressure-powered guns. The compressed air is blown from the gun where it is mixed with the sprayed material. The sprayed material can be either wet or dry. The shotcrete technology is commonly used in the construction and mining industries to repair concrete structures and for securing rock masses in tunnels and mines. The biggest user of this technology is the Swedish mining industry, but it has been also applied for the construction of underground tunnel systems. The LKAB Berg & Betong AB company produces yearly around 130 000 m^3 of shotcrete, which is mostly used to secure mine tunnels. Depending on the local seismic activity, the typical thickness of a shotcrete layer varies between 70 and 100 mm. The concrete mix usually has the W/C ratio of around 0.48 and is based on the Portland cement (OPC) produced by Cementa AB. It contains also usually accelerators and other chemical admixtures. Steel fibers and steel mesh are typically used as reinforcement, sometimes combined with r-bars, (Iad Saleh, 2016). The 28 days compressive strength is at least 30 MPa but often exceeds 45 MPa, while the early age compressive strength measured after 4 hours >4 MPa. The Södra Länken and Norra Länken road tunnels in Stockholm are two examples where the shotcrete technology was used. In those two cases, exposure classes XD3 and XF4 were considered. The used W/C ratio was 0.45, the target compressive strength class C32/40, the actual developed compressive strength was between 40 and 47 MPa. All mixes based on Portland cement, contained accelerators and other chemical admixtures (e.g., air entraining agent), (Iad Saleh, 2016). One of the main differences between shotcrete used in mines and in road/subways tunnels is the required significantly longer life span of the later ones.

Material requirements are tougher for shotcrete in comparison with cast in-situ or precast concrete. Shotcrete is exposed to severe conditions from the very first moment when being placed on the rock surface. The impact speed is very high, it is difficult to ensure effective curing conditions, the strength must develop very fast, shrinkage should be very low, etc. Other factors also include vibration from the ongoing nearby blasting, natural movement of mass rock, vibrations from machines, running of natural water or pressure changes due to passing vehicles. Moreover, the shotcreting process also produces a rebound material (waste) which affects economy. The rebound can be as high as 30 % in the dry process and 10 % in the wet process.

Locally in Sweden, shotcrete technology was extensively studied at KTH and CBI, (Ansell, 2004)(Holmgren, 2010a)(Ansell, 2005)(Ansell, 2007)(Ansell, 2010)(Bryne, Ansell and Holmgren, 2014)(Sjölander and Ansell, 2017)(Bäck, L., Oscarsson, 1995)(Bryne and Ansell, 2012)(Lagerblad, Fjällberg and Vogt, 2010). The research focused on the finite element analysis of loads subjected to Portland-cement based shotcrete. The considered loads included vibrations, dynamic loading in train tunnels, shrinkage cracking, and bond strength between concrete and rock, effects of various types of fiber reinforcement. Currently all concretes for shotcrete applications in Sweden contain 100 wt.% of Portland cement, which is known for its very high CO$_2$ footprint,

(700-900 kg of CO_2/ton of the produced cement). This in combination with a typically high binder content, well exceeding 450 kg/m^3, results in a negative environmental impact. Additionally, the high amount of cement combined with the used chemical accelerators results in a high shrinkage often leading to cracking and problems related to durability and operational safety. Normal concretes often contain large amounts of secondary cementitious materials (SCMs) to reduce the CO_2 footprint. The maximum SCMs amount in shotcrete is typically reduced to 6-20 wt.%, depending on the country, due to a slower strength development, problems with durability and a low robustness, (Iad Saleh, 2016) (Bäck, L., Oscarsson, 1995)(Monika Lundgren et al. 2018).

The sustainability of shotcrete can be also enhanced by a full replacement of Portland cement with other types of cementitious binders, which are more ecological. The common alternatives include calcium aluminate cements (CAC), phosphate base binders, reactive calcium silicate-based binders, binders based on precipitated calcium carbonate or magnesia, Figure 1, (Yang, Ann and Jung, 2019)(Ideker et al., 2019)(Jimoh et al., 2018)(Liska and Al-Tabbaa, 2009). The alkali activated binders have received a significant attention in the recent decade with many full-scale applications, (Cwirzen et al., 2014)(Cwirzen and Habermehl-Cwirzen, 2013)(Cwirzen, Metsäpelto and Habermehl-Cwirzen, 2018)(Alghamdi, Nair and Neithalath, 2019)(Park, Lee and Lee, 2018). Another alternative is a Ye'elimite-based cement. The main sub-types of that cement include calcium sulphoaluminate cement (CSA), calcium sulphoaluminate-belite cement (CSAB), Belite-rich calcium sulphoaluminate cement (BCSA), Belite-sulphoaluminate ferrite cement (BCSAF) and Alite-rich calcium sulphoaluminate cement (ACSA). Each has unique properties in addition to a lower CO_2 footprint in comparison with OPC.
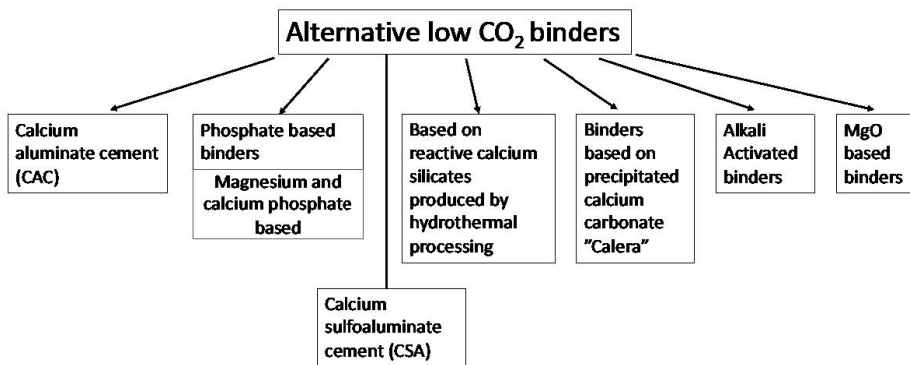
Figure 1. Examples of alternative cementitious binders.

The solution verified in this pre-study project replaced partly or fully OPC with calcium sulphoaluminate (CSA) and Belitic Calcium Sulphoaluminate (BCSA) cements. In comparison with OPC, both CSA and BCSA have lower CO_2 footprint, faster hardening, and lower drying shrinkage, (Yu, Wu, W. V. Liu, et al., 2018)(Chaunsali and Mondal, 2015)(Gastaldi et al., 2011). Both cements are not new products, and their manufacturing process is similar to Portland cement, (Ballou, 2013).

Table 1. Estimated CO_2 footprint reduction of selected cementitious binders.

Cementitious binder	Estimated CO_2 footprint reduction in comparison with Portland cement
Ordinary Portland cement (OPC)	reference
Calcium Sulphoaluminate cement (CSA)	25% - 50%
Calcium Aluminate Cements	53%
Alkali activated binders (gepopolymers)	35% -55%

The current report describes the main findings and results. The first stage (WP1) of the project was a literature study focusing on calcium sulphoaluminate (CSA), Belitic Calcium Sulphoaluminate (BCSA) cements, their combinations with OPC and reported applications in shotcreting. The next step included a limited laboratory testing (WP2, WP3) of selected properties followed by a simplified estimation of CO_2 emissions and costs. The study and the report were finalized with the formulation of conclusions and recommendations for future research, (WP4), Figure 2.
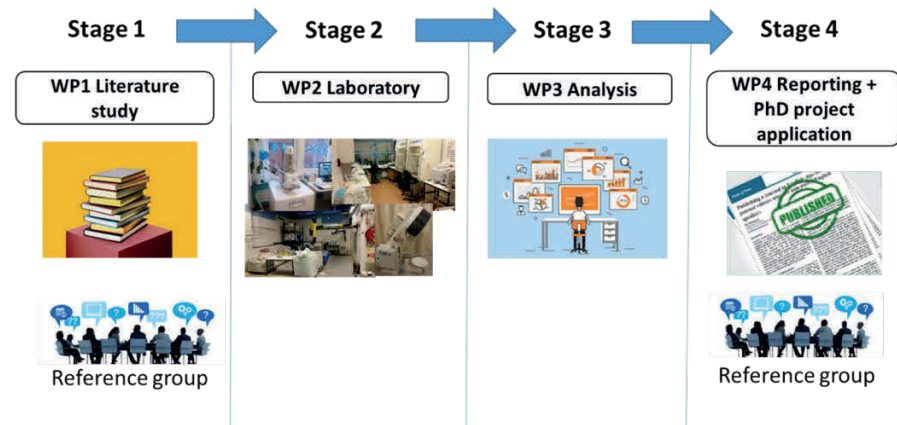

Figure 2. Outline of the project activities.

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2   LITERATURE REVIEW (WP1)

2.1   CSA cements - general

The family of calcium sulfoaluminate cements consists of a basic calcium sulphoaluminate cement (CSA), calcium sulphoaluminate-belite cement (CSAB), Belite-rich calcium sulphoaluminate cement (BCSA), Belite-sulphoaluminate ferrite cement (BCSAF) and Alite-rich calcium sulphoaluminate cement (ACSA), Figure 3. The main component of all CSA cements, i.e., Ye'elimite ($4CaO \ 3Al_2O_3 \ SO_3$, $C_4A_3\hat{S}$), was synthesized for the first time in 1957, is (Ragozina, 1957)(A. Klein, 1958)(Fukuda, 1961)(Ragozina, 1957). The first synthesis used heating of a mixture of tricalcium aluminate and gypsum to 1200 °C. Klein and Troxell published a scientific paper describing synthesis of $5CaO \ Al_2O_3 \ 2CaSO_4$ and $9CaO \ 4Al_2O_3 \ 3CaSO_4$ as a part of their study on expansive cements, (A. Klein, 1958). In that case, a mixture of calcium hydroxide, bauxite and aluminum sulphate was treated at 1350°C. Later, Fokuda published results describing a production of the $4Al_2O_3 \ 3CaSO_4$ by treating at 1350°C a mixture of bauxite, lime and $CaOCaSO_42H_2O$, (Fukuda, 1961). The official invention of CSA cement dates to 1963 when Alexander Klein applied for a patent on an expansive cement, which could reduce the shrinkage of Portland cement, (Klein, 1963). As described in that patent, calcium carbonate, alumina, and gypsum were mixed to produce a clinker having the formula of $C_aA_bS_c$+d. Klein indicated that s- should be 1-4, b- around 1-3 and d- around 1-2. The total amount of the free lime varied between 21 wt.% and 40 wt.% of the produced clinker. After grinding the mixture was heated to the incipient fusion at temperatures below 1600°C. An example mix used to prepare a CSA clinker contained 51.7% of calcium carbonate, 31.3% of gypsum and 17% of hydrated alumina. From the 1970s China has successfully produced and applied the significant amount of CSA cements to the various types of structures.

The second, studied type of CSA cement, was the Belitic CSA (BCSA) cement, (Bescher and Kim, 2019). The BCSA cement is very similar to CSA, has also lower shrinkage and faster strength development in comparison with OPC. The use of this cement has already exceeded two million tons in North America alone. The main applications are airports, the rehabilitation of concrete pavement. Serval companies have been also established in Europe to provide various types of CSA based cements.
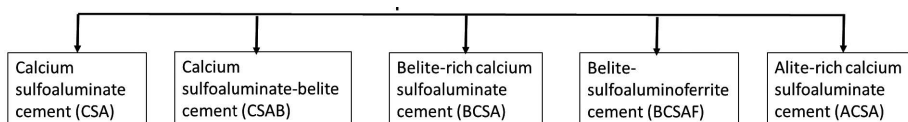
Figure 3. Main types of Calcium sulphoaluminate cements.

The production technology of CSA cements is comparable with OPC. However, the composition of raw materials fed into a kiln affects more the stability of Ye'elimite. The rotational kiln has a higher rotation speed to shorten the exposure time in a sintering zone. The aluminum needed for its production has been sourced typically from bauxite, and recently also from industrial various wastes, (Glasser and Zhang, 2001a)(Scrivener, John

and Gartner, 2018). The clinkering temperature varies between 1100 and 1350ºC, (Andac and Glasser, 1995)(Fernando Pacheco-Torgal, 2017)(Rungchet et al., 2016). The produced CSA clinker requires less grinding energy due to its higher porosity and it is inter-grinded with 16-25% of a $CaSO_4$, (Hargis, 2013)(Glasser and Zhang, 2001a)(Winnefeld et al., 2017). The density of CSA cements is usually slightly lower in comparison with OPC, (Fernando Pacheco-Torgal, 2017). The Ye'elimite content of a typica CSA cement varies between 25 and 75%. In the case of Belite Calcium Sulfoaluminate Ferrite or Belite-Ye'elimite-Ferrite (BYF, BCSA), the amount of the required aluminum is lower in comparison with CSA. Various types of steel slags have been used for its production to lower the price and to enhance its sustainability, (Adolfsson et al., 2007). The belite phase can be formed in CSA cement when SiO_2 is also present in the system. Usually BCSA cement contains 45-50% of belite (C_2S) in addition to 25-30% of Ye'elimite. The price of a BCSA cement is slightly lower due to the lower amount of Ye'elimite. It consists of Ye'elimite ($4CaO\ 3Al_2O_3SO_3$), belite ($2CaOSiO_2$) and calcium alumino-ferrite ($4CaO\ Al_2O_3\ Fe_2O_3$) (Fernando Pacheco-Torgal, 2017). BCSA cements are characterized by a slower strength development due to the presence of belite (C_2S), (Álvarez-Pinazo et al., 2013). To accelerate the initial strength development a formation of alite was induced to the clinkering process. Consequently, an Alite-rich calcium sulfoaluminate cement (ACSA) cement has been created. It contained in parallel to C_3S, C_2S etc. also Ye'elimite, (Hanein et al., 2019). The presence of all these phases enabled to combine advantages of OPC and CSA cements. Earlier studies showed that the production of CSA cement, which contains Ye'elimite and alite (C_3S) is impossible using the previously described process. Alite is stable at 1250ºC and forms rapidly at 1400ºC. On the contrary, sulfur contained in Ye'elimite becomes volatile and decomposes at >1300ºC, (Hu et al., 2016). Several methods have been developed to overcome this limitation, e.g., partially replacing Ca with Sr and Ba, (Chang, Shang and Zhao, 2015). Others lowered the clinkering temperature to 1250-1300ºC by the addition of a small amount of gypsum and CaF_2, (Odler and Zhang, 1996)(Zhang and Odler, 1996). Metal oxides including MnO_2, ZnO and CuO were observed to widen the coexistence temperature range, (Hu et al., 2016). In most cases clinker containing both phases showed an increased strength. Recently, (Hanein et al., 2019) produced CSA containing both C_3S and Ye'elimite employing the same process as used in the production of OPC, but additionally controlling the fugacity of oxygen and sulfur dioxide. The method stabilized Ye'elimite also at higher temperatures.

Table 2. Composition of the main types of CSA cements, (data adapted from (Wolfgang Dienemann Mohsen Ben HahaMohsen Ben Haha, 2018)(Skalamprinos et al., 2018))

Name (Acronym)	Main phase	(wt.%)	Minor phases	(wt.%)	References
Portland cement (OPC)	C_2S C_3S	10-20 55-75	$C4AF$ C_3A, CA, C_{12} SO_3	5-10 5-10 0,3-1,5	
Calcium sulfoaluminate cement (CSA)	$C_4A_3\hat{S}$	45-75	C_2S C_3S C_4AF $C\hat{S}$ $C_{12}A_7$	10-35 0-5 5-10 0-5 0-20	(Liang Zhang, 2000)
Calcium sulfoaluminate-belite cement (CSAB, BYF)	$C_4A_3\hat{S}$ C_2S	25-30 45-50	$C4AF$ $C\hat{S}$ $C12A7$ $C3A$	2 7-10 0	
Belite-rich calcium sulfoaluminate cement (BCSA)	$C_4A_3\hat{S}$ C_2S	20-45 45-75	$C4AF$ SO_3 C_3A, CA, C_{12} A_7, CA_2	2-30 6-15 0-5 0-5	(Gartner and Sui, 2018)
Alite-rich calcium sulfoaluminate cement (ACSA)	C_3S $C_4A_3\hat{S}$	48 50	C_2S $C4AF$	0-0.1 0-5	(Hu et al., 2016)(Hanein et al., 2019)
Calcium sulphoaluminate belite-ye'elimite-ferrite-ternestite cements (BY(F)T)	$C_4A_3\hat{S}$ $C_5A_2\hat{S}$ (ternesite)	35.1 28.6	C_2S C_2AS $C\hat{S}$	16.7 7.2 10.4	(Skalamprinos et al., 2018)

The main components of Calcium sulphoaluminate belite-ye'elimite-ferrite-ternesite cements (BY(F)T) are CaO, SiO_2 and SO_3 and other possibly incorporated elements, i.e., Al_2O_3, Na_2O, K_2O, (Skalamprinos et al., 2018). One- or two- stage sintering processes have been used. The one stage process included sintering at 1270ºC for 30 min, (Shen et al., 2015). The two-stage consisted of 8 hours of sintering at 1200ºC, flowed by a hold for one hour at 850 and at1000ºC, (Sherman et al., 1995a). Other methods, aiming to produce cements characterized by a higher hydration rate included for example sintered in the presence of soluble aluminum hydroxides, at 1280 and 1300ºC, (Bullerjahn, Zajac and ben Haha, 2015). Hydrocarbon fuels were also partially replaced by the combustion of chemically reduced forms of sulfur, which enabled to produce a belite-Ye'elimite-ternesite cement, (Galan et al., 2017). The ternesite appeared as being compatible with Ye'elimite and belite. This enabled to apply the single stage method and ensured the usage of optimized sintering process parameters. Another unique issue, while producing this type of cement, is the importance of a vapor phase, which in other clinkering processes can be neglected, (Skalamprinos et al., 2018). The stability of ternesite strongly depends on a temperature and the partial pressures of SO_2 and O_2, (Hanein et al., 2017).

The main problem related to the production of CSA cement is the need of expensive and limited in supply aluminum. The total CO_2 footprint is related to several production stages including sintering, grinding, raw material and waste management, Table 3, (N. Ukrainczyk, N. Frankoviæ Mihelj, 2013)(Ali, Gopal and Handoo, 1994). The reduction of CO_2 emission when considering CSA vs. OPC has been estimated to reach in the average around 30%, (Wolfgang Dienemann Mohsen Ben HahaMohsen Ben Haha, 2018). However, even lower emissions have been achieved when using SCMs, (Marta García Maté, 2014).

Table 3. Example production related advantages of CSA over OPC (data adapted from (N. Ukrainczyk, N. Frankoviæ Mihelj, 2013)).

Process	CSA	OPC (CEM II/B-M(S-V) 42,5N containing 15wt.% of BFS)	Difference
Sintering	0.3 tones $CaCO_3$ per tone of cement	0.85 tones $CaCO_3$ per tone of cement	-64%
Grinding of raw materials	11 kWh/tone of cement	16 kWh/tone of cement	-28%
Grinding of cement clinker	14 kWh/tone of cement	36 kWh/tone of cement	-40%
CO_2 emission related to raw materials	0.132 tones of CO_2 per ton of cement	0.374 tones of CO_2 per ton of cement	-64%
CO_2 emissions related to fuel	223 kg CO_2 /tone of cement	279 kg CO_2 / tone of cement	-20%

2.2 Hydration of CSA cements

The main phases forming during the hydration of CSA cement, are Ye'elimite, calcium sulphoaluminate ($4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O$) – AFm, and gibbsite ($Al_2O_3 \cdot 3H_2O$), (Pelletier, Winnefeld and Lothenbach, 2010). The main chemical reactions are summarized in Figure 4. Ye'elimite, which is the main compound of CSA cements, reacts with water resulting in the formation of AFm and Gibbsite. However, the presence of anhydrite triggers instead formations of Ettringite and Gibbsite. CSA systems containing belite, e.g., are characterized by the additional formation of calcium-silicate-hydrate (C-S-H) and calcium hydroxide (Portlandite), known from the hydration of OPC, Figure 4. The amount of added Gypsum has an important effect on the hydration process of CSA. It controls the ultimate phase composition of a solidified binder matrix. The increasing amount of Gypsum results in the formation of less AFm, C-S-H but more AFt, by (Liang Zhang, 2000). At the same time the formation of Gibbsite is affected only marginally. The hydration process itself can be divided into three stages. At an early age (<24 hours) the phase composition of hydrating CSA-based binder matrix depends on several factors, i.e., the amount of gypsum and the presence of other formed phases. The formation of ettringite dominates and leads to the development of a network skeletal immediately after mixing with water. This stage defines a time span between initial and final settings, and is characterized by a strong heat development, (Liang Zhang, 2000). The initially formed ettringite transforms into monosulphate, if no additional gypsum is added to the system,

(Hannawayya, 1975). Certain CSA cements, including for example expansive types, also showed the formation of Portlandite at the early stages of hydration, (Wang and Glasser, 1996). The presence of gypsum, along with available free lime leads to the formation of a significant amount of Portlandite. Later, but still before 28 days, when belite and ferrite starts to hydrate, the strength of matrix increases slowly. The binder matrix is built of a mixture of ettringite, aluminum hydroxide and C-S-H. The formed C-S-H has the Ca/Si ratio of around 1.2, which is lower in comparison with OPC. C_3A and C_4AF present in some binders can react with ettringite and cause its transformation into monosulphate (C_4ASH_{12}), (Beretka et al., 1996). After the 28-days of hydration, the water is incorporated into hydration products, similarly as seen in the OPC systems. When the available water is consumed no further reactions occur, thus resulting in unchanged mechanical properties. The water to cement ratio is an equally critical parameter in CSA and OPC systems, (Liang Zhang, 2000).
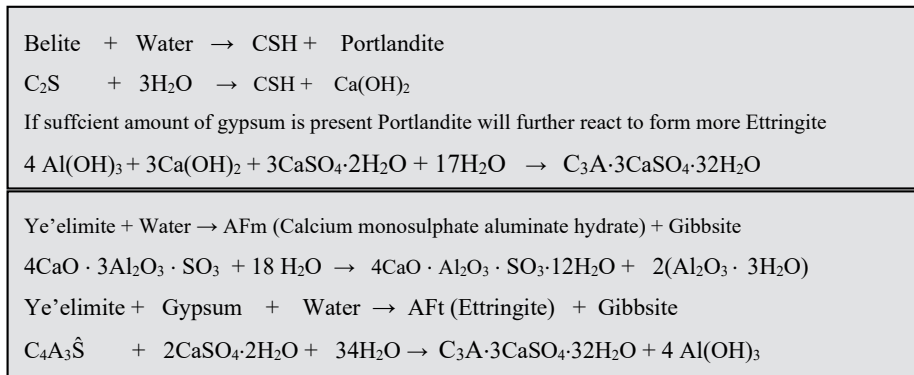

Belite + Water → CSH + Portlandite

C_2S + $3H_2O$ → CSH + $Ca(OH)_2$

If suffcient amount of gypsum is present Portlandite will further react to form more Ettringite

$4\,Al(OH)_3 + 3Ca(OH)_2 + 3CaSO_4{\cdot}2H_2O + 17H_2O \rightarrow C_3A{\cdot}3CaSO_4{\cdot}32H_2O$

Ye'elimite + Water → AFm (Calcium monosulphate aluminate hydrate) + Gibbsite

$4CaO \cdot 3Al_2O_3 \cdot SO_3 + 18\,H_2O \rightarrow 4CaO \cdot Al_2O_3 \cdot SO_3{\cdot}12H_2O + 2(Al_2O_3 \cdot 3H_2O)$

Ye'elimite + Gypsum + Water → AFt (Ettringite) + Gibbsite

$C_4A_3\hat{S}$ + $2CaSO_4{\cdot}2H_2O + 34H_2O \rightarrow C_3A{\cdot}3CaSO_4{\cdot}32H_2O + 4\,Al(OH)_3$

Figure 4. Main chemical reactions present during hydration of CSA cements.

2.3 Hybrid cements CSA with OPC

Hybrid binder combinations containing OPC, and CSA cements have been intensively studied during the last decade. The amount of CSA varied between 5 and 40 wt.% of the total binder amount. The ultimate properties of the hybrid binder depend on used cement types and their amounts. The hydration of such binders is a combination of processes typical for OPC and CSA cements, as well as additional new reactions, Figure 5. The additional reactions are related to the presence of alite and Portlandite originating from Portland cement. Generally, it has been observed that CSA present in OPC system does not alter the hydration mechanism of C_3S, but rather controls the dissolution of aluminate, (le Saoût et al., 2013).

The ultimate hydration of OPC+CSA hybrid systems is faster and develops a higher heat flow. For example, the heat flow of a mix containing 20 wt.% of CSA cement increased 2.5 times in comparison with OPC-based mix (first peaks), (Zhang et al., 2020). Faster wetting, dissolution and partial hydration were indicated as the main factors, (Hesse, Goetz-Neunhoeffer and Neubauer, 2011; Jansen et al., 2011). The amounts of sulphates

and free lime were observed to be higher in OPC-CSA systems and led to a higher heat release, (le Saoût et al., 2013). Furthermore, the hydration of Ye'elimite was very intense, (Trauchessec et al., 2015). The second- and the third- peak forming in OPC systems are related to the dissolution of C_3S and formation of C-S-H and CH. The lower amount of CSA (<10 wt.%) did not result in significant differences. However, the high additions of 15 and 20 wt.% delayed the formation of both peaks by 50 and 70 hours, respectively. The similar delay of C_3A hydration was seen earlier in OPC systems containing CaO and anhydrite, (Nocuń-Wczelik, Stok and Konik, 2010). The increased number of sulphates in the presence of unreacted calcium sulfates was proposed to bind to C_3A and to retard its hydration, (Minard et al., 2007). Others proposed that the simultaneous precipitation of calcium hydro aluminate and ettringite could decelerate the hydration of C_3S and delay the nucleation of C-S-H, (Brown, Liberman and Frohnsdorff, 1984)(Zhang et al., 2020).

Ye'elimite + Anhydrite + Portlandite + Water → Ettringite

$4CaO \cdot 3Al_2O_3 \cdot SO_3 + 8CaSO_4 + 6Ca(OH)_2 + 90H_2O → 2C_3A \cdot 3CaSO_4 \cdot 32H_2O$

Presence of Anhydrite

Portlandite + Gibbsite + Anhydrite + Water → Ettringite

$6Ca(OH)_2 + 2AH_3 + 6CaSO_4 + 52H_2O → 2C_3A \cdot 3CaSO_4 \cdot 32H_2O$

Absence of Anhydrite

Portlandite + Gibbsite + Ettringite → AFm

$6Ca(OH)_2 + 2AH_3 + C_3A \cdot 3CaSO_4 \cdot 32H_2O → 3CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O + 8H_2O$

Presence of Gibbsite

Alite + Gibbsite + Water → Strätlingite + Portlandite

$C_3S + AH_3 + 6H_2O → C_2ASH_8 + Ca(OH)_2$

Absence of Gibbsite

Alite + Water → C-S-H + Portlandite

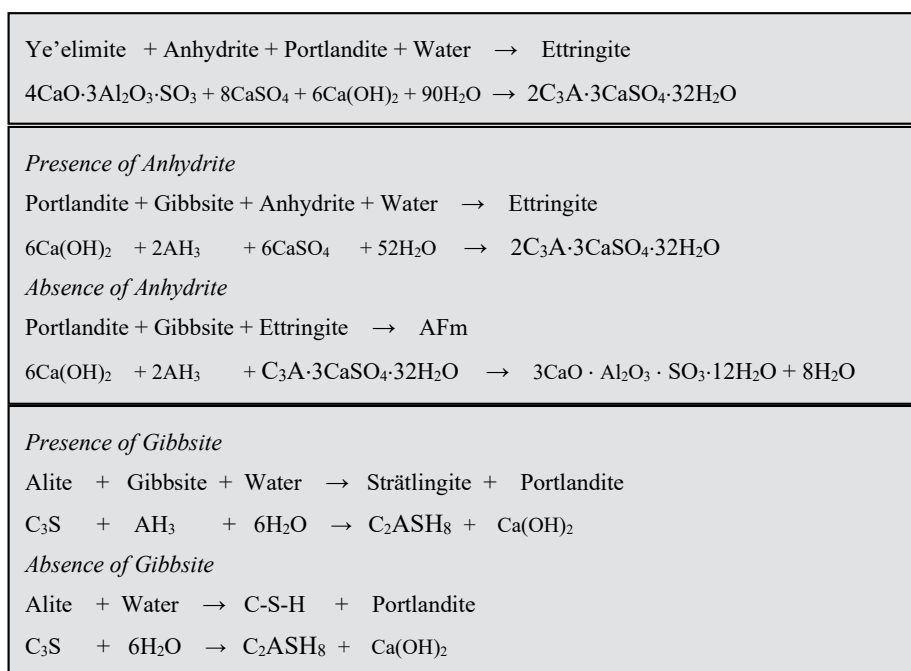$C_3S + 6H_2O → C_2ASH_8 + Ca(OH)_2$

Figure 5. Main chemical reactions developing during hydration of CSA+OPC combinations in addition to reactions listed in Figure 4.

Others assumed the extensive consumption of water by AFt, which slowed the hydration of C_3S, (Trauchessec et al., 2015). Ultimately, after the 28 days of hydration the amount of formed ettringite was higher at the expense of lower amounts of C-S-H and AFm. Generally, the composition and structure of C-S-H phase seem unaltered. For example, a ^{29}Si NMR study showed that an average tetrahedral chain length is the same, i.e., 3,9 vs. 3,8 and the Al/Si atomic ratio 0,08 vs 0,07. The degree of hydration was 75 vs 78, for OPC vs OPC+CSA, respectively, (le Saoût et al., 2013).

2.4 Microstructure

CSA binder matrix tends to be denser in comparison with OPC, due to the higher amount of chemically bound water resulting in a more extensive hydration, (N. Ukrainczyk, N. Frankoviæ Mihelj, 2013)(Beretka et al., 1996)(Bernardo, Telesca and Valenti, 2006). CSA cement sets and hydrates fast in the first hours after mixing with water. Its microstructure densifies rapidly during that time, while later changes are minor. On the contrary, OPC pore structure densifies slowly but still progresses even after 28 days. Pore size distribution and total porosity tend to be similar when measured after 2 hours in CSA and after 18 hours in OPC. CSA paste tends to have finer and less interconnected pores. This characteristic could potentially enhance durability, especial when the transport of aggressive media has a dominant role. OPC and OPC+CSA binder matrixes have similar microstructure; however, the number of Hadley grains is higher in an OPC+CSA matrix.

2.5 Fresh concrete properties

The time between initial and final setting is dominated by formation of ettringite, significant heat development and consumption of water. Generally, the setting times of CSA cements are shorter in comparison with OPC. This enables their usage as accelerators in OPC based concretes. For example, the replacement of 10 wt.% of OPC with CSA shortened the initial setting time from 195 min to 50 minutes and to 20 minutes when for a 20 wt.% replacement, Figure 6 (Zhang et al., 2020). Similar effects were also observed for final setting times, (Li et al., 2020).
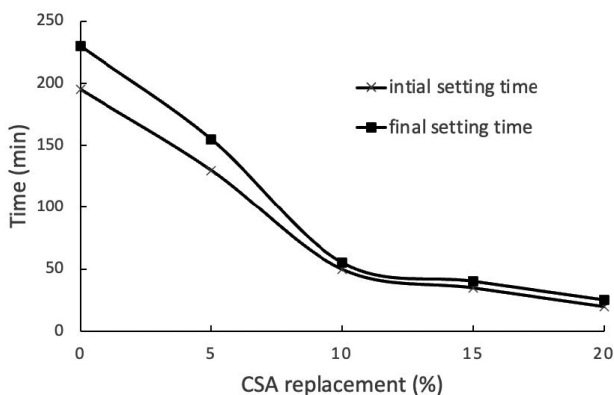

Figure 6. Effects of CSA replacement of OPC on initial and final setting times, data adapted from (Zhang et al., 2020).

2.6 Strength

The mechanical properties of matrixes based on the various types of CSA cements depend on their phase composition. Strength development can be slower or faster in comparison with OPC based systems. The early strength development of CSA cement depends on the

amount of added gypsum. The gypsum to CSA clinker ratio (C_T) appeared to predict well the mechanical properties of solidified matrixes, (Liang Zhang, 2000). An example comparing the strength development of OPC vs CSA based mortars is shown in Figure 7. CSA cement contained 53.0 wt.% of $C_4A_3\hat{S}$, 18.6wt.% of C, 13.2wt.% of α'-C_2S and 10.3 wt.% of $C_{12}A_7$. OPC was CEM I-A/L class 42.5 R Portland and contained 12% of limestone and 4.5% of gypsum.

The strength development of concretes based on the hybrid binders, strongly depends on the type and amount of added CSA. Generally, higher additions accelerate strength development, if the optimum amount of gypsum is present in the system to promote the ettringite formation, (Trauchessec et al., 2015).
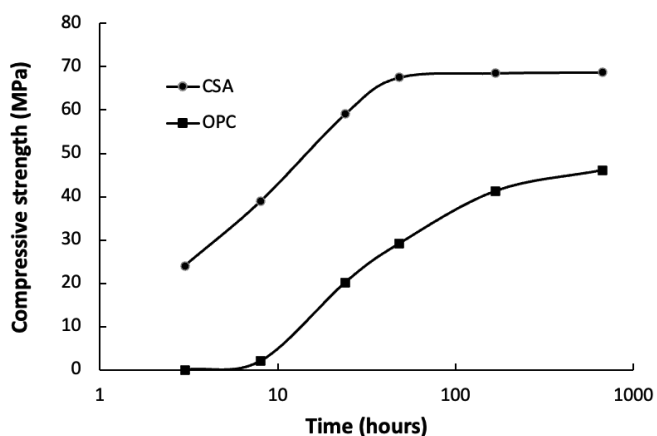

Figure 7. Compressive strength development, CSA vs OPC mortars, data adapted from (Bernardo, Telesca and Valenti, 2006).

2.7 Shrinkage

CSA cement was originally developed as a shrinkage reducing additive for OPC. The ultimate shrinkage and expansion of CSA cement depended on the amount of formed expansive or non-expansive ettringite. A higher ettringite nucleation rate has been indicated as a key factor enhancing the expansion, (Telesca et al., 2013)(Paulo Monteiro, 1993). Nucleation rate, and thus the expansion, increase at the higher concentrations of key elements, i.e., OH^-, Ca^{++}, SO_4^{--}, $Al(OH)_4^-$, in a strong alkaline environment, in the presence of lime and the higher amount of gypsum is added, (Beretka et al., 1996). For example, the expansion increased by the addition of 20-25 wt.% of gypsum, (Chen, Hargis and Juenger, 2012). The decrease of the water to cement ratio densifies the microstructure of a binder matrix. Consequently, the mobility of ions is limited by the lower volume of available free space. All these factors were indicated as being dominant to limit the early reaction of Ye'elimite, (Beretka et al., 1996). The lower water to cement ratio enabled the secondary formation of ettringite at later stages when an external water

was available, which led to the expansion, (Glasser and Zhang, 2001b). The late expansion was observed to be less than 1% and did not cause the cracking of a binder matrix, (Chen, Hargis and Juenger, 2012).

Earlier studies showed that the mixes containing 12 wt.% of fine CSA showed a rapid early age expansion but without induced cracking of binder matrix, (Cohen and Richards, 1982). The low amount of C-S-H was indicated as the main factor. Mixes containing coarser CSA expanded more and for a longer time. The formed binder matrix contained a higher amount of C-S-H, had higher strength and stiffness, which led to a sever cracking. The effect is known in OPC based system as delayed or secondary ettringite formation, when the additional supply of sulphate can transform monosulphate into ettringite, (Stark and Bollmann, 2000). This late formation can cause severe expansion and cracking of a solidified binder matrix. In some cases, the significant or complete loss of mechanical properties could occur. The expansion of an OPC binder matrix occurs only when ettringite forms in C-S-H phase, (Taylor, Famy and Scrivener, 2001). C-S-H with its pore diameters <10 nm creates an efficient special confinement needed to build the stresses created by forming ettringite. Thus, the expansion of CSA and CSA+OPC systems also depends on amount, microstructure, and strength of the C-S-H phase. Tests showed that the same amount of a formed ettringite caused a higher expansion in more porous matrixes and a lower expansion in less porous C-S-H matrixes, (Bizzozero, Gosselin and Scrivener, 2014a). Among several theories explaining this phenomenon, the crystallization pressure theory is indicated as the most accurate. The size of pores and crystallization pressure were related to the supersaturation of ettringite. To exclude the risk of a late expansion and to avoid the cracking of a binder matrix in systems based on OPC+CSA combinations, the formation of ettringite must be initiated at the right time, (Nocuń-Wczelik, Stok and Konik, 2010). The pressure created by its formation must be lower than the developed tensile strength of a matrix. Considering all described factors, the ultimate measured and reported shrinkage of pure CSA, and hybrid mixes, can wary significantly. Generally, the autogenous shrinkage of mixes based on CSA and OPC+CSA hybrids tends to be higher in comparison with OPC. Example values measured for the first 24 hours after mixing with water are shown in Figure 8. Systems containing CSA cement showed a more extensive autogenous shrinkage developing after the initial set than OPC. The observed trend was related to the rapid formation of ettringite at an early age of hydration. Others observed a similar chemical shrinkage in comparison with OPC at early ages, <40 hours, and higher at later times, (le Saoût et al., 2013). CSA cements tend to develop less drying shrinkage in comparison with OPC, Figure 9.
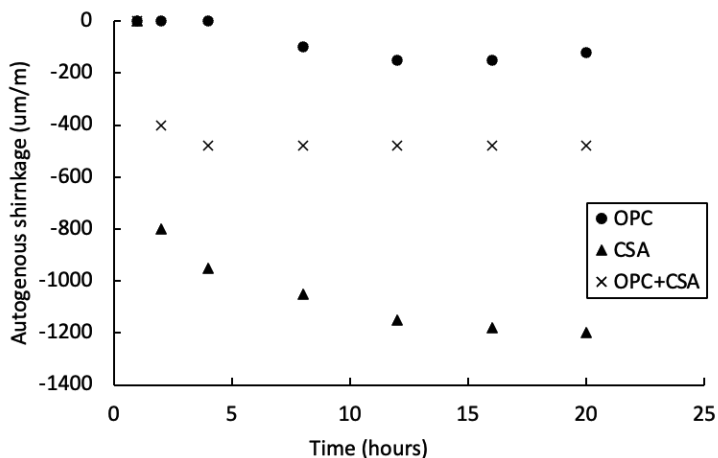
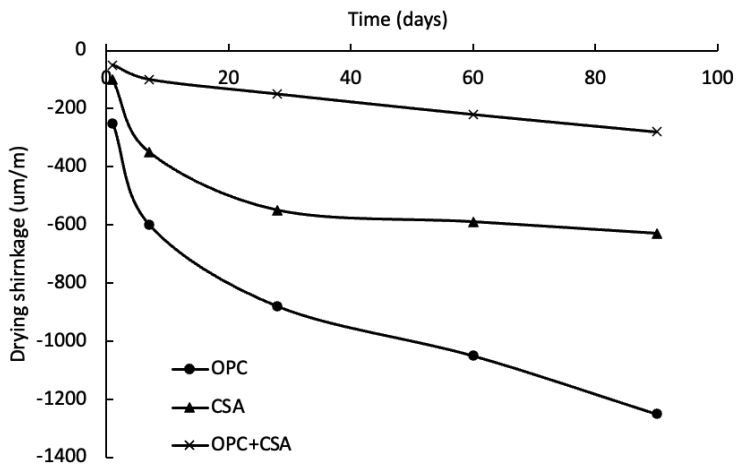*Figure 8. Autogenous shrinkage of OPC, CSA and OPC+CSA, data adapted from* (Sirtoli et al., 2019)

Figure 9. Drying shrinkage of concretes containing only Portland cement (OPC), only CSA cement (CSA) and mix of Portland and CSA cements in proportions 50/50 wt.% (OPC+CSA), data adapted from (Telesca et al., 2013).

The trend was related to the higher amount of C-S-H present in OPC-based systems and to its stronger ability to release water molecules in comparison with ettringite, (Telesca et al., 2013). Tests performed on hardened concretes containing 60 wt.% of CSA indicated that the amount of anhydrite was crucial for their dimensional stability. Concretes containing only CSA and OPC showed shrinkage but the addition of 6.5 wt.% of anhydrite resulted in an expansion. A very high amount (27wt.%) of anhydrite induced

an expansion related cracking and led to the destruction of test samples, (Trauchessec et al., 2014).

2.8 Creep

The creep of concretes containing CSA cements tends to be lower in comparison when OPC is used, Figure 10 (Sirtoli et al., 2019). Furthermore, the difference between basic and drying creep is smaller in systems containing CSA cements. Several factors were indicated to cause these trends, i.e., the faster hydration of CSA cement, the quicker densification of microstructure, the deficiency of water in the pore system due to the movement of the drying front from the surface inwards, larger difference between autogenous shrinkage and drying shrinkage observed in OPC, (Lura, Jensen and van Bruegel, 2003; Bizzozero, Gosselin and Scrivener, 2014b). The hybrid systems showed similar basic creep and drying creep when measured for 70 days. However, later, the basic creep was higher than the drying creep.
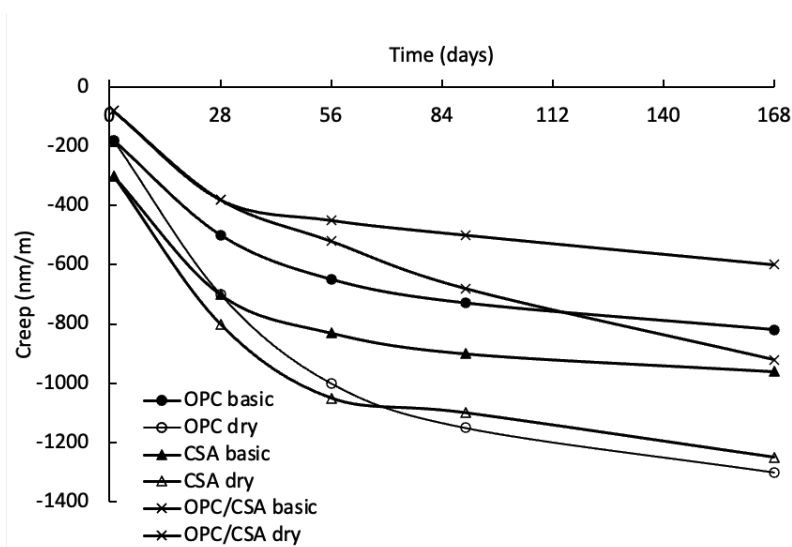

Figure 10. Creep of concretes containing a) OPC, b) CSA and c) 50wt.%of OPC + 50wt.% of CSA, data adapted from (Sirtoli et al., 2019)*.*

2.9 Durability

2.9.1 Carbonation and corrosion potential

Early published tests results were often contradicting to define whether CSA cements carbonate faster or slower than OPC, (Hargis et al., 2017). The accelerated carbonation test of CSA-based concretes showed a significant increase of the carbonation depth. The depth increased from 2 to 30 mm/year, (Hargis et al., 2017) (Alapati and Kurtis, 2018).

Furthermore, XRD and TG analyses showed a nearly full decomposition of ettringite, while the amounts of gibbsite, anhydrite, and hemihydrate have increased. The progress of carbonation tended to be slower and comparable with OPC-based systems which had lower water to cement ratios. The carbonation of an CSA-based concrete decreased the 28-days compressive strength by up 33%, (Sherman et al., 1995b).

The pH of the hydrated CSA binder is generally lower in comparison with OPC, thus increasing the risk of the reinforcement corrosion, (Fernando Pacheco-Torgal, 2017). The measured pH of CSA systems varied between 6 and 13, (Andac and Glasser, 1999; Carsana, Canonico and Bertolini, 2018)(Winnefeld and Lothenbach, 2010).

Hybrid binder systems containing both OPC, and CSA cements generally showed a higher alkalinity. For example, the mixes containing 60 wt.% of CSA and 40 wt.% of OPC reached pH of 12.5, (Carsana, Canonico and Bertolini, 2018).

Measured corrosion rates and corrosion potentials were slightly higher in CSA concretes and reached, $1\,\text{mA/m}^2$ and $-200\,\text{mV}$, respectively, (Carsana, Canonico and Bertolini, 2018). These tests showed also that the initial corrosion rate was higher. Carbonated concretes based on CSA and OPC+CSA cements showed higher carbonation and corrosion resistances in comparison with concretes based on OPC but containing limestone.

2.9.2 High temperatures

An OPC-based matrix sustains a gradual decomposition of the main hydration phases when exposed to high temperatures, mostly due to dehydration. The partial dehydration of ettringite already occurs below 200°C and the full dehydration at 300°C, (Sodol, Kaczmarek and Szer, 2020). Calcium aluminate hydrate C_3AH_{16} is known to be stable between 20 and 250 °C, while monosulphate starts to dehydrate at 290°C, (Jin Wang, 2016). The dehydration of C-S-H leads to a loss of interlayer water and hydroxyl over a wide range of temperatures, i.e., 105 and 1000°C, (Khoury et al., 2002). Portlandite dehydrates and decomposes to CaO and H_2O at temperatures between 400 and 500°C, (Sha, O'Neill and Guo, 1999)(Zhang and Ye, 2012).

The decomposition of CSA cements at high temperatures differs from OPC. Ettringite, which is the main hydration product next, to aluminum hydroxide, starts to decompose at 90°C and transforms into monosulphate and calcium sulfate, (Sodol, Kaczmarek and Szer, 2020). This transformation could lead to delayed ettringite formation when a CSA based concrete is subsequently exposed to a lower temperature, combined with wet or humid conditions, (Kaufmann, Winnefeld and Lothenbach, 2016). The exposure of ettringite to high temperatures at dry conditions led to its dehydration to 10-13H_2O meta-ettringite, (Zhou and Glasser, 2001). Upon heating and cooling cycles, the hydration and dehydration of ettringite lead to the formation of a meta-ettringite. Depending on the pressure/temperature ratio, two zones were identified, i.e., decomposition zone and reformation zone. Ettringite is stable in the reformation zone and could reform into the meta-ettringite. On the contrary, ettringite is unstable in the decomposition zone, and once decomposed it will not reform spontaneously, (Zhou and Glasser, 2001). At higher

temperatures, >110ºC, ettringite decomposes through a heterogenous mechanism, which leads to the formation of gypsum, hemihydrate and possibly also AFm. Ettringite-based matrixes, also including CSA cements, are believed to be safe to be used in humid climate at temperatures below 100ºC. Monosulphate starts to dehydrate at around 150ºC, while alumina trihydrate dehydroxylates at 200ºC. The dehydration of monosulphate begins above 450ºC, Table 4 (Sodol, Kaczmarek and Szer, 2020).

Table 4. Decomposition of CSA cement at high temperatures, adapted from (Sodol, Kaczmarek and Szer, 2020)*.*

Temperature	Decomposition process
>90ºC	Dehydration of Ettringite Decomposition of AFm to calcium sulphate
>150 ºC	Partial dehydration of monosulphate
200-230 ºC	Dehydroxylation of alumina trihydrate
>450 ºC	Dehydration of monosulphate

The comparative study of hybrid CSA+OPC cements indicated significant variations of their mechanical properties after an exposure to fire. For example, (Sodol, Kaczmarek and Szer, 2020) studied mixes, which contained 0, 25, 50, 75 and 100 wt.% of CSA and had the water to binder ratio of 0.5, Table 5.

Table 5. Mix designs used for testing of fire performance of CSA cement in combination with OPC. Data adapted from (Sodol, Kaczmarek and Szer, 2020)*.*

Sample	W/C	OPC wt.% of binder	CSA wt.% of binder
OPC	0,50	100	0
75OPC+25CSA	0,50	75	25
50OPC+50CSA	0,50	50	50
25OPC+75CSA	0,50	25	75
Z5	0,50	0	100

Samples were exposed to a maximum temperature of 800ºC, which was reached after 60 minutes. Temperatures which developed inside of the test samples varied between 220ºC and 480ºC. Compressive strength was measured at different times. All samples loss over 50% of their original strength. However, the samples made of CSA developed the smallest loss, Figure 11. At this stage temperature in the oven reached approximately 800ºC. Subsequently, between 15 and 60 minutes the temperature increased linearly to 950ºC. After 60 minutes the reference OPC concrete showed no mechanical strength, while the sample made of only CSA cement (Z1) retained around 10MPa. Samples containing combinations of CSA and OPC reached between 12 and 3 MPa. Interestingly, the best performing sample contained 75wt.% of OPC and 25 wt.% of CSA, while the worse performing sample contained 75 wt.% CSA and 25 wt.% OPC. Consequently, a moderate addition of CSA appeared to improve the fire resistance of tested concretes.
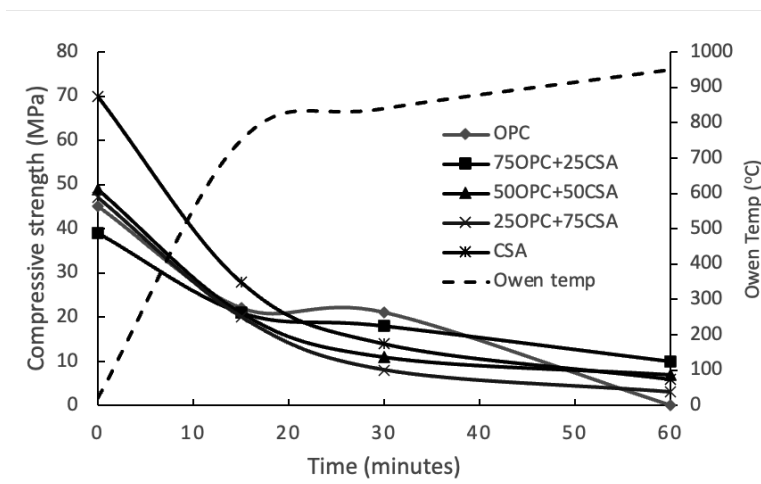
Figure 11. Effect of temperature and duration of exposure on the compressive strength. Data adapted from (Sodol, Kaczmarek and Szer, 2020).

2.9.3 Cold weather concreting and frost attack

CSA cements have been used at subzero temperatures as accelerators and antifreeze admixtures for OPC. The freezing point of cement pastes based on OPC but containing 20 wt.% of CSA decreased from -3.1°C to -5.5, (Zhang et al., 2020). Interestingly, the additional 4 hours of heat curing lowered it further to -8.2 °C. The applied heat curing accelerated hydration and enabled a full consumption of gypsum originating from CSA, which enhanced the compressive strength. The consumption of Ye'elimite in hybrid OPC+CSA binders is fast. Its full disappearance was reported to occur after 24 hours of curing at -5°C. On the contrary, the hydration of C_3S started only after 8 hours, followed by the formation of Portlandite and C-S-H. Binders containing higher amounts of CSA were dominated by the hydration of Ye'elimite and the rapid formation of Ettringite at an early age. The porosity of these systems tends to be increased.

Concretes based on the hybrid binders and cured at -5°C without an additional heat treatment, developed higher compressive strengths, (Zhang et al., 2020). The 5 wt.% replacement of OPC with CSA enhanced the one-day strength by 50%, while the 20 wt.% replacement gave an 120% increase. The 28-days compressive strength increased by a nearly 150%. A slightly higher increase was measured in the samples containing 15wt.% of CSA cement. The rapid early age formation of ettringite has been linked with the observed strength increase of the OPC+CSA mixes.

The durability of CSA-based concretes exposed to freeze-thaw cycles appeared to be comparable with corresponding OPC mixes when a proper air entrainment was used, (de Bruyn et al., 2017). Surface scaling tended to be generally lower in CSA concretes. Some observed problems were linked to a lack of compatibility between CSA cements and air

entraining admixtures, (Polivka, 1973). The recommended content of entrained air varied between 2.6 and 6 %, while the air void spacing factor should <500 microns, (JACOB PEERY, 2015). Others observed a more extensive internal damage due to higher total porosity and coarser pore size distribution, (Janotka and Krajči, 2000). The study also emphasized that CSA-based mixes setting faster were performing worse.

2.10 CSA cements for shotcrete applications

CSA cements have been used for shotcreting applications in situations where rapid setting and low shrinkage were important technological parameters. The short setting times of CSA cements prevented their direct usage in a wet-mix shotcrete, (Alexander Mache, 2020). However, when used in a dry-mix shotcrete the compressive strength reached 20 MPa in only two hours after shotcreting, (Reny and Ginouse, 2014). An extensive study of a CSA based shotcrete, applied as wet and dry was done by (Tadolini, Mills and Burkhard, 2018). The shotcrete achieved the compressive strength of 20 MPa after 1 hour, 75 MPa after 28-days, and the adhesion bond with substrate of 10 MPa 7 after days. Chloride penetrability was negligible, thus indicating a very good protection against the corrosion of steel reinforcement. Shotcrete applied in tunnels is susceptible to cracking caused by the shrinkage of concrete and the movement of rocks, (Yu, Wu, W. v. Liu, et al., 2018). Typical concretes based on OPC contain alkali-free accelerators, which tend to increase its shrinkage, (Holmgren, 2010b). To mitigate these problems, hybrid cements containing the combination of OPC, CSA and calcium sulphate have been used. For example, an optimum binder combination contained 20 wt.% of OPC, 40 wt.% of CSA and 40 wt.% of CS. The 28-days concrete compressive strength reached 20 MPa, while the expansion was 0.25% after 7 days and 1,25% after 20 days. The development of drying shrinkage was fully mitigated. Shotcrete containing CSA cement appeared to have better bond with a rock substrate, higher compressive strength, and lower shrinkage in compromission with OPC, (Alexander Mache, 2020). For example, the comparison of tests results from laboratory and from full scale mine operations showed in both cases final settings between 4 and 5 minutes. The rebound of concrete tended to be lower in comparison with the mix based on OPC but containing silica fume, thus indicating its good cohesiveness. The compressive strength of 12 MPa was reached after 1 hour and 15 MPa after 2 hours, (Eric Bescher, 2018). The initial surface temperature of sprayed substrates was only 5°C. The ultimate 28 days compressive strength was around 50 MPa. The addition of 0.1 wt.% of a citric acid delayed the setting of shotcrete composed of OPC and CSA. This enabled its application in a dry-mix method, (Alexander Mache, 2020). The partial replacement of an OPC/CSA binder with GGBFS increased the compressive strength of shotcrete between 28 and 90 days after shotcreting. The compressive strength of this concrete in a full-scale application was higher due to a better compaction. Shotcretes based on CSA cements have been used in an underground mining when a rapid strength development was required. Practice showed that it could be spayed in thinner layers due to a better bonding with substrates, (Eric Becher, Nick de Ocampo and Mike Ballou, 2013).

3 LABORATORY TESTING AND DATA ANALYSIS (WP2 AND WP3)

3.1 Materials

Two types of cements were used, i.e., Portland cement (OPC) and Calcium Sulfoaluminate cements (CSA). OPC was a Anläggningscement type CEM I 42,5N-SR from Cementa. CSA cements were Next Base SR03 from Buzzi Unicem Spa, ALI Cem from HeidelbergZement and Belicem produced by Caltra. The physical properties and chemical composition of all cements are shown in Table 6 and Table 7. The Anläggningscement was chosen as being commonly used for shotcrete in Sweden, (BESAB AB). It is a pure Portland cement without additional SCMs, relatively coarse, has low shrinkage and slow hydration. SR03 and ALI, had a similar fineness but slightly different chemical compositions. The SR03 contained 45 wt.% of Ye'elimite, which was the lowest amount of all tested CSA cements, while the ALI contained 58 wt.% and the BELI over 60 wt.% of Ye'elimite. The amount of added anhydrite varied between 10 and 25 wt.% for BELI and ALI cements, respectively. The BELI and SR03 contained additionally 25 wt.% and 20 wt.% of Belite, respectively.

Table 6. The physical properties of studied cements

	Cement name	Type	Producer	Fineness cm²/g	density g/cm³	Strength class [MPa]	CO$_2$ eq / ton
SR03	Next Base SR03	Belite-CSA	Buzzi Unicem Spa	>4800	2.8	42.5	n.n.
ALI	ALI Cem	CSA	Heidelbeg Zement	4700		62	599 (380)
BELI	Belicem	Belite-CSA	Caltra	5000	2.9	52.5	n.n.
OPC	Anläggningscement	CEM I 42,5N-SR	Cementa AB	3100	3.2	42.5	873

Table 7. The chemical composition of studied cements

	CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	MgO	Belite	Anhydrite (wt.%)	Ye'elminate (wt.%)
SR03	43,9	7,6	21,3	2,07	17,5	2,59	20	22	52
ALI	36-41	<9	27-33	<1,5	10-14	<5		25	58
BELI	40-44	6-10	>32	<2,2	9-10	<1.5	25	10	>60
OPC	62,9	20,9	3,2	4,0	2,8	2,5	14,7	0-5	0

Concrete mixes contained natural granite aggregates having the diameters of 0-8 mm and were obtained from Jehander Heidelberg cement group. A fine natural filler was provided by Skanska AB from Luleå. All concrete mixes had the water to binder ratio of 0.5 and the total binder content of 430 kg/m³, Table 8. The concrete mixes contained either 100 wt.% of OPC, or the OPC was replaced by 20 and 40 wt.% with the CSA. The workability of fresh concrete was controlled by an addition either 0.5 or 1.5 wt.% of a Polycarboxylate ether based (PCE) superplasticizer type "MasterGlenium ACE 30" (SP) from Master

Builders. The higher amount of the SP was used in concretes containing the BELI cement, to prevent a rapid loss of workability. Unfortunately, this led to an excessive flowability in the first minutes after mixing, Table 10. Concretes were produced using a Hobart type mixer. The mixing procedure included 2 minutes of dry mixing, followed by an addition of water containing the SP and mixed for another 2 min. The workability of concrete was determined as a slump following the SS-EN 12350-2:2019 standard. Compressive strengths were determined 1, 3, 7, 14 and 28 days after casting using 100 x 100 x 100 mm^3 cubes. Samples were cured in water until the time of testing. The test procedure generally followed the SS-EN 12390-3:2019 standard. Shrinkage was determined on concrete cores, which had the diameter of 100 mm and the height of 150 mm.

Table 8. The mix compositions of studied concretes.

Mix	W/B	OPC (kg/m³)	Cem. type	CSA (kg/m³)	SP (wt.% of binder)	Filler (kg/m³)	Granite 0-4 (kg/m³)	Granite 4-8 (kg/m³)
OPC	0,5	430	OPC	0	0,5	193	1135	578
OPC:BELI_80:20	0,5	344	BELI	86	1,5	193	1135	578
OPC:BELI_60:40	0,5	258	BELI	172	1,5	193	1135	578
OPC:ALI_80:20	0,5	344	ALI	86	0,5	193	1135	578
OPC:ALI_60:40	0,5	258	ALI	172	0,5	193	1135	578
OPC:SR03_80:20	0,5	344	SR03	86	0,5	193	1135	578
OPC:SR03_60:40	0,5	258	SR03	172	0,5	193	1135	578

Cement pastes were used to determine initial setting times, final setting times, and for the analysis of microstructure and phase composition. The mix designs of pastes are shown in Table 9. The W/B ratio has been lowered to 0.31 to account for the lack of aggregates and filler. Either 0.5 wt.% or 1.0 wt% (the wt.% of the total binder) of the SP added to all mixes.

Table 9. Pastes mix composition

Mix	OPC_CSA Wt.%	W/B ratio	SP (wt.% of binder)
OPC	100	0.31	0.5
ALI-20	60_40	0.31	0.5
ALI-40	80_20	0.31	0.5
BELI-20	60_40	0.31	1
BELI-40	80_20	0.31	1
SR03-20	60_40	0.31	0.5
SR03-40	80_20	0.31	0.5
ALI	100	0.31	0.5
BELI	100	0.31	1
SR03	100	0.31	0.5

3.2   Experimental setup

Semi adiabatic temperature measurements were performed using a setup shown in Figure 12. Concrete samples having dimensions of 60x60x60 mm^3 were cast directly into forms made of polystyrene. Each sample contained a thermocouple. The microstructure of concretes was analyzed by a Scanning Electron Microscope type Jeol, JSM-IT100 (JEOL, Ltd., Japan), Figure 13. All images were obtained using a back scattered electron mode and the magnification of 500x. The accelerating voltage was 15 kV and the accelerating current was 50 μA. The SEM was equipped with a QUAN-TAXEDX (Energy-dispersive X-ray spectroscopy) analysis system from BRUKER coupled with the ESPRIT 2 software (Bruker Corporation, USA). After cutting from test cubes, specimens were immersed in ethanol alcohol to remove a capillary water.

Figure 12. Semi adiabatic temperature measurements setup

Subsequently, the alcohol was evaporated, and samples were impregnated with a low viscosity epoxy resin under vacuum. After curing samples were polished using a Struers Labo-Force-100 machine produced by Struers from Denmark. Diamond sprays having the particle size diameters of 1, 3, and 9 μm were used.

Figure 13. Scanning electron microscope (SEM) integrated with an energy dispersive spectrometer (EDS) used for the characterization of microstructure and phase composition.

The total volume change of hardened concretes was measured using cylindrical specimens having the diameter of 100 mm and the height of 200 mm, Figure 14. Steel studs were glued with an epoxy resin to the sides of cylinders. Strain values were measured using an electronic manual strain gauge type DEMEC type produced by Mayes Instruments. The strain measurements started 24 hours after casting. All specimens were kept in a laboratory environment and exposed to drying.
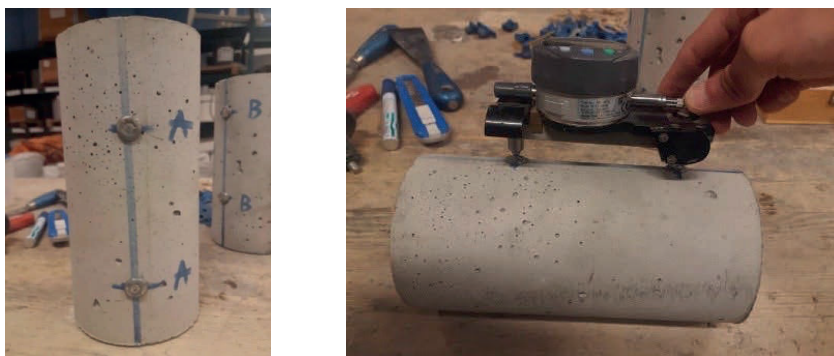

Figure 14. Setup used to determine volume changes of hardened concrete samples.

3.3   Tests results and discussion

3.3.1   Fresh concrete properties

The properties of fresh concretes were determined by measuring a slump directly after mixing. The amount of the SP was optimized to produce sufficiently workable mixes. The replacement of OPC with 20 and 40 wt.% of BELI and SR03 generally enhanced workability. The measured slump varied between 5 and 25 cm, Table 10. The addition of 1wt.% of the SP to mixes containing 20 and 40 wt.% of BELI cement produced a very good workability with no signs of segregation, Figure 15. The workability of fresh concretes was not determined at later times. However, visual observations indicated the tendency of mixes containing BELI cement to stiffen rapidly. These mixes developed also a short initial setting already after 4 minutes, Figure 18. The specific surface areas of CSA were larger in comparison with the OPC, 4000-5000 cm^2/g versus 3100 cm^2/g, Table 6. This presumably caused the higher adsorption of SP polymers on cement particles, which increased their effectiveness and produced more workable mixes, (Hu, Ge and Wang, 2014; Mardani-Aghabaglou et al., 2017). The visual observations of fresh mixes indicated a faster workability loss when CSA was present, with the strongest effect when BELI cement was used. PCE superplasticizers are known to initially decrease the yield stress of CSA pastes followed by its rapid later increase, (R. Belhadi, A. Govin and P. Grosseau, 2019). This trend was related to the formation of Ettringite on the side chains of PCEs, which weakened their dispersing effect, (Tan et al., 2017). Consequently, it could be assumed that PCE having longer side chains could support the formation of a thicker absorbed PCE layer, thus leading to a better dispersion, (Flatt and Houst, 2001).

Table 10. Slump measured directly after mixing.

Mix	SP (wt.% of binder)	OPC. (wt.%)	CSA (wt.%)	Slump (cm)
OPC	0,5	100	0	5
OPC:BELI_80:20	1,0	80	20	25
OPC:BELI_60:40	1,0	60	40	16
OPC:ALI_80:20	0,5	80	20	7
OPC:ALI_60:40	0,5	60	40	7,5
OPC:SR03_80:20	0,5	80	20	9
OPC:SR03_60:40	0,5	60	40	5

a)   b)

Figure 15. Example slump and slump flow tests of a) ANL OPC:BELI_80:20 b) OPC:BELI_60:40

3.3.2 Hydration

The studied CSA cements developed only one main exothermic peak with an additional shoulder. The first peak formed shortly after mixing and corresponded to the rapid dissolution of gypsum and Ye'elimite. This led to the oversaturation of pore solution, considering the formation of ettringite, (Jansen et al., 2017). The following peak could be related to the formation of ettringite and amorphous AH_3.

The induction period lengths were 250 minutes for OPC, 6 min for SR03, 25 minutes for ALI and 140 minutes for BELI cement, Figure 16. The main exothermic peak formed after approximately 40 minutes for SR03, 170 minutes for ALI and 230 minutes for BELI. The third exothermic peak, which usually forms due to the additional formation of ettringite, was not recorded presumably due to the low sensitivity of the used setup. The highest temperature in the BELI cement. The length of the induction period for mixes

based on hybrid binders containing 20 wt.% of CSA was 12-30 minutes and for mixes containing 40 wt.%, 4-18 minutes. The shortest induction period of around 4 minutes was measured for the mix containing 40 wt.% of the BELI cement, which also corresponded to the shortest measured initial setting time, Figure 18.

Generally, the partial replacement of OPC by CSA cement resulted in a faster hydration and increased hydration temperature, e.g., in the mix containing 40 wt.% of CSA, Figure 17. Mixes with 20 wt.% of CSA developed lower temperatures in comparison with the reference OPC. The OPC60+ALI40 hybrid binder developed the highest maximum temperature of a nearly 90°C. The very high content of sulfates (25 wt.%), additionally accompanied by the high amount of Ye'elimite (58 wt.%), were presumably the main contributing factors.
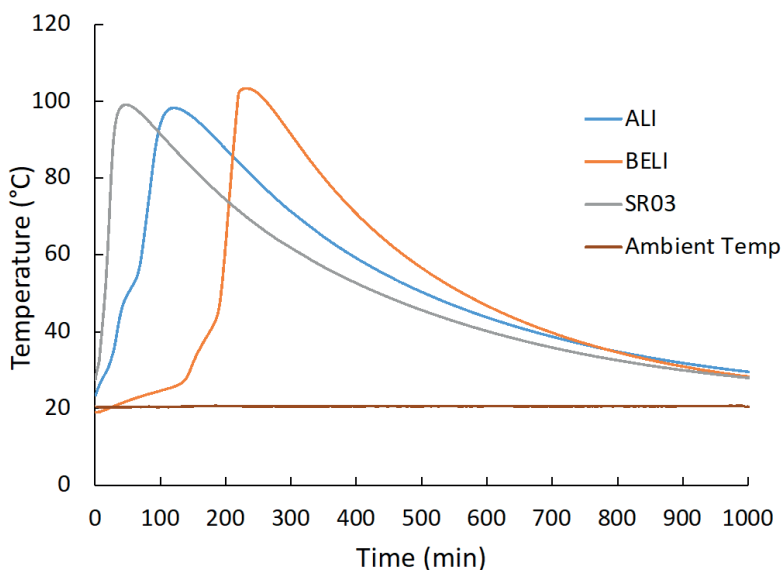

Figure 16. Semi adiabatic temperature development of CSA samples cured at 20°C.

The temperature increase rate developed after induction period was ≈0.5 °C/min for the reference OPC mix, ≈6.5 and ≈6.3 °C/min for mixes containing 40 wt.% of BELI and ALI cements, respectively. The rates decreased to ≈2.6 and ≈2.1 °C/min, when only 20 wt.% of OPC was replaced. The replacement of OPC with 40 and 20 wt.% of SR02 resulted in the rate of ≈2.4 and ≈3.5 °C/min. The lower rates could be related to the amount of Ye'elimite and to the enhanced formation of ettringite. The SR03 cement contained only 45% of Ye'elimite versus 58 and over 60 wt.% for ALI and BELI cements, respectively. An additional shoulder formed prior to the main peak in the CSA-OPC hybrid binders, Figure 16. Its formation could be related to the partial dissolution of gypsum and Ye'elimite followed by the precipitation of hydration products, Figure 17. The delayed formation of the second exothermic peak was observed between after 80

hours. The highest hydration temperature developed for a binder 20 wt.% of BELI. The second peak formed between 26 and 33 hours, while the third between 108 and 125 hours. At the same time a higher replacement (40 wt.%) of OPC with BELI lead to the formation of a very small second peak between 91 and 108 hours after mixing. The late release of heat was also measured in the hybrid binder incorporating 20 wt.% of ALI cement. Two peaks formed after 33-58 hours. The binder containing 40 wt.% of ALI cement showed a strong increase of the hydration temperature after 133 hours. Since, the temperature measurements were terminated after 150 hours, it was impossible to determine the maximum developed temperature and the exact position of that peak. The ALI cement did not contain additional belite.
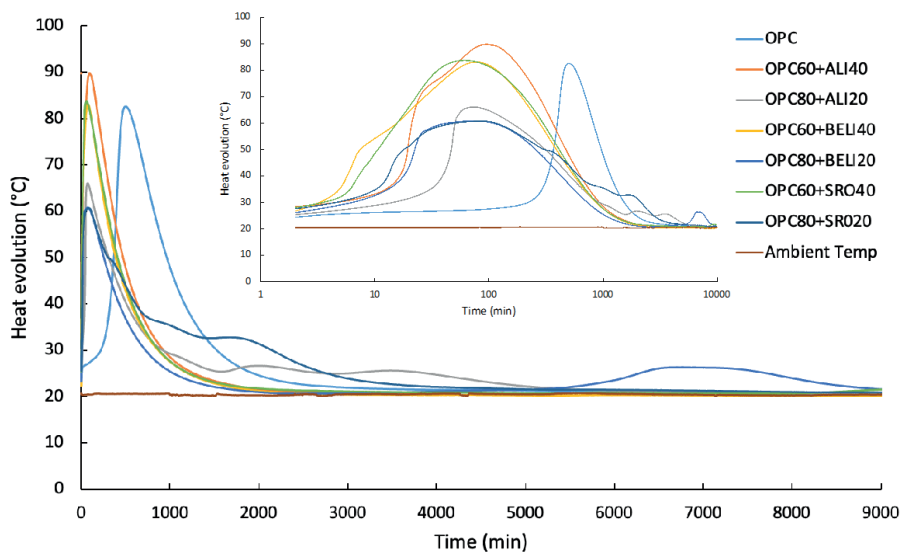

Figure 17. Semi-adiabatic hydration heat release shown versus normal and logarithmic time scales.

3.4 Setting times

The initial and final setting times of pastes containing CSA cements were generally shorter in comparison with OPC, Figure 18. The initial setting time of the reference OPC mix was 581 minutes. The increase of the ALI cement content from 20 to 100 wt.% shortened this time from 25 minutes down to 7 minutes. The hybrid binder containing 80 wt.% of OPC and 20 wt.% of SR03 set after 7 minutes, and instantly at a 100 wt.% replacement. The effects of BELI cement on setting times of hybrid binders were different. The reduction of an initial setting time was nearly the same as for the SR03 cement, but only until the replacement reached 40 wt.%. A mix containing only BELI cement initially set after 30 minutes. The shortest final setting times of around one hour were measured for hybrid mixes containing 80 wt.% of OPC and 20 wt.% of, either BELI or ALI cements. The interesting trend was observed for BELI cement, where its higher

amount delayed the final setting time. All observed trends could be directly related to the hydration processes, Figure 17.
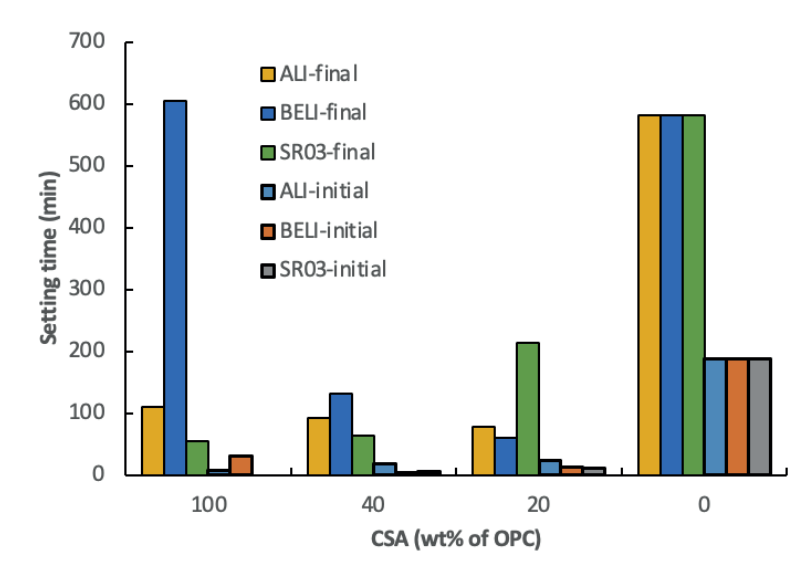

Figure 18. Initial and final setting times of hybrid OPC+CSA binders.

3.5   Microstructure and phase composition

The microstructure and phase compositions of hardened binder matrixes were studied using a combination of SEM and EDX. Resin impregnated and polished 28 days old concrete samples and 4 months old paste samples were used. Example images are shown in Figures 19-24. None of the analyzed samples showed extensive cracking of the binder matrix. The interfacial transition zone (ITZ) appeared similar and without any trend to form as wider or more porous when CSA cements were present. In all cases, some unhydrated OPC and CSA cement particles were visible throughout the binder matrix. The limited study of 4 months old samples exposed to a laboratory environment also did not indicate any significant changes of the microstructure.
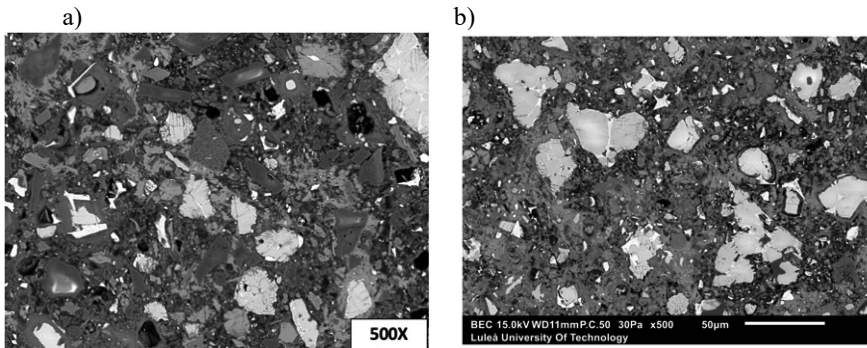
a)   b)

Figure 19. SEM image of 28 days old ANL cement: a) 28 days old concrete, b) 4 months old paste
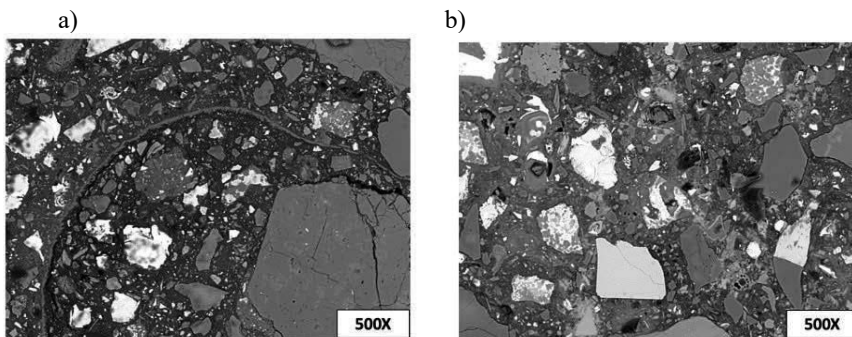
a)   b)

Figure 20. SEM images at 500x magnification of concretes based on hybrid OPC/CSA binder, a) 60 wt.% of OPC + 40 wt.% of ANL:BEL, b) 80 wt.% of OPC + 20 wt.% of ANL:BEL
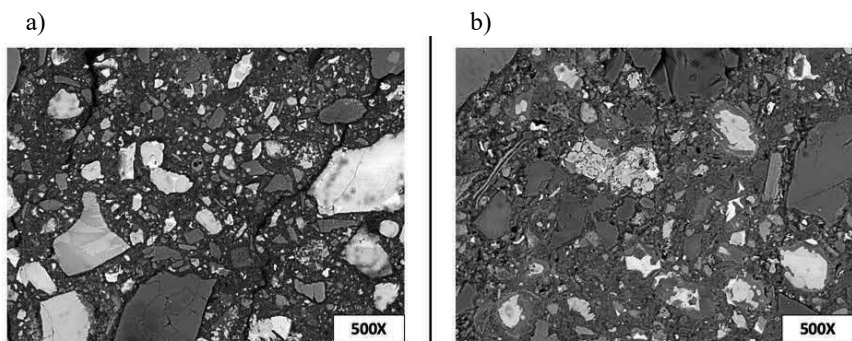
a)   b)

Figure 21. SEM images at 500X magnification of concretes based on hybrid OPC/CSA binder, a) 60 wt.% of OPC + 40 wt.% of ANL:ALI, b) 80 wt.% of OPC + 20 wt.% of ANL:ALI
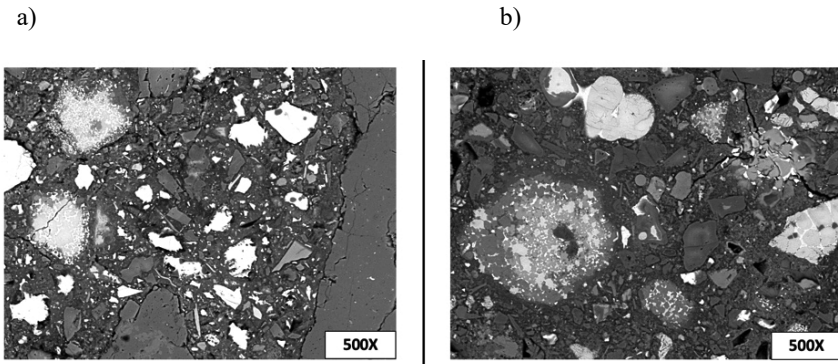
a)   b)

Figure 22. Effect of age on microstructure od CSA cements and CSA+OPC hybrid combinations. SEM images at 500X magnification of concretes based on hybrid OPC/CSA binder, a) 100 wt.% ALI:SR03, b) 80 wt.% of OPC + 20 wt.% ALI
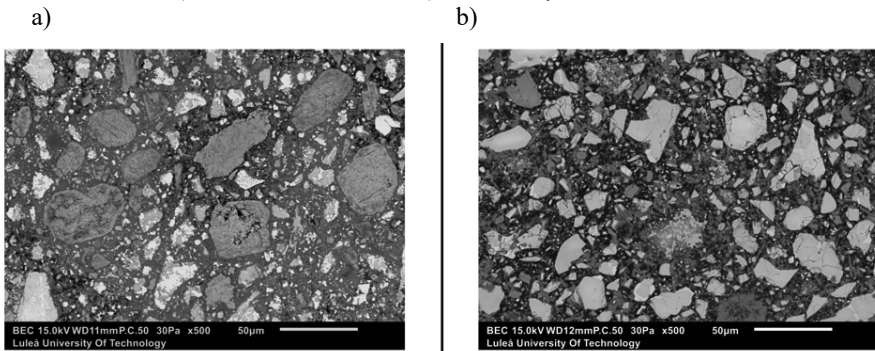
a)   b)

Figure 23. Effect of age on microstructure od CSA cements and CSA+OPC hybrid combinations. SEM images at 500X magnification of concretes based on hybrid OPC/CSA binder, a) 100 wt.% BELI b) 80 wt.% of OPC + 20 wt.% BELI
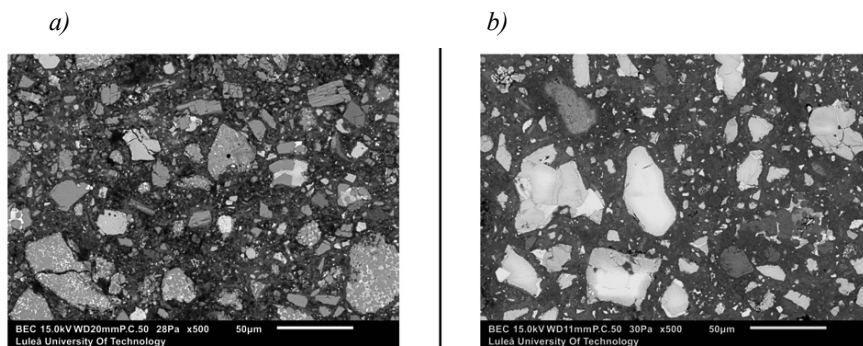
a)   b)

Figure 24. Effect of age on microstructure od CSA cements and CSA+OPC hybrid combinations. SEM images at 500X magnification of concretes based on hybrid OPC/CSA binder, a) 100 wt.% SR03, b) 80 wt.% of OPC + 20 wt.% SR03

The SEM-EDX spot analyses of hydrated binder matrixes were performed only on 4-month-old samples. Average atomic ratios, i.e., Ca/Si, Al/Ca and S/Ca are shown in Figure 25. The lowest Ca/Si atomic ratio of 3.6 was measured in OPC, which significantly higher than reported by others. Those studies indicated that Ca/Si ratios exceeding 1.5 indicate a presence of Portlandite, (A Cwirzen and Penttala 2005). The Portlandite could be either intermixed or located beneath the observed surface and thus unintentionally analyzed as C-S-H.

Hydrated binder matrixes, containing 20 wt.% of CSA and 80 wt.% of OPC, contained phases related to the hydration of both cements. Consequently, the Ca/Si ratio increased to 6-8 due to the simultaneous formation of C-S-H, portlandite, Ettringite, and Al(OH)$_3$. The exact contribution of each phase is unknown. However, several trends could be seen, i.e., higher amounts of C-S-H and Portlandite for binder containing BELI cement or increased Ca/Si ratio in mixes containing 20 wt.% of CSA cement.

The Al/Ca and S/Ca atomic ratios calculated for pure CSA cements, i.e., ALI, BELI and SR03, were higher in comparison with the hybrid binders containing CSA and OPC cements.
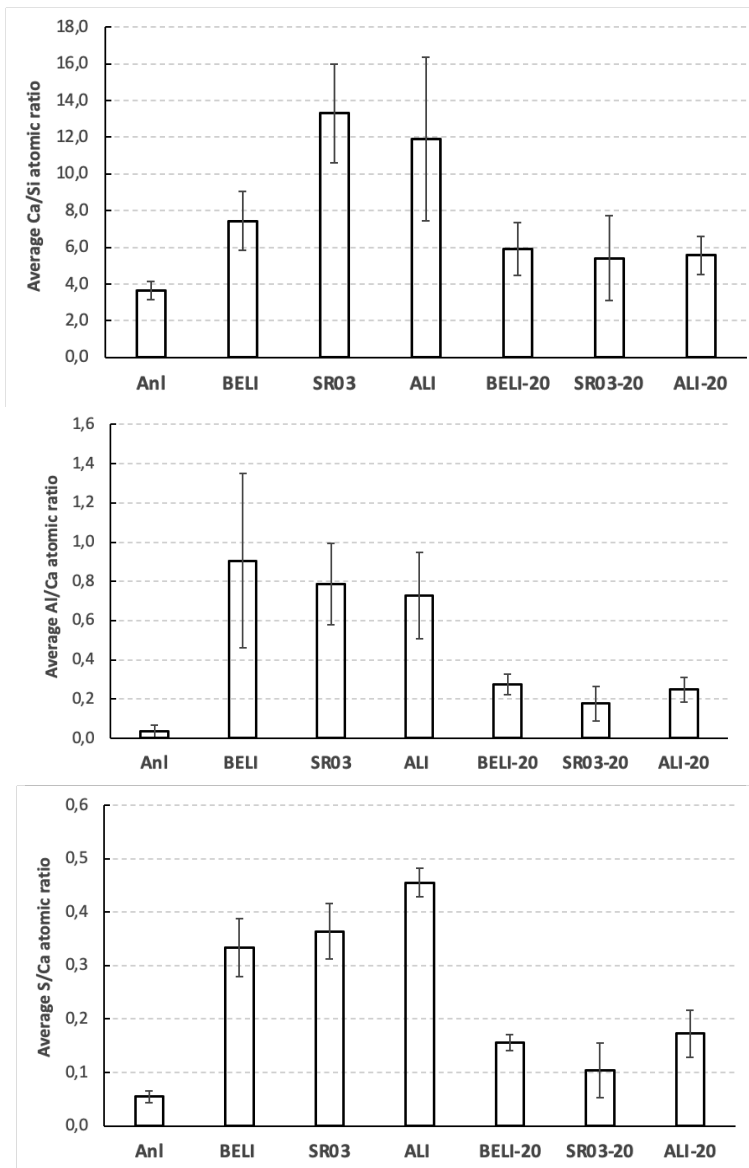
Figure 25. Average atomic ratios of EDX 4 months old pastes.

3.6   Mechanical properties

The determination of mechanical properties included measurements of the compressive strength using 10x10x10 cm^3 cubes after 1, 3, 7, 14 and 28 days of the standardized curing. The obtained results are summarized in Figure 26 for the 40 wt.% replacement and in Figure 27 for the 20 wt.% replacement. Mixes containing the higher amounts of CSA cements developed similar or higher compressive strengths than the OPC mix. Concretes containing 20 wt.% of CSA showed mixed results. For example, the one-day strength was the highest for the BELI cement and the lowest for the SR03 cement. The SR03 cement had a generally lower compressive strength measured after 1, 3 and 7 days when compared with the OPC mix. However, due to an unknown reason after 14 and 28 days the strength was similar. Furthermore, the same CSA cement produced the highest one-day strength when replacing 40 wt.% of the OPC. The obtained results did not indicate any strength regression up to the tested 28 days.

Despite these discrepancies the obtained results indicated that it is possible to replace up to 40 wt.% of OPC with CSA cements and to produce concrete mixes having similar compressive strengths and strength developments. The compressive strength can be assumed to increase also after 28 days similarly as observed earlier, e.g., Trauchessec et al measured increasing values even 100 days after casting, (R. Trauchessec et al. 2015). None of the earlier studies indicated the regression of the compressive strength with time.
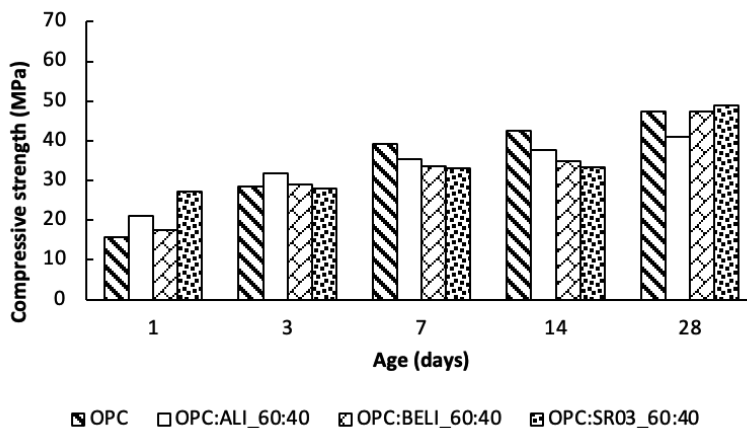

Figure 26. Compressive strength development of concretes based on hybrid binders containing 40wt.% of CSA and 60 wt.% of OPC.
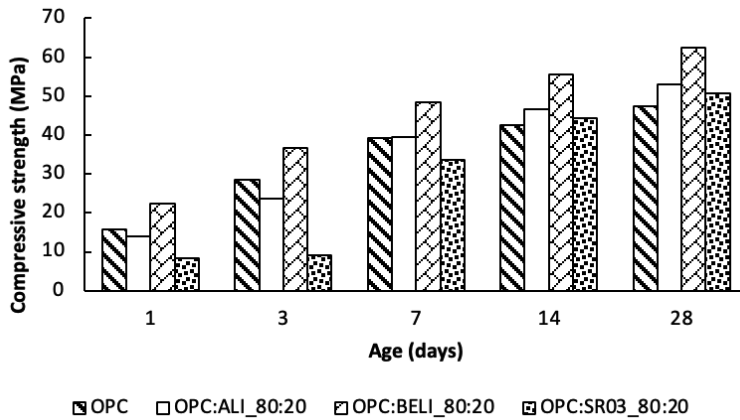
Figure 27. Compressive strength development of concretes based on hybrid binders containing 20wt.% of CSA and 80 wt.% of OPC.

3.7 Shrinkage

Shrinkage measurements started 24 hours after casting and were performed on specimens exposed to the laboratory environment without any additional protection. Therefore, the measured values correspond mostly to the drying shrinkage. The summary of the obtained results is shown in Figure 28. A slight expansion two days after casting was measured only for concretes containing Belite CSA (BELI), 74 μm/m and 29 μm/m for 40 and 20 wt.% replacement, respectively. Other concrete mixes developed only shrinkage. The maximum cumulative shrinkage measured after 28 days reached 420 μm/m for the OPC concrete, which is a relatively low value considering Portland cement-based concretes. Low calcium aluminate content and low specific surface area of that cement could be indicated as the main contributing factors. All mixes containing 20 wt.% of CSA cements showed higher-, while mixes with 40 wt.% replacement, lower- shrinkage values. The highest ultimate 28 days shrinkage reached 1200 μm/m and was measured for the concrete containing 20 wt.% of ALI CSA cement and the lowest, of only 78 μm/m, for the concrete containing 40 wt.% of Belite CSA (BELI).
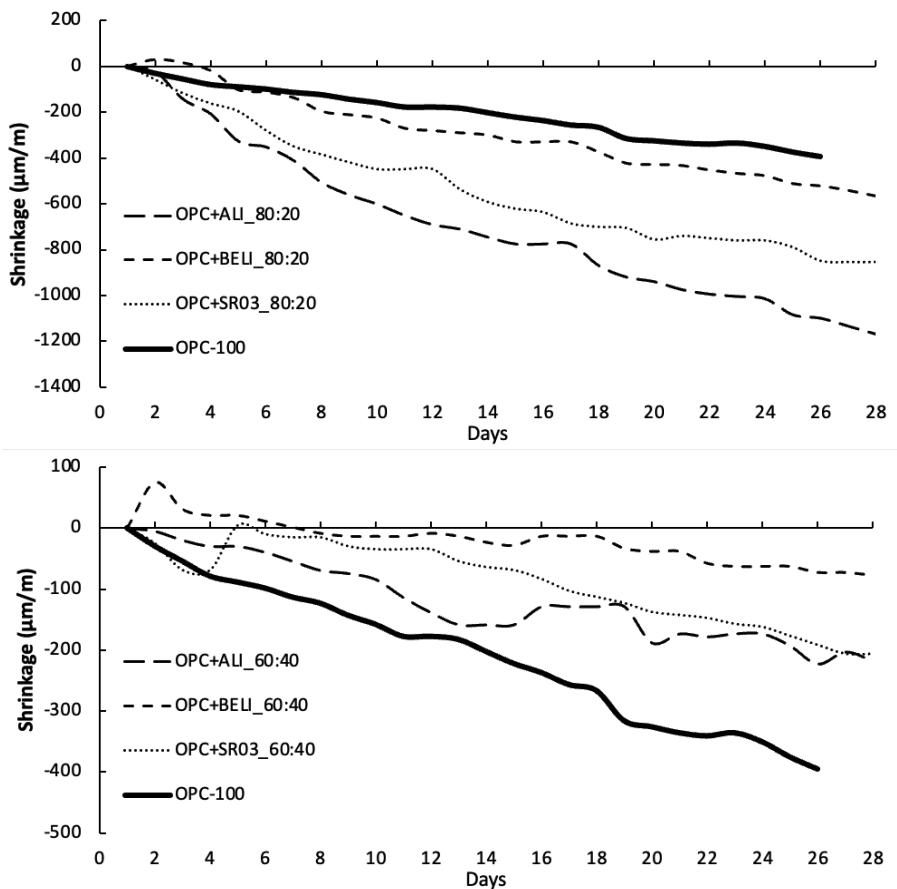
Figure 28. Total shrinkage

As described in the section 2.8, the autogenous shrinkage of CSA cements tends to be higher in comparison with OPC due to a rapid formation of ettringite after the initial setting. Later, the drying shrinkage appeared to be lower for these cements. Consequently, the recorded values corresponded mostly to the developing drying shrinkage. This could also explain the reduction of shrinkage measured in mixes containing 40 wt.% of CSA. The higher amount of CSA reduced the ultimate drying shrinkage, while the presumably higher autogenous shrinkage of these mixes was not recorded.

Summarizing, the obtained results indicate that CSA cements can significantly reduce the drying shrinkage of Portland cement-based concretes. In all studied cases the shrinkage was still developing after 28 days when the tests were stopped. This trend complies with the earlier studies that reported a continued development of the drying shrinkage after 90 days even in OPC based concretes, (Telesca et al. 2013).

4   SUSTAINABILITY AND ECONOMY

One of the main study aims was to evaluate the possible enhancement of a shotcrete sustainability through a partial replacement of OPC with CSA. The sustainability of concrete is affected by several factors, including CO_2 emissions related to cementitious binders or long-term performance and durability. Due to the limited resources and short duration of the project, the assessment of long-term performances and durability was based on the literature review, see Section 2.10. The calculation of CO_2 footprint was limited to cements only. The simplification was possible due to the usage of the same mix design.

The performed literature study indicated that the partial replacement of OPC with CSA cement can fully mitigate drying shrinkage and lower the crack risk of shotcrete. The loss of compressive strength due to an exposure to high temperatures and fire is lower. Both effects improve durability and enhance sustainability of concrete. Unfortunately, earlier studies also revealed several possible problems related durability. For example, the lower pH of pore solution could increase the risk of reinforcement corrosion. On the positive side, this risk appeared to be lower in comparison with ecological concretes containing OPC and limestone. Based on limited tests results, several studies also indicated a lower frost durability and the increased risk of a delayed ettringite formation in certain mixes containing CSA.

The described in this report, laboratory study showed a lower drying shrinkage of concretes containing 40 wt.% of CSA, while compressive strengths remained close to the reference OPC concrete. Microstructure was dense, homogenous and without the excessive microcracking of the binder matrix. Consequently, it could be assumed that durability, where the transport properties of a binder matrix is a key factor, should be enhanced or at least be similar to OPC concretes. Nevertheless, due to limited available data, the durability of OPC+CSA concretes should be studied in more details.

The CO_2 emission of all studied CSA cements was set as a constant value of 611 kg/t. This corresponds to a 30% reduction in comparison to the used in this research OPC (Anläggning cement), which emission is 873 kg/t, according with the producer declaration. The extend of the reduction was derived from the reviewed existing data. Therefore, the actual reduction could be higher, especially when SCMs would be used. The obtained results are shown in Table 11. The CO_2 emission of concrete based on the OPC and containing 430 kg/m^3 of the binder was estimated to reach 337 kg of CO_2/m^3. A partial replacement of the OPC with 20 and 40 wt.% of the CSA cements lowered this value by 14 and 28%, respectively.

The additional calculation of the CO_2 footprint was done for theoretical concrete mixes containing the new generation of an ecological OPC. An AnläggningFA cement was chosen, as being based on the OPC used in the performed laboratory tests. The CO_2 footprint of that cement was 680 kg/t, which is only 69 kg/t higher in comparison with the assumed emission of CSA cements used. The calculated reduction of CO_2 emissions of concretes containing 20 wt.% and 40 wt.% of were 12 and 25%, respectively, Table 12.

Table 11. The estimation of a total CO_2 footprint and its reduction as per m^3 of concrete, considering only the cementitious binders for Anlagning cement.

Mix	OPC (kg/m³)	OPC (kgCO₂/m³)	CSA - type	CSA (kg/m³)	CSA (kgCO₂/m³)	Total (kgCO₂/m³)	Reduction (%/m³)
OPC	430	337	Anl	0	0	337	0
OPC:BELI_80:20	344	269	BELI	82	19	290	-14
OPC:BELI_60:40	258	202	BELI	172	40	242	-28
OPC:ALI_80:20	344	269	ALI	82	19	290	-14
OPC:ALI_60:40	258	202	ALI	172	40	242	-28
OPC:SR03_80:20	344	269	SR03	82	19	289	-14
OPC:SR03_60:40	258	202	SR03	172	40	242	-28

Table 12. The estimation of a total CO_2 footprint and its reduction per m^3 of concrete, considering only the cementitious binders. For comparison substituting in calculations Anläggning OPC with an environmental OPC type Anläggning FA.

Mix	OPC (kg/m³)	OPC (kgCO₂/m³)	CSA - type	CSA (kg/m³)	CSA (kgCO₂/m³)	Total (kgCO₂/m³)	Reduction (%/m³)
OPC 1	430	292	Anl FA	0	0	292	0
OPC:BELI_80:20	344	234	BELI	86	23	256	-12
OPC:BELI_60:40	258	175	BELI	172	45	220	-25
OPC:ALI_80:20	344	234	ALI	86	23	256	-12
OPC:ALI_60:40	258	175	ALI	172	45	220	-25
OPC:SR03_80:20	344	234	SR03	86	23	256	-12
OPC:SR03_60:40	258	175	SR03	172	45	220	-25

The economic effects of using CSA cements in shotcrete were assessed by calculating the cost of binders, while the cost of remaining ingredients was excluded. The costs corresponded either to materials packed in 25 kg bags or delivered as in bulk. The prices for 25 kg bags were 1040 and 1430 €/t, for SR03 and ALI, respectively, Table 12. While the bulk price of the BELI cement was 443 €/t. The OPC price was 1100 and 150 €/t, for the 25kg bags and the bulk, respectively.

The total prices of test concretes were calculated also for these two types of packing/delivery methods, Table 13 and Table 14. Concretes containing 20 and 40 wt.% of CSA packed in 25 kg bags were either similar as OPC-based concretes or 6-12% more expansive. However, when considering the bulk prices, which are typically used in a concrete industry the cost of $1m^3$ of concrete containing 20 and 40 wt.% of CSA increased by 39 and 78%, respectively.

It must be emphasized that the final price of a shotcrete containing up to 40 wt.% of CSA would be significantly lower due to limited or excluded usage of certain chemical

admixtures, i.e., accelerators or shrinkage reducing admixtures. Certainly, a more extensive study is required to verify these effects and to determine the actual costs.

Table 13. Cement prices.

	Cement name	Type	Producer	Approximate Price €/tone *(incl. VAT)*	Price source
SR03	Next Base SR03	Belite-CSA	Buzzi Unicem Spa	1040	moertelshop.eu *(Packed in 25kg bags)*
ALI	ALI Cem	CSA	Heidelberg Zement	1430	moertelshop.eu *(Packed in 25kg bags)*
BELI	Belicem	Belite-CSA	Caltra	443	Caltra *(as bulk)*
OPC	Anläggnings cement	CEM I 42,5N-SR	Cementa AB	1100	Beijer AB *(packed in 25kg bags)*
				150	Cementa AB *(as bulk)*

Table 14. Cost comparison per m³ of concrete considering only cementitious binders which prices corresponds to the cements packed in 25kg bags.

Mix	OPC (kg/m³)	Price (€/m³)	CSA-type	CSA (kg/m³)	Price (€/m³)	Total price (€/m³)	Difference (%)
OPC	430	473		0	0	473	0
OPC:ALI_80:20	344	378	ALI	86	123	501	+6
OPC:ALI_60:40	258	284	ALI	172	246	530	+12
OPC:SR03_80:20	344	378	SR03	86	89	468	-1
OPC:SR03_60:40	258	284	SR03	172	179	463	-2

Table 15. Cost comparison per m³ of concrete considering only cementitious binders which prices correspond to the prices for the bulk cement.

Mix	OPC (kg/m³)	Price (€/m³)	CSA-type	CSA (kg/m³)	Price (€/m³)	Total price (€/m³)	Difference (%)
OPC	430	65		0	0	65	0
OPC:BELI_80:20	344	52	BELI	86	38	90	+39
OPC:BELI_60:40	258	39	BELI	172	76	115	+78

5   CONCLUSIONS

Generally, the performed pre-study showed a significant potential of CSA cements when used as the partial replacement of OPC for shotcrete and for other applications. The main conclusions formulated after the literature review (WP1) and laboratory studies (WP2, WP3) are summarized in the following two subsections.

5.1   Literature review

The literature study enabled to determine the main limitations and advantages of CSA cements when used as partial and full replacement of OPC in concrete.

Advantages in comparison with OPC based concretes:

- Possibility to control the final fresh and hardened concrete properties, as well as the hydration/hardening processes by the amount of the added anhydrite
- Over 30% reduction of CO_2 footprint when compared to OPC
- Shorter initial and final setting times
- Very fast strength development after shotcreting, reaching >20 MPa in one hour
- Improved adhesion bond between substrate and shotcrete, reaching 10 MPa, enabling shotcreting of thicker layers
- Possibility to fully mitigate drying shrinkage by the partial replacement of OPC with CSA.
- Lower crack risk of shotcrete
- Less rebound while shotcreting
- Higher strength development when cured at subfreezing temperatures
- Lower freezing temperature and possibility to exclude additional treatments when casting at -5°C
- Lower drying creep

Disadvantages in comparison with OPC based concretes:

- Higher price compared to OPC
- Strong dependence of fresh and hardened concrete properties on the amount of added gypsum, which in addition to potential benefits can also cause problems if not handled properly
- Limited availability of raw materials containing aluminum
- Lower pH of the pore solution
- Lower strength when exposed to high temperatures
- Possibly a slightly higher risk of reinforcement corrosion in concretes containing only CSA cement, but lower in comparison with ecological concretes containing OPC with limestone.
- Possibly worse frost durability of some mixes containing CSA (limited test results).
- Possibly increased risk of the delayed Ettringite formation (limited available data).

5.2   Laboratory study

The laboratory study was performed on three commercially available CSA cements and on one Swedish Portland cement. The studied CSA cements were unavailable in Sweden at the time of preparing this report and were obtained from Germany and Netherlands through regular purchase channels. The test program aimed to determine various effects when partially replacing OPC with CSA. Two replacement levels were used, i.e., 20 and 40 wt.%. The chosen concrete mix design represents an average industrial concrete. The binder content was 430 kg/m^3 and the water to cement ratio was 0,5. Granite aggregates and natural fine fillers were used in combination with a polycarboxylate based superplasticizer, which provided an adequate workability.

The obtained laboratory tests results can be summarized as:

- Partial replacement of OPC with CSA cement shortened the initial setting time significantly, in the most extreme case from 187 minutes (for OPC) to 4 minutes (for mix containing 40 wt.% of CSA BELI cement)
- The compressive maximum strength and the compressive strength development were comparable between all tested binder combinations.
- The drying shrinkage was reduced by up to 80% when 40 wt.% of OPC was replaced with CSA BELI cement.
- On the contrary the shrinkage increased by up to 178% when 20 wt.% of OPC was replaced with CSA ALI cement.
- The microstructure of the solidified binder matrixes appeared to be dense and homogenous for all concretes containing CSA cements. No enhanced macrocracking or ITZ having increased porosity were observed.
- The CO$_2$ footprint of concretes containing CSA cements was reduced by up to 28%
- Costs for replacing OPC with CSA cement varied between an increase by 78% and a reduction by 24%.

6   FUTURE RESEARCH AND OPEN QUESTIONS

The performed literature study revealed several advantages of using CSA as a partial replacement of OPC in shotcrete and in normal concrete. The limited laboratory study confirmed most of trends observed by others. Both indicate several areas, which require more detailed investigation, especially related to local Swedish conditions. The most important open questions include:

- How autogenous shrinkage develops in the first minutes after shotcreting?
- How shotcreting conditions affect shrinkage?
- What is the risk of cracking in various conditions and for different binder combinations?
- How CSA influences fresh concrete properties, which are specific for shotcreting, e.g., rebound, dusting, bond strength with substrate, maximum layer thickness?
- Is it possible to delay setting after mixing and before shotcreting operation?
- Is it possible, technologically, and logistically, for the contractor to add anhydrite on-site?
- How addition of various fibers affects properties of CSA/OPC concretes?
- How the partial replacement of OPC with CSA affects durability structure, especially including frost, fire, carbonation, chloride penetration, reinforcement corrosion, alkali silica reaction?
- Is it possible to produce shotcrete incorporating OPC+CSA and certain industrial and communal wastes to reduce its price and to enhance sustainability?
- What are advantages and possible problems (application technology, sustainability, price, and durability) related to the usage of SCMs in OPC+CSA systems.

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7   REFERENCES

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