Synthesis and characterization of calcium sulfoaluminate cements produced by different chemical gypsums

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Abstract

Calcium sulfoaluminate (CSA) cements show some desirable environmentally friendly features which include the possibility of using several industrial byproducts as raw materials in their manufacturing process. Four chemical gypsums (flue-gas desulphurization gypsum, fluorogypsum, phosphogypsum and titanogypsum) have proved to be suitable as total substitutes for natural gypsum (NG) in the raw meal. Mixtures based on limestone, bauxite, NG or one of the $\text{C}\bar{\text{S}}$ -rich by-products were heated in a laboratory electric oven from 1150° to 1300°C. The reactivity of raw mixtures to form clinker products was evaluated using X-ray diffraction (XRD) analysis. The raw mixtures containing industrial gypsum displayed better reactivity towards $\text{C}_4\text{A}_3\bar{\text{S}}$ than mixture made with natural gypsum. Moreover, conduction calorimetric measurements associated with XRD and differential thermal-thermogravimetric analyses showed that all CSA cements, obtained by adding commercial anhydrite to clinkers produced at the optimum synthesis temperatures, have similar hydration products but with different hydration kinetics.

Introduction

Portland cement (PC) production is one of the most energy-intensive processes in common use. In 2015, cement production was about 4.5 Gt (Activity Report, 2015; Shen and Qian, 2015) and contributed for about 7% of the global human atmospheric CO₂ emission; about 0.87 kg of CO₂ are generated per each kg of PC clinker produced (WBSCD, 2009), due to both limestone decomposition (about 60% of the total CO₂ emission) and fuel combustion (mainly fossil) (Xu, 2015) during pyro-processing the clinker-generating raw mixture. With increased awareness of carbon dioxide emissions from cement production, the main challenge of the cement industry is focused on reducing the carbon footprint to 1.55 Gt per year (about –45% of the current value) by 2050 (Barcelo, 2014). To this end, both cement industry and research community are stimulated to develop low-CO₂ alternatives to PCs (Buzzi et al., 2010; Gartner and Macphee, 2011; Juenger et al., 2011; Gartner and Hirao, 2015). Thus, there is a strong interest in calcium sulfoaluminate (CSA) cement due to both its many potential valuable technical properties as well as pronounced environmental benefits.

The most important technical properties of CSA cement (e.g. high early strength, rapid setting, shrinkage compensating (Glasser and Zhang, 2001; Bernardo et al., 2006; Winnefeld and Lothenbach, 2010; Chen et al., 2012A; Valenti et al., 2012; Bizzozero et al., 2014; Telesca et al., 2014) and resistance against several aggressive media (Bianchi et al., 2009)) are mainly regulated by formation of ettringite ($C_6A\bar{S}_3H_{32}$) originating from the hydration of $C_4A_3\bar{S}$ (the key-component of CSA cements) and calcium sulfates (as part of the clinker and/or added to the clinker). Besides these compounds, C_2S , $C_5S_2\bar{S}$, various calcium aluminates ($C_{12}A_7$, C_3A , CA , C_4AF , C_2AS , CAS_2) or lime can occur in CSA cements, depending on the synthesis temperature as well as the nature and proportioning of raw materials (typically limestone, bauxite and gypsum or anhydrite).

Compared to PC, CSA cement manufacturing process displays four major environmentally friendly features, namely: (1) reduced limestone requirement (about 60% less), therefore lowered kiln thermal input, and CO₂ generation, (2) clinkers obtainable at lower synthesis temperatures (about 150°-200°C less) and more friable (lower grinding energy required), (3) larger clinker dilutions with calcium

sulfate additions (as gypsum or anhydrite (Sahu et al., 1991, Hargis et al., 2014)), and (4) greater usability of industrial byproducts as kiln feed components (e.g. coal fly ash, flue gas desulphurization gypsum, fluidized bed residues, blast furnace slags, red mud, alumina powder, anodization mud, fertilizer plant wastes, municipal solid waste incineration fly ash, calcium looping spent sorbents, (Sahu et al., 1994; Palou and Majling, 1995, Singh et al., 1996; Arjunan et al., 1999; Adolfsson et al., 2007; Singh et al., 2008; Luz et al., 2009; Marroccoli et al., 2009 and 2010; Selçuk et al. 2010; Pace et al., 2011; Wu et al., 2011; Chen and Juenger, 2012b; Shen and Qian, 2015; Telesca et al., 2015a; Telesca et al., 2016; Xu et al., 2017).

In the title paper, four different chemical gypsums, namely flue gas desulphurization gypsum, fluorogypsum, phosphogypsum and titanogypsum, were separately used to replace calcium sulfate in the raw meal. Different laboratory-made CSA clinkers, obtained at temperatures ranging from 1150°C to 1300°C, were investigated by using X-ray diffraction (XRD) analysis as the main characterization technique. A reference mixture based on limestone, bauxite and natural gypsum underwent the same thermal treatments. The hydration behaviour of five CSA cements, obtained by adding a commercial anhydrite to CSA clinkers produced at the optimum synthesis temperatures, were investigated for curing times ranging from 4 hours to 28 days by means of conduction calorimetry linked to XRD and differential thermal-thermogravimetric analyses (DT-TG). Thermodynamic modelling using the geochemical GEMS-PSI software was used to predict the kind and amount of hydrates depending on the quantity of anhydrite added to the CSA clinker as previously established for CSA cements (Winnefeld and Lothenbach, 2011; Pelletier-Chaignat et al., 2012; Martin et al., 2015; Martin et al, 2017; Winnefeld et al., 2017).

2. Materials and methods

2.1. Raw materials and proportioning of CSA-clinker generating raw mixtures

The chemical composition of limestone (L), bauxite (B), gypsum (G) and industrial by-products, namely flue gas desulphurization gypsum (D), fluorogypsum (F), phosphogypsum (P) and

titanogypsum (T), used in the title study are presented in Table 1. Five mixtures (MR, MD, MF, MP and MT), having the composition shown in Table 2, were investigated: the first, MR, used as a reference, was based only on natural materials; the others (indicated with the same symbols of the included industrial by-products) separately contained, D, F, P, and T as total natural gypsum replacement, respectively. The proportioning of the raw mixtures was determined assuming that SO_3 and Al_2O_3 on the one hand, and SiO_2 , on the other hand, react to give only $\text{C}_4\text{A}_3\bar{\text{S}}$ and C_2S (the main constituents of CSA clinker) respectively, and supposing also that solid solution effects were absent. The alumina and silica amounts were the stoichiometric contents required for the synthesis of the above-mentioned phases. In order to hinder the calcium sulfoaluminate decomposition, the sulfur content was twice the stoichiometric amount needed for its formation; the residual calcium sulfate can therefore be available for the formation of $\text{C}_5\text{S}_2\bar{\text{S}}$ (at the expense of C_2S and stable until almost 1300°C , Sherman and Beretka, 1990), and/or $\text{C}_9\text{S}_3\bar{\text{S}}_3\text{-CaF}_2$ (when F is present) as well as CSA cement hydration. The theoretical $\text{C}_4\text{A}_3\bar{\text{S}}$ content of the five mixtures is reported in Table 3.

2.2. Burning of raw mixtures

Four 100 g batches of each clinker generating raw mixture were heated in an open tubular static electric oven for 2 hours at 1150° , 1200° , 1250° and 1300°C , respectively, with an accuracy of $\pm 2^\circ\text{C}$. The resulting CSA clinkers (comprised in the range 65-70 g) were finely ground in a Fritsch Pulverisette 6 (FP6) laboratory planetary mill (rotation speed 100 to 650 rpm, grinding bowl with a 500 ml capacity and silicon-nitride internal covered) to pass a $90\ \mu\text{m}$ sieve and characterized by XRD analysis in order to completeness of reaction and influence of the gypsum source.

2.3. Preparation of CSA cements

CSA cements were prepared by grinding the CSA clinkers with a commercial anhydrite (containing 96.6% by mass of CS) in the FP6 laboratory mill to pass the $90\ \mu\text{m}$ sieve. Clinker specific surfaces

according to EN 196-6 were in the range $4600 \pm 50 \text{ cm}^2/\text{g}$. The addition of anhydrite was based on attaining an M-value (moles $\text{C}\bar{\text{S}}$ / moles $\text{C}_4\text{A}_3\bar{\text{S}}$) of 1.4 for all the five cements; their mix design is summarized in Table 5. In particular, M-values lower than 1.5 are typical for CSA cements characterized by rapid setting and hardening properties (Zhang et al., 1994; Zhang et al., 1999). The CSA cements derived from the corresponding synthetic clinkers were denoted with the same symbols used for their generating raw mixtures (CEM_R, CEM_D, CEM_F, CEM_P and CEM_T).

2.4. Hydration experiments

CSA cement pastes were prepared with a 0.70 water/solid mass ratio, then cast into 15-mm-high and 30-mm-diameter cylindrical molds, and finally placed in polyethylene bags inside a thermostatic bath (at 20°C and 95% relative humidity) for curing times ranging from 4 hours to 28 days. At the end of each aging period, the specimens were crushed. Hydration was stopped by solvent exchange using first acetone and then diethyl ether. The pulverized samples were subsequently stored in a desiccator over silica gel and soda lime (to ensure protection against H_2O and CO_2) prior to further characterization.

2.5. Characterization techniques

2.5.1. X-ray fluorescence (XRF) analysis

XRF analysis was used for the determination of both the chemical composition of the raw materials and the CSA clinkers heated at the best synthesis temperatures. For the raw materials an energy dispersive BRUKER Explorer S4 apparatus (maximum power=1 kW; LiF200, PET, OVO-55, OVO-B as analyzing crystals) was employed. The CSA clinkers were analyzed according to EN 196-2 and ISO 12677 using fused beads. Loss on ignition was determined according to EN 196-2, and CO_2 content was quantified by combustion analyses using a C/S analyzer.

2.5.2 XRD analysis

XRD analyses were performed for the determination of the mineralogical composition of both the CSA clinkers and the hydrated cement pastes.

The CSA clinkers were ground for 30 min in isopropanol using a McCrone micronizing mill. A Panalytical X'Pert Pro instrument in a Θ - Θ configuration using $\text{CoK}\alpha$ -radiation and the X'Celerator detector was used. The samples were scanned at a step size of $0.017^\circ 2\Theta$ for 45 minutes between 5° and $90^\circ 2\Theta$. Rietveld refinement of the XRD patterns was performed using X'Pert Highscore plus V. 4.7 according to the procedure previously published (Pelletier-Chaignat et al., 2011; Le Saoût et al., 2013; Winnefeld et al.; 2017). For the refinements, the crystal structures suggested by Snellings (2015) were used with the exception that recently published structures for orthorhombic and cubic ye'elimite (Cuesta et al., 2013; Cuesta et al., 2014) were applied.

For the hydrated pastes a Rigaku Miniflex 600 ($\text{CuK}\alpha$ radiation and $0.02^\circ 2\Theta \text{ s}^{-1}$ scanning rate) was used. The samples were scanned at a step size of $0.02^\circ 2\Theta$ for 27.5 minutes between 5° and $60^\circ 2\Theta$.

2.5.3. Isothermal calorimetry

Isothermal conduction calorimetry was performed at 20°C using a Thermometric TAM Air equipped with admix ampoules (Wadsö, 2005) which allow to follow the hydration heat flow from the very beginning. After thermal equilibration 2.86 g of binder were mixed in-situ with 2.00 g water and stirred for 1 minute. The hydration heat flow was monitored for 168 h and integrated to determine heat of hydration.

2.5.4. Simultaneous DT-TG analysis

Simultaneous DT–TG analysis was carried out with a Netzsch Tasc 414/3 apparatus operating in the temperature range $20^\circ\text{--}1000^\circ\text{C}$, with a heating rate of $10^\circ\text{C min}^{-1}$ in 150 μL alumina crucibles. TG analysis was also used for the quantitative determination of ettringite, assuming that 24 water moles were lost by heating 1 mole of ettringite in the narrow temperature range corresponding to its strong endothermal effect (Richardson and Taylor, 2017).

2.6 Thermodynamic modelling

Geochemical modelling was used to predict the kind and amount of hydrates depending on the dissolution of the anhydrous phases. The geochemical GEMS-PSI software (Wagner et al., 2012; Kulik et al., 2013) was used together with the Nagra/PSI database (Hummel et al., 2002) and the cement-specific database CEMDATA18 recently published (Lothenbach et al., 2018). The volumes of hydrates formed upon hydration of the CSA clinkers blended with different (0–30 mass-%) amounts of anhydrite were calculated. The phase composition of the clinker as determined by quantitative XRD was used as input. For the various clinker phases reasonable hydration degrees were assumed based on literature data referring to a sample age of 28 d. Ye'elimite and mayenite were assumed to have reacted completely, for fluorellestadite a reaction degree of 60%, and for belite, ternesite and gehlenite reaction degrees of 30% (Bullerjahn et al., 2015; Martin et al., 2017; Winnefeld et al., 2017). Anhydrite was assumed to be 100% CaSO_4 and allowed to react completely. All other phases were assumed to be inert. The same water/cement ratio of 0.70 was applied as in the experiments.

3. Results and discussion

3.1 Synthesis of CSA clinkers

From an overall examination of the XRD data about the synthetic CSA clinkers it can be drawn that, at every investigated temperature, the conversion of reactants is complete and $\text{C}_4\text{A}_3\bar{\text{S}}$ is the main burning product as highlighted in a preliminary study (Telesca et al., 2015b); in particular, the best results were obtained at 1250°C for MR and MP (Cli_MR and Cli_MP), and at 1300°C for MB, MF and MT (Cli_MB, Cli_MF and Cli_MT). Furthermore, as secondary components, anhydrite $\text{C}\bar{\text{S}}$, sulfo spurrite (ternesite, $\text{C}_5\text{S}_2\bar{\text{S}}$) and gehlenite (C_2AS) are the most important phases encountered in all the clinkers while fluorellestadite was detected only in Cli-MF and Cli-MP in agreement with the significant fluorine contents detected by XRF. Finally, C_2S was observed as minor component together with perovskite and mayenite.

Table 4 reports both the chemical composition (in terms of main oxides) and phase contents of CSA clinkers heated at their best synthesis temperature. As far as the most hydraulically reactive phases are concerned, with the exception of Cli_MP (containing 57 mass-% ye'elimite), the others are approximately composed of 65% by mass of $C_4A_3\bar{S}$. Moreover, the silica present in the CSA-clinker generating raw mixes was more prone to form ternesite (due to the presence of an excess of $C\bar{S}$) and gehlenite instead of belite (Shen et al., 2015). Additionally, the lower amount of total sulfates for Cli_MT and Cli_MF was due to the volatilization of part of SO_3 .

3.2 Isothermal calorimetry

Isothermal calorimetry of CSA cements is often complex with several heat flow maxima, especially when the dissolution kinetics of the calcium sulfate are rather low or other phases are present (Palou and Majling, 1996, Winnefeld and Barlag 2009, Winnefeld and Barlag, 2010). As expected the cements investigated in this study also show this complex behavior, probably partly caused by the presence of two different types of anhydrite (the anhydrite as part of the clinker phase assemblage and the anhydrite blended with the clinker). However, in general the hydration heat flow is characterized by three main maxima, (i) an initial peak occurring in the first 15 – 30 minutes of hydration (Figure 1a), (ii) a second maximum between 1.25 h (CEM_F) and 28 h (CEM_T) and (iii) a third maximum between 6 h (CEM_F) and 40 h (CEM_T) (Figure 1b). Besides, depending on the cement, various smaller maxima or shoulders occur. From isothermal calorimetry it cannot be directly concluded if the maxima are associated with ettringite or monosulfate formation. Often, the third maximum can be associated with monosulfate formation after depletion of the calcium sulfate (Winnefeld and Barlag, 2009; Winnefeld and Barlag, 2010). However as two different types of calcium sulfate are present in the investigated cements also slowed down and afterwards renewed ettringite formation might be the reason for the second and third maxima (Gay, 1965).

The initial peak of CEM_R containing the clinker prepared using natural gypsum shows the lowest heat flow during the first two hours (Figure 1a), while all the cements prepared from clinkers

containing waste gypsum show a slightly (CEM_P) or significant higher (all other cements) heat flow during the first 2 hours. This indicates that the clinkers made from waste gypsum show a higher initial reactivity than the reference clinker. The occurrence of the 2nd and the 3rd main maxima also depends strongly on the origin of the clinker. The reference cement exhibits the 2nd maximum after 4 h and the 3rd maximum after 9 h. With one exception (CEM_T) the cements made from clinkers with waste gypsum have faster hydration kinetics than the reference cement. 2nd and 3rd maximum for CEM_F are 1.25 h and 6 h, for CEM_P 3.5 h and 8 h, and for CEM_D 4 h and 13 h. The cements with the earliest 2nd maxima are the 2 cements made from clinkers containing fluorine (CLI_MF, CLI_MP, see Table 4). Those clinkers contain fluorellestadite and no (CLI_MF) or only a small amount of ternesite (CLI_MP). Among all cements, CEM_F contains the lowest amount of anhydrite in the clinker, and thus the highest amount of added anhydrite, which could explain that this cement exhibits the fastest hydration kinetics. The slow hydration kinetics of cement CEM_T currently cannot be explained.

The different hydration kinetics of the studied cements is also mirrored by the cumulative heat of hydration (Figure 2). The reference cement CEM_R and CEM_P show the lowest heat of hydration after 7 d (319 J/g resp. 325 J/g), while the heat of hydration of the other three cements is around 430 J/g after 7 d.

3.3 Hydrate assemblage

Figure 3 displays the DT thermograms for the five CSA cements cured for times ranging from 4 hours to 28 days. With DT-TG temperature increase, ettringite and aluminium hydroxide were observed through the dehydration endothermal peaks at $158^{\circ}\pm 8^{\circ}\text{C}$ and $287^{\circ}\pm 8^{\circ}\text{C}$, respectively; no significant effects were recorded above 300°C .

From an overall examination of the DT-TG results it can be argued that ettringite and aluminum hydroxide are detected at all the curing periods, except CEM_F and CEM_T, where significant

amounts of AH_3 are detected only after 24 hours of curing; moreover, both ettringite and aluminium hydroxide formation increased with the increasing cure time.

Ettringite concentration (normalized to 100 g anhydrous CSA cement) vs. curing time for the five hydrating systems is displayed in Figure 4. In terms of ettringite-generating ability, the following sequence is observed: $\text{CEM_T} \sim \text{CEM_F} > \text{CEM_D} \sim \text{CEM_R} > \text{CEM_P}$; as expected, the lowest amounts of ettringite are produced when less $\text{C}_4\text{A}_3\bar{\text{S}}$ is available (see CEM_P).

The hydration rate of ye'elimite was also reflected in the amount of bound water, as obtained from TG analyses (Figure 5). As already seen in Figure 4, all systems display a similar trend in terms of formation of ettringite. With the exception of CEM_P , all reach comparable bound water contents after 28 days. AFm phases such as monosulfate and strätlingite could not be clearly detected due to overlaps of the signals in the TG.

The hydration process was also investigated by means of XRD analysis (Figure 5) which allows detecting the consumption of reactants, the presence of inert phases and the development of ettringite. The absence of AH_3 among the crystalline phases detected through XRD analysis is related to its amorphous nature (Marroccoli M. *et al.*, 2007). As for the DT–TG thermograms, a high similarity was observed among the XRD patterns of the hydrated CSA cements. Together with ettringite, peaks for monosulfate (not detected through DT-TG analysis, as its peak is overlapped by that of ettringite) as well as unconsumed reactants such as ye'elimite, anhydrite and gehlenite (only in CEM_F , CEM_P and CEM_T), fluorellestadite (only in CEM_F and CEM_P) and ternesite (only in CEM_R , CEM_D and CEM_T), were present.

3.4 Thermodynamic modelling

Figure 7a shows the calculated hydrate assemblages of clinker Cli_R blended with different amounts of anhydrite. The composition chosen for CEM_R is labelled. Without added anhydrite, ettringite is the main hydration product. Besides, the presence of monosulfate, microcrystalline aluminum hydroxide and strätlingite is calculated. The latter phase is formed from the hydration of the silica

bearing phases (belite, ternesite and fluorellestadite). With increasing addition of anhydrite, ettringite content increases on the expenses of monosulfate. When about 12 mass-% of anhydrite are present, C-S-H is predicted to form on the expenses of strätlingite. Beyond 16 mass-% of anhydrite, excess calcium sulfate remains, while strätlingite is no longer stable. This is in line with previous calculations, showing that strätlingite is not stable in the presence of calcium sulfate (Winnefeld and Lothenbach, 2016).

Figure 7b shows the hydrate assemblages of clinker Cli_T blended with calcium sulfate as an example for the clinkers synthesized with waste gypsum (in this case titanogypsum). As this clinker contains significantly less anhydrite compared to clinker Cli_R (6.3 and 13.0, respectively), plain Cli_T yields less ettringite and more monosulfate than Cli_R. Thus, more anhydrite needs to be added to achieve a hydrate assemblage with a molar ratio anhydrite / ye'elimite of 1.4 compared to Cli_R. Strätlingite occurs up to 22 mass-% of anhydrite addition, and small quantities of C-S-H are predicted to develop at anhydrite addition above 20 mass-%. Surplus gypsum remains at an anhydrite content exceeding 22 mass-%.

The modelling indicates the presence of monosulfate and strätlingite in both hydrated cements, however those phases could not be unambiguously identified by either by XRD nor by TG as (i) hydration degrees of the anhydrous phases might be lower than the assumptions made in the thermodynamic modelling (see 2.6), and (ii) identification of strätlingite has certain detection limits in TG (due to overlap with other AFm-phases) and (iii) by XRD (due to its low crystallinity).

4. Conclusions

It has been found that chemical gypsums (flue gas desulphurization gypsum, D, fluorogypsum, F, phosphogypsum, P, and titanogypsum, T) can be successfully employed as substitutes for natural gypsum in CSA clinker-generating raw mixtures. In terms of selectivity of reactants towards $C_4A_3\bar{S}$ formation, the best results are exhibited by raw meals based on D, F and T heated at 1300°C (Cli_D, Cli_F, Cli_T).

Outcomes from isothermal calorimetry up to 7 days indicate that, with the exception of CEM_T (Cli_T + anhydrite), CSA cements obtained from waste gypsum-based clinkers display faster hydration kinetics than the reference cement, and CEM_D, CEM_F and CEM_T show the highest heat of hydration among the investigated cements. As far as the ettringite-generating ability is concerned, DT-TG results on the specimens in question reveal an almost analogous tendency; once again, at the longest investigated curing periods CEM_T, CEM_F and CEM D exhibit the highest ettringite concentration. Thermodynamic modelling shows that similar hydrate assemblages in the different CSA cements can be achieved when the anhydrite contained in the clinker is included when adjusting the calcium sulfate addition. Thus, using waste gypsum instead of natural gypsum in the synthesis of CSA clinker is a suitable possibility to enhance CSA reaction kinetics without significantly changing the hydrate assemblage.

Despite all cements having been prepared in the same way, they behave differently upon hydration, which shows that the phase composition of the calcium sulfate source used to make the clinker strongly influences phase composition and hydration kinetics. More detailed and quantitative analyses of clinker phase dissolution rate, hydrate phase compositions and pore solution chemistry at various hydration times would be needed to unravel the underlying mechanisms.

4. References

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Table 1 Chemical composition of natural materials and industrial wastes, mass %

	<i>L</i>	<i>B</i>	<i>G</i>	<i>D</i>	<i>F</i>	<i>P</i>	<i>T</i>
<i>CaO</i>	55.2	-	30.1	31.9	37.2	32.6	31.7
<i>SiO₂</i>	-	5.9	3.0	3.3	0.5	0.1	0.1
<i>Al₂O₃</i>	-	50.0	0.8	1.0	0.4	0.1	0.5
<i>Fe₂O₃</i>	-	5.7	0.2	0.3	0.1	-	0.1
<i>MgO</i>	-	-	3.7	3.8	-	-	0.4
<i>TiO₂</i>	-	2.3	-	0.1	-	-	-
<i>SO₃</i>	-	-	36.2	36.9	54.0	45.4	44.5
<i>P₂O₅</i>	-	0.1	-	-	-	0.6	-
<i>l.o.i.*</i>	42.6	33.6	24.6	22.4	5.7	19.9	22.4
<i>Total</i>	97.8	97.6	98.6	99.7	97.9	98.7	99.7

**loss on ignition at 950°C, according to EN 196-2 Standard for cements*

Table 2 Composition of raw mixtures, mass %

<i>Mixture</i>	<i>MR</i>	<i>MD</i>	<i>MF</i>	<i>MP</i>	<i>MT</i>
<i>L</i>	29.3	29.1	32.4	30.3	30.4
<i>B</i>	41.1	41.5	45.5	44.2	43.9
<i>G</i>	29.6	-	-	-	-
<i>D</i>	-	29.4	-	-	-
<i>F</i>	-	-	22.1	-	-
<i>P</i>	-	-	-	25.5	-
<i>T</i>	-	-	-	-	25.7

Table 3: Potential contents of $C_4A_3\bar{S}$ in the CSA cement clinkers, mass %

<i>Mixture</i>	<i>Cli_MR</i>	<i>Cli_MD</i>	<i>Cli_MF</i>	<i>Cli_MP</i>	<i>Cli_MT</i>
$C_4A_3\bar{S}$	62.6	62.8	65.8	65.4	66.9

Table 4: Chemical (a) and mineralogical (b) composition of CSA clinkers, mass %, heated at the optimum synthesis temperature (OST)

(a)	Cl _i _MR	Cl _i _MD	Cl _i _MF	Cl _i _MP	Cl _i _MT
OST	1250°C	1300°C	1300°C	1250°C	1300°C
CaO	38.56	40.56	40.31	39.33	39.83
SiO ₂	7.70	7.07	7.73	7.60	7.92
Al ₂ O ₃	30.90	28.58	32.10	31.82	32.07
Fe ₂ O ₃	2.00	1.83	2.10	2.03	2.03
TiO ₂	1.49	1.37	1.45	1.44	1.66
MgO	1.36	0.55	0.57	0.60	0.57
SO ₃	16.15	18.39	14.24	15.55	14.38
Na ₂ O	0.15	0.14	0.14	0.16	0.17
K ₂ O	0.28	0.16	0.17	0.17	0.18
P ₂ O ₅	0.09	0.09	0.10	0.26	0.10
Cr ₂ O ₃	0.06	0.05	0.06	0.06	0.06
SrO	0.19	0.05	0.05	0.06	0.06
BaO	0.01	0.02	0.01	0.01	-
F	0.06	0.07	0.35	0.19	0.07
L.O.I.	0.97	1.04	0.820	0.790	0.83
(b)					
C ₄ A ₃ $\bar{S}$ orthorhombic	15.4	16.1	19.4	18.0	19.5
C ₄ A ₃ $\bar{S}$ cubic	44.9	50.4	46.9	39.0	48.0
C ₁₂ A ₇	0.6	0.4	0.4	0.3	0.4
C ₂ S	2.9	2.7	3.1	1.2	2.4
C ₂ AS	8.0	4.5	9.6	18.0	10.3
C ₅ S ₂ $\bar{S}$	11.5	12.7	-	2.7	9.7
C ₉ S ₃ $\bar{S}$ ₃ -CaF ₂	-	-	13.9	8.1	-
CT	3.6	2.8	2.9	2.5	3.4
C $\bar{S}$	13.0	10.4	3.7	10.1	6.3
S	0.1	-	-	0.1	0.1

Table 5 Mix design (g/100g cement) of the investigated systems, mass%.

	CEM R	CEM D	CEM F	CEM P	CEM T
CSA clinker	95.9	93.3	89.4	96.4	88.6
Anhydrite	4.1	6.7	10.6	3.6	11.4
Total	100.0	100.0	100.0	100.0	100.0

Figure 1. Hydration heat flow of the CSA clinkers blended with anhydrite during a) the first 2 hours of hydration and b) between 0 and 168 h of hydration. Please note that in b) the scale of the x-axis changes at 24 h.

Figure 2. Development of heat of hydration of CSA the clinker blended with anhydrite up to 168 h of hydration.

(a)

(b)

(c)

(d)

(e)

Figure 3. DT thermograms for CEM_R (a), CEM_D (b), CEM_F (c), CEM_P (d) and CEM_T (e) cured at various ages. First endothermal peak: ettringite (= E; $158^{\circ}\pm 8^{\circ}\text{C}$); second endothermal peak: aluminum hydroxide (= AH₃; $287^{\circ}\pm 8^{\circ}\text{C}$).

Figure 4. Ettringite content as determined by TG up to 28 d of hydration (normalized to 100 g anhydrous CSA cement) for CEM_R, CEM_D, CEM_F, CEM_P and CEM_T vs. curing time.

Figure 5. Bound water as determined by TG up to 28 days of hydration (normalized to CSA cement) for CEM_R, CEM_D, CEM_F, CEM_P and CEM_T vs. curing time.

(a)

(b)

(c)

(d)

(e)

Figure 6. XRD patterns for CEM_R (a), CEM_D (b), CEM_F (c), CEM_P (d) and CEM_T (e) cured at various ages. A=anhydrite, E=ettringite, F=fluorellestadite; G=gehlenite, M=monosulfate; T=ternesite; Y=ye'elimite.

Figure 7. Hydrate assemblages calculated by thermodynamic modelling of a) Cli_R and b) Cli_T as a function of clinker replacement by anhydrite. Reaction degrees of 100% for ye'elimite, mayenite and anhydrite, of 60% for fluorellestadite and of 30% for belite, ternesite and gehlenite are assumed. A water/cement ratio of 0.70 was used in the calculations. The positions of CEM_R and CEM_T, respectively, are marked by dashed lines.