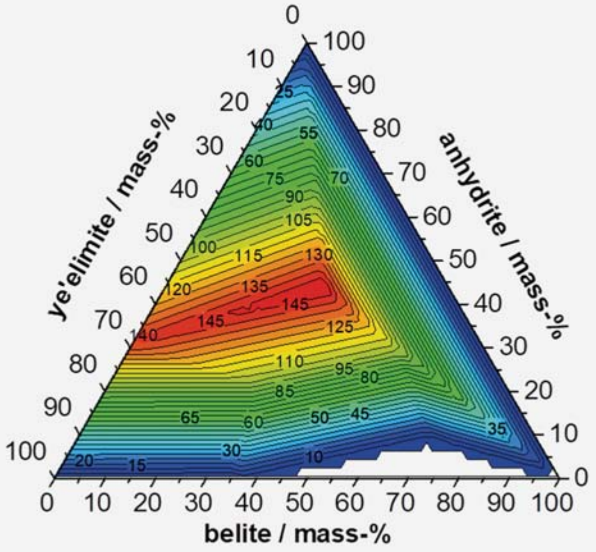
INTERNATIONAL WORKSHOP ON

# Calcium sulfoaluminate cements



Theoretical amount of ettringite calculated by thermodynamic modelling
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# PREFACE

Calcium sulfoaluminate cements are receiving increasing interest as an environmentally friendly alternative to Portland cement and as they can be used to formulate mortars and concretes with special properties such as fast setting, high early strength or shrinkage-compensation. Thus in the recent years the number of publications in this field increased rapidly, and new products came on the market.

This workshop aims at exchanging state-of-the-art knowledge regarding production, hydration, properties, durability and application of calcium sulfoaluminate cements. In this booklet the one-page abstracts of the work presented are compiled.

The following topics were addressed in the workshop:

- Clinkering: Raw materials, lab and industrial clinkering, mineralizers, kiln operation
- Hydration mechanisms: Kinetics, hydrate assemblages, mineral additions, ternary binders with Portland cements, admixtures, phase stabilities, thermodynamic properties
- Properties: Mechanical properties, volume stability (expansion, shrinkage, creep)
- Durability and sustainability: Sulfate resistance, chloride ingress, carbonation, rebar corrosion, life cycle analysis
- Application: Mortar, concrete, waste encapsulation, standardization

Selected papers will in addition be published in a special issue of “Advances in Cement Research” which is scheduled to appear in 2019.

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# OBITUARY ELLIS GARTNER

Ellis Gartner, 68, Visiting Professor in Civil and Environmental Engineering at Imperial College, London and prominent cement scientist, passed away on February 13 in Lyon, France. He made many contributions to the field of cement and concrete and was the senior associate editor on the journal Cement and Concrete Research for the last 14 years. He was an inspiring friend and mentor to many of us; he will be sorely missed.

Ellis was born on January 18th, 1950, in London, to a family of Eastern European extraction. He completed his MA and then PhD in Physical Chemistry at Cambridge University, UK. He then took up a post as Higher Scientific Officer at the UK Building Research Establishment. At that time, the early 1970s, there was a lot of concern about the provision of aggregates for construction. At the same time industries such as coal mining, iron and steel production, and the mining of slate and china clay were producing very large amounts of waste. Ellis contributed to finding uses for these wastes in the construction industry. One memorable contribution was to design and build a pilot scale fluidized-bed furnace to demonstrate how slate waste could be expanded to make a lightweight aggregate.

In 1977, he moved to the Portland Cement Association in Skokie, Illinois, USA, where he worked on the chemistry of cement manufacture and cement hydration. One landmark contribution from this time was on the influence of sulfate source on Portland cement hydration.

In 1985, Ellis joined W.R. Grace at the Washington Research Center in Columbia, Maryland (USA). He led the cement additive and concrete admixture research effort as a Senior Research Scientist and a Research Manager. During his tenure, he was responsible for the discovery and understanding of many new technologies, including higher molecular weight alkanolamines as strength enhancers for cement [1], polycarboxylate ether-based high range water reducers, and shrinkage control agents for concrete. The continual global success of these transformational technologies is the direct result of the scientific rigor Ellis exercised during the development of these products. He also hired, mentored, and coached an entire generation of scientists that have had an impact within and outside of Grace and GCP Applied Technologies.

In 1996, Ellis moved back across the Atlantic, to join Lafarge Central Research (LCR) in Lyon, France, where he became head of the newly created organic-mineral Interaction team. For him there was no frontier between mineral chemistry and organic chemistry on the contrary, he made a specialty of the organo-mineral interactions, leading key research projects in this area. The development of admixtures greatly benefited from his brilliant scientific approach. Unfortunately, little of this work was published as it was considered of great commercial importance in the control of concrete quality. This work also led to a strong collaboration with Japanese colleagues at Taiheiyo cement.

He became Principle Scientist and then Scientific Director for Chemisty at LCR where he then focused on the development of low $CO_2$ clinkers. His contribution in this field was outstanding. Not only did he work on internal projects in Lafarge leading to the development of the Aether cement, but he published several seminal papers giving an in-depth analysis of the possibility for $CO_2$ reduction given the limitations of the geology of the earth. These contributions drew on his incredibly depth of knowledge on both cement production and hydration chemistry. They include key note papers at the last 3 International Conferences on Cement Chemistry and most recently he was one of the leading authors on a report from the United Nations Environment Program on Eco Efficient cements: Potential, economically viable solutions for a low-$CO_2$ based cement based materials industry. His work here will continue to be very influential.

In parallel to his work in the industry, Ellis pursued his passion for Cement Chemistry, particularly in the field of hydration. His papers on C-S-H growth in 1995 [2] and the role of water in the formation of C-S-H published just last year [3] demonstrate his ability to come up with completely new ideas, which will stimulate research in this area for many years to come. He also contributed by organizing conferences and workshops, where he built many bridges with experts from other disciplines. In this respect, he was also a lynchpin of the Nanocem network which brings together industry and academia for fundamental research into cementitious materials. He had a knack of getting to the heart of a problem and outlining what had to be done to solve it. His judgements were always influenced by a deep understanding of the physical chemistry of cements as well as the commercial practicality of new inventions and discoveries. His wisdom will be missed.

Towards the end of his career with Lafarge and into his retirement, he took up a post as visiting Professor at Imperial College, London.  Here he gave lectures and supervised students. He was very popular with students, dedicated and incredibly generous with this time and knowledge.

Ellis was an inspiration to many of us, and an excellent mentor to many younger scientists. He had a great sense of, very British, humor with an ability to make plays on words across both English and French.  He had friends and colleagues across many cultures: “English style, Japanese style, French style, American Style, whatever it did not matter, we just had good time”. He is survived by his wife, Noriko and children, Maya, Yuma and Abi.

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Karen Scrivener

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# BELITE-YE'ELIMITE-FERRITE (BYF) CEMENTS AS POTENTIAL LOW-CARBON ALTERNATIVES TO PORTLAND CEMENTS: CURRENT LIMITATIONS AND RESEARCH PERSPECTIVES

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BYF cements are based on clinkers comprising both belite and ye'elimite as major phases, but with belite preponderant, and usually also accompanied by an appreciable amount of a calcium aluminoferrite phase. Such clinkers fall outside the range of the CSA-based clinkers developed over the last few decades for specialty cement applications, and thus merit consideration as a class apart. They were proposed for the replacement of Portland clinkers in cements intended for a wide range of large-scale, non-specialty construction applications, aimed at providing significant global $CO_2$ emissions reductions in the manufacture of cement and concrete.

Currently, BYF clinkers and cements are still in the R&D phase. As much of this work has been done in industry, a lot of it remains unpublished. But it appears that many significant problems remain to be solved before such cements can compete with Portland-based cements at $CO_2$ emissions costs in the range expected to be reached in the coming decade. The two main technical challenges are both related to control of hydraulic reactivity, but on different time scales. Firstly, although it is relatively easy to achieve acceptable early strength development by hydration of ye'elimite together with sufficient calcium sulfate (either anhydrite or gypsum) to give ettringite as the major binder phase in the first day or so of hydration, this high initial reactivity brings with it the challenge of controlling the rheology and setting time of the cement to give long-enough working times for demanding applications such as self-compacting ready-mix concretes. The retarders and dispersants needed for this level of set and rheology control may well be somewhat different to those currently used for control of Portland cement concretes. Secondly, for the strength development to continue smoothly from the first day onwards, to give a strength gain vs. time profile similar to OPC, it is necessary that the belite be sufficiently reactive. There are currently two main approaches to achieving this: use doping with borates to make the belite reactive; or use excess sulfate in the clinker to stabilise ternesite ($2C_2S$•C$), a phase distinct from belite but which can be considered in this context to be equivalent to a belite incorporating excess calcium sulfate. Both of these approaches have benefits and drawbacks. Borate doping can increase belite reactivity while simultaneously reducing ye'elimite reactivity, thus also helping to solve the problem of initial set control; and it also helps the kiln feed to self-nodulize, facilitating manufacture in energy-efficient preheater/precalciner kilns. But borate-rich raw materials are relatively costly. The sulfate-based approach has the advantage of requiring only inexpensive sulfur as the activator, which can in principle be provided in the form of an inexpensive high-sulfur kiln fuel. But it has the disadvantage that high sulfur levels and/or an unusual temperature profiles are required in the kiln system, which may either cause operating problems or require equipment modifications, with the associated cost implications. It can also produce cements with high water demand and short setting times. Optimal BYF manufacture requires very careful control of clinkering conditions, the composition of the kiln feed (including minor elements) and also of the cement.

In addition to the above cement manufacturing issues, which can greatly influence the cost and thus the commercial competitivity of a BYF approach, there are some hydration incompatibility issues that also require further research. Surprisingly, the hydration of the active belite phase in some BYF clinkers can be retarded by the presence of limestone fines. Thus, dilution of BYF clinker by fine fillers works best if the fillers are siliceous rather than calcium carbonate-based. In theory highly reactive pozzolans such as metakaolin should be good extenders for BYF cements because they can permit generation of additional hydrate volume and lower $CO_2$ emissions by stabilization of strätlingite rather than siliceous hydrogarnets. More research is required into the reaction kinetics of such combinations to determine whether their theoretical potential for improved hydration volume efficiency and stability are practically achievable.

# CLINKERING OF CALCIUM SULFOALUMINATE CLINKERS: POLYMORPHISM OF YE'ELIMITE

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The manufacture of CSA cements is more environmentally friendly than that of OPC as it releases less $CO_2$. This reduction depends on CSA composition and is due to three factors: i) less emissions from decarbonation in the kilns; ii) lower clinkering temperature, consequently less fuel is needed, and iii) it is easier to grind, implying a depletion in indirect emissions.

CSA cements are prepared by mixing the clinker with different amounts of calcium sulfate as a set regulator. Their main performances are fast setting time (followed by a rapid hardening), good-chemical resistance and, depending on the amount of the added sulfate source they can work as shrinkage controllers.

CSA cements present a wide range of phase assemblages, but all of them contain over 50 wt% of ye'elimite ($C_4A_3\bar{S}$) jointly with belite ($C_2S$), tetracalcium aluminoferrite ($C_4AF$) and other minor components such as CA, $C\bar{S}$, $C\bar{S}H_2$ and so on [1]. Ye'elimite is also included (~25 wt%) in BYF (Belite-Ye'elimite-Ferrite) or BAY (Belite-Alite-Ye'elimite) clinkers.

Ye'elimite has a sodalite type structure with general composition, $M_4[T_6O_{12}]X$. Stoichiometric ye'elimite crystal structure at room temperature will be described in detailed. The role of different amounts of minor elements on the synthetic procedure and crystal structures will be also presented [2,3].

This keynote will be also focused on a revision of the effect of raw materials on the mineralogical composition of CSA, BYF and BAY. Specifically, the role of main elements contents in the ye'elimite formation in these systems will be described. Moreover, the effect of minor elements on the polymorphism of both ye'elimite and belite, especially on BYF and BAY clinkers, will be presented [4,5,6].

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# PROGRESS AND FUTURE PERSPECTIVES OF CSA CEMENTS IN CHINA

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Calcium sulfoaluminate ($C_4A_3\underline{S}$, CSA), due to its lower formation enthalpy and half of the embodied $CO_2$ compared with tri-calcium silicate ($C_3S$), has been intensively investigated and utilized especially in combination with di-calcium silicate ($C_2S$), another low energy mineral, for low energy and low carbon clinker cement preparation and application. China takes the lead in developing CSA series cements and using CSA cements on commercial basis since 1970s. The evolution of CSA-derived cements in China in terms of fundamental research on chemistry of clinkering and hydration, cement and concrete performance, industrial production and application is reviewed and latest progress on belite based CSA (BCSA) introduced.

Two main types of CSA cements were defined: normal CSA with 55-75% of $C_4A_3\underline{S}$ and 8-37% of $C_2S$ and 3-10% of ferrite in clinker mineralogy, and ferro-aluminate cement, specially iron-rich CSA containing 33-63% of $C_4A_3\underline{S}$ and 14-37% of $C_2S$ and 15-35% of ferrite. Further study revealed different composition of ferrite in the two CSA cements with $C_4AF$ for the former and $C_6AF_2$ for the latter due to the difference in clinkering temperature. Interesting is that latter iron-rich CSA cement, though containing less $C_4A_3\underline{S}$, exhibits higher reactivity of $C_6AF_2$ than $C_4AF$.

Through comprehensive study on CSA cements properties, hydration mechanism and microstructural analysis and thanks to the first publishing of Chinese Standards for normal CSA cements in 1981 and for iron-rich CSA in 1987 which lead to the booming of the two CSA cements used both in structural and non-structural application in China as well as the use of modern calcining kilns from the earliest hollow rotary kiln to the latest new dry process kiln with pre-calciner for the manufacturing of CSA cements, which further improves the capacity, energy efficiency and $CO_2$ mitigation. What is worth mentioning is that the SOx emission that has been concerned was proved to be far less than expected with the use of new dry process kiln.

Different CSA-derived cements with specific properties have been defined and produced by adjusting the dosage of gypsum or CSA/gypsum ratio, including rapid-hardening and high-strength CSA cement typically used for fast construction and precast products, expansive CSA cement used for shrinkage compensation concrete, self-stressing CSA cement used for producing pressure pipes for delivery of water and oil, and low alkalinity CSA cement ($pH \leq 10.5$) widely used for producing glass-fibre reinforced cement (GRC) products.

Both lab evaluation and field application showed excellent performance of CSA-derived cements as high early and final strength, high impermeability, good resistance to corrosion and freezing and thawing. The retrogression in flexural strength with higher dosage of gypsum was effectively controlled by the combined addition of gypsum with limestone. The durability of CSA concretes has been demonstrated, though controversy exists even now, through decades of field application in many engineering projects in China, particularly in saline marine environment.

Another two alternative clinker systems, i.e., alite based CSA and BCSA, are also introduced, particularly BCSA. Salutes to the first-generation CSA researchers in China who made systematic exploration through both in lab and trial production, leading the way to today's intensive R&D of BCSA as a promising alternative clinker cements for future cement and concrete sustainability. The dawn has appeared by commercialization of BCSA in China for non-structural purpose now. We have the reason to be optimistic for BCSA as future alternative binder to Portland cement in view of its lower energy input and environment impact as well as its better performance in general purpose application.

# POTENTIAL OF CALCIUM SULFOALUMINATE CEMENTS FOR STABILIZATION / SOLIDIFICATION OF RADIOACTIVE WASTE

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Alternative inorganic binders may offer new solutions for the conditioning of low- or intermediate-level radioactive waste with a view to minimizing the amount of packages to be produced, obtaining cement-waste forms as inert as possible from the physical and chemical points of view, and / or providing new options for the conditioning of deleterious waste. This presentation points out the main advantages of calcium sulfoaluminate cements (CSAC) with a high ye'elimite content (>50 wt.%).

Due to the different chemistries of Portland cement (PC) and CSAC, the retarders of PC may be less influent on CSAC hydration. For instance, borate ions, which are widely used in PWR nuclear plants as neutron moderators, are strong inhibitors of PC hydration, but only weakly retard CSAC, especially at low gypsum content [1]. In a similar way, ashes resulting from the incineration of technological wastes with neoprene and polyvinylchloride, contain substantial amounts of soluble zinc. Zinc cations delay the setting of PC-based materials but exert an accelerating effect on the hydration of CSAC [2].

Hydrated CSACs also exhibit a favourable mineralogy for waste immobilization. As for PC, the rather high pH of the interstitial solution of CSAC pastes makes it possible to precipitate many radionuclides as hydroxides. Moreover, the main hydrates of CSAC are ettringite and calcium monosulfoaluminate hydrate. These two phases exhibit a rather flexible structure and can accommodate many substitutions on their cationic or anionic sites. In addition to AFt and AFm phases, aluminium hydroxide may also play a key role in the entrapment of pollutants such as heavy metals [3].

The chemical water demand (minimum amount of water for full hydration of the anhydrous phases) of CSACs is higher than for Portland cement. It increases with the initial calcium sulfate content, up to a maximum which corresponds to the highest precipitation of ettringite. A high water demand makes it possible to increase the incorporation rate of aqueous wastes in a cement-based matrix while keeping acceptable properties of the final cement-waste form. In a material with a low water content, it leads rather easily to dry internal environments due to self-desiccation. This property is used to design composite cement-based materials, containing getters of the $Ag_2O/MnO_2$ type, in order to limit the outgassing of tritium from cemented waste packages. Minimizing the residual amount of free water within the capillary porosity is a key issue to keep a good efficiency of the getter.

Finally, recent results show that when CSAC-based materials are submitted to gamma irradiation, their radiolytic production rate of dihydrogen is of the same order of magnitude as that measured for PC-based materials with the same water content.

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# OVERVIEW OF RECENT BYF STUDIES

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This paper aims to give an overview of recent studies on the performance of a specific type BYF binder. As a reminder, prior to its merger with the Holcim group, Lafarge had been working on BYF type clinkers and had patented a manufacturing process in 2004 [1]. The objective was to design a low-$CO_2$ clinker alternative to ordinary Portland clinker. The BYF clinker is composed of, as its name suggests, belite, yeelimite and ferrite. The component proportions and the added calcium sulphate were adjusted to design cements mimicking the mechanical performance of Ordinary Portland Cement (OPC).

Thanks to internal and European funding (Life+ from 2010 to 2013, and SILC from 2014 to 2015), clinker was produced in cement plant (5000 tons) and the BRE was part of the consortium to evaluate the performance of a cement made with the clinker produced [2]. The BRE cast a large number of concrete specimens. Different compositions were scanned in terms of cement content and water-to-cement ratio. The follow-up focused on the development of mechanical strengths of cubes stored at three different temperatures (5, 20 and 38 ° C) at 100% relative humidity and at 20 ° C and 65% relative humidity. Stability was verified by dimensional measurements of prisms kept under the same conditions. Large samples reinforced with steels were also exposed outside the laboratories at the BRE exhibition site. Resistance to external sulfate attack was also evaluated, as well as resistance to diffusion penetration of chlorides. The monitoring performed by the BRE showed the absence of active corrosion of the reinforcing steel, a regular increase of the mechanical resistances, the absence of deleterious swelling in the water, a reduced drying shrinkage, a very good resistance in a medium highly concentrated in sulphates, and a good resistance to the penetration of chlorides. Once the European financing was over, the group that became LafargeHolcim asked the BRE to continue the monitoring at their facilities. This gives results of up to 5 years for the first samples.

In addition to this follow-up on concrete, comprehension studies have been carried out internally and with external partners, on neat paste and mortar. First, the modeling of the hydration process was discussed with Lothenbach [3]. Then, through his thesis work, Koga was able to show the effective passivation of the steel embedded in BYF cement tested by the BRE and explained the phenomena involved [4]. Resistance to external sulphate attack has also been studied in more detail by electron microscopy. Studies at the microstructure scale show the strong dependence of performance as a function of clinker composition and calcium sulphate addition. These results must therefore be associated with the composition of the cement considered, and cannot be widen to other BYF or CSA in general. There are still many things to check before replacing Portland cement to make structures with a guaranteed service life of 50 years. We can mention the European project Ecobinder which deals with the performance on several compositions of BYF cements [5].

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# ADVANCED SYNCHROTRON STUDIES OF YE'ELIMITE-BASED CEMENT PASTES

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Synchrotron characterization techniques [1] are being used to study Portland-based cements and recently also CSA and related cements. A key property of these techniques is that they do not require sample preparation, so the microstructures of the pastes can be preserved. The classical application of synchrotron tools is powder diffraction used to determine the crystalline phase content evolution with hydration including the overall amorphous fraction. Furthermore, other most advanced techniques are being applied to ye'elimite-containing pastes such as i) Total Scattering Synchrotron Powder Diffraction (TS-SXPD), and ii) Ptychographic Synchrotron X-ray Computed Tomography (PSXCT). All these applications will be reviewed here.

TS-SXPD data coupled with the Pair Distribution Function (PDF) analysis methodology [2] allows having a better insight about the nanocrystalline/amorphous atomic arrangements in the gels. It has been very recently shown that nanogibbsite with very small particles, ≈3nm, is the main constituent of ye'elimite-gypsum hydration paste [2]. Nanogibbsite particles being smaller than those originated from the hydration of monocalcium aluminate. In addition, PSXCT is a tomographic technique that profits from the partly coherent nature of the synchrotron beam to provide better (smaller) resolution, which can be lower than 100 nm. It also provides the mass densities if the chemical stoichiometries are known. This technique has been applied to ye'elimite hydration to determine the microstructure and chiefly the bulk densities of nanogibbsite [3]. The microstructure evolution at early age was also followed [4]. Figure 1 shows an example of a slide of the electron density tomogram for a ye'elimite paste at 8 days of hydration and the corresponding histogram for the full volume with all phases identified. We highlight that it is possible to distinguish different hydrated phases which is not the case with standard (absorption-based) synchrotron X-ray computed tomography.

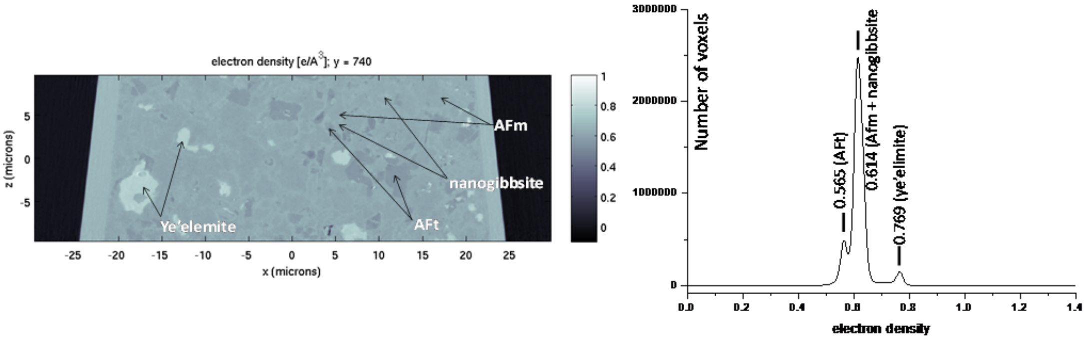

Figure 1: (Left) vertical slice of the electron density tomogram and (right) histogram of the electron densities for a ye'elimite paste at 8 days of hydration [3], as an example.

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# OPTIMIZE ETTRINGITE FORMATION AS A WAY TO REDUCE ENVIRONMENTAL FOOTPRINT

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They are several publications which demonstrate that Portland Cement (PC) industries is one of the main contributor to $CO_2$ footprint emissions of the building sector. In a recent report of the United Nation Environment Program [1], two mains areas for $CO_2$ reduction were identified: increased use of supplementary cementitious materials (SCM) as partial replacements for PC and more efficient use of PC in applications. In applications where high performance (fast drying, rapid hardening, shrinkage compensation …) are required in the first hours after mixing, Ettringite precipitation is critical. This hydrate comes from of a combined hydration of various Ettringite precursors as ye'elemite, calcium aluminate cement and calcium sulphate which react with PC's components ($C_3S$, $C_3A$ and sulphates). The environmental foot-print of these systems can be reduced by optimizing the hydration degree of these precursors at early age and then by reducing the total binder content.

In this study, the intrinsic dissolution rate of various Ettringite precursors are compared (Figure 1): (i) two ye'elimite rich cements, (ii) a CA-rich cement and (iii) two amorphous calcium aluminate cements. They contains respectively 77%wt. (CSA1), 69%wt. (CSA2), 63%wt. (CA-CAC) and 95%wt. (ACAC) of hydraulic compounds ($C_2S$ is not taken in account). Portland cement and calcium sulphates are taken as reference. Dissolution rate is measured by quantifying the amount of calcium after 2min of dissolution at 0.1g/L and 20°C (this concentration is chosen to be undersaturated with respect to Ettringite).

A solution to maximize the formation of Ettringite could be to obtain a better synchronisation between Ettringite precursors and PC. In PC-Rich system aluminate ions are often the limiting reactant. It is necessary to bring these ions quickly into the solution and to get a full $C_3A$ hydration in the first hours. Figure 1 shows that the dissolution rate of ACAC is in the same range that the PC one. In addition, its higher content of hydraulic phases allows to reduce the amount of PC without impacting the performances in application.

To go further, a simplified life cycle analysis (LCA) study has been done, in order to compare the environmental footprint of different formulations of ettringitic binder made with CSA and calcium aluminate cements with regards to their performances in application. A more theoretical approach is also proposed for the comparison of different binders formulated to lead to the formation of the same amount of Ettringite.

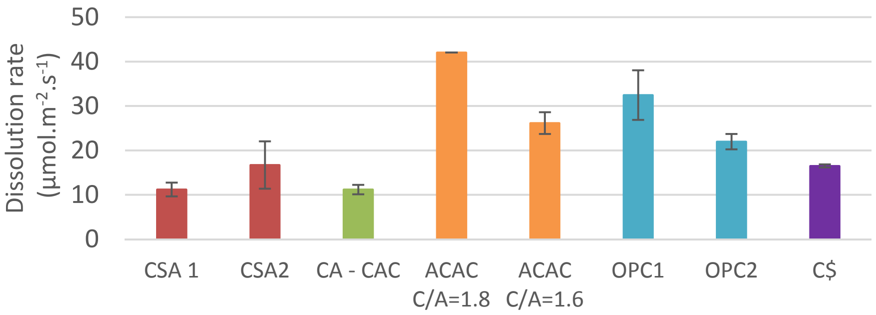

Figure 1: Intrinsic dissolution rate of Calcium at 20°C for various binders.

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# CSA AND SLAG: TOWARDS CSA COMPOSITE BINDERS

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Green binders, eco-friendly cementitious materials, low embedded-$CO_2$ cements: different names for the same purpose, i.e. to reduce the environmental impact of cement production.

CSA cements supply a valid alternative to ordinary Portland cements (OPC), since they couple the advantages of a lower environmental impact production with well-known high early-performance and dimensional stability. Their use, once limited, due to a lack of regulations, is today increasing thanks to the development of dedicated standard processes [1]. The combination of CSA cement with OPC has been widely investigated [2,3], and a few products, characterized by peculiar features, such as high early strength and shrinkage compensating effect, have been developed and are already available on the market [4].

Supplementary cementitious materials (SCMs) are widely used for improving the durability performance and lowering the clinker content, as described in the EN 197-1. High levels of substitution have allowed to improve performance indicators in terms of $CO_2$, but on the other hand, mechanical strengths at early ages can be affected.

The combination of sulfoaluminate cement with SCMs opens the route towards a wide range of innovative composite binders, where good mechanical performance and significant $CO_2$ reduction are achieved. Within this topic, a huge laboratory trial regarding the use of blast furnace slag in combination with sulfoaluminate cement alone, or in mixture with OPC, has been performed, revealing that composite CSA cements can supply innovative solutions for many applications.

Through a multi-technique investigation based on XRD, TG/DSC and SS-MAS NMR, the hydration mechanisms involving CSA clinker and slag could be explained, permitting the elaboration of dedicated strategies for improving performance of different mixtures.

For example, a blend of sulfoaluminate and Portland cement with a third part of slag reached strengths of about 20 MPa at 24 hours and 70 MPa after 90 days. Further, the addition of slag to a low shrinkage system enabled a greater improvement of this performance.

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# BELITIC CALCIUM SULFOALUMINATE CEMENT IN AMERICA: A 60-YEAR HISTORY OF DEVELOPMENT, CHEMISTRY, AND APPLICATIONS.

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The history of calcium sulfoaluminate (CSA) cement traces back to Professor Alexander Klein in the 1950s. His studies on the expansive properties of CSA are well documented and led to the development of Type-K cement. Initially, this new cement technology was used in various applications including highway pavement, chemically pre-stressed precast concrete members, airfield pavement, water treatment plants, parking structures, and various other applications. In the decades following, shrinkage compensating cement technology was widely used in large distribution center warehouse floors with joint spacing up exceeding 50 meters.

In the 1970s, the chemistry of Klein's original CSA cement was modified to develop a standalone CSA cement exhibiting a very high early strength, rather than as an additive to portland cement for shrinkage-compensation. The main constituent of this new cement was belite, (about 45% by weight), and CSA (roughly 25%), a combination known as belitic calcium sulfoaluminate (BCSA) cement.

The development of a new single component cement is a complex path fraught with many challenges; the chemistry must fit a large enough need to support mass production, yet regulatory approvals must be met. BCSA was granted a CAS number in the US in the 1990's. The growth of BCSA in the United States was fostered by the commercial need for fast repair mortars and quick return of rehabilitated concrete to service, especially in highly populated states like California where closing highway pavements for more than overnight closures is economically and politically difficult. In the past 30 years, more than 2 million metric tons of BCSA cement have been produced in the United States. To-date, the California Department of Transportation has placed more than 3,000 lane-kilometers of BCSA concrete pavement. At Seattle-Tacoma Airport, more than 35,000 cubic meters of BCSA concrete has been used for overnight rehabilitation of the main runway and has shown excellent long-term durability.

This presentation will cover the history of the use, chemistry, and performance of belitic calcium sulfoaluminate cement produced and used in the United States. Hydration mechanisms and their relationship to the performance of materials in the field will be discussed. An emphasis will be placed on how the chemistry and materials science of this material have strived to meet the needs of a civil infrastructure under increasing pressure. New opportunities in concrete pavement design will be described,

In the history of cement, a 60-year history of the development of chemistry, specifications and regulatory approvals is a significant-enough time period to warrant an objective summary of challenges past, present and future, as well as a review of the opportunities for scientists, engineers and infrastructure policymakers.

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# STUDY OF CALCIUM SULFOALUMINATE CEMENTS AND PORTLAND CEMENT BLENDS

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Calcium sulfoaluminate cements (CSA) are receiving increasing attention because, in comparison to Ordinary Portland Cement (OPC), they provide a low-$CO_2$ alternative [1] as well as specific properties [2]. OPC-CSA blends containing a low proportion of CSA cement can be used to modify the binder early strength or dimensional stability [3]. However, CSA cements properties (composition, finesse, etc.) vary and could affect the blend properties.

Therefore, the current research study the mechanical properties and hydration of CSA-OPC (25%-75%) mixtures using one CSA cement (CSA1) and two blends of 85% of CSA clinkers and 15% of anhydrite (CSA2 and 3). OPC was also studied as reference. Compressive strength (0.25, 1, 3, 7 and 28 days) were determined on mortars. Hydration was studied on paste using isothermal calorimetry, X-ray diffraction and thermal analysis. A second part of the investigations analyses the modification of the anhydrite percentage for CSA2 and CSA3 cements.

Results show that CSA binder composition can have a large influence in the early hardening and hydration. For example, mortars compressive strength (figure 1a) and hydration heat (figure 1b) highlight the CSA binder influence on the blend properties. Beyond the quantity of ye'elimite, complementary experiments with addition of anhydrite in CSA2 and CSA3 point out the major influence of the ye'elimite/anhydrite ratio on the properties of OPC and CSA blends.

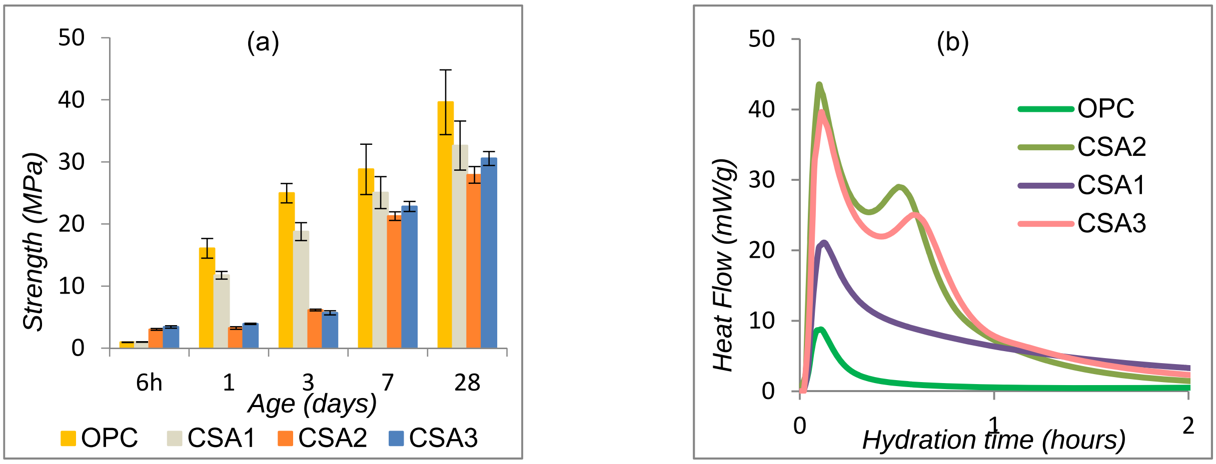

Figure 1: a) Compressive strength at 6h, 1d, 3d, 7d, and 28d and (b) isothermal calorimetry of blends with 25% of CSA (1, 2, 3) cement – 75% OPC and OPC.

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# A POSSIBLE ALTERNATIVE TO ALKALI ACTIVATION IN LOW CLINKER CEMENTITIOUS MATERIALS

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Concrete production is responsible for about 5-8% of manmade $CO_2$ emissions and 2-3% of total global energy consumption. One of the most successful approaches to reduce the high environmental impact of Portland cement, the main binding component of concrete, is clinker substitution with supplementary cementitious materials (SCMs). Nevertheless, high levels of replacement decrease the performance, specifically the early mechanical strength of concrete, due to the lower reactivity of SCMs. A common strategy to overcome this drawback is the activation of SCMs with moderate concentrations of alkali solutions. However, strong incompatibilities are shown in combination with polycarboxylate ether (PCE) superplasticizers, needed in concrete technology in order to decrease the water demand while maintaining a high workability. This issue is mainly due to the competitive adsorption between the anionic species present in solutions and the PCEs, that penalizes the flow properties of concrete. Marchon et al. [1] developed a criterion that allows to partially resolve this drawback. In particular, they defined PCEs molecular structures effective in NaOH activated systems, based on their high adsorption equilibrium constant. A feasible alternative to alkali activator solutions is the use of moderate amount of calcium sulfoaluminate cement (CSA), which leads to higher mechanical strength and maintains a high initial fluidity. Specifically, CSA as accelerating agent allows to prevent the process of competitive adsorption and, consequently, the requirement of a specific PCE. Moreover, it avoids the critical handling of alkali activators solutions during cement and concrete manufacturing.

In this work, we have studied a new blended cement containing 50% of Portland cement and 50% of SCMs that are available in Switzerland, such as limestone, burnt oil shale and fly ash. The limited reactivity and early mechanical strength of this blend have been increased by the addition of alkali solutions, such as NaOH and $Na_2SO_4$. Their competitive adsorption with different PCEs has been investigated. Furthermore, clinker replacement with moderate amount of CSA has been assessed as a possible alternative to alkali activated systems. The hydration kinetics, the rheological properties and the mechanical strength over 90 days have been studied.

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# CHARACTERISATION AND HYDRATION OF YE'ELIMITE CONTAINING CEMENTS - EFFECT OF IRON

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Calcium sulphoaluminate cements (CSA) with the main phase ye'elimite ($C_4A_3\bar{S}$) are a class of non-Portland cements, which are considered as promising low-$CO_2$ or so called ''green'' binders [1]. The hydration kinetics of CSA cements varies strongly, even for cements with similar composition and fineness [2]. Understanding the origin of this variation was the main motivation for this work. Earlier studies indicated that the type and composition of ye'elimite was related to the different hydration kinetics. The formation of iron-rich solid solution of ye'elimite seems to correlate with a faster reaction [3]. This is particularly of importance for belite-rich CSA cements, sometimes referred to belite ye'elimite ferrite (BYF). BYF clinkers are often produced using iron-bearing industrial by-products as raw materials to replace expensive bauxite [4]. The literature reports that stoichiometric ye'elimite has an orthorhombic symmetry at ambient conditions, whereas a cubic symmetry is stabilized by the presence of iron [5]. Thus, previous to this work, it was often assumed that there was a link between the presence of iron, the polymorphism and the hydraulic reactivity. Understanding the origin of the different reactivity of the ye'elimite, e.g. by studying the formation of iron-bearing solid solution and the change of the polymorphism, was the main motivation for this work.

Stoichiometric ye'elimite forms fast at 1250 °C, and iron even further accelerates its formation. A fraction of the iron-rich solid solution ye'elimite starts to decompose during the applied sintering period. The decomposition results in the volatilization of sulphur and the formation secondary phases such as krotite, mayenite and calcium ferrite. We studied the hydration of the stoichiometric and solid solution ye'elimite in paste and suspensions covering a broad range of water to binder (w/b) ratios. We could determine two main hydration reactions, five periods and the main controlling parameters. The hydration reactions and sequences were the same for stoichiometric and iron-rich solid solution ye'elimite but the kinetics vary. The differences in kinetics could be mitigated and even suppressed by increasing the w/b ratios in paste. Furthermore, in some cases no acceleration was detected for solid solution ye'elimite even when the cubic form was present. That demonstrates that the polymorphism alone cannot explain the differences. On the contrary, we could simulate the hydration kinetics of iron-rich ye'elimite by blending stoichiometric ye'elimite with synthetic mayenite. It therefore appears that the presence of small quantities of mayenite, rather than polymorphism, explains the different kinetics. The effect of mayenite was explained by its rapid dissolution and the altered solution composition, favouring the nucleation and growth of ettringite.

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# STRATEGIES TO EXTEND CALCIUM SULFOALUMINATE CEMENT CONCRETE WORKING TIME

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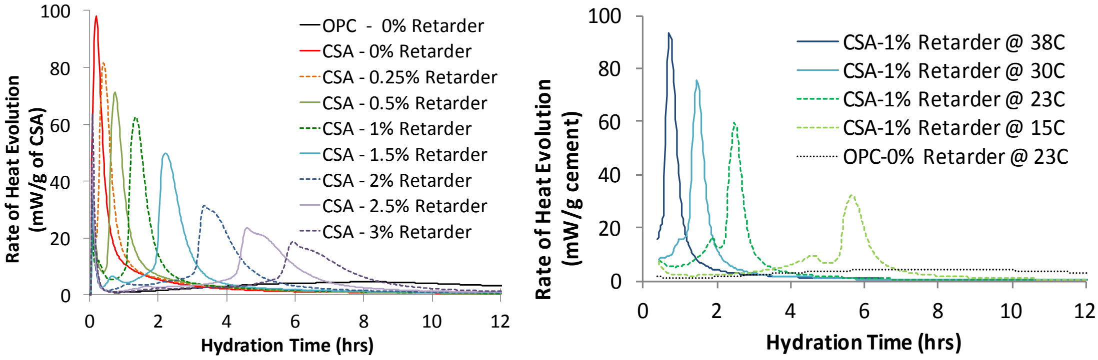
Ever increasing demand for concrete infrastructure coupled with the significant quantities of associated $CO_2$ emissions from portland cement production has made development of more efficient cement technologies necessary for achieving global emissions standards. Calcium sulfoaluminate cements (CSA) show great promise in this respect, having been shown to embody emissions reductions of as much as 49% [1,2] compared to traditional OPC. However, despite their clear environmental advantages, adoption in the U.S. has been slow. One of the biggest hurdles to upscaling production of CSA concrete is the rapid set time of this material, which limits its use predominantly to small scale applications and transport in volumetric mix trucks, both of which allow for onsite mixing operations. Ready mix concrete producers are hesitant to adopt usage of this material due to the risk of equipment losses should mixtures harden prior to reaching the job site, and will require working times surpassing 180 minutes before traditional batch plant production and truck transportation will be considered seriously [3].

Previous work has demonstrated that CSA cements are highly responsive to chemical retardants, with citric acid shown to be effective in extending working time from 15 minutes to 120 minutes (Figure 1a) [3], as well as temperature changes (Figure 1b). However, the limits of the total time to which mixture working time can be extended without harming hardened binder properties, has not previously been fully evaluated. To this end, this work will discuss several techniques for extending the working time of CSA mixtures, including use of chemical retardants and temperature control mechanisms, to evaluate the degree to which CSA working time can be extended and its impact on hardened properties. Additionally, the use of hydration reaction heat release to predict setting time will be introduced in order to develop procedures for understanding real-time field mixture behaviour.



(a) (b)

Figure 1: Influence of (a) citric acid (citation) and (b) temperature on CSA hydration kinetics.

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# HYDRATION OF A CALCIUM SULFOALUMINATE CLINKER WITH TERNESITE

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The discovery of the reactivity of ternesite ($2C_2S{\cdot}C\$$) has led to the early stage development of a new reduced-carbon footprint cement, "belite-(ferrite)-ye'elimite-ternesite" cement [1,2] whose compositional ranges have not yet been defined [2].This study aims to explore the reactivity of synthetic ternesite when blended with a CSA clinker with low or zero content of respectively $C_2S$ and $C_4AF$, cement phases that contribute to late strength development. To do this, hydration of a CSA cement (CSAC), a CSA clinker (CSAK) and a mix of CSA clinker with ternesite (CSAT) (2:1 by mass, w/s=0.4), at 2 and 28 days, was studied by means of XRD, DTA-TG and conduction calorimetry analyses. Moreover, mechanical strength of small cylindrical specimens (diameter=10.5mm, height=11mm) was determined at same time periods.

DTA-TG and XRD results revealed that ettringite and aluminum hydroxide were the main hydration products in all the samples and that $CAH_{10}$ also precipitated at 28 days in CSAK and CSAT. Only ye'elimite was completely consumed at 28 days in the sample with ternesite (CSAT). However, the reaction of this latter did not yield crystalline silicate phases. Further to calorimetry analyses and compressive strength measurements, the sample with ternesite exhibited at 2 days the lowest content of hydration products and lowest strength (5.6 MPa) as expected. Nonetheless, after 48 hours in this sample was registered the highest heat of hydration and after 28 days the highest increase in the precipitation of hydration products and strength development.

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# EARLY-AGE EXPANSION OF ORDINARY PORTLAND CEMENT-CALCIUM SULFOALUMINATE CEMENT BLENDS

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Traditionally developed as shrinkage compensating cement, calcium sulfoaluminate cement (CSAC) has lower carbon footprint than ordinary Portland cement (OPC). This presentation reports early-age expansion behavior of OPC-CSAC blends with CSAC amount varying up to 30% (by wt.). A commercially available calcium sulfoaluminate-based admixture was used as a CSAC, having 19.3% ye'elimite, 15% gypsum, 16.1% anhydrite, 9.4% bassanite, 34.8% belite, and 2.1% ferrite phases. It was shown that supersaturation with respect to ettringite plays critical role in giving rise to crystallization stress which is the precursor for expansion. Tensile stresses were estimated using various elasticity-based models including one based on poromechanics. All models enabled a reasonable prediction of tensile failure of OPC-CSAC blend with 30% CSAC. A significant difference in measured strain and calculated elastic strain highlighted the role of early-age creep on expansion characteristics.

# COMPARISON OF DIFFERENT PREPARATION METHODS FOR YE’ELIMITE CLINKER SYNTHESIS

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Calcium sulfoaluminate cement (CSA) is a low energy cement produced at the temperature range between 1200 to 1300°C. It has lower energy consumption and less limestone in the raw meal, leading to less $CO_2$ emission compared to Portland cement. The main component of CSA is ye’elimite. High purity clinker synthesis in lab scale generally uses pressing disc, nodulizing method or compacted materials in the crucible [1], where only a relatively low amount of clinker can be produced at once. Recently, a protocol has been suggested for alite synthesis, the so-called “cylinder method” [2], which allows to synthesize up to 400 g alite per synthesis and is well reproducible. The method starts with homogenizing the raw meal together with some water in a ceramic jar. The slurry is ground at least 24 hours, then casted in carton cylinders. After drying at 105°C for 48h, the cylinders have enough strength to be demoulded, dislocated to the furnace and sintered, as shown in Figure 1. This method can increase the productivity of clinker synthesis up to kilogram scale.

This cylinder method protocol was used to synthesize ye’elimite. The composition of the obtained ye’elimite was compared between the pressing disc method and the cylinder method by X-ray diffraction (XRD) when using the same heating profile and the same furnace for the synthesis. The compositions of different parts of the cylinder were also determined to confirm the homogeneity of the clinker.

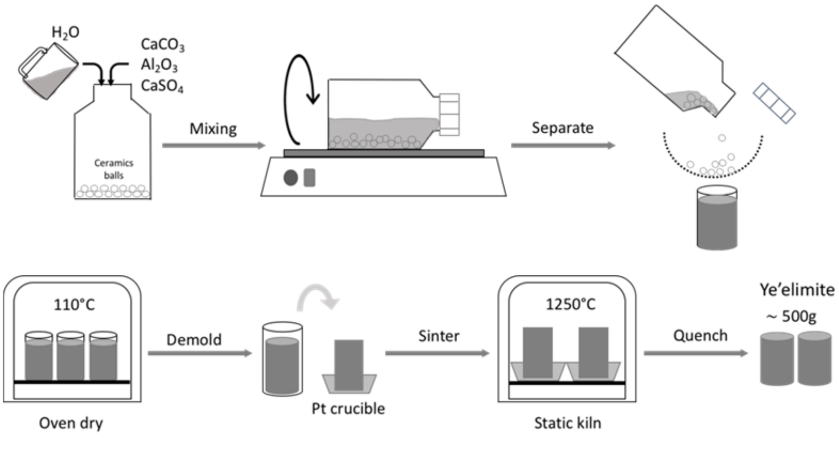

Figure 1: Schematic drawing of the procedures for ye’elimite synthesis (cylinder method); adapted from [2].

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# STUDY OF THE VOLUME CHANGE PROPERTIES OF DIFFERENT OPC/CSA MORTAR SYSTEMS

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The use of Calcium Sulfoaluminate (CSA) cement has progressively increased in the last few years. One advantage of CSA derives from its lower $CO_2$ emissions during production compared to ordinary Portland cement (OPC). Another advantage is the early development of mechanical properties allowed by CSA, which enable these cements to be used in applications in which high early-age mechanical performance and volume stability are required.

Although several experimental campaigns have been performed in order to study the mechanical properties of mortars made with CSA binders, the knowledge about volume changes of OPC/CSA blends is limited. In order to understand the fundamental mechanisms governing the mechanical performance and the shrinkage and creep response of these blends, an extensive study in both in autogenous and drying conditions was carried out on blends with different proportions and fixed water-to-cement ratio (w/c) of 0.50. In addition to measurements of mechanical properties, shrinkage and creep, also the moisture loss or gain, the internal relative humidity in sealed conditions and the relative humidity gradients in large, drying specimens were measured. Finally, the residual stress development due to restrained volume changes was measured by means of dual rings. Both the mechanical properties and the volume changes can be qualitatively explained by considering that the CSA reacts quickly in the first couple of days, while the OPC reacts slowly for several weeks. Systems with higher OPC content might experience self-desiccation despite the relatively high w/c, because the rapid reaction of the CSA binds a substantial amount of the mixing water.

# YE'ELIMITE SYNTHESIS FROM PHOSPHOGYPSUM

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Due to the use of calcium carbonate as a raw material, the manufacture of Portland cement is a source of $CO_2$ emissions at the time of clinker firing, which can be detrimental to the environment. Making binders that produce less $CO_2$ is an alternative solution. Calcium sulfoaluminate cement (CSA) are very promising candidates. Phosphogypsum (PG) is a by-product discharged from the production of phosphoric acid, in a relation of 1 ton of phosphoric acid to 4.5-5.5 tons of PG. At present only 15% of this by-product is recycled. However, PG contains the sulfates of calcium. Therefore, PG can be used to substitute for natural gypsum to prepare the CSA cement. The objective of the present work is to study synthetic CSA cement using PG and to understand the influence of the impurities in PG on the formation of ye'elimite (the major phase of CSA cement) and stabilization of their cubic form. The acquired ye'elimite was characterized by Rietveld quantitative phase analyses. Results demonstrate the successful utilization of PG as a raw material to prepare CSA cement. PG allowed on the formation of 98.5% of ye'elimite with only one sintering, and the simultaneous presence of $Fe_2O_3$, $SiO_2$, $Na_2O$ and $P_2O_5$ stabilized the cubic form of ye'elimite.

# SOLID-STATE SYNTHESIS OF PURE YE'ELIMITE

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The current cement industry is one of the most emitting of $CO_2$, Greenhouse gases (GHG), because of the massive use of calcium carbonate $CaCO_3$ as a raw material and high clinkering temperatures (1450 °C). An alternative solution is to develop cements that would produce less $CO_2$ during their manufacture such as sulfoaluminate cements (CSA). CSA clinker releases less $CO_2$ than ordinary Portland clinker for essentially two reasons: the clinkerization temperature is around 1250 °C and the calcium carbonate proportion is lower [1]. The aim of our work is the determination of synthesis optimal conditions of CSA clinkers and more specifically of the major phase which is ye'elimite $Ca_4(Al_6O_{12})(SO_4)$. The optimal synthesis conditions and the microstructural evolution during ye’elimite synthesis, by solid-state reaction from pure oxide raw materials ($CaCO_3$, $Al_2O_3$ and $CaSO_4.2H_2O$) is investigated. During ye'elimite synthesis, thermal behavior was studied using dilatometric analysis, differential thermal analysis and gravimetric thermal analysis coupled with mass spectroscopy. Microstructural evolution according to temperature was investigated by monitoring the dimensional variations using dilatometric analysis and by porosity measurement using Archimedes principle compared to BSE image analysis. The results of these different analyzes allowed us to define thermal events during ye’elimite synthesis and to suggest an optimal thermal cycle allowing to synthesize pure orthorhombic ye'elimite. The purity of the synthetized product was confirmed using quantitative Rietveld analysis.

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# THE STABILISATION OF α' DICALCIUM SILICATE IN CALCIUM SULFOALUMINATE CLINKER

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Calcium sulfoaluminate cements are widely used as special cements and, because of low specific $CO_2$ emissions relative to Portland cement, have potential for use in general construction. However, their widespread application has been limited by the relatively high cost of aluminous raw materials. A novel process has been developed for the production of calcium sulfoaluminate cement whereby its sulfur source - typically provided by gypsum in conventional feeds – instead, through the combustion of elemental sulfur, oxidises sulfur into sulfate which becomes part of the clinker product [1-3].

As part of a broad program on the optimisation of these cements, we have reformulated the clinker mineralogy to enhance the activity and strength contribution of the silicate phases. Preservation of the α' $Ca_2SiO_4$ phase to ambient is described. Both commercially available raw materials and reagent grade chemicals have been used and clinkers have been made at scale ranging from laboratory (10 to 100g) to small rotary kiln scale at 10-100 kg/hr. Preservation of the alpha belite phase to ambient is achieved by a combination of chemical doping with control of the furnace atmosphere and fast cooling of the clinker. It is hypothesised that α $C_2S$ is stabilised by using a hyper-stochiometric atmosphere, one containing a slight excess of $SO_2$ and $O_2$ relative to equilibrium. This enables the formation of a sulfated and alkali impurity substituted belite which can be stabilised to ambient during subsequent clinker cooling.

The scope of the study is that, ultimately, clinker with alpha prime belite, ye'elemite and ferrite can be optimised to create a new generation of low cost sulfoaluminate cements with improved performance and large potential energy savings relative to Portland cement. The metastability at ambient of the belite produces a reactive clinker in the course of hydration, contributing to enhanced early strength development. Hydration kinetics studies are planned to analyse the influence of varying combination of sulfur and alkali impurity fractionation in belite on the reactivity of belite.

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# DESIGN OF SELF DESSICATING BINDERS USING CALCIUM SULFOALUMINATE CEMENT: INFLUENCE OF THE CEMENT COMPOSITION AND CALCIUM SULFATE SOURCE

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Calcium sulfoaluminate (CSA) cements with a high ye'elimite content are of interest to produce self-desiccating binders. Their hydration is usually fast and their chemical water demand, which depends on the hydrates assemblage, can be tailored by adjusting the composition of the cement.

The main hydrates are indeed ettringite (AFt) and calcium monosulfoaluminate hydrate (AFm), the former being progressively replaced by the latter by decreasing the calcium sulfate content. This work thus investigates the influence of the cement composition and calcium sulfate source on the content of water bound by hydration, with the goal of designing non-expansive materials with dry internal environments.

A thermodynamic approach was first carried out. Ten cement compositions were prepared by blending a CSA clinker comprising 54.3% ye'elimite and 29.1% belite with anhydrite and calcium oxide, respectively within the range [80–95%], [5-20%] and [0–15%]. Cement suspensions (w/c = 6) were fully hydrated under stirring at 20°C. The cement comprising 80% clinker and 20% anhydrite led to the highest contents of ettringite and bound water, which was well simulated by thermodynamic calculations.

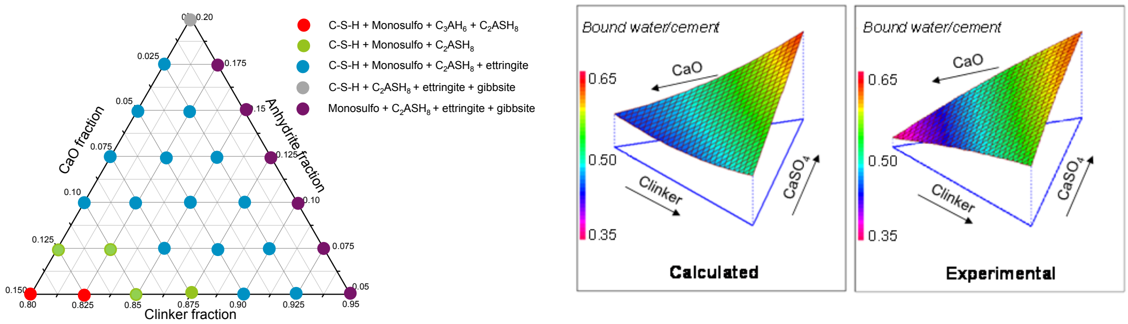

*Figure 1: Calculation of the phase assemblage of fully hydrated cements (left) and bound water / cement ratio (center) using thermodynamic modelling, comparison with experimental findings (right).*

Then, *a kinetic study was performed on cement pastes (w/c* = 0.5 or 0.6), the cement comprising 80% clinker and 20% $CaSO_4$, introduced as anhydrite or gypsum. Gypsum, which dissolved faster than anhydrite, led to the rapid formation of dense layers of hydrates, which tended to limit the progress of hydration at later age. With the use of anhydrite, higher hydration degrees were reached and specimens cured in a wet or dry environment exhibited smaller volume changes.

# CSA-BASED FAST HARDENING CONCRETES

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Fast hardening concretes are developed for three main applications: to save time on a construction site by faster removing wall moulds, to be able to make a traffic lane operational as fast as possible after repair (mainly used for airport runways), or for prefabricated concrete pieces (to avoid curing at high temperatures or to accelerate production rate).

In all these cases, concrete should have a given workability time and lead rapidly to a sufficient mechanical strength. We decided to work with an S4 consistency (fluid concrete) during one hour. Our target compressive strength is 16 MPa, which is the request to unmold a wall.

Three different binders were tested in our concretes:

- CEM I 52.5 Portland cement
- CSA cement
- a mix of Portland and CSA cements (70/30)

Our results show that CSA based binders are interesting options to accelerate setting compared to Portland cement. However, they exhibit two different behaviours: CSA alone leads to very high early age strength while the mix show a lower early age mechanical resistance but higher 28 days resistance.

# 5 YEAR OF EXPERIENCE OF AN EUROPEAN TECHNICAL APPROVED CSA CEMENT

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CSA cements are not classified as cements according to EN 197-1 therefore for an application in structural concrete in most cases these binders need a technical approval. In order to open the market of CSA cement also to concrete application Buzzi Unicem initiated a request of a European Technical Approval (ETA) for 3 CSA binders that was concluded in 2013 with the achievement of a CE label on one type of CSA cement (Next Base SR03, fulfilling the ETA requirement 13/0417), and two blended cement (Next binder SL05 NF fulfilling the ETA requirement 13/0418 and Next binder SL05 fulfilling the ETA requirement 13/0419) based on the combination of CSA cement and respectively Portland cement and Portland limestone cement. The ETA specify the chemical (chloride content, cement composition), physical (blaine value, density,) mineralogical composition ($C_4A_3\$$ content), performances (mechanical strength at early and late age, setting time, soundness) and the evaluation and attestation of conformity (system 1+) approved by a certification body. The approved certification body is in charge of the initial type testing of the products, of the inspection of the factory, of the continuous surveillance of the management system (one audit every year) and also of the testing of the CSA samples taken at the factory (six samples for each CSA cement every year) following a conformity verification which is well known for the EN- 197 cements.

On the July 2016 Buzzi Unicem obtained also an authorisation of use in Germany (Zulassung Z-3.15-2130) for the product Next Base SR03, which was authorized as sulphate resistance cement (SR) also in Germany, but with some restriction for application in structural concrete.

The history of this authorisation process evidence that the standardisation of a new type of hydraulic binder is a very long process and this is mainly due to the lacking of a long term experience on the durability performances of the binder. The ETA obtained by Buzzi Unicem open a first door for the acceptance of this innovative binders also in structural concrete and boost the research toward cement optimisation [1], CSA concrete application [2], durability performances of CSA concrete [3], behaviour of the steel embedded in CSA concrete [4], the research of alternative non corrodible reinforcement (i.e. glass fiber reinforced polymer - GFRP or Carbon reinforcement) to be used in combination with CSA cement [5].

The ETA and the conformity verification have also a relevant meaning for the customers, as the producer of an authorized product is forced in a continuous optimisation of the quality, performances, raw material, but also for what concern the production process.

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# AN ALTERNATIVE METHOD OF PRODUCING ALITE CALCIUM SULFOALUMINATE CEMENT

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Alite calcium sulfoaluminate (a-C$A) cement is a cement hybrid currently gaining research interest and undergoing development. It is believed that such cements can combine the favourable characteristics of Portland cement with those of calcium sulfoaluminate cement. More importantly it is understood that a-C$A cement can help bridge the gap in reactivity between ye'elimite and belite that is responsible for some physical and mechanical shortcomings observed in hardened belite-calcium sulfoaluminate cement. Current methods for the synthesis of a-C$A cement involve either lowering the formation temperature of alite via entropy stabilization by fluorine substitution or by stabilizing ye'elimite to higher temperatures via the addition of foreign elements such as barium and strontium.

A thermodynamic study is conducted here in order to explore the routes for the co-formation of ye'elimite and alite. It is revealed that the production of a-C$A clinker is possible without the use of mineralizers such as $CaF_2$ or the doping with foreign elements. It is established that a-C$A cement can be readily produced by controlling the oxygen and sulfur dioxide gas concentrations in the process atmosphere. The proposed fugacity control allows for the stabilization of ye'elimite to the higher temperatures that are required for simultaneous alite stability.

# MOLTEN SALT SYNTHESIS OF YE'ELIMITE

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Ye'elimite ($C_4A_3\$$) is the major component of calcium sulfoaluminate (C$A) based cements which are promising alternatives to Portland cement (PC) in general use around the world. The main advantage of C$A based cements over PC is their lower carbon footprint per mass which arises due to the lower lime factor, energy, and temperature required for their production. In this work, an alternative process for the production of ye'elimite is presented where the ye'elimite is produced in a molten salt fluxed system. Other important components of C$A cements, including belite and ferrite have already been synthesized via molten salt synthesis [1,2]. The flux allows ye'elimite to be produced at temperatures ≤1000°C as opposed to that in conventional C$A cement manufacture; ≈1300°C. The products are then separated from the salt using various solvents, based on the solubility difference of the compounds.

A lower production temperature allows for further reduction in temperature and energy requirements associated with C$A cement manufacture and could allow the use of alternative fuels and non-fossil fuels for the pyro-processing of C$A cement; indirect heating from sustainable sources can also be considered for this method of cement manufacture. In summary, this work presents an innovative cement production process which promises to lower the temperature requirement and thus the $CO_2$ emissions from cement manufacture that are partly responsible for the global warming of our planet.

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# FURTHER INSIGHTS INTO CALCIUM SULFOALUMINATE CEMENT EXPANSION

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The present study aims to build upon the growing body of evidence that crystallization pressure is responsible for expansion in CSA cement based systems by investigating the hydration of a variety of CSA cements with calcium sulfate to ye'elimite molar ratios (M ratios) ranging from 0.1 to 2 and monitoring their expansion from approximately 30 minutes to 182 days. By monitoring the hydration over a much broader period of time compared to prior studies, the present study sought to further the knowledge on CSA expansion and bring additional insights on how crystallization pressure is affecting CSA cement expansion. Tests conducted included pore solution analysis, thermal gravimetric analysis, quantitative X-ray diffraction, mercury intrusion porosimetry, dimensional stability, and autogenous strain.

Utilizing the ion concentrations from the expressed pore solutions, saturation indices for the hydration products were calculated using the Gibbs Free Energy Minimization Software, GEMS. The maximum crystallization pressures that can be developed due to a given supersaturation of a phase were then calculated according to Correns' equation for gibbsite, stratlingite, $CAH_{10}$, ettringite and monosulfate. The five crystalline hydrates were all supersaturated in CSA pastes at some point during hydration with ettringite and stratlingite having the highest supersaturations at early ages and gibbsite and stratlingite having some of the most persistent supersaturations. Although ettringite had some of the highest supersaturations because of its large molar volume, its maximum crystallization pressures were below those of gibbsite, stratlingite, monosulfate, and $CAH_{10}$ at times. This leads to the question as whether ettringite is the sole culprit of CSA expansion or whether the crystallization of other hydrates is contributing to expansion.

# TERNESITE-CALCIUM SULFOALUMINATE CEMENT PREPARED WITH PHOSPHOGYPSUM: SYNTHESIS, CHARACTERIZATION AND HYDRATION

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Ternesite has been proved to have some cementitious properties in calcium sulfoaluminate cement (CSA). However, due to the different rapid formation temperatures of ternesite and calcium sulfoaluminate, it is hard to prepare a ternesite rich CSA clinker by a single calcination process. In this study, phosphogypsum was utilized to prepare ternesite-calcium sulfoaluminate cement (TCSA) clinker by a single calcination regime. The results demonstrates that the impurities in phosphogypsum could promote the rapid formation of calcium sulfoaluminate at low temperature which contributes to the coexistence of calcium sulfoaluminate and ternesite in the clinker. By the calcination process at 1125-1175 °C for 15-30 min, the TCSA clinker could be prepared and the clinker exhibits an excellent grindability. To make a deep understanding of TCSA cement hydration. A comparative study of the hydration TCSA and belite calcium sulfoaluminate cement (BCSA) with equal calcium sulfoaluminate content was conducted. Results demonstrates that calcium sulfoaluminate in TCSA exhibits a higher hydration activity at the early age and higher hydration degree at the late age. Therefore, TCSA cement exhibits a higher compressive strength. Besides, due to hydration of ternesite at the late age, the compressive strength of TCSA keeps a consecutive growth.

# THE INFLUENCE OF $Li_2CO_3$ ON THE DEVELOPMENT OF THE WATER CONTENT IN THE AL-HYDROXIDE-GEL OF YE´ELIMITE BINDERS

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Ye´elimite ($C_4A_3\$$) is a major phase in CSA cements. Due to its very fast reaction with water, especially in mixes with calcium sulfates, it´s reaction is a crucial factor for working time, workability and early strength of binders containing ye'elimite. It was already published that new insights into ye'elimite hydration with calcium sulfates can be achieved from combination of insitu XRD, pore water analysis and especially $^1$H-NMR [1].

In the present study a nominally pure ettringite binder system of synthetic ye'elimite, anhydrite and high water content was investigated with XRD, $^1$H-NMR, pore water analysis, calorimetry and TGA. XRD and TGA confirm the findings from thermodynamic modelling [according 2] that ettringite and aluminium hydroxide are the major phases formed. The influence of lithium carbonate on the system and in particular the influences of the lithium carbonate on the water content of the AH-phase Al-hydroxide-gel was investigated.

$^1$H-NMR gives a clear idea that the formation of the $AH_3$-gel shows different stages during hydration without lithium carbonate, starting from a high hydrated gel with more than the usually postulated 3 water and develops to $AH_3$ (Gibbsite) which is very often postulated in literature. With addition of Lithium carbonate the water content of the gel is lower at the early beginning of hydration than in the system without lithium carbonate but develops continuously. In comparison to the system without Li there is no stage detectable where water is again removed from the amorphous Al-hydroxide-gel (see figure 1).

On the basis of the data received from the present study, already published hypothesis for the action of Lithium carbonate in CSA cements can be evaluated for the first time by the use of a directly measured physical value, namely the direct measured water content in the gel phase formed during hydration, highly time resolved.

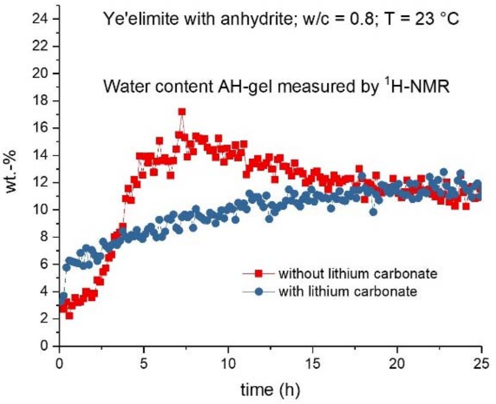

Figure 1: Comparison of directly measured water content in Al-hydroxide-gel during hydration of ye'elimite with anhydrite

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# USE OF BAUXITIC INDUSTRIAL BY-PRODUCTS FOR THE PRODUCTION OF BELITE-CALCIUM SULFOALUMINATE CLINKER

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Belite-Calcium Sulfo-Aluminate (BCSA) is a novel and promising clinker type owed to its low environmental footprint combined with equivalent (or better) performance compared to Ordinary Portland Cement clinker (OPC) [1-4]. The main mineralogical phases of BCSA are Belite $C_2S$, Ye'elimite $C_4A_3\hat{S}$ and Ferrite $C_2A_xF_{(1-x)}$ (C:CaO, S:$SiO_2$, A:$Al_2O_3$, $\hat{S}$:$SO_3$, F:$Fe_2O_3$). The study and production of BCSA clinkers contains significant ongoing research as the formation and development of the mineralogical phases is influenced by several parameters including raw materials composition, raw mix design and production conditions [5-6]. In addition to other parameters, the cost of aluminum-rich raw materials is critical towards the implementation of BCSA type clinkers to production. This work aims to contribute to the matter by presenting BCSA clinker synthesis using bauxitic wastes as alternative raw materials.

Accordingly, BCSA clinker with approximate composition of 40 wt.% belite and 40 wt.% ye'elimite was designed, using bauxitic wastes as aluminum source. Following DTA/TG analysis of the raw mix, clinker phase formation was studied at different clinkerisation temperatures (1270°C, 1300°C, 1320°C and 1340°C), each at three different time intervals (20min, 30min and 60min). The evaluation of clinker phase development in terms of morphological and mineralogical characterization was performed by electron microscopy (SEM/EDS) and X-ray diffraction (XRD / QXRD), respectively. Finally, the compressive strength of hydrated mixtures prepared by the developed clinker samples was determined.

The results of this study provide new insight on the essential role of clinkerisation temperature and duration on the formation and development of clinker phases. The clinkers produced at lower temperatures (1270°C) led to a low quality clinker as the consumption of the raw materials and the formation of the main phases was incomplete, while at higher (1340°C) partial decomposition of $C_4A_3\hat{S}$ was observed. As far as the effect of clinkering duration period, when 60min clinkering time was applied an improvement, in terms of completing the formation of the main clinker's mineralogical phases, was observed.

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# PREDICTION OF THICKENING TIME OF CLASS G CEMENT SLURRIES INCORPORATING CALCIUM SULFOALUMINATE (CSA) CEMENT

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The present study aims to predict thickening time of API Class G cement slurries incorporating calcium sulfoaluminate (CSA) cement and chemical admixtures such as retarder and superplasticizer (SP). Hydration kinetics of cement are well described by Avrami-type equations which can be used to predict the time, $t_{LOP}$, (thickening time) when the consistency of slurries reaches to 100 Bc, *limit of pumpability*. In this study, cement slurries (w/b ratio of 0.4) were prepared using 768 g of Class G cement, 16.6 g of CSA cement and 7.2 g of gypsum. Retarder and SP amounts were 0.5 % and 0.5 % (by weight of binder), respectively. At constant T and p, if we assume that the thickening time corresponds to a fixed degree of reaction, we can obtain [1]

$$\exp\left[-\frac{4(\Delta E^{\ddagger}+p_0\Delta V^{\ddagger})}{RT_0}\right] t_{LOP}^4(T_0,p_0) = 4\int_0^{t_{LOP}}\left(\int_{t'}^{t_{LOP}} q_G[T(t''),p(t'')]dt''\right)^3 q_I[T(t'),p(t')]\mathrm{d}t'$$

If the activation energies ($\Delta V^{\ddagger}$) and activation volumes ($\Delta E^{\ddagger}$) are known, $t_{LOP}$ can be calculated for any thermal and pressure cycles by using this equation.

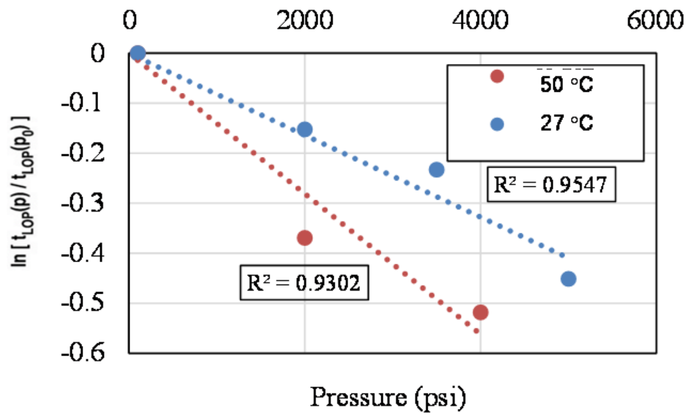

**Figure 1**: Relationship between $\ln[\frac{t_{LOP}(p)}{t_{LOP}(p_0)}]$ values and pressures obtained from consistometer test of API Class G cement slurries incorporating CSA and gypsum

The thickening time of the slurries was measured from consistometer tests under the two temperature conditions (27 and 50 $^{\circ}$C) and the four pressure conditions (100, 2000, 3500, 5000 psi). In Figure 1, a slope of trend line corresponds to activation volume on the basis of theoretical background. However, at 27 and 50 $^{\circ}$C, the measured thickening time does not fit well with the trend line since the constant temperature and pressure were not maintained due to the experimental error. If constant pressure and temperature conditions can be maintained during the test, activation volume is obtained from the trend line slope. Accordingly, it is possible to predict the thickening time of cement slurries incorporating CSA cement.

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# CORROSION BEHAVIOUR OF CARBON STEEL IN CSA: PRINCIPLES AND METHODS

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The paper deals with the study of the passive film formation on steel reinforcements embedded in traditional and CSA-based binders by means of combined electrochemical techniques. In the specific, the corrosion behaviour of steel was evaluated by means of open circuit monitoring (OCV) and Electrochemical Impedance Spectroscopy (EIS) in concretes manufactured with ordinary portland cement (OPC) and CSA-based binders. The work examines the fundamental aspects that determine the protective behaviour of carbon steel reinforcements in concrete made with traditional binders based on Portland cement and defines the peculiarities with respect to CSA-based binders [1]. The paper analyses the role of alkalinity and its maintenance on the corrosion behaviour of carbon steel. The protective action of Portland cement and passivation kinetics are strictly dependent upon the pH of the pore solution [2] – i.e. the availability of hydroxyl ions - and the oxygen content just since the early periods of exposure, in fresh conditions [3]. The pH and alkalinity reservoir also play a fundamental role for the qualification of the new binders for the building industry as far as the resistance to the depassivating effect of chlorides is concerned (Figure 1). New methodologies are proposed for the assessment of pH of cement matrix in order to determine the protective action respect to carbon steel reinforcements. Qualitative test is proposed by using an alternative indicator to phenolphthalein and quantitative technique based on indirect pH measurement of the cement matrix are presented. Corrosion tests confirm different passivation kinetics moving from traditional to innovative binders. Data collected by means of EIS tests showed a marked shift-to-the-left of the time constant over time since early exposures for rebars embedded in OPC compared to CSA. Behaviour that is more complex was noticed for rebars embedded in CSA-based binders.

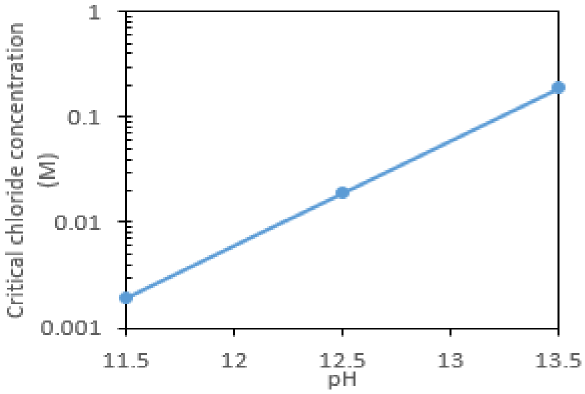

*Figure 1: Critical chloride concentration in function of pH*

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# CALCIUM SULFOALUMINATE CEMENT CLINKER INFLUENCE ON THE HYDRATION OF PORTLAND-LIMESTONE CEMENT

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Calcium sulfoaluminate(CSA) as a sustainable cementitious binder, with the benefit of lower carbon footprint and provided more hydrate assemblages. This study investigated the contribution of calcium sulfoaluminate(CSA) into Portland limestone cement(PLC) by control the content of limestone powder unchanged, replaced Portland Cement(OPC) with different ratio, investigated ternary system mechanical properties, hydrate assemblage and hydration degree. Adding CSA increase hyaration calorimetric of cement at very early age, but strongly delayed the hydration of OPC. During the earlu hydration, CSA converted to ettringite and AFm phase, improved the hydration of limestone to form more carboaluminate hydration products. Compared to without CSA, the appearance of hemicarboaluminate(HC) advanced to 1d, and then converted to monocarboaluminate(MC), consumed more AFm phase and stabilized the existence of ettringite[1-2].

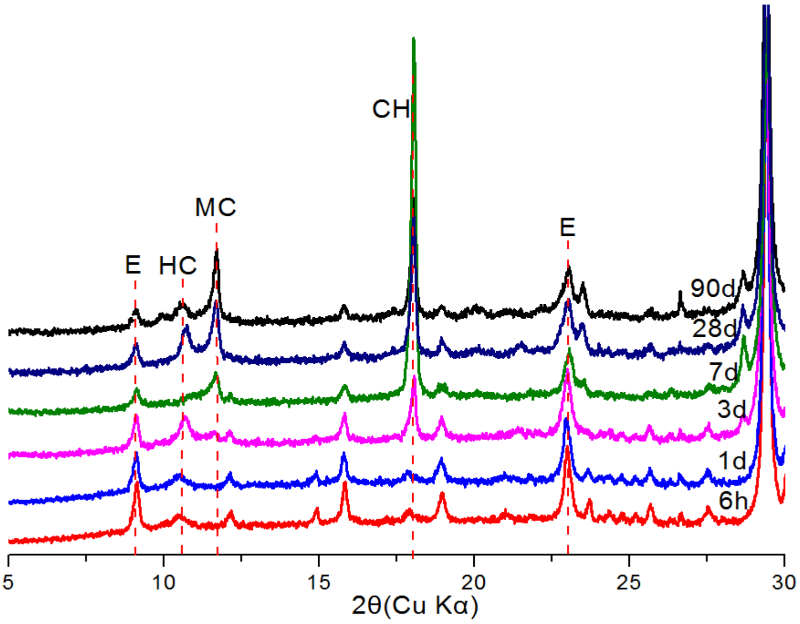

Figure 1: X-ray diffraction patterns of 60%OPC10%CSA30%LS at 0.5W/cm after 6h, 1,3,7,28 and 90 days of sealed curing(Note:E is ettringite; HC is hemicarboaluminate MC is monocarboaluminate and CH is portlandite)

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# IMPACT OF ADDITION OF COMMERCIAL INORGANIC SALTS ON CSA CEMENT PERFORMANCE

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Calcium sulphoaluminate cement (CSA) are usually used in combination to Ordinary Portland Cements (OPC) for formulating special mortars and concretes used for different applications (self-levelling screeds, self-levelling underlayment, repairing, grouting) where rapid-hardening and shrinkage compensating behavior are required. Such kind of formulation normally includes the use of different admixtures, the most important are the retarding agents, necessary for obtaining a suitable pot-life. The widely used retarders are organic acids that, other than the setting time, strongly affect the early strength development. For this reason the use of accelerating agents becomes necessary for counterbalancing the negative effects of the retarding agents. The effect of retarding agents on the performance and hydration of CSA based formulations have been recently widely investigated by different authors. This study is instead focused on the impact of the addition of several commercial inorganic salts, utilised as accelerating agents, on the hydration and final performance of CSA cement. Physical-mechanical tests as well as dimensional stability have been monitored in the presence of different percentage of additions at standard curing conditions (20°C). In all the considered mixes the systems, the effect on the hydration kinetic and hydration products assemblage has been monitored by means of the Isothermal Conduction Calorimetry (ICC), XRD in-situ, SEM, TGA and MIP analyses in the first 28 days of hydration.

# HYDRATION AND TECHNICAL PROPERTIES OF BLENDED-CALCIUM SULFOALUMINATE CEMENTS

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Portland cement (PC) is the most widely used hydraulic binder in construction industry and its manufacture determines about 7% of the global anthropogenic $CO_2$ emissions. This has driven both cement producers and scientific community to develop new cementitious materials whose production process is characterized by a reduced $CO_2$ generation [1].

In this regard, calcium sulfoaluminate (CSA) cements undoubtedly represent an important alternative to PC; as a matter of fact, CSA cements are special hydraulic binders obtained from non-Portland clinkers whose peculiar composition can be exploited not only for achieving considerable technical properties (e.g. rapid hardening, shrinkage compensation, chemical resistance) but also for giving a more pronounced environmentally friendly feature to their manufacturing process [2-3]. Compared to PC, they need a lower synthesis temperature and a reduced limestone requirement which determines a strong decrease of kiln thermal input and $CO_2$ emissions. On the other hand, due to the use of bauxite in the clinker generating raw mix, the price of CSA cements is higher than that of traditional binders; in order to lower the costs and further reduce the amount of carbon dioxide associated with their manufacture, they can be mixed with supplementary cementitious materials (SCMs) such as industrial wastes and/or natural materials [4].

In this paper, water potabilization sludges (WPS) were employed as SCM in CSA-blended cements; WPS were preliminarily thermally treated (TT) at different temperatures in order to obtain an industrial pozzolanic material. The effect of TTWPS on both hydration properties and technical behaviour of different CSA blended cements was investigated by means of differential thermal-thermogravimetric and X-ray diffraction analyses, mercury intrusion porosimetry (for the former) and shrinkage/expansion and compressive strength measurements (for the latter).

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# OPTIMIZATION OF SULFATE CONTENT IN CALCIUM SULFOALUMINATE CEMENTS FOR ENGINEERING APPLICATIONS

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Calcium sulfoaluminate (CSA) cements are usually formulated by considering the stoichiometry of the potential reactions between the ye'elimite in the clinker, calcium sulfate and water [1, 2]. Two reaction cases – one for gypsum and one for anhydrite – may be presented as follows:

$$C_4A_3\overline{S} + 2C\overline{S}H_2 + 34H \rightarrow C_3A{\cdot}3C\overline{S}{\cdot}32H + 2AH_3 \qquad (1)$$

$$C_4A_3\overline{S} + 2C\overline{S} + 38H \rightarrow C_3A{\cdot}3C\overline{S}{\cdot}32H + 2AH_3 \qquad (2)$$

However, if the ye'elimite content of the CSA clinker is high, a significant quantity of mixing water – possibly higher than 60wt% – would be needed to balance these reactions. For most engineering applications (e.g. structural concrete), meeting such a high chemical water demand is not feasible as water contents are usually minimized to ensure that strict performance criteria are met. Therefore, with not enough water available for reactions (1) and (2), it is not always correct to conclude that the system is fully optimized.

This study seeks to improve on the above methodology by considering the water:binder ratio (w/b) of the end application. With w/b as an additional input parameter, the quantity of additional sulfate can be estimated based on the actual quantity of mixing water that is added rather than the theoretical quantity required for full hydration. Therefore, a new formula was devised to account for this. Unlike the traditional approach, the new formula outputs the theoretical mass (%) of calcium sulfate (gypsum or anhydrite) to be fully consumed in the reaction with ye'elimite and the mixing water only. Following this, an experimental study was undertaken to compare the performance of CSA cement pastes optimized using the conventional 'full hydration' approach with pastes optimized using the new 'target w/b' approach. Early mechanical and durability testing revealed that the new methodology led to improved cement paste performance compared with control specimens that were formulated using the conventional approach.

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# EFFECT OF LIMESTONE FINENESS ON CSAB CEMENT HYDRATION

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The current study investigated the hydration characteristics and materials properties of calcium sulfoaluminate-belite (CSAB) cement blended with limestone powder of varying fineness. The presence of limestone powder accelerated the hydration of CSAB cement regardless of its fineness. The limestone powder took part in the hydration of CSAB cement, forming hemicarboaluminate and monocarboaluminate, which could possibly decrease the porosity of the pastes and increase the strength. Specifically, large fineness of limestone accelerates the degree of hydration more due to the increased surface area. It provides more nucleation sites for hydration product to form. On the other hand, the strength improvement was only observed where finder limestone powder than the clinker was used. This indicates that the positive influence of forming carbon-containing AFm phases with additional ettringite can be reduced by the reduction in clinker component. Thermodynamic modelling of the system provided that the total solid volume of the cement increased with increasing limestone content up to 6 wt%. This provides the evidences of improvement of strength as well as reduction of pore volume of the cements.

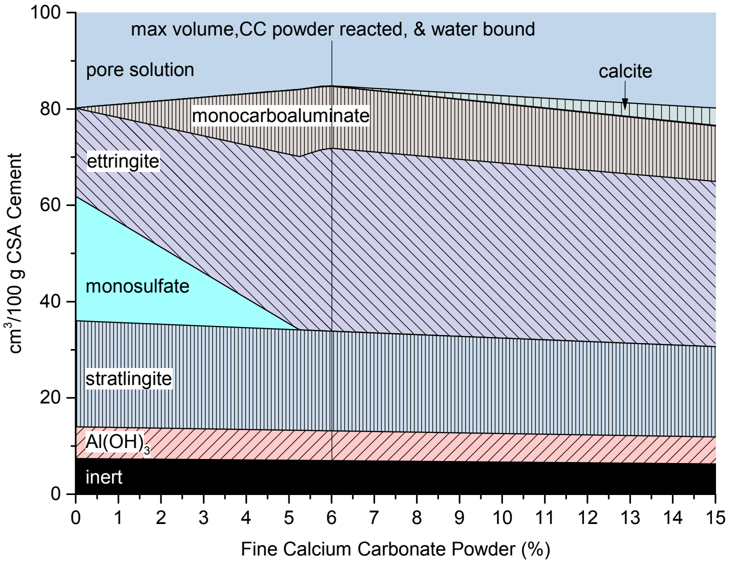

**Figure 1.** Results of modeling cement hydration with different limestone contents under conditions of full hydration [1].

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# THE POTENTIAL OF MICROSCOPY FOR THE INVESTIGATION OF THE CSA CLINKER MICROSTRUCTURE

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Clinker microscopy is an often used method for the characterization of ordinary Portland cement (OPC). The crystal size, the shape and the distribution of the minerals within the matrix gives a lot of information about the raw materials, the burning and the cooling process and an idea about the properties of the later cement. But in case of calcium sulfoaluminate (CSA) clinker the microscopic investigation is much more difficult. CSA is burned at lower temperatures than on OPC and different clinker minerals are formed. Additionally, the developed crystals are mostly very small within a sometimes very heterogeneous matrix. This is a huge handicap for the investigation of polished sections by light microscopy. The identification of the minerals is very tricky, sometimes impossible. An additional investigation of the samples with the scanning electron microscopy gives much more information. The investigation of the polished sections by back scattered electrons (BSE) improves the differentiation of the several phases in spite of the small crystal size, and an additional elemental analysis by EDX makes the identification of the different phases possible.

This study shows the potential of the investigation of CSA clinker with the combined methods of light and scanning electron microscopy to get more information about the burning process and the later properties of cement in case of CSA clinkers. CSA clinkers from three different kilns were investigated and characterized comparing the microscopical results with the physical properties of the different cements.

# PHASE SINGULARITIES IN C-S-A-F-S-(H) SYSTEMS

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Sulphoaluminate Belite Cements (SAB) considered as Low Energy and Low Carbon Cements have been developed as alternative to Portland cement, at least to its partial replacement in specific cases [1-2]. In spite of the excellent experimental results obtained throughout laboratories and the numerous manifested advantages, their industrial scale production has not received a favorable echo among cement producers and some doubts remain regarding their use as a masonry material in civil engineering. The scientific challenge regarding the development of SAB was the establishment of phase compatibilities in the framework of $CaO$-$SiO_2$-$Al_2O_3$-$Fe_2O_3$-$SO_3$ five oxide system, in which 52 phase diagrams (assemblages) were identified, each consisting of five phases coexisting thermodynamically at clinkering temperature lower than 1450 °C. 18 phase diagrams are relevant to SAB [6]. Our studies have established, from a map of raw materials necessary to produce SAB cements the existence of five-phase systems as areas, four-phase systems as lines separating the areas and three-phase systems as intersection of at least 3 areas [7]. Until now, only cement within $C_2S$ - $C_4A_3\bar{S}$-$C_4AF$- C- $C\bar{S}$ and $C_2AS$-$C_4A_3\bar{S}$-$C\bar{S}$-$C_2S$ were deeply explored because of the similarity between their hydration products with that of Ordinary Portland cement. Indeed, $C_2S$ produces by hydration calcium silicate hydrate (CSH) responsible for later strength development according to Eq1.

$$C_2S + H \Leftrightarrow CSH + CH \tag{1}$$

In the presence of C and $C\bar{S}$, $C_4A_3\bar{S}$ reacts with water to form ettringite for fast early development of compressive strength.

$$C_4A_3\bar{S} + 8C\bar{S} + 6CH + 90\,H \quad \Leftrightarrow \quad 3C_6A\bar{S}_3H_{32} \tag{2}$$

When is anhydrite only, $C_4A_3\bar{S}$ hydrates to form ettringite, according to Eq. 3.

$$C_4A_3\bar{S} + 2C\bar{S} + 38\,H \Leftrightarrow \quad C_6A\bar{S}_3H_{32} + 2AH_3 \tag{3}$$

The secondary reaction between CH, $AH_3$ and C-S-H and water leads to the formation gehlenite hydrate according to Eq. 4.

$$CSH + CH + AH_3 + 3H \quad \Leftrightarrow \quad C_2ASH_8 \tag{4}$$

At a specific singular composition of SAB, two thermodynamically products can be formed: ettringite ($C_6A\bar{S}_3H_{32}$) and gehlenite hydrate ($C_2ASH_8$) with possible formation of solid solutions.

The ongoing research in this field is to investigate the mechanism and kinetics of ettringite and gehlenite hydrate formation in a particular singular composition.

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# THE EFFECT OF METAKAOLIN AND LIMESTONE ON THE HYDRATE PHASE ASSEMBLAGES AND HYDRATION KINETICS OF CALCIUM SULFOALUMINATE – METAKAOLIN – LIMESTONE BLENDS

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Calcium sulfoaluminate (CSA) cement attracts currently significant attention as an alternative to ordinary Portland cement because of its lower $CO_2$ footprint. A further reduction in $CO_2$ emission may potentially be achieved by a partial replacement of CSA cement with supplementary cementitious materials such as calcined clays. The present work focusses on a commercial CSA cement with 20 wt.% replacement by mixtures of metakaolin (MK) and limestone (LS), where our primary goal is to obtain an improved understanding of the hydration products and kinetics and to explore the potential of SCM's in CSA cement.

Five blends corresponding to MK/(MK + LS) ratios of 0, 0.25, 0.5, 0.75 and 1 have been prepared with a water-binder ratio of 0.7 and a gypsum/ye'elimite ratio of M = 0.5. Additionally, a pure CSA blend has been prepared as a reference. The hydration reactions of all blends have been studied by powder X-ray diffraction, thermogravimetric analysis, as well as $^{27}$Al and $^{29}$Si NMR. In addition, compressive strengths have been obtained for the corresponding mortar samples after 1, 2, 7, 14, 28, 91 and 182 days of hydration.

Ettringite and calcium aluminate hydrate are the main hydrate phases formed during hydration of pure CSA cement and when belite starts to react after approx. 7 days, strätlingite is also formed. At later hydration times, ettringite dissolves and monosulfate forms, which results in a decrease in compressive strength. The presence of limestone results in the formation of hemicarbonate at the expense of monosulfate, which stabilizes ettringite in the system, and no decrease in the compressive strength is observed for these blends. The addition of metakaolin leads to an increased compressive strength possibly due to a refined pore structure. The $^{27}$Al MAS NMR spectra in Fig. 1 show the difference in AFt/AFm ratio after 182 days of hydration as a result of partial replacement by LS and MK.

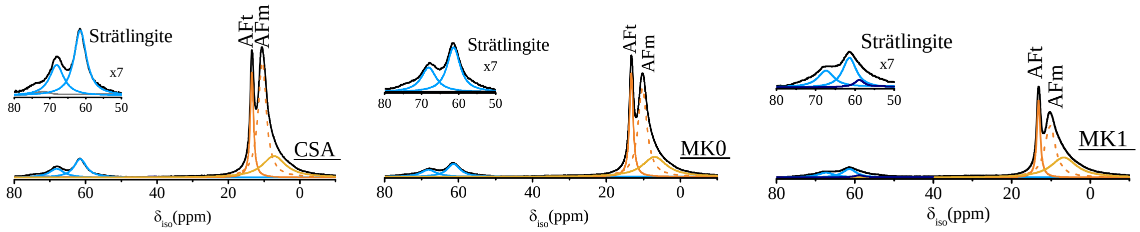

Fig. 1 $^{27}$Al MAS NMR spectra (14.1 T) of the CSA blend, and the blends containing only limestone (MK0) and metakaolin (MK1) after hydration for 182 days.

Both metakaolin and limestone accelerate the hydration of ye'elimite at early hydration times, which is ascribed to a filler effect and the increased effective water to cement ratio in these blends. Furthermore, the presence of limestone results in an increased degree of reaction for belite, whereas the lower space availability in the metakaolin containing blends gives a decrease in the reaction degree for belite. In conclusion, the combination of metakaolin and limestone shows great promises as potential SCM's in CSA cement systems at the studied replacement level of 20 wt.%.

# ON THE HEAT OF FORMATION OF YE’ELIMITE USING DENSITY FUNCTIONAL THEORY AB-INITIO CALCULATIONS

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Ye’elimite is the key component in novel, low $CO_2$ clinkers and cements [1]. Thermodynamic calculations are nowadays widely used to optimize clinkering conditions [2] and to investigate and understand hydration behaviour [3]. The reliability of the obtained calculation results depends directly on the quality of the underlying Gibbs energy data. In the case of ye’elimite, the available data is scarce with considerable error bars. There is only one calorimetric measurement for the heat of formation of this compound using acid solution calorimetry at room temperature [4]. All other data values are derived from hydration measurements and are based on assumptions/estimations [5-7].

A modern way to determine thermodynamic properties of individual substances and solutions is the used of ab-initio first principles calculations using density functional theory. The application of this method for cement clinker related compounds was already shown [8]. In the case of ye’elimite, the structural characteristics of the cubic and orthorhombic modifications were determined recently by Cuevas et al [9]. In this contribution the focus is set on the energy of formation of both modifications of ye’elimite with respect to CaO, $Al_2O_3$ and $CaSO_4$ and $CaAl_2O_4$ and $CaSO_4$. The VASP (Vienna Ab-initio Simulation Package) [10] is used with a plane-wave basis and the projector augmented wave (PAW) method [11]. Three different exchange-correlation functionals are used: LDA, GGA and SCAN (meta-GGA). The calculated results for the energies of formation for the two potential reactions cited above and the simulated lattice parameters for both modifications will be compared to the available literature information and to the work of Cuesta et al.

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# STUDY OF NUCLEATION AND GROWTH PROCESSES OF ETTRINGITE IN SUPERSATURATED DILUTED SOLUTIONS

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Ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ is one of the major hydrates formed during cement hydration. Ettringite forms in Portland cement from the reaction between tricalcium aluminate $C_3A$ and calcium sulfate. Ettringite is also present in calcium sulfoaluminate cements in which it is the major hydrate, formed by the reaction between yeelimite and calcium sulfate.

Development of ettringite is a crucial parameter of cement chemistry, however several concerns remain about the factors influencing its nucleation-growth process. To make progress toward the understanding of existing phenomena, a specific study of nucleation and growth of ettringite was made.

First ettringite nucleation was studied in ionic aqueous solutions, with controlled but different experimental conditions, as different supersaturation degrees (β), different pH or presence of exogenous ions. Through induction time measurements, interfacial ettringite crystals solution energies (γ) were determined. Growth of ettringite in supersaturated solutions was also studied through chain crystallization reactions. Specific BET surface area measurements and SEM observations seemed to prove that growth process is favored over the nucleation process when ettringite crystals are initially present in a solution with a low supersaturation degree with respect to ettringite.

During all these experiments, initially present ions are consumed to form ettringite in such a way that the supersaturation degree with regard to ettringite is decreasing over time. To avoid this phenomenon a device compensating the drop of ions concentrations by adding some more solutions, and therefore always have constant ionic concentrations, was used. This constant β recreates the conditions of the beginning of cement paste hydration, when the dissolution of solid reagents compensates the consumption of ions to form hydrates. This device allowed the determination of the ettringite precipitation speed as a function of the supersaturation degree β. By taking samples at different time during ettringite precipitation and doing BET measurements, we were able to determine the interfacial growth rate of ettringite in $m^2/s$. This data is important to see whether or not ettringite grows with a constant rate over time. If not this will be proof that there is a limit size from which ettringite crystals have difficulties to keep growing.

Results obtained about the nucleation-growth process of pure ettringite in aqueous solutions were then transposed to cementitious systems. Ettringite formation was studied in systems such as $C_3A+CaSO_4$ or yeelimite+$CaSO_4$, still with controlled parameters. Ettringite formation process and morphology were also studied in these systems through conductivity and calorimetry measurements, XRD analysis or SEM observations.

This work will lead to a better understanding and control of ettringite formation during hydration of different cements, in particular calcium sulfoaluminate cements. This study will also ultimately define the impact of ettringite formation process on the rheology of cement pastes at early age, which is a crucial parameter from a practical point of view.

# CALCIUM SULPHOALUMINATE CEMENT VS. CALCIUM ALUMINATE CEMENT- SULPHATE BASED BINDER. COMPARISON OF THE HYDRATION KINETICS AND PHASE ASSEMBLAGE.

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Although calcium sulphoaluminate cement (CSA) and calcium aluminate cement (CAC) blended with calcium sulphate ($C\overline{S}$) might lead to the formation of the same hydrates, their kinetics can differ [1]. The comparison of the hydration kinetics and phase assemblage of a calcium sulphoaluminate cement (CSA) and a calcium aluminate cement- calcium sulpahte (CAC-$C\overline{S}$ based binder has been presented. In the CAC-$C\overline{S}$ system, gypsum was used as a sulpahte source. The hydration kinetics and the phase evolution was investigated in terms of calorimetry, XRD, TGA and SEM. The phase assemblage was followed quantitatively at discrete ages of 1, 7, and 28 days. Experimental results from XRD and TGA showed ettringite, monosulphate and $AH_3$ as main hydration products. Monosulphate was found to be X-ray amorphous in both cases and its presence was verified by thermal analysis. Quantitative X-ray analysis confirmed that the amount of ettringite content varied between both systems, with the CAC-$C\overline{S}$ system developing higher amount of ettringite. SEM observations indicated morphological differences in between the hydration products. Poorly crystallized ettringite, with consequently a denser matrix was observed in the hydrated CSA, while well-crystallized needle like ettringite were formed in the CAC-$C\overline{S}$ binder.

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# EVALUATION OF PROPERTIES OF ALITE-CALCIUM SULFOALUMINATE (A/CSA) CEMENT PRODUCED FROM ASIAN ASH

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This work summarizes the use of fly ash produced at the Zhungeer Power Station located in the Province of Inner Mongolia, China, in the production of Portland/Calcium Sulfoaluminate (OPC/CSA or A/CSA) cements. The unusually high $Al_2O_3$ content, up to 55% by weight, makes the Zhungeer fly ash a candidate for the production of CSA or A/CSA clinkers without the need to add bauxite or other sources of aluminum. Previous work presented at the Asian Coal Ash Association in 2016 [1] demonstrated this feasibility. This study focused on the production of almost 2kg of A/CSA clinker with the Zhungeer fly ash as the source of alumina. The clinker composition was approximately: 28 wt.% $C_3S$, 22 wt.% $C_2S$, 2 wt.% $C_4AF$, and 41wt.% $C_4A_3\acute{S}$. The optimal calcium sulfate content for both gypsum and anhydrite were determined using isothermal calorimetry. Both forms of calcium sulfate were interground with the clinker and this cement was used in production of cement pastes and mortar cubes. The hydration process was followed by analyzing the cement pastes with X-ray diffraction (XRD) and thermogravimetry analyses (TGA). The compressive strength of the mortar cubes was determined using the European standard, EN-196, and the results were found to be very promising out performing OPC at early strengths. The work demonstrates that the production of A/CSA cement is another potential high value added material for the Zhungeer fly ash.

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# THE β→γ TRANSFORMATION OF $Ca_2SiO_4$

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Due to the use of calcium carbonate as a raw material, the manufacture of Portland cement is a significant source of $CO_2$ emissions during clinker firing, which can be detrimental to the environment [1]. An alternative solution is to develop a new type of hydraulic binders that would produce less $CO_2$ during the clinker formation. Sulfoaluminate Cements (CSA) are promising candidates. Among the crystalline phases contained in these cements is the dicalcium silicate, $Ca_2SiO_4$. Moreover, Belite, which is a solid solution based on dicalcium silicate, is also present in Portland cements. Dicalcium silicate belongs to the family of ortho-silicates. It has five polymorphs ($\alpha$, $\alpha'_H$, $\alpha'_L$, $\beta$ and $\gamma$), whose β form is the best known in cements [2]. The stable form at low temperature is the γ-$Ca_2SiO_4$ phase. This form has no hydraulic activity. Therefore, this is a phase to avoid in the manufacture of cements. Thus, the stabilization of the β-$Ca_2SiO_4$ phase during cooling of the clinker is a goal to be achieved to ensure the hydraulicity of this phase. This goal requires a good understanding of the factors that influence the β→γ transformation. In the present work, the influence of $Ca_2SiO_4$ particle size on the stabilization of the β form has been studied. The $Ca_2SiO_4$ phase was prepared by polycondensation reactions and calcined at different temperatures (800°C, 1000°C, 1200°C and 1400°C). The control of the particle size was ensured by the change in the firing duration at 1400°C. The phases formed after each treatment were characterized by X-ray diffraction and quantified by the Rietveld method. The microstructure of the obtained particles was studied by scanning electron microscopy (SEM) in order to see the effect of this transformation on the microstructure of the obtained grains. The presented results will focus on the correlation between the particle size and the stabilization of the β phase. A critical particle size above which γ-$Ca_2SiO_4$ can be formed will be defined. A thermodynamic model, which enables to predict the critical particle size, will be presented.

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# IMPROVED WORKABILITY OF CSA CEMENT BY POLYMER ENCAPSULATION

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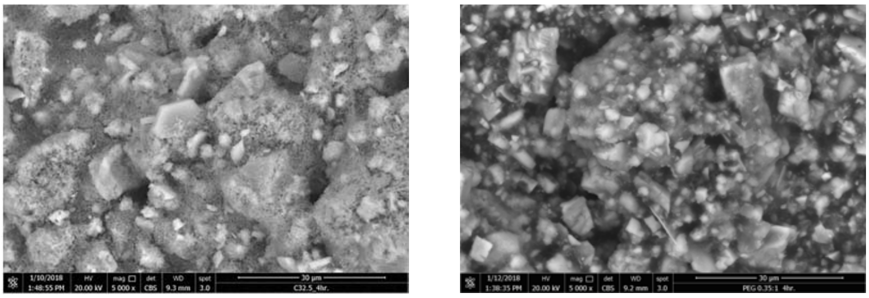
This study focuses on the modification of calcium sulfoaluminate (CSA) cement by encapsulating conventional CSA cement in a matrix structure. Polymers (e.g. polyethylene glycol, PEG) act as a matrix for cement particles to disperse. The purpose of this new class of CSA is to improve its workability. When the modified CSA cement contacts with water, the polymer matrix acts as a water barrier, and thus, delays hydration reactions. The hydration of conventional CSA cement and modified CSA cement were examined with simultaneous differential thermal-thermogravimetric (DTA-TG) analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM) over 4 weeks. The DTG analysis confirmed that at an early stage of hydration, conventional CSA cement generates more ettringite than modified CSA cement, which is also observed under SEM, as shown in Figure 1.



(a) (b)

*Figure 1. Scanning electron micrographs of (a) conventional CSA cement and (b) modified CSA cement at 4 h of hydration.*

This results in better workability of the modified CSA cement when compared to that of the conventional CSA cement. Within the first 7 days, conventional CSA cement expands more significantly than the modified CSA cement. However, the amount of ettringite generated from both cements increased and eventually reached the same amount after 2 weeks. At 28 days, no significant difference in drying shrinkage was seen from both cements (Figure 2).

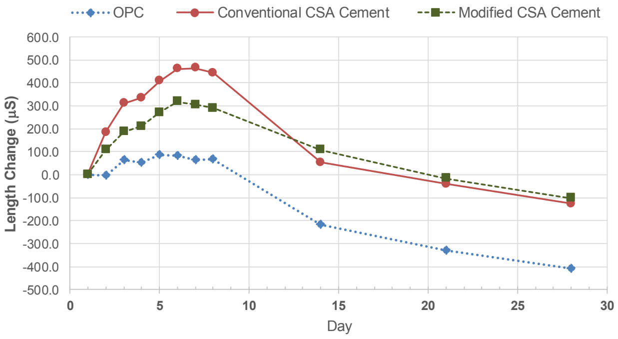


*Figure 2. Comparison of drying shrinkage of mortar prepared from OPC (♦), Conventional CSA (●) cement and Modified CSA cement (■).*

# CHARACTERIZATION OF CALCIUM SULFOALUMINATE CEMENT COMPONENTS AND HYDRATION REACTIONS BY $^{19}$F, $^{27}$Al AND $^{29}$Si MAS NMR SPECTROSCOPY

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Calcium sulfoaluminate (CSA) cements receive currently significant research interest, as they may be a low-$CO_2$ alternative to Portland cement. The present study investigates the potential of solid-state NMR spectroscopy to follow the hydration reactions of major and minor phases in CSA cement and reports some of the fundamental NMR parameters for the individual components.

The principal phase in CSA cement is ye'elimite ($Ca_4Al_6O_{12}SO_4$) which include eight crystallographically independent $AlO_4$ sites in its orthorhombic structure [1,2]. The $^{27}$Al quadrupole coupling and chemical shift parameters have for the first time been determined for these eight sites from a combined analysis of $^{27}$Al MAS and MQMAS NMR spectra (Fig. 1) acquired at several magnetic field strengths (4.7 – 22.3 T). These parameters are assigned to the individual Al sites in ye'elimite by DFT calculations, and their agreement with the calculated $^{27}$Al electric-field gradient tensor elements are used to evaluate the proposed structures from neutron powder diffraction [1] and a combined neutron and X-ray powder diffraction study [2]. DFT refinements of the two proposed structures result in the same and a refined crystal structure for ye'elimite.

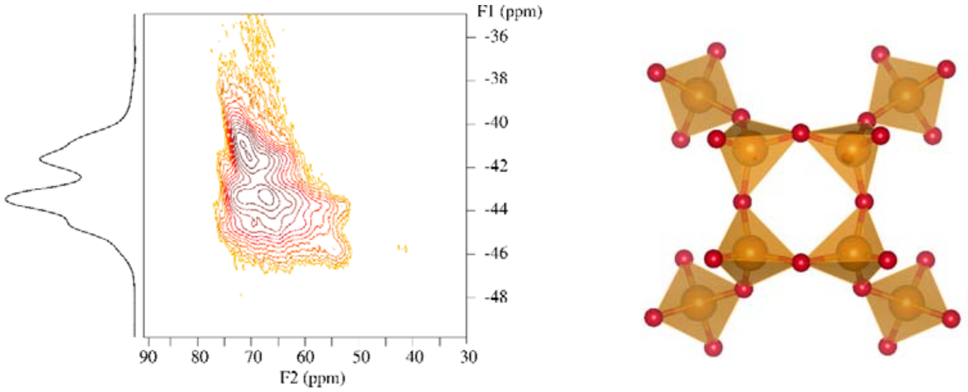

Fig. 1: $^{27}$Al MQMAS NMR spectrum (14.1 T) of ye'elimite and the $AlO_4$ sites of its crystal structure.

The $^{27}$Al NMR parameters form also the basis for a reliable quantification of ye'elimite in hydrated CSA cements by $^{27}$Al MAS NMR as illustrated for a commercial cement which contains ye'elimite, belite ($Ca_2SiO_4$), fluorellestadite ($Ca_{10}(SiO_2)_3(SO_4)_3F_2$), and bredigite ($Ca_7MgO_8(SiO_2)_4$) as the principal phases. The two latter phases have been synthesized and characterized by $^{29}$Si NMR to obtain the $^{29}$Si chemical shifts, which provide the basis for the identification of these two components in CSA cements. Moreover, fluorellestadite can be selectively detected by the $^{19}$F{$^{29}$Si} cross-polarization experiment, which transfers magnetization from $^{19}$F to the $^{29}$Si spins. The above-mentioned NMR techniques are used to characterize the hydration reactions for the commercial CSA cement in a semi-quantitative manner.

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# SYNTHESIS AND CHARACTERIZATION OF CALCIUM SULFO-ALUMINATE CEMENTS PRODUCED BY DIFFERENT CHEMICAL GYPSUMS

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Nowadays there is a renewed interest towards calcium sulfoaluminate (CSA) cement due to both its valuable technical properties and pronounced environmentally friendly features, widely recognized by the international scientific community and greatly appreciated during the last years [1-2].

Compared to ordinary Portland cement (OPC), the production process of CSA cement requires a lower synthesis temperature (around 1300°C), a reduced amount of limestone in the kiln raw mix and, consequently, reduced thermal input and $CO_2$ emission. Moreover, CSA cement can be synthesized from a wide range of industrial wastes whose reuse and disposal is often quite complicated [3].

In this work four different chemical gypsums (flue gas desulphurization gypsum, fluorogypsum, titanogypsum, and phosphogypsum) were separately used as total calcium sulphate substitute in the CSA clinkers generating raw mixes (also containing limestone and bauxite). Different laboratory-made CSA clinkers (obtained at temperatures ranging from 1150°C to 1300°C) were investigated using XRD analysis as main characterization technique. A reference mixture, based on limestone, bauxite and natural gypsum underwent the same thermal treatments. It has been found that a very good selectivity towards high contents of $C_4A_3\$$, even better than that achieved by using only natural raw materials, was displayed by chemical gypsums-based raw mixes.

The hydration behaviour of five CSA cements, obtained by adding a commercial anhydrite to CSA clinkers produced at the optimum synthesis temperatures, has been experimentally investigated for curing times ranging from 4 hours to 28 days. In this regard, conduction calorimetric measurements associated with X-ray diffraction and differential thermal-thermogravimetric analyses showed that all CSA cements produced have a similar hydration behaviour. A thermodynamic hydration model based on cement composition using the geochemical GEMS-PSI software was set up [4]. The modelled phase composition, depending on hydration time, shows a good agreement with the experimental results of the investigated cements.

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# A COMPARISON BETWEEN CALCIUM SULFOALUMINATE CEMENT AND FLY ASH-BASED GEOPOLYMER AS SUSTAINABLE BINDERS FOR NON-STRUCTURAL AND STRUCTURAL MORTARS

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This work is focused on the study of calcium sulfoaluminate (CSA)-based cements and fly ash-based geopolymeric (GEO) binders as environmentally-friendly alternatives to ordinary Portland cement (OPC) to produce mortars for construction applications. According to the European standard EN 1504-3 "Products and systems for the protection and repair of concrete structures", six different mortars, conceived for both non-structural (R1 ≥ 10 MPa and R2 ≥ 15 MPa) and structural (R3 ≥ 25 MPa) applications, were prepared; mixtures belonging to the same mechanical strength class (one per each binder) were tested and compared. Binder pastes were prepared in order to study their hydration behavior by means of differential thermal-thermogravimetric and X-ray diffraction analyses; afterwards, porosity development in hydrated pastes was determined by means of mercury intrusion porosimetry (MIP). MIP measurements were also carried out on the corresponding mortars, which were also compared in terms of mechanical compressive strength, dynamic modulus of elasticity, and water vapor permeability. Tests based on capillary water absorption, free and restrained drying shrinkage, and resistance to sodium sulfate attack were carried out in order to study also the durability of mortars. All CSA-based mixtures reached their final highest compressive strength value faster than GEO mortars, due to the high formation rate of ettringite [1,2]. Moreover, they exhibited both a lower free drying and restrained shrinkages [3], thanks to their high modulus of elasticity [4] as well as the initial expansion [5]. CSA and GEO mortars showed the same total porosity values; however, compared to GEO mortars, the lower CSA mortars pores size determined a worse resistance to sulfates; they caused the formation of expansive products which induced higher tensile stresses. However, the presence of smaller pores contributed to a lower permeability to water vapor and retarded the capillary absorption of water at short periods of time in CSA mortars.

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# FLEXURAL STRENGTH OF MORTARS CONTAINING CALCIUM SULFOALUMINATE CEMENT

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Beyond compressive strength ($\sigma_c$), for many applications (road, screed, etc.), tensile strength is also an important mechanical property which depends on various parameters (cement paste porosity, aggregate shape, reinforcing fibres, etc.). In absence of fibers, flexural strength ($\sigma_f$) of mortars [1-2] or splitting strength of concrete can be predicted from compressive strength using power relations ($\sigma_f = K x \sigma_c^{\alpha}$).

The aim of this study is to control if calcium sulfoaluminate (CSA) cement and Ordinary Portland Cement (OPC) have the same mechanical behaviour. Analysis of 130 strengths measurements on mortars [3-4] containing CSA cement, OPC and OPC-CSA cement blends shows that mortars made with CSA cement have lower flexural strength (25% in average). Power relations predict the flexural strength with an average error of 0.6 MPa and 0.5 MPa for CSA cement and OPC, respectively. These tests being done mainly on standard mortars (EN 196-1), new measurements were made with four different water/cement ratio (W/C=0.4, 0.50, 0.55, 0.6) and two type of 0/4 sand (siliceous and calcareous) after 28 days of hydration.

These results (Figure 1) confirm that mortars with CSA cement develop lower flexural strength regardless of the type of sand (i.e. the cement paste-aggregate bond) or the water/cement ratio (i.e. the paste porosity). Therefore, this mechanical behaviour of mortars containing CSA cement and OPC is discussed regarding their differences in terms of hydration product and microstructure.

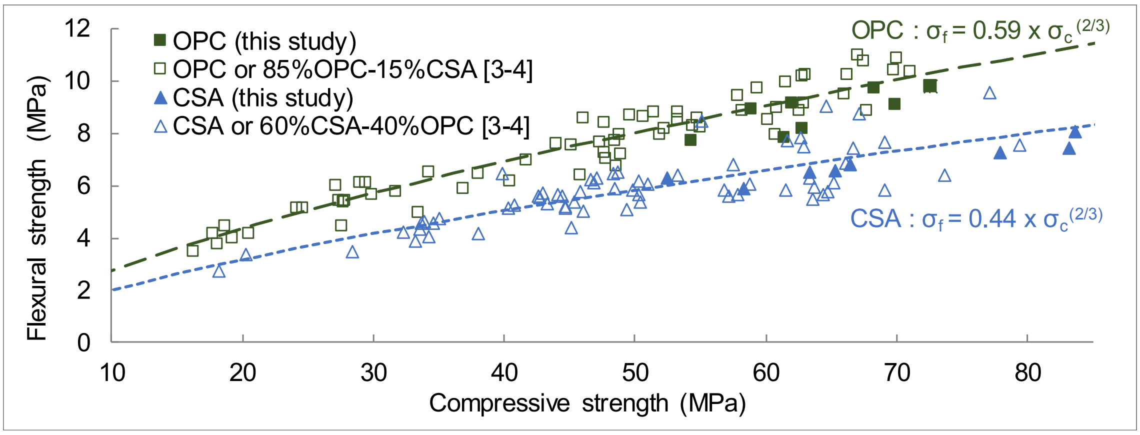

Figure 1: Flexural and compressive strengths of mortars containing OPC and CSA cement

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# ACCELARATED FOAMED CONCRETE BASED ON CSA CEMENT

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Calcium Sulfo Aluminate cements are based on the formation of ettringite. On hydration a crystal is formed which holds approximately 32 water molecules. In theory this means an excellent fire resistant material (f.e. gypsum holds only 2 water molecules).

At increased temperature (> 90°C) the crystal starts losing its bound water - releasing enough moisture to significantly reduce the temperature.

In practice there is no demand for any load bearing so strength is of no importance and was not measuredt

Aim of our investigation was to make heat insulation panels or mortar using CSA cement as prime binder with a density of 180~200 kg/m$^3$.

From earlier tests and literature we learned that foamed concrete based on OPC tend to get unstable at densities below 400 kg/m$^3$ - primarily due to the collapse of the air bubbles in the matrix. With a more fast setting material stability of the bubbles is better guaranteed. In this respect the use of CSA cement is the favourable type of binder as it normally sets within 20 minutes.

Other benefits of aerated concrete are found to be:

- sound insulation
- thermal insulation
- low weight
- cost effective
- ease of handling

This paper presents the results of the imperial study done.

# FURTHER INSIGHTS IN THE CARBONATION RESISTANCE OF CALCIUM SULFOALUMINATE CEMENT MORTARS

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Calcium sulfoaluminate (CSA) cement is an alternative to Portland cement (PC) and has been proposed as a low carbon cement. Compared to PC, there have been relatively few durability studies investigating CSA cement, hampering a broader application of CSA based concretes. Carbonation of concrete and subsequent corrosion of the steel reinforcement is one of the major deterioration mechanisms of concrete. Prior research, see [1] and the references cited therein, presents conflicting results as to whether CSA carbonates faster than PC.

This study is investigating potential physical and chemical parameters that could govern the carbonation rate of CSA mortars and endeavors to elucidate the microstructural and chemical factors that govern CSA cement's carbonation rate in laboratory experiments and out-door exposures.

The kinetics of the carbonation process is investigated on CSA systems with different calcium sulfate sources and different calcium sulfate to ye'elimite molar ratios. Plain PC mortar serves as reference. The impact of the carbonation process on physical-mechanical and durability performance of mortars is correlated at microscale level to the hydrated phase evolution characterized by means of analytical techniques such as thermogravimetric analysis, X-ray diffraction, infrared spectroscopy and mercury intrusion porosity. Thermodynamic modelling is applied as potentially valid tool to predict hydrated phase evolution and thermodynamic stability of hydrated carbonated phases.

The results reveal that CSA mortars show a carbonation resistance similar to PC mortar provided that sufficient calcium sulfate is present in the CSA cement. Such systems exhibit a very dense pore structure, allowing only a slow ingress of $CO_2$. In the carbonated region (detection using the phenolphthalein test) ettringite, the main hydration product of CSA, is still present. Thus, no strength loss of carbonated CSA mortars was observed.

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# HYDRATION KINETICS IN A HIGH OPC TERNARY CSA SYSTEM

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Ternary blends consisting of calcium sulfoaluminate cements, OPC and a sulfate carrier are of particular interest for certain applications as they combine the advantages of CSA hydration, such as high early strength and good volume stability with the advantages of OPC hydration products such as high strength after long hydration times [1]. These systems also tend to produce relatively high amounts of ettringite in the hydrating pastes and are therefore often used in applications where rapid drying is desired. As the calcium content of CSA cements is comparatively lower than in Ordinary Portland cements these blends can furthermore be used to reduce the environmental impact arising from the calcination of limestone during the manufacturing process. Yet the hydration kinetics in OPC-CSA-C$ mixes have not been fully described with respect to their hydration kinetics derived from quantitative phase development  for the early time frames.

For this study we chose a system with a high OPC content (55 wt.-% in the dry mass). According to thermodynamic modelling via the GEMS software the Ca-sulfate should be completely incorporated into AFt-Phases (ettringite) for a w/c value of 0.8. From the thermodynamic simulation we expect a high ettringite content after full hydration (approx. 52 wt.-% of the paste), which is nearly reached already after 2 days of hydration.

The ettringite formation in the first 48h processes in a multi-step hydration arising from the interaction of the CSA and OPC components and the three different reaction pathways which lead to ettringite formation. We can correlate the stepwise ettringite formation from in-situ XRD with several maxima of heat flow curves and ultrasonic pulse velocity measurements (Fig. 1).

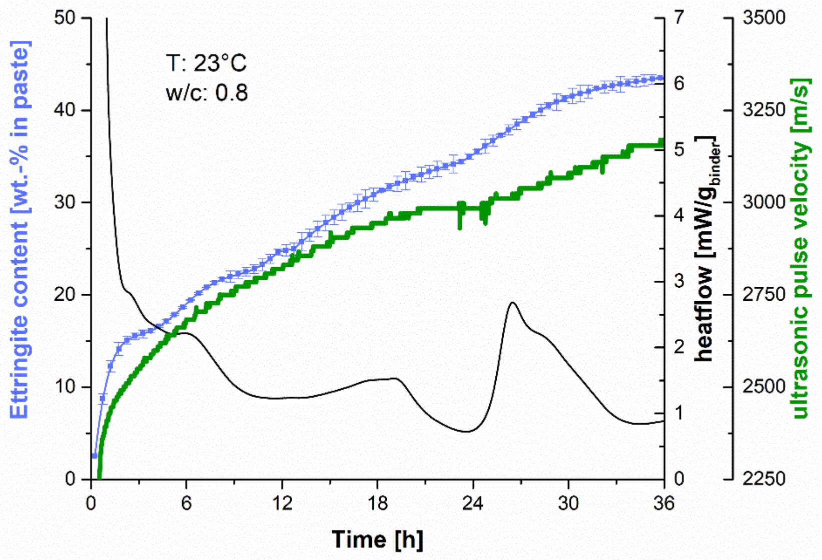

Figure 1: Comparison of ettringite content in the hydrating paste during the first 48h with heat flow calorimetry and ultrasonic pulse velocity.

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# MODELLING OF THE HYDRATION AND PERFORMANCE EVOLUTION OF BYF CEMENT

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In recent years, belite - calcium sulphoaluminate – ferrite type binders (BYF) are in the scope of the research and development at industry. This type of cements may exhibit similar performance as the ordinary Portland cements (OPC) thought offers the potential to reduce the environmental footprint of the building industry [1]. However, the introduction of a new type of binder to the building practice is challenging. Since there is a lack of empirical data, the definition of the perspective rules is not possible. To address these needs, the prescriptive concrete design needs to be replaced by a performance-based design and the long-term experience by predictive modelling of material performance.

In order to address these challenges we undertake the effort to understand the reaction mechanisms of various BYF cements characterized by the different sulfate content and resulting evolution of performance, i.e. compressive strength and elastic properties. As a first step, we characterized the hydrating samples by multimethod approach to assess the evolution of their hydrates assemblages and porosities. This data was supplemented with measurements of the mechanical performance evolution. Subsequently, we applied currently available thermodynamic (GEMS) and micromechanical models to quantitatively predict the hydrates assemblage and mechanical performance evolution, respectively [2] [3].

The results demonstrate that strength and E-modules and compressive strength evolution of the BYF cement strongly depends on the sulphate dosage: the higher the sulphate dosage the higher the early compressive strength. Addition of sulphate accelerates early hydration and retard later hydration of the clinker. The early hydration is dominated by the reaction of ye'elimite, calcium sulfate and calcium aluminate phases. The main crystalline hydrate is ettringite. Analysis of the phase assemblage by means of experimental techniques and thermodynamic modelling reveals that the volume of the XRD-amorphous phase is important at early period. The reaction of belite, which reacts at later times, results in significant changes to the phase assemblage. This is demonstrated by an important phase transformations, mainly of the XRD-amorphous phases. These processes modify the initial microstructure and the resulting mechanical performance. The micromechanical modelling employed further contributes to the understanding of the origin of the performance evolution and reveals the role of individual hydrates and reactions in the strength evolution.

We show that the models available are generally applicable to model the strength of mortars based on the hydrates assemblages predicted by the thermodynamic modelling and on material properties of hydrates reported in the literature. However, the modelling needs to be further improved by better definition of the XRD amorphous phases and their properties.

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# RAPID HARDENING HIGH-BELITE CALCIUM SULFOALUMINATE (HB-CSA) CEMENT: A LOW-$CO_2$ CEMENT

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Calcium sulfoaluminate (CSA) cement is a promising cement of low $CO_2$ emission. Compared to ordinary Portland cement (OPC), the decomposition of CSA clinker raw materials generates less $CO_2$, and CSA clinker is formed at lower temperature and easier to be ground. Manufacturing CSA cement needs a large amount of high-quality bauxite, which provides $Al_2O_3$ to form CSA, the primary mineral in the clinker. Bauxite is an expensive resource and this elevates the material cost of CSA cement and limits its applications.

Recently, a high-belite calcium sulfoaluminate (HB-CSA) cement has been developed. HB-CSA clinker is made of low-quality bauxite or 100% industrial by-products, such as fly ash, blast-furnace slag and FGD gypsum. HB-CSA clinker is produced by calcining raw materials at 1300±50°C, 150-200°C lower than OPC clinker and 50–100°C lower than CSA clinker. In general, the $CO_2$ emissions associated with HB-CSA cement manufacturing is about 30%–60% of OPC and about 50%–80% of CSA cement.

HB-CSA cement shows excellent mechanical properties, volume stability and durability, such as rapid-hardening, high early strength (2h-compressive strength over 10 MPa) and later strength (28d-compressive strength over 70 MPa), low hydration heat (around 210 J/g within first 7 days), low shrinkage (about 1/10 of Portland cement) and good resistance to chemical attacks.

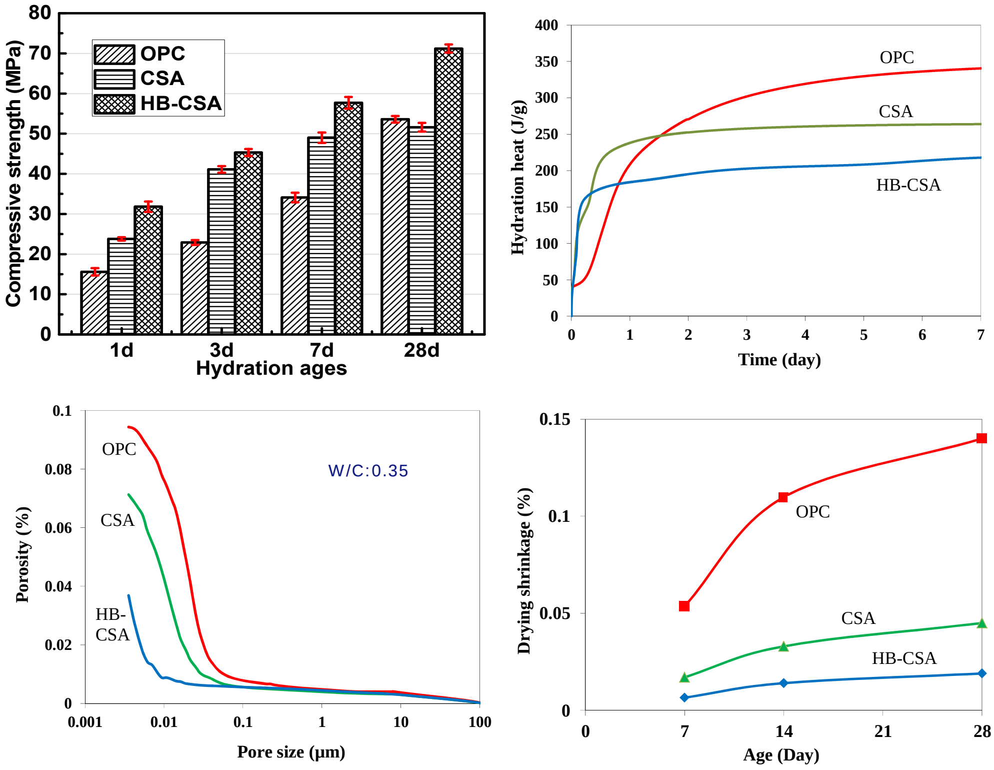

Figure 1: Properties of OPC, CSA cement and HB-CSA cement.

# MICROSTRUCTURE OF BELITE SULFOALUMINATE CLINKER AND ITS INFLUENCE ON CLINKER REACTIVITY

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Belite sulfoaluminate cements are promising low-$CO_2$ binders as their physical and mechanical properties are comparable with conventional Portland cements [1]. Many studies address the synthesis and hydration of belite sulfoaluminate clinkers or cements [2] [3], yet clinker microstructure is seldom investigated comprehensively. One of the issues that have not been addressed satisfactorily is the relationship between belite sulfoaluminate clinker microstructure and its reactivity. In this study, the microstructural characteristics of clinkers of two various phase compositions were investigated: (i) phase composition KBA-1: 65wt.% $C_2S$, 20wt.% $C_4A_3\$$, 10wt.% $C_4AF$; and (ii) phase composition KBA-2: 50wt.% $C_2S$, 35wt.% $C_4A_3\$$, 10wt.% $C_4AF$ (Figure 1). In each raw mix 5wt% of minor phases were assumed. The main raw mix components were limestone, flysch, bottom ash and titanogypsum, while bauxite was used only in small amounts. Raw materials were proportioned by adapting the modified Bogue calculation. Prepared raw mixtures were homogenized in a laboratory ball mill, using isopropanol as the grinding medium. Pressed pellets were prepared from each mixture and heated at a constant rate of 10°C/min up to the maximum temperatures of 1200°C, 1250°C or 1300°C, holding time at the final temperature for 60 min, and naturally cooled in a closed furnace.

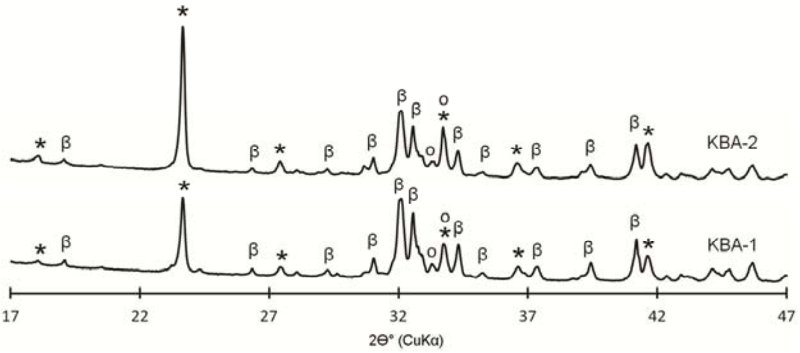

Figure 1: Selected range of the XRD-patterns for the two clinkers heated at 1250°C (* = $C_4A_3\$$, β = β-$C_2S$, o = $C_4AF$).

Clinker phases, determined by the Rietveld quantitative phase analysis, were in good agreement with the predicted phases. The microstructure was studied by scanning electron microscopy (SEM) and optical microscopy. The clinker phases were additionally characterized by elemental distribution, performed by energy dispersive spectroscopy (EDS). Clinker reactivity was investigated by isothermal calorimetry and the determination of compressive strength of cements prepared from those clinkers. As a result, the relation between clinker microstructure and clinker reactivity was thoroughly examined.

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