

**Calcium aluminate based cement for concrete to be used as thermal energy storage
in concentrated solar power plants**

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Abstract

A new type of thermal energy storage (TES) using concrete is proposed for concentrated solar power plants (CSP). The concrete mix developed is based on high alumina cement (CAC) blended with blast furnace slag (BFS) that allows controlling conversion. Concrete has been exposed up to 75 thermal cycles within the range 290-550°C. The dehydration processes of hydrated cement paste have been correlated with mechanical properties loss, porosity changes and ultrasound analysis. Stabilization of damage under thermal fatigue conditions due to heat cycling is found. The aggregate size (max 12 mm) and their thermal stability have demonstrated to affect the performance of concrete with the charge / discharge heat-cycles defined. The material developed can become in a near future a more cost efficient solution for CSP plants with storage.

Keywords: CAC concrete, thermal storage, conversion, high temperature

1. Introduction

An increased interest on environmental issues has been rising since the Kyoto Protocol came into force, focusing on electricity production with no CO₂ emissions. One of the main challenges for renewable energy technologies is finding solutions to problems derived from the varying or intermittent nature of most renewable resources. Among these resources, solar energy has some major advantages, not only because it is much more abundant than any other source but also because the hours of solar radiation for a certain location are easier to predict and measure. Concentrated solar power plants (CSP) that use direct solar radiation for the production of electricity were introduced in the early 1980's in California, USA, the so called SEGS plants. Compared with other solar energy forms, CSP has a key: thermal energy storage, so that extra energy collected can be stored for later usage during the night or on cloudy periods [1]. Energy storage is essential for improving the performance of CSP plants and its dispatchability, which is a valuable asset and allows CSP plants to be managed like fossil-power plants or hydropower plants [2]. This enables CSP plants to operate if necessary on a peak shaving mode during the day, making possible to produce power either when is most needed or when prices are more attractive, depending on the strategy. Without TES, CSP would be an intermittent power resource depending exclusively on solar radiation availability, as it is the case of photovoltaic systems. Therefore the development of an efficient and more economical solar energy storage system is of major concern, and a key feature of CSP plants.

The current state of the art in commercial CSP plants with TES is based on sensible heat storage with an indirect 2-Tank system using a binary mixture of molten salts [2]. In Europe, Andasol-1 was the first plant, in 2009, to have such a system implemented, after that, several other plants have followed.

Mainly because of the lower initial investment cost issue and the long term material availability, thermal energy storage using solid materials like concrete becomes an attractive option for

storing sensible heat [3,4]. Concrete as a solid storage material is a challenge, as it is easy to handle, possible to manufacture in-situ, available all over the world and in general its construction is a technology mastered by local companies. Based on the relatively low cost and high heat capacity of concrete, in recent years it has been given priority for research as a thermal energy storage solid medium.

First studies considering concrete as potential material for thermal energy storage show that conventional phases present in Portland cements, as monosulphoaluminates, ettringite or Friedel salt, have demonstrated to have high capabilities for sensible heat storage [6]. Two concepts that use concrete as part of a thermal energy storage system for CSP have been considered up to now:

- 1) using concrete with a heat exchanger (steel) medium [7-11] and
- 2) using concrete as filler in a thermocline tank [2,12].

Applications of solar concrete-heat exchanger started with domestic hot water, but the maximum working temperature is limited by the high steam pressure reached due to the use of water as heat transfer fluid (HTF) and the working temperature is below 100°C [7-9]. In concrete heat exchanger design, the thermal storage efficiency depends, among other parameters, on concrete conductivity [9]. High thermal conductivity and high thermal capacity of the concrete mix helps to achieve a more uniform heat distribution in the concrete bulk. Recently higher temperature storage concrete mixes have been designed and validated up to 400°C having steam as the heat transfer media [3,4,10,11]. This high temperature concrete mix contains blast furnace slag cement, aggregates with thermal properties such as iron oxides, gravel, basalt and sand in the composition, and polypropylene fibers (PPF) to reduce any risk of spalling [10]. Currently the trend in the CSP world is that plants must be designed to operate up to 550-570°C for higher efficiency operation. Thus, developing and validating new mixtures is quite relevant.

Concerning the thermocline energy storage design, concrete has been also considered [12] with

the ultimate objective of identifying a concrete mix suitable for usage as filler inside the thermocline tank with molten salts. Ordinary portland cement (OPC) and calcium aluminate cement (CAC) with fly ash and silicafume as mineral additions were evaluated; also polypropylene fibers (PPF) were added. Limestone was used as coarse aggregate together with siliceous river sand. The concrete was heat-cycled (30 heat-cycles) between 300 °C and 585 °C or maintained 500 h at 585°C, in air and in molten salts [12]. The findings show that plain OPC concrete retains only 14% from its initial compressive strength value and severe cracking after cycling were observed, while the blended OPC concretes and CAC concretes maintain at least 30% of their initial strength. In addition it was found that the aggregate size affects the thermal response, as coarse aggregates exhibited the highest reduction in compressive strength. With molten salts higher residual strength in blended CAC is obtained than in blended OPC concrete. Future challenges in storage systems imply the increase of the maximum temperature of the transfer fluid and the storage media. Developing solid media like concrete with higher thermal stability, for instance refractory concretes is a relevant research topic that this article addresses.

Refractory concrete seems a suitable material for uses in structures that have to work for long periods under temperatures ranging from 500 up to almost 2000°C [13]. As the concrete temperature requirement in CSP heat storage plants has to bear temperatures up to at least 600°C, a refractory concrete design should be considered.

Refractory concretes are used primarily as a protective lining, so that can be considered as a consumable material that needs to be replaced after an appropriate service life. However attention has been given recently to the possibilities of using refractory concretes for large load-bearing structures, as for nuclear power plants [14].

Many different materials can be used for refractory purposes and some of them are based on the use of hydraulic cements: OPC allows limited refractory applications and the refractory properties are mainly provided by the use of appropriate aggregates in the mix. Calcium silicates hydrates (CSH) from the hydrated OPC decompose at temperatures above 105°C and calcium hydroxide (CH) at temperatures around 450°C, both forming CaO as main dehydrated

residue [15]. After cooling, the CaO can be easily rehydrated again by absorbing moisture from the atmosphere with the consequent swelling of the hardened paste, increasing cracking; also it causes powdering of the cement paste after been exposed to temperatures above 500°C. Therefore, thermal cycling could result in severe disruption and damage [16,17]. Blended cements, using blast furnace slag or natural pozzolans as mineral additions generate more CSH and less CH than plain OPC, so that dehydration follows similarly as in the Portland case except for CH and then, the residual strength can be higher after cooling than in the case of pure OPC [18].

For the reasons mentioned above, attention is then focused on high alumina cements (CAC). It is a hydraulic cement that combines water to harden and increase strength. At normal temperatures and moisture the first hydrated phases are CAH_{10} and C_2AH_8 and colloidal aluminium hydrate AH_3 [19-21]. Hydration takes place very rapidly allowing high mechanical strength after 24 h [20]. However, these initial hydration phases are chemically unstable and conversion reactions to more stable hydrated phases take place, C_3AH_6 and AH_3 [19,20]. The density of this last cubic phase is higher (2.53g/cm^3) than that of the initial hexagonal phases (1.72g/cm^3) [22]. This increase in density is accompanied by a reduction in volume and so an increase in the porosity of the paste, which is considered to be the main cause of the strength decay. Several actions have been considered to retard or completely eliminate the conversion of hexagonal phases to cubic ones [23-28]. More commonly used solutions are based on the incorporation of mineral blends containing high silica content, as blast furnace slag (BFS), fly ash (FA) or silica fume (SF) to avoid the C_3AH_6 transformation from early hydration ages due to the preferential formation of hydrogranet phases [25,28]. These calcium aluminates contain silica in their structure and [25,28,29], are promoters of the formation of Afm phases [23,26,27]. Even mixes with OPC/CAC can control the conversion process in CAC [30].

There are relatively few studies on CAC dehydration compared with the ones available for Portland cement paste. Research conducted [14,28,31] shows that above 105°C the chemically combined water of CAC paste is gradually lost from hydrated aluminates. Most important

changes occur up to 300°C: dehydration of CAH_{10} and AH_3 . At temperatures between 400-500°C the dehydration of aluminate hydrate should be completed [31]. As occurs in case of hardened Portland cement paste, the density and porosity of CAC pastes change due to dehydration above 100°C. Porosity of CAC concrete can increase by about 25% up to 500°C [32]. These changes in porosity and in density affect the strength of CAC paste. From 200 to 600°C CAC paste strength decays around 50% [14]. At higher temperatures no significant changes occur until melting above 1300°C. Additionally, the dehydrated CAC is more stable after cooling, reducing swelling risk [14].

Besides CAC concretes are considered to show also higher chemical resistance in aggressive environments than OPC concretes [14,29,33,34], being this aspect relevant if the concrete structure has to resist aggressive environments at high temperature like the molten salts storing energy in CPS facilities.

The suitability of the refractory concrete for TES in CSP plants is the topic of this paper, presenting the development of a high temperature resistant CAC-based concrete stabilized with BFS. The influence of the aggregate composition and size is considered, and the mechanical and the microstructural properties are analyzed after treatments in air at temperatures in the range of 290 to 550°C. Different number of thermal cycles: 25, 50 and 75, corresponding roughly to 1, 2 and 3 months of CSP plant operation are considered.

2. Experimental set-up

2.1. Samples preparation

Calcium Aluminate Cement (CAC cement) blended with blast furnace slag (BFS) to stabilize the conversion process was used. A binder mix of 70 % CAC + 30% BFS was selected. The chemical compositions of both components are included in table 1, in % weight. Accordingly to [35], for special refractory concretes the total alumina content shall be above 32% and the ratio alumina (Al_2O_3) to lime (CaO) shall be between 0.85 and 1.3. The CAC used in the present

work has 40% Al_2O_3 and a $\text{Al}_2\text{O}_3/\text{CaO}$ ratio of 1, so that meets with the mentioned basic requirements of hydraulic binding agent in refractory concretes. In addition the iron content also has a relevant role; contents around 15% Fe_2O_3 limits the maximum temperature of use to 1370°C , comfortably meeting the requirements in a CSP with heat storage system.

<Table 1>

The particle size distribution of both components is included in table 2; mean particle size of BFS is three times lower than that of CAC cement.

<Table 2>

Figure 1(a) includes the XRD of CAC cement and BFS. The main crystalline component of CAC cement is calcium monoaluminate (CaAl_2O_4 , CA); other phases in less proportion are C_{12}A_7 , C_4AF and Al_2O_3 . The BFS shows massive presence of amorphous phases together with some crystalline phases like calcite, gehlenite (calcium aluminosilicate) and calcium-magnesium aluminosilicates ($54\text{CaO}\cdot 16\text{SiO}_2\cdot \text{Al}_2\text{O}_3\cdot \text{MgO}$).

<Figure 1>

Mortar and concrete specimens were prepared using CAC and BFS mixtures as a binder. Mortar samples of 4x4x16 cm using standard siliceous sand (1-4 mm), binder to sand ratio of 1/3, water to cement ratio of 0.44 and 1% of superplasticizer by cement weight (sikament-180) were prepared with a fluidity of 17-18 mm. For concrete design, two types of aggregates were used, from 0 to 12 mm size:

- 1) Natural aggregates from crash stone with siliceous-calcareous composition (SCA) mainly constituted by quartz and calcite, and
- 2) Aggregates from industrial waste slag from ore processing (SSA). This slag-waste aggregate shows a partially crystalline structure; XRD of SSA in figure 1(a) indicates

Comentado [MSM1]: Repetitivo?

the presence of quartz. Also a variation of 25-40% in SiO_2 content can be observed by Energy-Dispersive X-Ray microanalysis, EDS. Other main component is Fe_2O_3 (40-60%, EDS), while the contents of Al_2O_3 and CaO are residual (less than 3%). The TG/dTG of figure 1(b) shows that SSA aggregate suffers progressive mass loss through all the temperature range. The most relevant losses are those at temperatures below 300°C, probably associated to iron components by loss of bound water and oxidation at high temperature. A crystalline transformation of the quartz phase from α to β -quartz occurring at 550°C is also detected.

Comentado [MSM2]: Con el TG se detecta que es una transformación cristalina?

Two different concrete dosages were prepared maintaining the same type and content of CAC+BFS binder, but varying the type of aggregate. The name CAC refers to concrete prepared with 100% of SCA, while the CAC+ identifies concrete made with a mix of 75% SCA+ 25% SSA. The mix dosages for CAC and CAC+ concretes were made following Bolomey method; the final distribution selected is included in figure 2(a) for both concretes. It can be seen that the introduction of SSA covers more homogeneously the distribution of all ranges of particle size. The aspect of the different aggregate ranges used is included in figure 2(b).

<Figure 2>

The final dosages of CAC and CAC+ concretes are included in table 3. Superplasticizer 0.8% by cement weight (Sikament 180) was used and this proportion was maintained in both concretes to obtain a good workability. After some trials it was chosen $w/c_{\text{CAC}} = 0.5$ and $w/c_{\text{CAC+}} = 0.57$, since the SSA needs some more water to maintain the same workability without bleeding of concrete. The slump of both type of concretes varied among 5.5 and 6 cm. Once the composition of the two mixes was well defined, cylindrical concrete samples of 7.5 cm in diameter (\emptyset) and 15 cm in height (H) were prepared.

<Table 3>

Mortar (CAC-M) and concrete (CAC and CAC+) samples were cured for 7 days under standard conditions in a chamber at $100\% \pm 5\% \text{RH}$ and $22 \pm 2^\circ\text{C}$. After curing, each concrete sample was cut in two halves allowing an $\text{Ø}/\text{H} = 1$.

Compressive and flexural strengths were measured in mortar samples at 24 h and 7 days of curing, followed by XRD and TG/dTG to determine the initial hydrated phases. In concrete, compressive strength measurements at 7 days were performed. Also XRD and mercury intrusion porosimetry analysis were done in concrete samples.

2.2. Sample preconditioning and heating protocol

After curing, the series of mortar and concrete samples were pre-dried before the exposure to heating cycles to minimize risk of spalling during the first heating cycle. The drying protocol was 3 days drying at 105°C to eliminate most of the free water in the capillary pores, but without significantly affecting the hydrated solid phases. During this drying process % water loss for CAC M was $3.74 \pm 0.18\%$; for CAC concretes was similar $3.54 \pm 0.23\%$.

The heating resistance of concretes was evaluated throughout the exposure of the samples to heating/cooling cycles with a t 24 h period inside an electric furnace, as shown in figure 3(a), being the maximum temperature $550 \pm 5^\circ\text{C}$ and the minimum $290 \pm 5^\circ\text{C}$. A heating rate of $1^\circ\text{C}/\text{min}$ was selected for the first heating step, to minimize thermal damage and crack developing as consequence of strong temperature gradients in the bulk of the samples respect to the concrete surface, guaranteeing that the changes were mainly consequence of the dehydration of cement paste. For the next cycles a heating rate of $9^\circ\text{C}/\text{min}$ up to 550°C followed by cooling to 290°C at a rate $< 1^\circ\text{C}/\text{min}$ were used. This temperature was maintained until starting the next heat-cycle. Periods of 5 cycles of 24 h ($550^\circ\text{C}/290^\circ\text{C}$) followed by 2-3 days stays at 290°C were considered until complete 8 heat-cycles for CAC-M and 75 heat-cycles for CAC and CAC+ concretes.

Every some cycles in mortar or 25 cycles in concrete, samples were removed from the furnace and introduced in a preheated stove at 290°C to follow a slow cooling process (<1°C/min) to 20°C to minimize thermal gradients. The rest of the samples continued in the oven for next series of 550°C/290°C cycles. During the heat-cycles the temperature inside the oven and at the surface level of the samples were recorded to continuously identify the thermal regime performance, as shown in figure 3(b).

<Figure 3>

Samples subjected to heat/cool cycles were characterized using different techniques from macro to micro level. At the macro level, in the entire concrete sample, the ultrasound velocities and the compressive strength were determined and, in mortar samples, compressive and flexural strength were measured. At the micro level, DRX (concrete and mortar), TG/DTA (mortar), mercury intrusion porosimetry (concrete), SEM back-scattering microscopy with EDS characterization (concrete) and thermal conductivity (concrete) were done. Mass loss after heat-cycles was also determined in mortar and concrete samples, as can be observed in figure 4.

<Figure 4>

It is relevant to point out that most of mass loss takes place the during first cycle associated mainly to dehydration processes of cement paste. After 5 cycles the mass loss is practically stabilized in CAC-M (figure 4(a)). In the case of concretes the mass losses follow a similar trend, with small changes after 25 heat-cycles (figure 4(b)). However, higher mass losses are detected in CAC+, probably associated to the progressive alteration of SSA aggregates, also observed from TGA results, Figure 1(b). To confirm this point, powder from SSA aggregate was heated for 24 h at 550° and a mass loss above 3% was detected.

3. Results and Discussion

3.1. Stabilization of CAC due to BFS addition.

As stated in the introduction, the well-known CAC conversion phenomena of metastable hydrates, CAH_{10} and C_2AH_8 , with hexagonal structure, to C_3AH_6 with cubic form can be avoided introducing in the binder system a mineral addition with high SiO_2 content, as BFS [25,28]. DRX of Figure 5(a), taken after 24 hours and 7 days of curing, shows that the crystalline forms associated to CAH_{10} and C_2AH_8 are present at the initial stage, but after 7 days curing CAH_{10} and grossular-hydrogrossular solid solution with Si in their composition (hydrogranet type $C_3AS_{3-x}H_{2x}$) are detected. The formation of the Si-hydrogranet is also confirmed by TGA/DTA in figure 5(b), where two singular exothermal peaks appear between 100-250°C as also confirmed in [36]. More than 80% of the total mass loss takes place within this range of temperature due to the dehydration of these phases, what agrees with the fact that CAC hydrates contain in their structure more bounded water than the C-S-H of OPC paste [28].

Comentado [MSM3]: Para poder hablar de exotérmico/endotérmico hay que poner el TGA, no el dTG.

<Figure 5>

The control of the conversion process due to the incorporation of amorphous SiO_2 rich mineral addition during curing allows to detect an increase in the evolution of the mechanical strength. Thus, the strength decay associated to conversion evolution and C_3AH_6 formation is avoided due to lower volume of the later [22,25]. An increase of 47% in compression and 37% in flexural strength has been measured in CAC-M (table 5) from 1 d curing to 7 d curing..

Comentado [A4]: Esta frase no se entiende, demasiado larga. No sé muy bien cómo cambiarla. Conviene que alguien la revise a fondo.

3.2. Thermal fatigue of CAC concrete under heat-cycles.

CAC cement paste follows a dehydration process at high temperature that evolves with the concrete mixes alteration at macro and microstructure.

3.2.1. Alteration of mechanical properties

The mechanical properties of blended CAC mortar and concrete mixes are affected by heating up to 550°C, as observed from figures 6 and 7 respectively. This temperature level that can be expected during normal CSP operation is above the stability of CAC hydrates. A decay in compressive strength up to 50% after the first heating cycle is detected. Similar observation was detected in [12] with a CAC concrete containing fly ash.

It is very noteworthy to point out that further heat-cycles do not follow the same trend decay and the compressive strength tends to stabilize. In the case of mortar, either in compression (figure 6(a)) and flexion tests (figure 6(b)) the % compression and flexural strength losses are in 8 and 14 respectively. The small size of aggregates (maximum size 4 mm) softens the fatigue effect due to the thermal heat-cycles, as also noticed in [10] using OPC+BFS.

Comentado [A5]: Ojo, en el eje de ordenadas de las gráficas pone Rcom y Rflex. Hay que traducirlo.

<Figure 6>

The decay in compressive strength with the heat-cycles is also observed in CAC concretes with higher maximum size of aggregate, figure 7(a). Similar compressive strength decay is detected in both concretes mixes independently of the aggregate type, SCA alone or mix SCA+SSA, despite the additional mass loss occurring during the heating of concrete with this aggregate (figure- 4(b)). The damage evolution due to thermal cycles is more pronounced in concretes mixes than in mortar, probably as consequence of the higher aggregate size (maximum 12 mm) that can affect the deterioration process, as also suggested in [12]. The damping in compressive strength fits well with potential function, of the type $R=29 \cdot e^{-0.02 \cdot C}$ (R: compression strength, C: heat-cycle number). The repetitive expansions and contractions taking place during each heat-cycle can contribute to the crack propagation, as shown in figure 8, what explains the progressive decrease of ultra-pulse

Comentado [A6]: ¿Merece la pena ponerlo como ecuación o mejor dentro del texto?

velocities (UPV) measured with heat-cycles. This point is confirmed by the good correlation found between the compression strength and the UPV as observed in figure 7(b).

<Figure 7>

<Figure 8>

From the UPV values, the dynamic elastic modulus of concrete has been estimated using the equation (1) [37,38]:

$$E = \frac{C_p^2 \rho (1+\nu)(1-2\nu)}{(1-\nu)} \quad (1)$$

E: dynamic elastic modulus (GPa), C_p : pulse propagation speed (m/s), ρ : concrete density (kg/m^3) and ν : Poisson coefficient. The ν value usually assumed for concrete is 0.2 [39,40] for the initial state but after high temperature exposure the ν value decreases up to even 0.08, as suggested in [40]. These two values of ν have been used for E estimation in the present work. Figure 9 shows the evolution of E with heat-cycles (E1, using ρ calculated from mass and volume of sample, E2 with ρ obtained from MIP and n_T considering the influence of temperature in ν) giving very similar results and showing the loss of E due to heating cycles.

Comentado [MSM7]: ¿Definir?

<Figure 9>

The alteration of mechanical properties in compression, flexion and elastic modulus, indicates that the concrete behavior both during pre- and post- heating cycles should be considered, to guarantee at least the minimal performance requirements during the service life of the structure exposed to high temperature. The stabilization on the progressive strength decay is fundamental, which suggests that additional measures to reduce the fatigue effect due to heating cycles should be included in TES-concrete.

3.2.2. Changes in the microstructure of CAC concretes.

All the mentioned changes, observed at the macro level in mortar and concretes exposed to heating cycles, should be a consequence of the changes occurring at the micro level.

Similar crystalline composition is observed in both concretes with XRD analyses, represented in figures 10 and 11. From a microstructural point of view, calcium aluminous cement with high slag mineral admixture has allowed to control the conversion process. That is, the initial hexagonal hydrates, CAH_{10} y C_2AH_8 of a pure calcium aluminate cement, have not evolved to the cubic C_3AH_6 and gibbsite (AH_3) phases; instead, part of the hexagonal hydrates have evolved to the formation of a grossular-hidrogrossular solid solution with Si in their composition, $(C_3AS_{3-x}H_{2x})$ or to strätlingite (C_2ASH_8), as also found in [36]. Also quartz and calcite are identified as part of the aggregate composition. After 25 heat-cycles, calcite and quartz are present; also peaks near to the CAC cement anhydrous phases containing calcium and aluminium, as CA ($C_{12}A_7$) ($Ca_{12}Al_{14}O_{33}$), are detected, together with phases containing silica in their crystalline structure, such as , magenite, also detected by Neutron Diffraction Spectroscopy [36], during dehydration up to 500°C.

Comentado [MSM8]: ¿Y esto qué implica?

Comentado [MSM9]: Igual estaría bien dar la fórmula como en el resto de compuestos.

<Figure 10>

The chemical changes due to heating are also confirmed in TGA test, Figure 10(b) for mortar samples. It is important to notice that after the first heating at 550°C all dehydration processes in CAH and $CASH$ have been developed and further heating cycles are not inducing more chemical transformations, as shown in figure 10(a) and 11(b). Additional mass losses after cycles in CAC and CAC+ concretes are more associated to progressive chemical transformations of the aggregates and to the alteration of dehydrated paste/aggregate interface, as shown later.

<Figure 11>

The heating cycles have induced changes also at pore level. The increase in porosity detected in figure 12 after 25 heat-cycles explains the decay in mechanical strength; both the pore structure distribution and the pore size are affected. A clear increase is observed in capillary pores below 3 μm due to the dehydration of the cement paste. The pore distribution and the total porosity after 25 cycles (21%) is similar in both concretes, what explains the similar mechanical response found for both concretes. The main difference is in the initial porosity of CAC+ having less capillary pores (total porosity 10.6%) but in the same pore region than CAC (total porosity 12.9), a possible consequence of the different distribution of aggregate size in CAC+ concrete using SSA showed in figure 2.

Comentado [MSM10]: Esta frase queda rara.

<Figure 12>

All these transformations are confirmed through scanning electron microscopy and EDS. The first to be analyzed were the changes in the microstructure and in the density of the cement paste that can be visualized in figures 13 and 14. Before heat-cycles (figure 13), a quite dense cement paste is observed in both concretes, containing some more crystalline zones and others with more amorphous shape. The main differences between these two zones are that the regions with more amorphous aspect contain those phases with higher Si/Ca ratio (points N 16, 17, 18 in CAC and 14, 16, 17, 19, 20 in CAC+), associated to hydrogrossular phases incorporating Si as solid solution from the hydration of BFS with CAC. The more crystalline regions contain higher Al/Ca ratio and no or low Si content, as (points N 14, 15 in CAC).

<Figure 13>

<Figure 14>

After heat-cycles the cement paste is less dense due to dehydration of aluminates (figure 14),

but also solid regions with geometrical aspect are observed, which composition indicates that of quartz or BFS (points N 11, 12, 13 in CAC) and (points N 2, 3, 4, 11 in CAC+). Other phases shape that bring back the CA anhydrous composition, confirmed with EDS analysis (points N 1, 2, 3, 4, 5, 6 in CAC) or (1 in CAC+), and also identified in XRD (figures 10 and 11).

Comentado [MSM11]: Esta frase es rara

Other important aspect to be analysed through SEM is the interface of cement paste with aggregates (interfacial transition zone, ITZ). Differences in thermal expansion between the aggregates and the cement paste favour the cracking of the paste surrounding the aggregates that also grow towards the dehydrated cement paste, as shown in figure 15. These microcracking, both at the interface between the aggregate and the cement paste and in the bulk region, contributes to the damage evolution and to the loss of mechanical properties found in figures 6, 7 and 9, even after the first heat-cycle. The thermal compatibility of these two main components of concrete, cement paste and aggregate, in relation to thermal deformation is of significant importance for concrete resistance under high temperature cycles, as those employed in present work 290-550°C. It is therefore not surprising that the concrete mixtures containing coarse aggregates exhibit the highest reduction in compression strength subsequent to elevated temperature exposure, as suggested to occur in [12].

This effect of the aggregate size in microcracking generation and evolution has been detected measuring the gap in the Interfacial Transition Zone (ITZ) in various aggregate sizes; results included in table 6. Small aggregates (< 0.5 mm) show less ITZ than higher aggregate size (1-2 mm in figure 14). After heat-cycles, the ITZ increases 3 to 5 times from its initial size.

<Figure 15>

Finally, other aspect to consider is the shrinkage of cement paste during dehydration, that is overcome by the increase of volume of the aggregate at high temperature. Also the repeated heat-cycles can contribute and favour the microcracking.

<Table 6>

3.3. Design of concrete for TES in CSP plants

CSP is for now the only solar technology with significant thermal energy storage capacity. TES allows electricity to be generated consistently at times when solar radiation is not available. The effectiveness of TES systems depends critically on the thermo-physical properties of the storage material: thermal conductivity, density, viscosity, melting and freezing points for molten salts, and thermal conductivity, heat capacity and diffusivity for the case of concrete. All these characteristics have an impact in the design, performance and cost of the TES.

Concrete for sensible heat storage shows the advantage of not requiring large facilities and equipment for their casting and it can be produced in-situ at ambient temperature. In addition, the properties can be easily modified by an appropriate design and the incorporation of suitable components (e.g. steel register, fibers, mineral additions, additives etc.) in fresh state during production. Thus, this gives the advantage that concrete with different and multiple functionalities can turn into a very appropriate material to be considered for TES systems.

The operation conditions of a real CSP plant vary according to its location and weather conditions, among others. During its service life the most extreme operating condition at continuous high temperature environment (currently 400°C for parabolic troughs and in the range of 550-565°C for brand new developed tower plants), are coupled with heating cycles, as those tested in the present work in the range 290 to 550°C.

The requirements of the main concrete components will be analyzed now in relation of the existing knowledge and that acquired in present work:

3.3.1. Cement role.

As mentioned in the introduction, two main hydrating cement materials can be considered, those based on calcium silicates, like OPC, and those based on calcium aluminates, like CAC. The hydrated phases of both type of cements suffer from dehydration when exposed to high temperatures, between 100 and 400°C, that causes decay of mechanical properties. Thus, the capability to respond to high temperatures and cycling is of major importance. The presence of portlandite in the case of OPC and the conversion phenomena in case of CAC are the main limitations for the usage of both plain cements. A CAC mix shows a better behavior at high temperatures than OPC. The incorporation of mineral admixtures seems to be a requirement, as demonstrated in [12] and also in the present work. But for temperatures above 450°C, CAC blended with mineral additions with high silica content are more suitable due to its higher stability after dehydration.

Comentado [MSM12]: Yo esta frase la quitaría, da lugar a confusión. Ya se ha seleccionado el CAC frente al OPC.

Concerning the chemical stability, CAC exhibits better chemical resistance in aggressive environments, as suggested in [14,29,33,34] even in the presence of molten salts [12,32]. Nevertheless, detailed research on this aspect is still needed.

All in all, CAC is thermally more stable than OPC and CAC is more adequate to resist chemical attack than OPC. Nevertheless, binder optimized mixes including even hybrid cements based on CACOPC have to be analyzed more in detail in order to achieve an optimum solution from the technical-economic point of view.

3.3.2. Aggregate role.

The aggregate is a very relevant component in the design of TES-concrete. Not only is important the type of aggregate but also the maximum size of aggregate is a relevant parameter to take into account. Concerning the type of aggregate, the main aspect to consider is the stability at high temperature both from a chemical and physical point of view. Aggregates suffering transformations at temperatures in the region of TES heat-cycles that could affect the

concrete mechanical integrity should be analyzed, and also their thermal expansion. High thermal expansion aggregates must be limited (siliceous alone or calcareous), as they can significantly affect the mechanical resistance under high temperature environments and also under thermal fatigue cycles. Concerning the size distribution it is important to compensate the changes in the concrete volume due to the thermal expansion and the dehydration reactions of the cement paste. According the results in literature and in the present work, it is highly recommended not to use aggregates above 10-12 mm. . The aggregate/cement paste ITZ is affected by the aggregate size and shape. The limitation of the maximum size of aggregate is relevant but also the progressive grade distribution must be taken into account to get homogenous compactness and interfaces, as it was done with the incorporation of SSA in the present work. The use of hybrid aggregates with different thermal stability, as performed in present work (SCA+SSA), could be attractive in order to increase the overall mix adaptability to thermal stresses. Future research is needed focused on the optimum type and percentage of aggregate with adequate granulometric curves.

3.3.3. Thermal response and requirements.

One main interest of concrete use in TES is the ability to store sensible heat. The heat capacity of a concrete varies with the composition of concrete. Concretes with heat capacity of 0.8 kWh/m³ K is possible and adequate for TES and [10,41] have been developed. Other relevant thermal parameter is the thermal conductivity (λ) of concrete expected to be around 2W/m K; the concrete used in present paper has a $\lambda_{0\text{cycles}} = 2.05$ W/m K and $\lambda_{25\text{cycles}} = 1.16$ W/m K. To control this decay after heat cycles, additional components for the concrete mix able to enhance the thermal conductivity of concrete are needed, for instance: silane, steel fibers, carbon fibers, carbon nanotubes, graphene, graphite powder [41-43]. An alternative during the TES module construction phase would be the application of additional heat transfer structures, that is, graphite or aluminum foils placed between the layers of the precast concrete [4,10,11].

3.3.4. Measures to compensate thermal properties loss and thermal fatigue of TES concrete

In order to prevent spalling, that could occur mainly during the first heating cycle, it is recommended the use of polypropylene fibers. However, these fibers melt at temperatures near 160°C and decompose after 300°C. Therefore this process can result in opening paths to allow aggressive media, like molten salts, penetrating and also affecting the mechanical properties of concrete. Other types of fibers, stable at high temperature, seem to be more attractive for compensating the thermal fatigue, as carbon fibers, glass fibers or steel fibers. That is a topic which needs further investigation.

3.3.5. Risk of molten salt contact.

Both in the two tanks system and in the thermocline tank, molten salts are in direct contact with the container. The actual limitations with metal containers is the high deterioration due to corrosion of carbon steel grades above 400°C. At such high temperatures, this metal heavily corrodes through mechanisms of local corrosion and pit formation, leading to a high cost for repair and maintenance.

When concrete is used as heat storage solid material in contact with a metallic heat-exchanger or as tank container itself, the possible contact with molten salts requires a high chemical resistant material, and a specific coating developed for this aim might be an appropriate solution. OPC concrete in general shows low chemical resistance; however, CAC could better supports the chemical attack [14,32].

4. Conclusions

In this paper the authors set out to develop and to analyze a new cementitious based mix that could conduct and store heat at high temperatures, namely with thermal cycles in the range 290-550°C, making it suitable for a Thermal Storage System in Concentrated Solar Power plants.

The main results can be summarized in the following way:

1. The incorporation of blast furnace slag to CAC mix controls the conversion phenomena and Si-Hydrogranet phases, type CASH, are formed.
2. CAC concrete with conversion control also suffer dehydration at high temperature, accompanied by a decay in the mechanical strength. However, after the first heat-cycle the CAC concrete evolves to stabilize the thermal fatigue induced by further heat-cycles
3. The use of correct grading of aggregates (max 12 mm) is fundamental for the resistance under high temperature heat-cycles of TES-concrete.
4. SSA waste from ore mining production used as aggregate for concrete has shown similar mechanical performance as SCA. Additionally, using aggregates with different thermal stability can be a benefit for the overall paste adaptability to thermal stress.
5. The ITZ is significantly affected with the aggregate size. High size of aggregates increases the thermal fatigue of concrete during heat-cycles.
6. .
7. Concrete based on blended CAC with an appropriate design can be employed for TES up to 550°C in CSP plants.

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