Thermal conductivity of concrete at high temperatures for thermal energy storage applications: Experimental analysis

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ABSTRACT

Thermal conductivity plays an important role in energy storage when the materials are charging and discharging. This paper presents an experimental investigation of the evolution of thermal conductivity up to 600 °C in different concretes. Moreover, the thermal conductivity was measured during thermal fatigue cycles when temperature ranged between 300 and 600 °C, simulating the operation conditions in a storage system of molten salts in a Concentrating Solar Power Plant (CSP). Five concrete compositions were analysed using diverse types of aggregates with different thermal response, covering a wide range of the initial thermal conductivity. The results confirm that the loss of thermal conductivity with temperature during the first heating is mainly due to the free water loss. Moreover, the type of aggregate influences the overall thermal performance of concrete due to its thermal conductivity and the volumetric differences with the cement paste. Siliceous aggregates underwent the highest decrease of thermal conductivity of concrete (+50%) with regard to room temperature. Regarding the cooling phase, thermal conductivity recovers between 20% and 40% depending on the type of aggregate. The outcomes of the present study demonstrate that the assumption of a constant thermal conductivity value in numerical simulations to predict its thermal capacity for energy storage is not appropriate.

1. Introduction

The continuous increase in the global energy demand has intensified the negative effects on climate change. The world energy production, mainly based on fossil fuels, is the principal source of CO₂ emissions. The fossil fuel depletion has been considered as a future challenge and some researchers highlight the need for a holistic solution (Höök and Tang, 2013). Solar energy is an alternative energy source whose main advantages are the sustainability and the no-generation of greenhouse emissions.

The limitation of the Solar Thermal Power Plants (STPP) is the intermittence of the source because of the lack of solar radiation at nights or in daily periods with clouds. Thermal Energy Storage (TES) systems are the solution to the problem since they ensure the viability of the STPP by satisfying the demand of energy when the solar input is insufficient. Moreover, the development of thermal energy storage technology achieves a higher level of sustainability of the STPP (Adinberg, 2011; Monjurul Ehsan et al., 2020; Mehrpooya et al., 2020).

TES can be divided into 3 categories: sensible, latent and

thermochemical heat storage (Rao et al., 2018). Sensible heat storage is produced by differences of temperature in the material. Latent heat is produced when the material experiences a phase change at an almost constant temperature. Thermochemical heat storage and discharge are produced when the molecular bonds are broken or reformed. The amount of energy stored for a specified system is defined by the energy density and depends on its heat capacity (Nazir et al., 2019). Latent heat storage materials are characterised by having higher energy density, but its lower thermal conductivity makes them materials with slower storage rate (Rao et al., 2018). Regarding the thermochemical heat storage materials, they are more complex and expensive at the current level of development.

Sensible heat storage materials are characterised by low-medium energy density, but its moderate cost and broad knowledge make them a valuable solution for thermal storage (Gil et al., 2010). In addition, sensible heat can be stored in liquid and solid materials. The problem when using liquid storage materials is that the technology employed needs high dimensions for the tanks and heat exchangers, which increase the cost of the storage application (Oró et al., 2012).

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Nomenclature

Acronyms

CAC	Calcium Aluminate Cement
CSP	Concentrating Solar Power
CTE	Coefficient of Thermal Expansion
CTES	Concrete as a Thermal Energy Storage
EPS	Expanded Polystyrene
HTF	Heat Transfer Fluid
NSC	Normal Strength Concrete
OPC	Ordinary Portland Cement
PPF	Polypropylene Fibres
SCC	Self-Compacting Concrete
STPP	Solar Thermal Power Plants
TES	Thermal Energy Storage
w/c	Water/Cement Ratio

2. Background

In recent years, many experimental studies have demonstrated the usefulness of concrete as solid material for thermal energy storage (CTES) (Cao et al., 2017; Cabeza et al., 2020; Liu et al., 2018). In addition, there are studies that have probed its appropriateness as CTES in Concentrated Solar Power Plants (CSP) (Alonso et al., 2016; John et al., 2013; Laing et al., 2012; Buscemi et al., 2018; Bataineh and Gharaibeh, 2018; Salomoni et al., 2014). Concrete presents several advantages such as its worldwide availability at a relatively low price, it is easy to handle, and it can be worked onsite (Alonso et al., 2016).

The use of concrete under high-temperatures regimes has been probed in real prototypes such as EnergyNEST and HEATCREATE (Hoivik et al., 2019; Laing et al., 2012). Those prototypes have been useful for measuring some thermal and mechanical parameters of concrete during the operation at high temperatures up to 400 °C. Numerical simulations of CTES have also reported the feasibility and cost-effectiveness of this type of thermal energy storage material (Vigneshwaran et al., 2019). However, most simulations are made assuming thermal properties with constant values, that is, considering them as temperature-independent properties (Vigneshwaran et al., 2019; Xu et al., 2017; Bai and Xu, 2011; Chen et al., 2019; Jian et al., 2015; Buscemi et al., 2018; Bataineh and Gharaibeh, 2018; Giannuzzi et al., 2017; Salomoni et al., 2014). Additionally, due to the high difficulty of evaluating these properties at high temperatures, in many studies, the thermal conductivity obtained at room temperature is used for the simulations (Doretti et al., 2019).

The analysis of the heat transfer at high temperatures for applications of thermal energy storage is of interest to predict the appropriateness of the application analysed in working conditions. In particular for CTES, when concrete is heated, the conduction is the dominant heat transfer mechanism within the solid medium. The thermal conductivity is the parameter that governs the conduction and gives the proportion between the heat flux and the thermal gradients that take place between the core and the external surface of the material (Incropera, 2006). Some authors highlight the temperature dependence of the thermo-physical properties of the storage materials for the overall performance of the storage applications (Rao et al., 2018). For that reason, a better knowledge in the evolution of the thermal conductivity with temperature in the heat storage system is of interest for the optimisation of concrete working under thermal fatigue cycles at high temperatures.

In concrete, around 70% of the volume is comprised by the aggregates. Consequently, the overall thermal response is heavily influenced by their behaviour, playing an important role in heat transfer. In addition to the aforementioned parameter of thermal conductivity, key for heat transfer processes, another parameter of interest is the thermal expansion of aggregates, which will influence the expansion/shrinkage

response of the material producing stresses and/or cracks. Table 1 summarises the thermal conductivity and thermal expansion coefficient (CTE) at room temperature of different conventional aggregates in rocks or concrete, obtained from the literature. Siliceous aggregates reach the highest thermal conductivity and thermal expansion, whereas calcareous aggregates achieve the lowest (Bonnell and Harper, 1950).

Nevertheless, since aggregates' behaviour at high temperatures is different from its behaviour at room temperature, their thermal parameters will have different values, which will influence the overall thermal performance and energy stored. Fig. 1 shows the evolution of thermal conductivity of different type of rocks at temperatures up to 600 °C obtained from the literature (Birch and Clark, 1940; Kanamori et al., 1968; Zoth and Hänel, 1988; Kawada, 1964; Birch et al., 1942; Sakvarelidze, 1973; Touloukian et al., 1971). Siliceous aggregates obtained the highest values at room temperature but also experienced the biggest drop when they are heated up to 600 °C. The loss of thermal conductivity is more pronounced in siliceous ($\approx 50\%$) than basalt and calcareous aggregates, whose decrease in the thermal conductivity is less accentuated.

Another parameter of interest in thermal storage applications is the specific heat. Fig. 2 summarises the evolution of the thermal parameter at temperatures up to 600 °C for different types of rocks, obtained from the literature (Goranson, 1942; Leonidov, 1967; Winkler, 1952). The differences found among the types of rocks analysed are lower and, in all cases, the specific heat ranges between 1 and 1.2 kJ/kg·K when the temperature reaches 600 °C. However, the value is increased ($\approx 50\%$) when is compared with the one obtained at room temperature. The importance of having data on the evolution at high temperatures is once again highlighted for making better predictions and simulations of the behaviour in operating conditions.

Nonetheless, the response of concrete at high temperatures changes due to several factors: chemical changes in the cement paste, mechanical changes due to the expansion of aggregates, and shrinkage of the cement paste (Bažant et al., 1996; Pimienta et al., 2018). These physicochemical changes take place at different temperatures and all these changes affect thermal conductivity. Regarding the cement influence, Calcium Aluminate Cement (CAC) withstands severe operating conditions because its heat capacity is higher than the Ordinary Portland Cement (OPC) concretes at temperatures up to 700 °C, 1.5 and 1 kJ/(kg·K), respectively (Dolado, 2018). The thermal conductivity of CAC pastes at high temperatures ranged between 0.96 and 1.1 W/mK at 25 and 80 °C, respectively (Ukrainczyk and Matusinović, 2010). At higher temperatures, one study reported (Yuan et al., 2014) that the values of thermal conductivity of CAC pastes measured in residual conditions decreased from 1.187, measured at 105 °C, to 0.621 and 0.542 W/mK, after being exposed to 350 and 900 °C, respectively. The dehydration of CAC cement paste takes place up to 300 °C with the decomposition of hydrated phases, mainly CAH_{10} and AH_3 . Regarding the OPC cement, CSH gels decompose from 100 to 400 °C and portlandite, CH , decomposes between 400 and 500 °C (Alonso and Fernandez, 2004).

The publications reporting the evolution of thermal conductivity on concrete at high temperatures are limited in number. Several authors reported measurement of thermal conductivity on concrete used for TES,

Table 1

Thermal conductivity and thermal expansion coefficient of rocks and concretes with different aggregates at room temperature. Source: (Bonnell and Harper, 1950; Bažant et al., 1996).

Type	Rock or concrete	Thermal conductivity [W/(m·K)]	CTE $\times 10^6$ [°C ⁻¹]
Siliceous	Rock	1.8–3.9	9.3
	Concrete	2.4–3.6 [OPC]	11.4
Basalt	Rock	1.7	6.4
	Concrete	1–1.6 [OPC]	9.3
Calcareous	Rock	1.2–1.4	5.5
	Concrete	1.9–2.8 [OPC]	8.6

Fig. 1. Evolution of thermal conductivity of different aggregates with temperature. Graph representing data published in (Touloukian et al., 1971; Birch and Clark, 1940; Kanamori et al., 1968; Zoth and Hänel, 1988; Kawada, 1964; Birch et al., 1942; Sakvarelidze, 1973).

Fig. 2. Evolution of specific heat of different aggregates with temperature. Graph representing data published in (Goranson, 1942; Leonidov, 1967; Winkler, 1952).

but the maximum temperature evaluated was 450 °C (Laing et al., 2012; Hoivik et al., 2019; Grosu et al., 2018). Recently innovations in the molten salts have demonstrated its stability at temperatures of 600 °C (Bonk et al., 2020). For that reason, it is important to evaluate the thermal performance of concrete reaching higher temperatures.

The studies performed at high temperatures show that the measure of thermal conductivity of concrete at high temperatures is heavily affected by many parameters such as porosity, moisture content, type

and amount of aggregates (Millard and Pimienta, 2019; Mindeguia, 2009; Jansson, 2004; Xing et al., 2015). In fact, the reduction of thermal conductivity when heating is more remarkable in concretes with siliceous aggregates in its composition than with calcareous or lightweight aggregates (Mindeguia, 2009; Jansson, 2004; Xing et al., 2015).

The lack of thermal conductivity tests on concretes up to 600 °C and the need to improve the input data in CTES numerical models made necessary this experimental study. In addition, the evolution of the

thermal parameter under successive thermal fatigue cycles between the temperature regime 300–600 °C has only been analysed in one study (Lucio-Martin et al., 2019) for two concrete types, to the knowledge of the authors.

The main focus of this study is to analyse the evolution of thermal conductivity up to 600 °C and after repetitive thermal cycles between 300 and 600 °C, to simulate working conditions as close as possible, as well as to define a test protocol for measuring the parameter at high temperature. A set of 5 different concrete compositions were studied with different type of aggregates, using CAC cement and incorporating polypropylene fibres. The study was divided into two parts: 1) the first part related to the first heating up to 600 °C where the effect of the aggregates and the heating rates were evaluated, and 2), the second part which comprises the effect of the thermal fatigue between 300 and 600 °C under service conditions and the final cooling down to room temperature.

3. Experimental setup and methodology

3.1. Materials

A set of five concrete mixes made of CAC cement and different aggregates type were analysed. The concrete compositions analysed had the same water/cement (w/c) ratio and aggregates volume (Table 2). The CAC was used due to its refractory properties and good response at high temperatures and during heating cycles (Bazant et al., 1996). The aggregates used in the five concrete mixes studied are: 1) fine CAT aggregate (named 1-C); 2) basalt aggregate (2-B); 3) a ternary mix combining basalt, CAT and a waste Slag from *São Domingos mine* (Pérez-López et al., 2008; Freitas et al., 2004) (3-B-C-S); 4) calcareous aggregate (4-CAL); and 5) siliceous sand (5-S).

One concrete batch of each concrete composition was produced. The mixing process consisted on these steps: 1) mixing the solid materials, aggregates and cement, during five minutes, 2) introduction of water with the plasticizer already diluted in it during one minute, 3) mixing during three minutes, 4) introduction of the polypropylene fibres during one minute, and 4) mixing during one minute. The mixes were poured inside prismatic moulds of 40 × 40 × 160 mm³ and compacted using a compacting rod. Since the size of the largest aggregates (7 mm) is smaller than 1/5 of the wide of the concrete sample (40 mm), the homogeneity of the material is ensured. Specimens were demoulded 24 h after casting and left in a humidity chamber at 95% of relative humidity and 20 °C until the age of testing.

3.2. Methodology

3.2.1. System description

A test protocol to measure properly the evolution of thermal

Table 2
Mix compositions used in this work.

kg/m ³	1-C	2-B	3-B-C-S	4-CAL	5-S
Cement CAC	600	600	600	600	600
Water	258	258	258	258	258
Aggr. 1 – Basalt 0–6 mm	0	1568.5	691	0	0
Aggr. 2 – CAT 0.25–4 mm	1736.5	0	745	0	0
Aggr. 3 – Slag 0.25–2 mm	0	0	133	0	0
Aggr. 4 – Slag 3–7 mm	0	0	141	0	0
Aggr. 5 – Calcareous 0–6 mm	0	0	0	1456.4	0
Aggr. 6 – Siliceous 0–3 mm	0	0	0	0	1456.4
Polypropylene fibres	0	0	2	0	0
Plasticizer	0.9	0.9	0.9	0.9	0.9
Water/cement (w/c)	0.43	0.43	0.43	0.43	0.43
Strength class	C70/ 85	C60/ 75	C45/ 55	C50/ 60	C40/ 50

conductivity at high temperatures (up to 600 °C) and during cyclic operation (during charging and discharging) has been designed. The test system for measuring the thermal conductivity comprises of various components, as it is shown in Fig. 3 and Fig. 4. The electrical furnace used is from Eurotherm and has 15 kW of power, and the model of the chamber furnace is MLR11 305/16. The maximum operating temperature of the oven was 1100 °C and it has a control system able to carry out the heating and cooling cycles with controlled rates. The equipment used for measuring the thermal conductivity was QTM-700 from Kyoto Electronics Manufacturing. This equipment is based on the hot wire method and measures the increase in temperature produced when an electrical current passes through the wires. The high-temperature probe of thermal conductivity is located between two concrete samples that are placed inside the oven, as shown in Fig. 3. The wires of the probe are connected to the equipment outside the furnace. Those wires were protected with ceramic covers in the region close to the door in order to insulate the connections from the metallic parts of the furnace. The thermal conductivity measurements have an accuracy of ±0.001 W/(m·K). To control and monitor the evolution of the temperature inside the concrete, one temperature sensor (K-type thermocouple) was embedded in the geometrical centre of the sample. Another two temperature sensors were located inside the furnace to follow the thermal response and to record the evolution of temperature at the external surface of the samples. The calibrated K-type thermocouples have accuracy in line with the specification of ±0.1 °C. All temperature data were collected and recorded through a data acquisition system (Model: Agilent 34970A) directly by an external data logger. In summary, the test comprises of the following components: furnace, two concrete samples, high-temperature thermal conductivity probe, K-type thermocouples and data logger (Fig. 3 and Fig. 4).

The equipment for measuring thermal conductivity had two different probes: one to measure the thermal parameter at room temperature and another for measuring high temperatures, up to 1000 °C. The room temperature probe covers a surface of 100 × 40 mm and the high temperature probe covered an area of 160 × 40 mm. Both probes cover a wide region of the surface of the concrete specimens. The values of thermal conductivity at room temperature were measured with both probes to compare their measures.

The lack of standardized tests methods for measuring the parameter at temperatures up to 600 °C made necessary to develop a protocol

Fig. 3. Graphical layout of the test facility and equipment.

Fig. 4. Experimental set-up of the real test facility.

taking into account the physicochemical changes that take place within the concrete while the material is being heated and cooled down. Two identical concrete samples of $40 \times 40 \times 160 \text{ mm}^3$ were needed for carrying out the test. The sample located at the bottom has a thermocouple embedded for recording the evolution of temperature in the centre of the specimen. An additional weight placed over the samples is needed to achieve full contact among the two samples and the probe.

Before start measuring, the wires of the high-temperature probe had to be calibrated. The wires used were able to measure up to 1000°C , but the sensors started to suffer damage from temperatures above 600°C . For that reason, the wires were calibrated before starting each test to ensure that they were not damaged.

In order to obtain an accurate measurement, the system needed to achieve constant temperature along both concrete surfaces in contact. For that reason, a time of 30 min after furnace reached the target temperature was needed in order to homogenize the temperature in the concrete samples in the processes of heating and cooling. Once those 30 min were elapsed, the thermal conductivity test started. The measures were discrete and the time for measuring was established in 60 s. During this time, the oven has to be under steady-state conditions to obtain an accurate value. If the electrical resistances of the furnace switched on at the end of the 60 s testing time, the transient conditions affected the value of thermal conductivity measured and the result had to be discarded. During these transient conditions, the convection inside the oven affected the measurement and the value was mainly affected by air-forced convection instead of the conduction within the solid medium. To obtain a more representative value of thermal conductivity, ten measurements at each temperature were taken, and only stable measures were considered.

3.2.2. Thermal regime

The evolution of the thermal parameters at the operating temperatures regime is of relevant importance to assess the heat transfer within the concrete structure and for determining the real energy storage. For that purpose, this paper deals with the maximum operating regime of the Heat Transfer Fluid (HTF) in CSP plants, commonly molten salts between 300 and 600°C . For that reason, the thermal conductivity was measured during the first heating up to 600°C and in successive heating and cooling cycles between 300 and 600°C .

The thermal conductivity has been measured during the thermal exposure of concrete, which has been divided into three stages: drying, dehydration and thermal fatigue stage.

Firstly, the concrete samples were dried up to 105°C for 72 h. In this stage, the loss of free water in the pores takes place. The time of 72 h was established after carrying out many tests on samples with the same

geometry and after verifying that all the free water was lost by weighting the samples. Secondly, the dehydration stage covers from 105 to 300°C , in the case of CAC concretes. During this stage, the dehydration of cement paste occurs. Finally, the thermal fatigue stage covers the subsequent heating and cooling cycles between 300 and 600°C .

The thermal conductivity was measured every 100°C from room temperature to 600°C during the first heating. During the first cooling stage, samples were cooled down to 300°C using the same temperature step. The second heating was performed up to 600°C again, measuring thermal conductivity every 100°C . Finally, the samples were cooled down to room temperature and the thermal parameter was evaluated at 400 , 200 and 25°C . All heating rates were programmed at $1^\circ\text{C}/\text{min}$. Regarding the cooling process, the oven controlled the evacuation of the heat using a trapdoor located at the top of the furnace, which was detailed in Fig. 3 and Fig. 4. The control system of the furnace regulated the degree of openness of the trapdoor. When the temperature had to decrease in more than 10°C than the theoretical programmed temperature, the furnace opened the trapdoor completely. For that reason, the furnace experienced a cooling process by following a natural draft. The thermal cycle and the stages are detailed in Fig. 5, and the measurements were performed at the temperature plateaus. The drying stage (blue surface) covers the first heating up to 100°C during the first 72 h of testing. After that, the first heating (1H) up to 600°C was performed (red area). During this heating, the dehydration of the CAC at 300°C takes place (dashed line). The thermal fatigue stage follows the cycle with a first cooling (1C) down to 300°C (violet surface), a second heating (2H)

Fig. 5. Thermal cycle with the stages in different colours.

up to 600 °C (orange surface) and the second cooling (2C) down to room temperature (purple surface). The duration of one complete test lasted 10 days.

The output parameters measured were the thermal conductivity, the temperature of the furnace, and the temperature in the core of the concrete samples. The experimental test was carried out in the five concrete mixes in order to evaluate the effect of the type of aggregates. Two samples per concrete mix were tested at the same time. An additional test was performed for the evaluation of the effect of the heating rate on the 3-B-C-S mix at 0.5 °C/min.

Additionally, a microscopic analysis was carried out when the samples were cooled down to room temperature, following the 2C process. Some pictures were taken at the surface of the samples by using an optical microscope (model SZ61TR from OLYMPUS) with a resolution of $\pm 1 \mu\text{m}$. The crack width was measured with the software OLYMPUS Stream Essentials in order to quantify the effect of the thermal exposure in all the concrete mixes.

3.2.3. Methodology for data analysis

The probes of the thermal conductivity equipment need to be calibrated before starting the test. The calibration procedure is carried out at room temperature using the patterns of different materials provided by the manufacturer. The calibration procedure consists of measuring the thermal conductivity of some patterns whose thermal conductivity is known for a selected current of the equipment. The calibration is done when the probe achieves three measures with a standard deviation lesser than 3% and a mean value similar to the value of the pattern.

After that, the test started with the thermal regime explained in Fig. 5. A set of 10 measurements were carried out at every single temperature once the material reached the equilibrium in the temperature located in the centre of the specimen. The weighted mean was taken from the right measurements and was the estimation of the real value. The uncertainties (U) were calculated and evaluated following the instructions summarised in (Moffat, 1988). The first step is the calculation of the standard deviation (σ) following the equation Eq. (1):

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X}_n)^2}{n-1}} \quad (1)$$

where σ is the standard deviation and is half of the U at 95% of confidence stated for each measurement X_i . The mean value is $\bar{X}_n$ and n is the number of measurements carried out at different stages of temperature.

The uncertainty (U) of the measurements were obtained by expression in the equation Eq. (2):

$$U_x = \frac{2}{\sqrt{\sum_{i=1}^n \frac{1}{\sigma_i^2}}} \quad (2)$$

4. Results and discussion

4.1. Evolution of thermal conductivity

4.1.1. Room temperature

Fig. 6 shows a comparison between the thermal conductivity measured with both probes: the room temperature probe (RT) and the high temperature probe (HT). The measures were carried out when samples were taken from the humidity chamber at room temperature. The values measured with the two probes show significant differences between them because the high-temperature probe is not appropriate for measuring the thermal conductivity at low temperature. This suggests the importance to employ the adequate probe system for the measurement of this parameter. The results obtained with the two probes display a linear dependence. Being the thermal conductivity measured at room temperature, k_{RT} , and the ones measured at high temperature, k_{HT} , the

Fig. 6. Thermal conductivity at room temperature measured with the two probes.

relation between them is shown in Fig. 6, with a coefficient of determination, $R^2 = 0.9525$.

4.1.2. First heating (Room temperature to 600 °C)

Fig. 7 shows the evolution of thermal conductivity measured during the first heating up to 600 °C. The legend shows the first heating (1H) followed by the name of the concrete mix. The values at room temperature represented in the chart are the ones measured with the high temperature probe so as to make a better comparison among them by using the same probe of measure.

The results obtained show that thermal conductivity decreases with temperature, especially for the siliceous mix. Thermal conductivity experienced the highest loss after drying the concrete at 105 °C for 3 days. Basically, the loss of evaporable water during drying up to 105 °C decreases thermal conductivity because the air replaces water in concrete pores. This is justified since water has higher thermal conductivity than air, with values of 0.607 W/(m·K) and 0.02551 W/(m·K) respectively at room temperature (Incropera, 2006). From temperatures below 100 °C, thermal conductivity is supported by both solids and liquids within the material. When the temperature exceeds 100 °C, the

Fig. 7. Evolution of thermal conductivity up to 600 °C for the CAC concrete mixes.

conduction is mainly supported by the solids inside the material. Additionally, the temperature affects the creation of air gaps and microcracking inside the material. That is the main reason why the parameter decreases during heating up to 105 °C.

When the samples were heated up to the maximum temperature of 600 °C, CAC concretes experienced decreases in the thermal parameter due to the dehydration of the cement pastes (up to 300 °C for the CAC (Antonović et al., 2013)) and the volumetric changes that take place due to the shrinkage of the cement paste and the expansion of the aggregates (Bažant et al., 1996). The results indicate that the thermal response of the concrete is influenced by the thermal response of the aggregates and the mix design. The biggest reduction of thermal conductivity took place in the siliceous mix (5-S) when heating up to 100 °C, achieving values nearly 2 W/(m·K). Many authors reported a similar decrease when heating up to 300 °C (Collet, 1977; Millard and Pimienta, 2019), but the test was done continuously and the drop was linear, what indicates the importance of giving time for homogenise the temperature and to produce the physicochemical changes in the whole specimen. Concrete with calcareous aggregates (4-CAL) also experienced a significant decay of conductivity when heating up to 100 °C. More stable aggregates such as basalt (2-B) experienced the lowest drop up to 100 °C and then the thermal response remained almost constant.

The decreasing trend in the thermal conductivity is consistent with many tests on concrete at high temperature carried out by different authors (Lucio-Martin et al., 2019; Bažant et al., 1996; Xing et al., 2011; Millard and Pimienta, 2019), highlighting the aggregates effect and the degree of saturation of the concrete. In this research, the siliceous mix (5-S) experienced the highest scattering, but this dispersion was verified as originated by the probe. On the contrary, another literature reported an increase of the thermal conductivity with temperature when adding graphite (Guo et al., 2010), but that would be a property of a special material.

In this work, thermal conductivity change with the temperature has been compared with the results of other studies in Fig. 8.

The projects HEATCRETE (Hoivik et al., 2019) and EnergyNEST (Laing et al., 2012) measured the evolution of thermal conductivity at high temperatures for their use in CTES. In these projects, tests to measure thermal conductivity were carried out up to 400 and 450 °C, respectively but with different initial conditions. Moreover, in both projects, the type of cement and aggregate composition are not described by the authors. In the case of HEATCRETE, the thermal conductivity of concrete was measured after being exposed at 430 °C for 100 h, obtaining values of around 1.92–1.78 W/(m·K) at 300 and 400 °C, respectively. In the EnergyNEST project, the thermal conductivity of concrete was measured after a simultaneous drying and dehydration process at 400 °C, obtaining 1.2 W/(m·K) at 450 °C.

Fig. 8. Measured thermal conductivity of CAC concretes and comparison to concretes from the literature (European Committee for Standardisation, (CEN), 2004; Hoivik et al., 2019; Laing et al., 2012; Xing et al., 2015; Jansson, 2004).

Other studies that reported values at high temperatures analysed: a) two Normal Strength Concretes (NSC) with OPC cement and siliceous and calcareous aggregates, named OPC-NSC-S and OPC-NSC-C, respectively (Xing et al., 2015), and b) a Self-Compacting Concrete (SCC) with PP fibres (OPC-SCC-PPF) (Jansson, 2004).

Fig. 8 shows the evolution of the thermal conductivity at high temperature measured in the concrete mixes of this work and the results obtained in the literature for the HEATCRETE (Hoivik et al., 2019), EnergyNEST (Laing et al., 2012), the NSC (Xing et al., 2015) and the SCC (Jansson, 2004) concretes. Additionally, the limits of thermal conductivity given in Eurocode 2 (European Committee for Standardisation, (CEN), 2004) are represented in the chart. It is worth noting that Eurocode 2 curves are adjusted from tests of concrete structures under fire conditions and take into consideration only the moisture transport. However, it is one of the most relevant resources of thermal conductivity and, for that reason, it was included in Fig. 8.

The curves obtained for the mixes analysed in this work are in accordance with those reported in the literature. Regarding the siliceous concretes, both compositions (OPC-NSC-S and 5-S) experienced the highest drop when are heated up to 100 °C, but the lack of measured values at 600 °C in the literature made not possible to compare the second decrease between 400 and 600 °C. The calcareous mixes experienced a lesser decrease at high temperatures in both tests up to 300 °C, however, they may not be appropriate for operating up to 600 °C, as reported in this work. The calcareous mix (4-CAL) experienced a decrease in the parameter of 20% when was heated from 400 to 600 °C. The suitability of the HEATCRETE and EnergyNEST for operating above 400 °C is not reported and, therefore, cannot be compared for that range.

To sum up, the mixes 1–3 analysed in this study can work properly up to 600 °C without significant variation of the thermal conductivity between 300 and 600 °C and showing low dispersion. Their thermal behaviour is almost steady under the cyclic operating conditions, as will be shown later. In contrast, the mixes containing calcareous and siliceous aggregates experienced the biggest losses and high variations of thermal conductivity (–30% for 4-CAL and –40% for 5-S) at temperatures above 300 °C. The results obtained in this work do not support their use for CTES applications under operating temperatures up to 600 °C.

4.1.2.1. Uncertainty analysis. There exist a discrepancy of results obtained with the high temperature probe among the siliceous 5-S and the other concrete mixes. It is worth noting that the boundary conditions in all tests were the same and the changes were mainly produced by the different materials tested. The repetition of the tests was done following the same procedure, i.e. the calibration process, thermal regime, heat source, power and thermal conductivity probes. The uncertainties in engineering experiments were described as “variable but deterministic” and are the errors that change during an experiment (Moffat, 1988). In fact, the author highlighted that in experiments including heat transfer and high temperature the source of errors might be produced for several factors such as system disturbance effects or interactions between the system and the sensor among others. For that reason, these conceptual disturbances difficult to find the connection between the estimation and the source of error.

Table 3 shows the mean values and the interval of the uncertainty of thermal conductivity for the first heating. The 5-S experienced bigger variation at high temperatures. Several sources might have been caused the errors such as the creation of air gaps due to microcracks in the material. The cracks affect negatively the thermal conductivity and the probe is very sensitive to changes in the thermal performance. On the other hand, a previous study showed that siliceous mixes loss more mass during the drying stage due to water evaporation, indicating that the high value of thermal conductivity at room temperature was owing to higher humidity in the composition (Lucio-Martin et al., 2019). The humidity might be altered the wires of the probe and for that reason, the

Table 3

Mean values and uncertainties of thermal conductivity for the first heating up to 600 °C.

Material	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C
1-C	1.18 ± 0.20	1.35 ± 0.26	1.03 ± 0.17	0.92 ± 0.07	1.03 ± 0.22	1.06 ± 0.24
2-B	1.32 ± 0.52	1.34 ± 0.61	1.36 ± 0.32	1.28 ± 0.64	0.97 ± 0.16	1.45 ± 0.77
3-B-C-S	1.23 ± 0.47	1.15 ± 0.33	1.12 ± 0.24	1.04 ± 0.15	0.96 ± 0.11	0.99 ± 0.14
4-CAL	1.11 ± 0.28	1.23 ± 0.24	1.23 ± 0.13	1.09 ± 0.12	1.04 ± 0.10	0.86 ± 0.10
5-S	1.96 ± 0.45	2.08 ± 0.95	2.23 ± 0.68	1.34 ± 0.30	1.2 ± 0.10	1.30 ± 0.11

measurements from 100 to 600 °C showed the biggest variation in the repeated measurements.

4.1.2.2. Effect of the aggregates. Not only the thermal conductivity of the aggregates is important but also the thermal expansion. More thermal expansive aggregates might induce a higher risk of microcrack formation, and this effect is increased because of the shrinkage of the cement paste (Bažant et al., 1996). The $\Delta L/L_0$ experienced by the aggregates up to 600 °C ranges from 0.5 to 1.5% depending on the type of aggregate and the cement paste varies from −1 to −2% of length change (Bažant et al., 1996). The cracks are originated from 100 °C and when the temperature rises the density of cracks is increased, as reported in (Pimienta et al., 2018). The appearance of cracks implies the creation of gaps within the material and, thus, the creation of another thermal resistance inside the material. In dry conditions, these interstices are filled with air, whose thermal conductivity differs orders of magnitude from the solid medium. Heat transfer is affected because there is not only conduction but convection also as mechanisms of transporting the heat.

Siliceous aggregates are more thermally conductive but also expansive. The CTE grows with the temperature, as reported in (Bažant et al., 1996). As a consequence, a concrete mix with siliceous aggregates can be more prone to crack under certain conditions (Senadheera and Zollinger, 1996; Lucio-Martin et al., 2019). In fact, in this study, the 5-S mix experienced another significant drop in the thermal conductivity at temperatures between 300 and 400 °C, achieving similar values of thermal conductivity than compositions with more thermally stable and less heat conductive aggregates. On the other hand, thermal conductivity is not only affected by the generation of cracks but also for changes in the crystallinity in the aggregates, as it was reported in (Touloukian et al., 1971).

4.1.2.3. Effect of the heating rate. Additionally, another test was done in the 3-B-C-S mix for evaluating the effect of using different heating rates: 0.5 and 1 °C/min. The results (displayed in Fig. 9) indicate that using these two heating rates the evolution of the thermal conductivity

followed the same pattern: i) decrease when heating up to 100 °C, ii) slightly increase at 200 °C, iii) another decrease at 300 °C, and iv) slight decrease or constant value when heating up to 600 °C. This test shows that heating rate may have some effects in the measured thermal conductivity, but the trend is maintained. In this research, the heating rate of 1 °C/min was selected, since it is a commonly used heating rate (Alonso et al., 2016; Pimienta et al., 2018).

4.1.3. Thermal fatigue stage (cycles from 300 to 600 °C)

This section presents the evolution of thermal conductivity when temperature ranged between the operating regime (300–600 °C). The code used for the different stages was: first heating up to 600 °C (1H); first cooling from 600 to 300 °C (1C); second heating from 300 to 600 °C (2H) and the second cooling down to room temperature (2C). The legend shows the previous code followed by the type of cement, CAC and the type of aggregate: C (CAT), B (basalt), B-C-S15 (basalt, CAT and Slag), CAL (calcareous) and S (siliceous). The results are presented in two subsections related to the heating and cooling processes. Both sections show graphs including the first processes (1H or 1C) with solid lines and the second processes (2H or 2C) represented with dashed lines.

4.1.3.1. Effect of the heating in the thermal fatigue cycles from 300 to 600 °C (1H and 2H): Fig. 10 shows the evolution of thermal conductivity during the two heating processes up to 600 °C in all concrete mixes. Whereas the first heating is a process mainly influenced by physicochemical changes, the successive heating cycles are expected to be affected by the degradation of the material due to the thermal fatigue.

The specimens followed the same pattern during the first heating (1H) and during the second heating (2H). In the second heating, the thermal conductivity decreased until reaching the same previous value obtained at 600 °C during the first heating. The mixes recorded similar values at 600 °C in both heating cycles, but the siliceous composition (5-S) had a decrease of 7% with respect to the thermal conductivity obtained in the first heating. Despite this slight difference, the experimental tests have proved similar patterns and stability during the cycles performed.

The experimental tests showed a slow degradation of thermal conductivity that seems to stabilize, but the long-term performance is not demonstrated in this work. Cyclic operating conditions above the 3rd thermal cycle are not reproducible at lab-scale with the setup of this study, since the time of testing of each sample exceeded 10 days and the degradation of the wires of the high-temperature probe made not possible to obtain accurate measurements at longer testing times.

Regarding the variation between the two heating processes, Fig. 11 shows the percentage of modification experienced by the concretes at the same temperature of testing. There exists a stabilization between 400 and 500 °C with a variation lesser than 10% in all cases excluding the basalt composition. When the temperature increased up to 600 °C, the calcareous mix experienced another significant drop, with a percentage of change of nearly 20%, whereas the other mixes remained with changes around 10%.

4.1.3.2. Effect of the cooling in the thermal fatigue cycles from 600 to 300 °C (1C and 2C): The evolution of thermal conductivity during the two cooling processes is shown in Fig. 12. Thermal conductivity of the concrete mixes might be assumed constant within the fatigue tests

Fig. 9. Evolution of thermal conductivity up to 600 °C for the 3-B-C-S with different heating rates.

Fig. 10. Evolution of thermal conductivity when heating from 300 °C to 600 °C during the 1H and 2H for the CAC concrete mixes.

Fig. 11. Percentage of variation between the two heating processes.

between 300 and 600 °C only for the ternary mix. Despite having more thermal stable aggregates, the basalt mix (2-B) test showed scattered values, in this case due to the damage of the high-temperature wires while testing. The mix with calcareous aggregates in 4-CAL obtained the

highest variability of the thermal conductivity. When the temperature decreased to 300 °C, there was a slight recovery of the thermal conductivity in all the mixes, which was more notable for the 4-CAL (40%) and 5-S (22%) mixes. In the second cooling down to room temperature, calcareous and siliceous mixes recovered between 15 and 30% of the value of thermal conductivity at 600 °C, while the mix with basalt aggregates experienced a decrease of 8% and the ternary mix showed almost constant values.

In the literature, several authors reported that the thermal conductivity remained almost constant when concrete was cooled down (Ödeen and Nordström, 1972; Jansson, 2004). In one study (Jansson, 2004), the values were measured by using the transient plane source for an SCC concrete with PP fibres, and the temperatures analysed when cooling were 500, 200 and 20 °C, and these differences do not allow a fair comparison with the tests carried out in this work.

Regarding the variation in the cooling processes, Fig. 13 shows the percentage of modification experienced by the concretes at the same temperature of testing. The most significant is the variation of the thermal conductivity at room temperature between the value before and after the test, ranging between 25 and 45% for the concrete mixes. For temperatures of 200 and 400 °C, the changes were below 8% in the mixes, excluding the basalt composition.

Fig. 12. Evolution of thermal conductivity when cooling from 600 °C to 300 °C (1C) and from 600 to 25 °C (2C) for the CAC concrete mixes.

Fig. 13. Percentage of variation between the two cooling processes.

4.1.4. Microstructure after the thermal fatigue stage

Fig. 14 shows an example of a picture taken on the surface of one 5-S concrete sample after two thermal cycles. The crack width values are included in different locations of the picture. The widths were measured ten times in all concrete compositions. The microcracks appeared close to the pores and in the interface between the cement paste and the aggregates. It is important to note that those cracks are the result after the thermal test because the pictures were taken at residual conditions. At higher temperatures, during real operating conditions, when aggregates are increasing their volume the cracks might be even lower than the ones represented in Fig. 14.

Regarding the microcracks, all concrete mixes experienced cracks of widths below 80 μm (Fig. 15). The mixes with calcareous and siliceous aggregates (4-CAL and 5-S) experienced the biggest microcracks with mean values of 15 and 55 μm , respectively. The biggest cracks found in the 5-S explained the highest decay in the thermal conductivity experienced by this concrete mix compared to the other materials tested. According to the more stable aggregates, the ternary mix (3-B-C-S) and basalt composition (2-B) experienced the narrower crack widths with values below 10 μm and 12 μm , respectively. These results are in accordance with other values reported in the literature for residual conditions, whose concretes experienced cracks between 50 and 80 μm after one thermal fatigue cycle between 290 and 550 $^{\circ}\text{C}$ (Alonso and Puentes, 2020).

Fig. 14. Example of microscopic analysis after the thermal exposure for the 5-S composition (each value of “length” indicates the crack width measured at the point indicated).

Fig. 15. Crack width for the concrete mixes after the thermal cycle.

4.1.5. Relationships for thermal conductivity at high temperatures

Recently, the number of simulations of CTES has increased due to its suitability for working at high temperatures. However, the evolution of concrete thermal conductivity at temperatures up to 600 $^{\circ}\text{C}$ is required to be used for those simulations and to improve the knowledge and the results of the heat transfer theoretical models.

To provide new information in this matter, this work aims to provide equations to calculate thermal conductivity as a function of temperature based on the experimental results obtained at high temperatures. Five compositions of CTES have been tested using CAC cement and different aggregates. The formulas for the thermal conductivity were obtained by curve fitting and are collected in the Appendix A. These relationships can be used as an input for numerical heat transfer models at high temperatures.

Fig. 16 shows the evolution of thermal conductivity of the 3-B-C-S mix with the temperature for the 2 thermal cycles, differentiating the heating and cooling stages. The curves were obtained from the fitted equations collected in Appendix A and followed a polynomial equation of second order. The evolution of thermal conductivity highlights the dependence with the temperature for the range of operation of applications of CSP. For that reason, assuming a constant value may not be suitable for making predictions on the overall thermal performance of certain applications of concrete working at high temperatures.

Regarding the stability of the thermal parameter during the long-term operation, additional thermal cycles are needed to make an appropriate prediction. With the present data available in this work, a linear regression was made to have a first approach on the stabilization

Fig. 16. Evolution of thermal conductivity of 3-B-C-S with temperature for successive heating and cooling processes obtained from fitted equations.

Fig. 17. Estimation of thermal conductivity at 600 °C during the thermal cycles of 3-B-C-S concrete mix.

of the thermal conductivity at both 300 and 600 °C along with the thermal fatigue cycles. The prediction for the 3-B-C-S mix is shown in Fig. 17. For this concrete composition working under heating and cooling cycles between 300 and 600 °C the stabilization of thermal conductivity would be reached around the 10th cycle, achieving a value of 0.95 W/mK at 600 °C and 1.01 W/mK at 300 °C. Nonetheless, this preliminary model needs further verification with additional experimental tests, which could not be performed due to the limitations in the durability of working at high temperatures of the available wires for this research. Additional research aiming to add insights in this matter should target to at least 10 cycles to verify if thermal conductivity equation converges. Anyway, the long-term performance should be tested at up-scaled levels in a real prototype of CTES in a CSP, since the data available of the behaviour of this material at operating conditions is still scarce.

In summary, assuming a constant value of thermal conductivity in simulations of heat transfer when concrete is exposed to high temperatures seems not accurate, at least for the first thermal cycles. After a certain number of thermal cycles (estimated around 10 cycles), the equation describing thermal conductivity change with temperature between 300 and 600 °C may stabilize, which in case of being confirmed experimentally, would smooth the modellers task.

5. Conclusions

In this paper, the evolution of the thermal conductivity of different concrete compositions exposed up to 600 °C and during repetitive thermal cycles was carried out. In particular, an analysis of the effect on the aggregates, heating rate and the thermal fatigue under service operation between 300 and 600 °C has been analysed in detailed. Based on the experimental results presented in this work, the following conclusions can be drawn:

- The thermal conductivity of concrete at high temperatures depends on the concrete mix and the aggregates. At room temperature, the values of thermal conductivity range for most of the concrete studied between 1.2 and 2 W/(m·K), range obtained in concretes with calcareous, basalt, CAT and their combinations of aggregates. Using siliceous aggregates improved thermal conductivity nearly up to 5 W/(m·K).
- In all the mixes, the biggest loss in the thermal conductivity takes place during the drying stage due to the loss of free water. When heating up to 600 °C, the siliceous mix experienced the biggest drop in the thermal conductivity, while CAT and ternary mixes displayed more stable behaviour.
- In the first cooling down to 300 °C, the thermal conductivity of most concrete mixes does not vary significantly, but siliceous and calcareous mixes recovered between 20 and 40% of the value at 600 °C. In the second heating, the thermal conductivity achieves again the previous values at the equivalent temperatures. The last cooling produced a slight recovery in the thermal conductivity when samples were cooled at 200 °C in mixes using siliceous, calcareous and basalt aggregates whereas the other mixes maintained the same value of the thermal parameter.
- The assumption of constant thermal conductivity in simulations of CTES is not appropriate for the first operating cycles and has to be decided depending on the concrete compounds. For longer-term cycles, further research is needed.

CRediT authorship contribution statement

T. Lucio-Martin: Conceptualization, Investigation, Resources, Methodology, Data curation, Validation, Visualization, Writing - original draft, Writing - review & editing. **M. Roig-Flores:** Conceptualization, Investigation, Resources, Data curation, Writing - original draft. **M. Izquierdo:** Conceptualization, Supervision, Writing - original draft. **M. C. Alonso:** Conceptualization, Funding acquisition, Supervision, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

Evolution of thermal conductivity with temperature

The following expressions for the evolution of thermal conductivity with the temperature of concrete based on different types aggregates can be used as an input data for modelling the behaviour of concrete at temperatures up to 600 °C. The proposed relationships can be of interests in applications of concrete for thermal energy storage or as a structural element exposed to fire.

1. First heating up to 600 °C (1H):

- CAT aggregate concrete – CAC cement (1-C):
 $100 \leq T \leq 600 \text{ °C: } 1.4587 - 0.0019T + 2 \cdot 10^{-6}T^2 \text{ (} R^2 = 0.4689 \text{)}$

- *Basalt aggregate concrete – CAC cement (2-B):*
 $100 \leq T \leq 600 \text{ }^{\circ}\text{C}: 1.5173 - 0.0015T + 2 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.1185\text{)}$
- *Basalt, CAT and Slag aggregate concrete – CAC cement (3-B-C-S):*
 $100 \leq T \leq 600 \text{ }^{\circ}\text{C}: 1.3311 - 0.001T + 7 \cdot 10^{-7}T^2 \text{ (R}^2 = 0.9477\text{)}$
- *Calcareous aggregate concrete – CAC cement (4-CAL):*
 $100 \leq T \leq 600 \text{ }^{\circ}\text{C}: 0.989 + 0.0017T - 3 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.944\text{)}$
- *Siliceous aggregate concrete – CAC cement (5-S):*
 $100 \leq T \leq 600 \text{ }^{\circ}\text{C}: 2.1622 - 0.0004T - 2 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.6628\text{)}$

2. First cooling down to 300 °C (1C):

- *CAT aggregate concrete – CAC cement (1-C):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: -0.1958 + 0.0068T - 8 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.5933\text{)}$
- *Basalt aggregate concrete – CAC cement (2-B):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: 2.887 - 0.0089T + 10^{-5}T^2 \text{ (R}^2 = 0.9657\text{)}$
- *Basalt, CAT and Slag aggregate concrete – CAC cement (3-B-C-S):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: 0.7119 + 0.0015T - 2 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.9317\text{)}$
- *Calcareous aggregate concrete – CAC cement (4-CAL):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: 0.768 + 0.0025T - 4 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.7618\text{)}$
- *Siliceous aggregate concrete – CAC cement (5-S):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: 2.528 - 0.0041T + 3 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.9861\text{)}$

3. Second heating up to 600 °C (2C):

- *CAT aggregate concrete – CAC cement (1-C):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: -0.4386 + 0.0088T - 10^{-5}T^2 \text{ (R}^2 = 1\text{)}$
- *Basalt aggregate concrete – CAC cement (2-B):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: 2.8374 - 0.0079T + 8 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.6669\text{)}$
- *Basalt, CAT and Slag aggregate concrete – CAC cement (3-B-C-S):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: 2.1378 - 0.0056T + 6 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.8783\text{)}$
- *Calcareous aggregate concrete – CAC cement (4-CAL):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: 2.3181 - 0.0053T + 5 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.9861\text{)}$
- *Siliceous aggregate concrete – CAC cement (5-SIL):*
 $300 \leq T \leq 600 \text{ }^{\circ}\text{C}: 3.5903 - 0.0096T + 9 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.9166\text{)}$

4. Second cooling down to room temperature:

- *Basalt aggregate concrete – CAC cement (2-B):*
 $25 \leq T \leq 600 \text{ }^{\circ}\text{C}: 0.7897 + 0.0024T - 4 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.4072\text{)}$
- *Basalt, CAT and Slag aggregate concrete – CAC cement (3-B-C-S):*
 $25 \leq T \leq 600 \text{ }^{\circ}\text{C}: 0.9371 + 0.0006T - 9 \cdot 10^{-7}T^2 \text{ (R}^2 = 0.4238\text{)}$
- *Calcareous aggregate concrete – CAC cement (4-CAL):*
 $25 \leq T \leq 600 \text{ }^{\circ}\text{C}: 1.2557 + 0.0004T - 10^{-6}T^2 \text{ (R}^2 = 0.8382\text{)}$
- *Siliceous aggregate concrete – CAC cement (5-SIL):*
 $25 \leq T \leq 600 \text{ }^{\circ}\text{C}: 1.7776 + 0.0006T - 3 \cdot 10^{-6}T^2 \text{ (R}^2 = 0.7691\text{)}$

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