Evolution of thermal conductivity on CAC concrete at high temperatures and during thermal fatigue tests

T. Lucio-Martin¹, M.C. Alonso¹,*, M. Roig-Flores¹,² & L. Guerreiro³
¹Eduardo Torroja Institute for Construction Sciences (IETcc-CSIC), Madrid, Spain
²Universitat Politècnica de València, Valencia, Spain
³University of Évora, Évora, Portugal

* Corresponding author (tamara.lucio@ietcc.csic.es, Serrano Galvache 4, CP: 28033, Madrid, Spain)

ABSTRACT

Heat transfer plays an important role when concrete works at high temperatures. For many applications, it is important to evaluate the effect of heat transfer on concrete to predict the thermo-mechanical response. Inside concrete, the dominant mechanism of heat transfer is conduction, and the main parameter involved is thermal conductivity. Heat transfer may play also a relevant role when spalling occurs.

In this paper, the evolution of thermal conductivity of concrete with temperature has been studied for different concrete types up to 600°C. The effect of cooling and thermal gradients are followed.

Results indicate that during the first heating, thermal conductivity decreases in several steps with temperature, first due to pore free water loss and second after dehydration up to 300°C. The mass loss and the temperature gradients are also affected. Thermal gradients play a role in the risk of concrete spalling. When cooling, thermal conductivity recovered almost the same value at 300°C. Repetitive thermal cycles do not modify the thermal performance of concrete.

KEYWORDS: heat transfer, thermal conductivity, thermal gradients, thermal fatigue

INTRODUCTION

There are infrastructures of concrete which operate at high temperatures during its service life. Applications such as nuclear and geothermal power plants condition concrete structures to work at high temperatures. Nowadays, concrete is being considered as a material for thermal energy storage systems for Concentrating Solar Power Plants (CSP). For such application concrete has to operate under high temperature for long periods and heating cycles of charge and discharge. Several authors have already demonstrated at lab scale the potentiality of concrete up to 600°C [1-3].

Nevertheless, when concrete is exposed to high temperatures, the spalling risk increases owing to thermal gradients between the surface and the core and pore pressures. The spalling caused by thermal gradients, which originates stresses, is one mechanism that has been widely accepted to explain the spalling phenomenon in concrete under fire [4-6].
Several authors have studied other factors that affect spalling such as pore pressures, thermal dilation of aggregates and shrinkage due to cement paste dehydration and the thermal incompatibility between the components of concrete [7-8]. Moreover, different thermal expansion coefficients between aggregates and cement paste inducing severe cracking can even produce further spalling risk [9-10].

In order to understand deeper concrete spalling phenomenon, the analysis of heat transfer mechanism when concrete is exposed to heat is of great interest for applications of concrete working at high temperatures. The heat transfer plays an important role in the spalling risk of a concrete. Thus, a better understanding of the thermal performance of concrete will be helpful for the design of concrete as well as for the thermal operation of these type of infrastructures.

When concrete is being heated, thermal conduction within the material is the dominant heat transfer mechanism. Thermal conductivity is the parameter that governs in conduction. By definition, this parameter gives the proportion between the heat flux and the temperature gradient between the external surface and the core. In conventional concrete, around 70% of the volume is occupied by the aggregates having a relevant role in the heat transfer. Since the wide types of aggregates that can be used in concrete have different thermal conductivity, the concrete response to heat will be different. The thermal conductivity of the concrete with siliceous aggregates is around 3 W/mK and the value is reduced to the half using basalt aggregates (1.5 W/mK) [11-12]. Nonetheless, these thermal conductivities are measured at ambient conditions before heating and, when concrete is exposed to high temperature, the thermal response changes significantly. There is limited information in the concrete thermal behaviour, and especially at high temperatures. There are different methods to obtain the thermal conductivity of concrete at high temperature which can be divided into steady or transient methods. Pimienta et al. [12] affirm that under moist conditions the steady state methods give an underestimation of the thermal conductivity due to moisture migration. Transient methods, and specifically, the hot-wire method are the more common methodology for the evaluation of thermal conductivity. The lack of thermal conductivity values and abroad databases of properties results and standardised test methods to measure this parameter at high temperatures make this study necessary to increase the knowledge on the heat transfer phenomenon on concrete and its contribution to the risk of spalling.

This paper deals with the evolution of thermal conductivity of concretes in a wide range of temperatures up to 600°C, during heating and cooling. Different type of aggregates are considered and the relationship with the spalling risk is analysed.

**EXPERIMENTAL PROCEDURE**

The aim of the experimental work performed is to design first a test protocol for measure the thermal conductivity of concrete at high temperature and to evaluate the evolution at temperatures during heating and cooling between 300-600°C.

**Materials and mix design**

Two different concrete mixes (Table 1) were used for the experiments with the same cement paste and w/c ratio. The Calcium Aluminate Cement (CAC) was used due to its refractory properties and good response at high temperatures. The effect on concrete thermal conductivity when using aggregates with different thermal response has been considered. One concrete composition with siliceous aggregate was selected representing a high thermal conductivity. Another concrete composition is a ternary mix with low thermal expanded aggregates, containing clinker of CAC (CAT), basalt and a waste slag from São Domingos mine.
The specimens prepared were prismatic of 40 × 40 × 160 mm³ and were cured in a humidity chamber at 95% relative humidity and 20°C until the age of 7 days. At the time of testing, the ageing of the siliceous mix was 98 days and the ternary mix 45 days.

**Thermal regime**

To completely determine the thermal conductivity evolution of the concrete during the thermal exposure, three stages are analysed in the thermal regime studied: 1) properties at room temperature and drying up to 105°C during 72 hours, when loss of free pore water takes place, 2) dehydration of cement paste process produced during the first heating between 100-300°C and 3) thermal fatigue stage during heating and cooling cycles from 300 to 600°C. The heating and cooling rates were established at 1°C/min in all stages of the thermal test. During the dehydration and thermal fatigue stages, thermal conductivity was measured at increasing temperatures with a step of 100°C until reaching 600°C, and afterwards, cooled down to 300°C using the same temperature step. Thermal conductivity was measured at each temperature step since the equipment needs constant temperature for evaluating the parameter. Figure 1 shows the thermal regime used during the test.

![Thermal cycle with stages](image-url)
Parameters under measure were: 1) temperatures of the furnace and in the core of the concrete samples, 2) mass loss during drying for both concrete samples and during all heating stages for the ternary mix, and from thermogravimetry test in hydrated CAC powder of the ternary concrete mix and 3) the evolution of thermal conductivity for all the heating and cooling stages in concrete samples.

For measure thermal conductivity, the equipment used was QTM-700 from Kyoto Electronics Manufacturing. This equipment is based on the hot wire method and measures the increase in temperature produced by the pass of electrical current through the wires. Due to the lack of standardised test methods for measuring thermal properties of concrete at high temperatures, a test protocol has been designed.

Samples of $40 \times 40 \times 160 \text{ mm}^3$ were used to performing the tests. Two identical samples were employed in each test. One of them contained a thermocouple embedded to record the evolution of temperature inside the concrete. The sensor wires for measuring thermal conductivity were placed between the two samples, the setup is shown in Figure 2. The whole system was placed inside the furnace. The accurate measurement of the thermal conductivity needs to reach stable temperature of the concrete. The time for each measurement was established in 60 seconds. The preliminary tests performed during the development of the protocol showed minimum dispersion for the same concrete mix. On the other hand, the test carried out displayed significant dispersion on the results when the electrical resistances of the furnace were switched on while the equipment was measuring. This fact motivated a specific analysis to obtain an adequate protocol. The experience showed that the value of thermal conductivity could be right or wrong depending on the situation of the furnace during the exact moment when the equipment measured. The strategy followed consisted of carrying out 10 measurements for each temperature and identify their stability during the measurement.

**Figure 2**  Setup for the thermal conductivity test

RESULTS AND DISCUSSION

1) Thermal evolution during free water loss (room to 105°C)

In general terms, the measurements obtained of thermal conductivity decreased with the temperature having the highest drop after the first heating at 105°C (see Figure 6). Thus, the
decrease in this parameter can be considered to be produced mainly during the drying phase, where the loss of evaporable water from the pores produced substitution of the volume of water by volume of air in the pores. Air has lower thermal conductivity than water and, for that reason, the thermal parameter decreases.

Since the highest drop in thermal conductivity occurred during heating up to 105°C, the evolution of mass loss and thermal gradients was also analysed. The evolution of mass loss quantifies the loss of evaporable water before starting the heating. Figure 3-left shows the mass loss in time for the two different compositions. The siliceous mix lost more mass than the ternary mix, which is in accordance with the loss on the thermal conductivity during heating up to 100°C, indicating that part of its higher conductivity was produced by its higher humidity. Moreover, the higher thermal conductivity of siliceous aggregates increases the heat conduction favouring the increase in concrete temperature and hence, the escape of free water out of concrete, as can be seen in Figure 3-right.

**Figure 3**  Evolution of mass loss during drying left) in time and right) with temperature in the core of the concrete and thermal conductivity before/after drying.

![Figure 3](image)

Regarding thermal gradients, Figure 4-left represents the evolution of temperature in the centre of the samples for the first hours of drying for both concrete compositions. Figure 4-right shows the evolution of thermal gradients between the geometrical centre of the sample and the external surface, which is at the same temperature than the furnace. As the thermal conductivity of the concrete with siliceous aggregates is higher than concrete with the ternary mix (see Figure 6), the increase of internal temperature in the specimen from the first group was transferred at a higher heating rate, while the second group had higher thermal inertia. This difference in the internal evolution of the temperatures is produced because conduction is the governing heat transport mechanism, based on Eq. (1).

\[
q_x' = -k \frac{dT}{dx}
\]

(1)

Where, \(q_x'\) is the heat flux per length unit [W/m], \(k\) is the thermal conductivity [W/mK], \(dT/dx\) is the thermal gradient between the distance, \(x\) [K].

As thermal conductivity is directly proportional to the heat flux, thermal gradients between the surface and the core were lower in siliceous dosage for the same heat flux. For that reason, higher values of thermal conductivity improve heat transfer to the centre of specimen, reducing the spalling risk due to thermal gradients up to 100°C. This could be
appreciated in Figure 4-right where the siliceous mix had lower thermal gradients for all the time of heat exposure at 105°C. After 1.5 hours of starting the test, thermal gradient (ΔT) in the siliceous mix was 20°C, whereas the ternary mix achieved double ΔT. In spite of having stable aggregates at high temperature, the risk of spalling could be higher with low thermal conductivity aggregates. However, siliceous aggregates make the concrete thermal response more easily to adapt to the temperature for the drying phase, but the amount of vapour generated (mass loss) is higher for the same heat flux, figure 3-left, increasing in this way the risk of spalling.

Figure 4 Evolution of left) temperature and right) thermal gradients during drying

2) Dehydration of cement paste stage (100-300°C)

During this stage, two mechanisms work simultaneously: the chemical changes of cement paste with loss of bound water and volume changes in aggregates and expansion followed by shrinkage of cement paste. The microstructural changes in the cement paste are due to dehydration of CAH₁₀ at 120°C and AH₃ produced between 210-300°C [13]. Figure 5-left shows the critical temperature of change with mass loss between 200 and 300°C. This is in accordance with the results of concrete mass loss (Figure 5-right), where the highest mass loss was reached when heating up to 300°C, achieving around 4% between 100-300°C. Z. Xing et al. [14] studied the evolution of thermal conductivity, heat capacity and thermal diffusivity of OPC concrete with siliceous aggregates and also found the highest drop on thermal conductivity at 150°C.
During this stage, the risk of spalling is higher owing to high thermal gradients between the external surface and the core, that affect all these processes in different level inside the concrete. The higher thermal conductivity in siliceous concrete respect to ternary mix make easier the flux heat transport and the dehydration processes in cements paste to occur liberating more vapour increasing the risk of spalling due to pore pressures. With the purpose to reduce the risk of spalling, the heating rate was established at 1°C/min. Moreover, to reduce the thermal gradients and vapour released and so the spalling risk, every 100°C the temperature was maintained constant. These temperature plateaus were useful for making the temperature homogeneous in the whole sample during heating up to another temperature and to have stable conditions for measuring the thermal conductivity. Thermal conductivity between 105°C and 300°C remain almost constant but after 300°C thermal conductivity suffered another drop more clearly appreciated in the siliceous mix (see Figure 6).

3) Thermal fatigue during heating 300 to 600°C

Figure 6 shows the evolution of thermal conductivity for both siliceous and ternary mixes during the thermal cycle for the first heating up to 600°C, followed by a cooling to 300°C and a second heating up to 600°C. Having the same volume of cement paste, the differences found between the concretes are related to the type of aggregates and their response when they are exposed to high temperatures after dehydration of cement paste. The higher thermal conductivity the siliceous concrete makes faster the increase of temperature inside the concrete.
Figure 6  Evolution of thermal conductivity for the first heating (1H), first cooling (1C) and second heating (2H) for both concrete.

Ternary mix had a more stable response when it is heated up to 600°C because low thermal conductivity aggregates experienced slower temperature increase and also lower volumetric expansion. Siliceous aggregates are more thermally conductive, but they also originate more volumetric expansion and probably more prone to crack generation. Cracks affect negatively heat transfer because of the creation of air gaps and once they appear, heat transfer is no longer produced by conduction exclusively, and convection mechanisms also participate. Thus, at high temperatures (and after cracking), for the same heat flux, conduction and thermal conductivity decrease significantly in the siliceous mix despite having more thermal conductive aggregates. Moreover, not only is heat transfer affected by thermal cracks, but also by the changes in crystallinity produced in the material components [15]. During the fatigue stage (cooling down to 300°C and second heating up to 600°C) the thermal conductivity remained almost constant.

These results are consistent with the loss of thermal conductivity with temperature also reported by different authors [16-17], as produced by the loss of water (evaporable water and chemically bounded) and thermal cracking.

Analysing the evolution of the thermal parameter, the results led to the conclusion that the most significant and critical stages are the drying and dehydration, especially when using siliceous aggregates.

For the thermal storage application, a balance between more thermal conductive aggregates or stable aggregates at high temperature must be achieved. While the first ones (siliceous in the case studied) improved heat transfer during the drying stage because of having higher thermal conductivity, when are exposed to temperatures up to 600°C its response is negatively affected due to their higher thermal expansion. The dehydration of cement paste and thermal conductivity of the aggregates affects heat flux transport and the rate of vapour generation and also the risk spalling process to occur.

CONCLUSIONS

The work carried out from thermal conductivity measurements at high temperature has led to the following conclusions:
The thermal conductivity decreased with temperature because of free water loss. The dehydration of cement paste produces the critical loss of thermal conductivity and its value remained constant at higher temperatures. The siliceous mix achieved higher values of thermal conductivity at room temperature due. However, it also registered the highest drop in thermal. The ternary mix with lower thermal conductivity aggregates, with basalt, CAT and São Domingos Slag, is more thermally stable at high temperatures than the siliceous mix as measured by the almost constant result in thermal conductivity. Higher thermal inertia is showed during the heating stage.

ACKNOWLEDGEMENTS

The research was financially supported by the H2020 project NewSol, New StOrage Latent and sensible concept for high efficient CSP Plants (Project ID: 720985).

REFERENCES