Compatibility Tests Between High Temperature Concrete and Molten Salts to be Used for a Thermal Energy Storage

F. Felizardo[1, a)], L. Guerreiro[1], M. Roig-Flores[2], M. C. Alonso[2] and M. Collares-Pereira[1]

[1]*University of Évora, Largo dos Colegiais 2, Évora, 7004-516, Portugal*
[2]*CSIC - Eduardo Torroja Institute for Construction Science, Madrid, 28033, Spain*

[a)]Corresponding author: facf@uevora.pt

Abstract. Solar Energy is an abundant resource and can be stored for use at any time of the day. One of the most efficient methods of storage is the thermal process at high temperature (> 400 ºC) usual for solar concentrators using molten salts stored in two tanks. In order to reduce total storage costs, an alternative solution would be to store in a solid medium using concrete with thermal properties optimized as a storage medium. The present paper focuses on performing a compatibility evaluation, by analyzing at a laboratory scale, small concrete cubes uncoated and concrete cubes covered with protective refractory coatings that were put in contact with molten salts subject to a heating cycle up to 500ºC. In this investigation, thermal cycles between 290 ºC and 500 ºC were tested by placing cubic samples (40x40x40 cm) in a bath with a ternary mixture of molten salts in a furnace to simulate loading and unloading cycles The results show that a good concrete mix (suitable binder, suitable aggregates, admixtures) is critical for good thermal performance and adequate durability.

INTRODUCTION

With the increasing share of renewable energies for the production of electricity, cost-effective, efficient and clean energy storage solution need to be further developed. Among various solar energy technologies, concentrated solar power (CSP) is attractive considering the high efficiency, operating cost and scale-up potential [1]. Within the strong efforts that are made to decrease the cost of CSP produced electricity, new solutions are proposed to replace the conventional molten salt two-tank system [2].

With cost reduction in mind, a new storage system with low-cost materials like concrete could be suitable in case it proves to be compatible and durable with the energy storage fluid used, in this case molten salts of K, Na and Ca. Factors such as the mechanical strength of the mixture when submerged and subject to temperature cycles, as well as its stability when placed in direct contact with molten salts under high temperatures cycles at high temperatures have been analysed.

According to existing literature, Alonso et al. [3] conducted tests to evaluate a new cement-based blend that could conduct and store heat at high temperatures with thermal cycling in the range of 290 to 550 ° C, making it ideal for a thermal storage system in solar thermal power plants. The authors proposed to develop and analyze samples of calcium aluminate cement (CAC), containing 40% alumina, mixed with blast furnace slag (BFS) to control any risk of early conversion and to improve thermal performance at high temperatures. Long-term performance was however not investigated.

Investigation about the contact between concrete mixtures and molten salts was developed by Emerson et al. [4]. The work was based on the evaluation of selected mixtures with different binder and aggregate types (sandstone, limestone and syenite) for which they performed a series of tests at high temperature. The number of mixtures investigated was 26. In a first test, these mixtures were pooled and tested in a molten salt bath at 585 °C for 500 hours. The samples were also exposed to 30 thermal cycles between 300 °C and 585 °C when submerged in molten salt. A separate batch was subjected to drying cycles with forced air circulation for 30 times between 300 °C and 600 °C.

SolarPACES 2018
AIP Conf. Proc. 2126, 200019-1–200019-8; https://doi.org/10.1063/1.5117734
Published by AIP Publishing. 978-0-7354-1866-0/$30.00

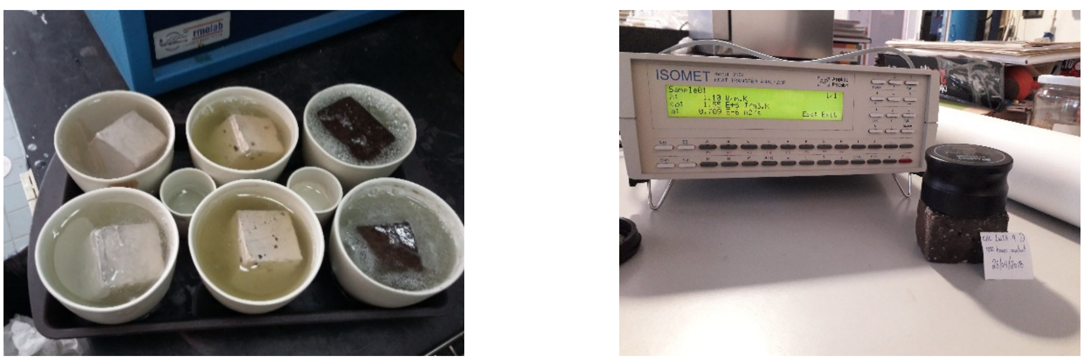
MATERIALS AND METHOD

The molten salt under investigation is a ternary mixture of K-Na-Ca Nitrates recently developed but not used yet in commercial applications. It has a low melting point (131°C). It has a volumetric heat capacity of 1.8 $MJ \cdot m^{-3} \cdot K^{-1}$, a thermal conductivity of 0.5 $W \cdot m^{-1} \cdot K^{-1}$ and a density 2.21 $kg.m^{-3}$ at 200°C. At 500°C has a volumetric heat capacity of 1.4 $MJ \cdot m^{-3} \cdot K^{-1}$, a thermal conductivity of 0.44 $W \cdot m^{-1} \cdot K^{-1}$ and a density of 1.89 $kg \cdot m^{-3}$. The concrete under study is a concrete with selected aggregates (size < 4mm) divided into two batches as in Table 1. The experimental work consisted in putting in contact molten salts with concrete samples (50×40×40 mm) after 28 days curing. The first batch has 6 aggregate combinations (siliceous, limestone, basalt, calcium aluminate synthetic sand, Sao Domingos slag) and was meant to be a preliminary study of 300 h to select the best aggregate for a deeper investigation. Batch two had 36 samples and the contact period was extended to 1500 h (Table 1). Additionally, two refractory materials were tested as protective layers. Six concrete cubes were placed into a molten salt bath and put in the oven, including two crucibles with only molten salt as references (Figure 1). In the first batch, the thermal conditions consisted of a constant temperature at 290°C and for the second batch thermal cycles changing the temperature between 290 ºC and 500 ºC every work day. The goal was to measure and evaluate changes in the thermal properties of the concrete and to understand if there is degradation of those properties with time.

TABLE 1. Experimental program description.

Batch	Number samples	Contact with molten salts	Protection Layer
1	18 with 6 aggregate combinations	300 h	• Uncoated • Coated with refractory paint • Coated with alumina mortar
2	36 with 1 aggregate combination	1500 h	• Uncoated • Coated with refractory paint • Coated with alumina mortar

The thermal properties of concrete were measured after 28 days curing, and later after 1000h and 1500h in contact with molten salts, using a portable measurement equipment ISOMET 2104 equipped with a surface probe, with a measured uncertain of 10% (Fig. 1-b).



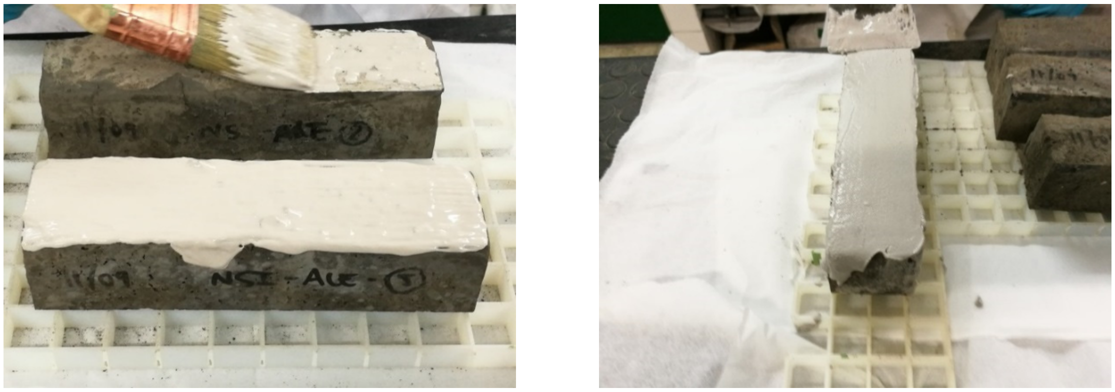
a) b)

FIGURE 1. a) Bath of concrete samples and molten salts references in crucibles. b) Thermal measurement after 1000 hours of contact with molten salts.

The use of protective layers for concrete mixes may represent an important step in this research in order to improve the stability of materials at high temperature and in direct contact with molten salts.

Materials that exhibit resistance to high temperature and extreme environments have already been developed and are available on the market. However, coatings that resist a heat-treated process of exposure to high temperature and in contact with molten salts are not yet known at present, for this reason, the study performed was a challenge. Some properties under consideration for the protective layers are the ability to withstand high temperature, resistance to contact with molten salts, resistance to thermal cycling and compatibility with a cementitious matrix.

After a pre-selection of possible commercial products, two products for testing were selected. One zircon based paint and one high alumina content refractory mortar. The selected products have characteristics such as a bulk density of 1800 kg/m^3 for the zircon paint and 2500 kg/m^3 for the vitset mortar. Some characteristics of these products are, for example, the grain size (in the case of zircon paint it is less than 0.1 mm, while in the vitset it is less than 0.5 mm). The method of application of the selected coatings, is displayed in Figure 2, for the case of zircon paint (Fig. 2-a) the application is done using a brush, in the case of vitset mortar, it is done with a spatula.



a) b)

FIGURE 2. a) Application of the paint with a brush. b) Application of the mortar with a spatula.

After application and drying, the zircon paint presented small cracks, while the refractory mortar had visually no defects. Therefore, the vitset mortar is the preferred material for the detailed interaction tests, additionally the paint shows a smoother surface due to its much easier application for the size of the samples.

The thickness of the samples was measured (Figure 3) before and after applying the protective layer (coatings), the measurement of the thickness was made three times (1,2 and 3) in the same face (faces A, B and C) (Fig. 3-b).

a) b)

FIGURE 3. a) Measure of the thickness of the cubes before the application of the coating. b) Three directions of the measurements performed on the prisms.

Table 2, presents the individual thicknesses, before and after paint and mortar application respectively showing an average thickness of 0.32 mm for the zircon paint and 1.85 mm for the vitset mortar.

TABLE 2. Measure of the thickness before and after applying the coatings.

BEFORE COATING

SAMPLE	Cube	Dimension A (mm) h_{A1}	h_{A2}	h_{A3}	Dimension B (mm) h_{B1}	h_{B2}	h_{B3}	Dimension C (mm) h_{C1}	h_{C2}	h_{C3}
Uncoated	1	40.52	40.43	40.31	40.50	40.27	40.44	51.05	51.10	51.30
	7	39.85	40.07	40.81	40.22	40.14	40.13	51.08	51.19	51.15
Zircon Paint	17	41.18	40.98	40.89	40.54	40.22	40.28	50.87	51.00	51.25
	23	41.87	41.87	42.39	40.22	40.33	40.29	51.43	51.21	51.33
Vitset Mortar	35	40.36	40.11	40.01	40.95	41.04	41.13	51.07	51.19	51.35
	36	40.12	40.13	40.13	41.42	41.43	41.44	50.83	51.44	51.34

AFTER COATING

SAMPLE	Cube	Dimension A (mm) h_{A1}	h_{A2}	h_{A3}	Dimension B (mm) h_{B1}	h_{B2}	h_{B3}	Dimension C (mm) h_{C1}	h_{C2}	h_{C3}
Uncoated	1	=	=	=	=	=	=	=	=	=
	7	=	=	=	=	=	=	=	=	=
Zircon Paint	17	42.61	42.12	42.25	40.88	41.30	40.89	51.78	51.95	51.83
	23	42.48	42.19	42.32	40.74	40.76	40.62	51.46	51.43	51.98
Vitset Mortar	35	43.69	43.57	43.47	42.57	42.98	52.85	53.48	54.65	54.64
	36	42.58	42.96	42.84	45.16	44.07	53.50	53.69	52.82	52.82

RESULTS AND DISCUSSION

The parameters in evaluation were the surface degradation of the uncoated and coated samples, changes in the thermal properties, and pore size distribution of the concrete mix at different depths, to analyze the penetration of the molten salt.

After a contact of 300 hours at a constant temperature of 290 ºC no visible cracks were detected. Nevertheless, the molten salt penetration was confirmed due to the mass of the sample increased in all cases between 9 and 18% of the initial mass before the contact. After a contact of 1500 hours and 32 temperature cycles performed, uncoated concrete samples had no visible cracks to the naked eye, while those coated with the refractory paint showed degradation of the paint in some areas and those coated with the alumina mortar were intact.

Figure 4 to Figure 6 present images taken in two surfaces of the three areas (A, B and C) measured, showing a visual registration of the degradation. Figure 4 shows a sample cube without coating that suffered thermal cycles of 290 to 500°C during 1500h in contact with a ternary mixture. Its visual appearance of the surface A and C shows only slight degradation of the surface, but no visible cracks.

a) b) c)

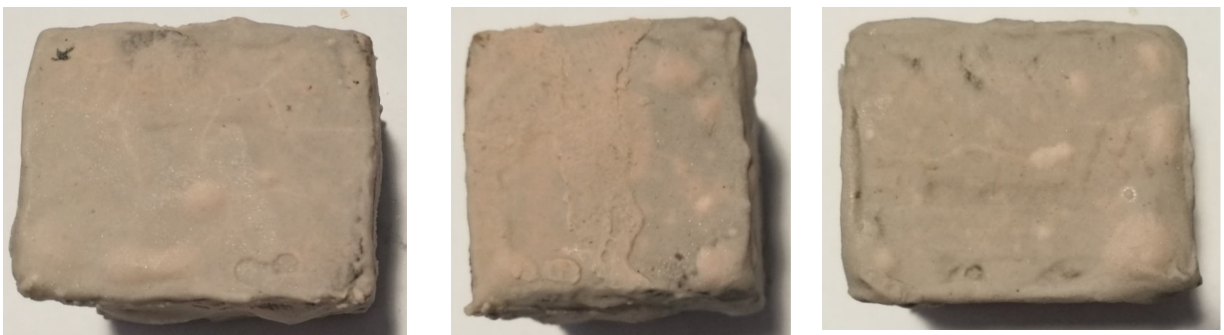
FIGURE 4. Visual appearance of an uncoated cube after 1500 hours in contact with the molten salts in surface A, B and C.

The surface degradation of coated samples is important to evaluate the protection layer. The cube sample 23 coating with the zircon paint has been analyzed after the thermal cycles for 1500h in contact with a ternary mixture of molten salt. Its visual appearance shows clear degradation of the coating (Figure 5), especially in surface A and C.

The same analysis was performed for samples coated with vitset mortar, after suffering the abovementioned cycling conditions. The results (Figure 6) show good integrity of the mortar but with a slight start of cracking in some faces.

a) b) c)

FIGURE 5. Visual appearance of the cube sample 23 coated with zircon paint after 1500 hours in contact with the molten salts in surface A, B and C.



a) b) c)

FIGURE 6. Visual appearance of the cube sample 35 coated with vitset mortar after 1500 hours in contact with the molten salts in surface A, B and C.

The surface degradation of the samples with zircon paint were calculated and are as high as 30% of the exposed surface. The process followed is summarized in Figure 7. The degraded area was selected as the area with a specific color range (Adobe Photoshop CS6 feature), using as reference the concrete color. This area was colored in red for clarity, and this area was evaluated (in pixels) and compared with the number of pixels in the whole section.

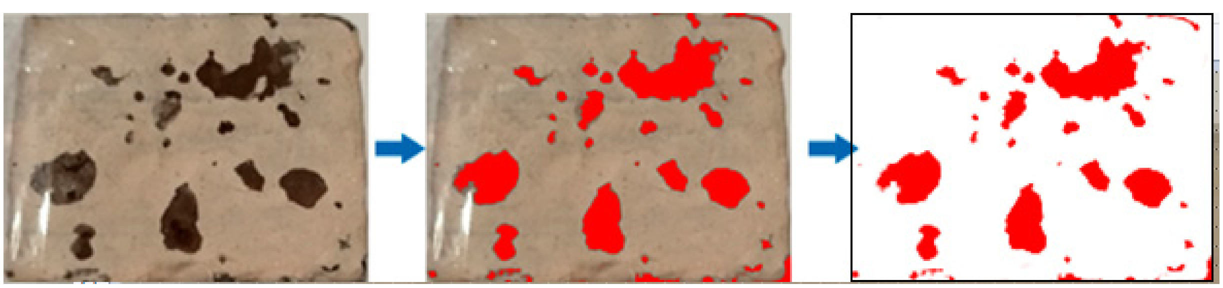


FIGURE 7. Image processing for the evaluation of the percentage of area degraded from surface "A" exposed to molten salt.

The values of the amount of surface where the coating disappeared calculated with this method are:

- Zircon Paint A: 17.2% - Surface area 20 cm^2
- Zircon Paint B: 1.7% - Surface area 16 cm^2
- Zircon Paint C: 28.4% - Surface area 20 cm^2
- Vitset A, B, C, no visual degradation (0%)

Thermo-physical measurements reveal a slight increase of thermal conductivity (λ) after 300 hours contact at constant temperature of 290 °C, possibly related to an internal deposition of the salts, and a very slight decrease after the 1500 hours contact with thermal cycles (Table 3). Specific heat values obtained before and after the contact are maintained fairly constant around $1.5 \cdot 10^6$ $Jm^{-3}K^{-1}$.

TABLE 3. Thermal conductivity measured before and after temperature cycles.

Batch	Thermal conductivity range before contact	Thermal conductivity range 300 hours	Thermal conductivity range 1500 hours
1	$\lambda \in [0.88 - 1.98]$ $W \cdot m^{-1} \cdot K^{-1}$	$\lambda \in [0.89 - 2.14]$ $W \cdot m^{-1} \cdot K^{-1}$	-
2	$\lambda \in [1.08 - 1.53]$ $W \cdot m^{-1} \cdot K^{-1}$	-	$\lambda \in [\ 0.88 - 1.15]$ $W \cdot m^{-1} \cdot K^{-1}$

In order to evaluate this penetration capacity, one sample that was never in contact with molten salts neither thermal cycles (7) was used as a reference. From the samples that suffered thermal cycles and contact with the molten salts, two positions were compared, one in the external part of the sample (where higher penetration was expected) and another in the interior of the sample, at a distance of approximately 2 cm from the surface. Using this method, the presence of pores will indicate the effectiveness of the coating.

The results obtained when using zircon paint and vitset mortar are displayed in Figure 9 and Figure 10, respectively, showing that for the external points, after the contact all the pores were completely filled by the molten salt, despite the presence of the coating. However, in the interior of the sample, vitset mortar achieved certain protection of the concrete, which can be deduced by the presence of pores of the size over 25 µm. The pore size distribution indicates that finer pores will be completely filled.

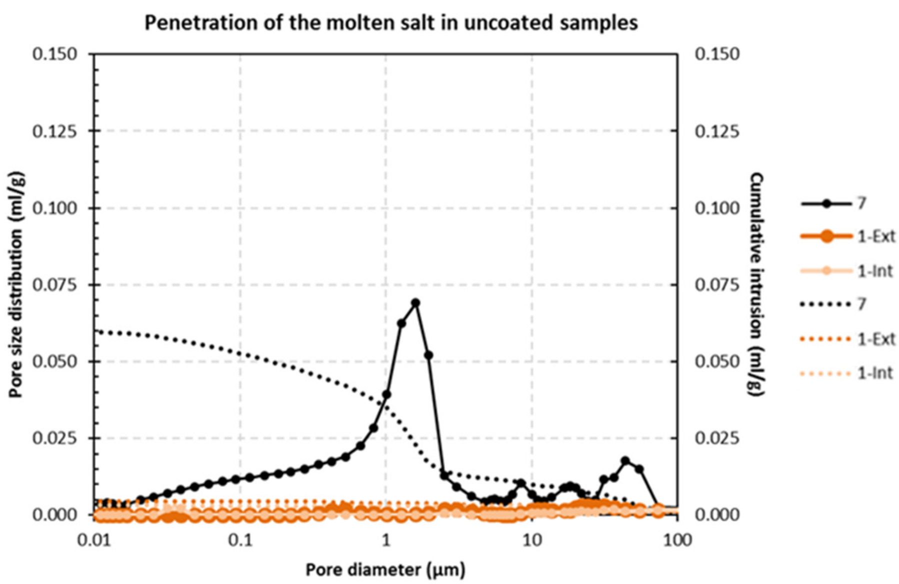


FIGURE 8. Pore size distribution for a reference concrete sample (7) and two zones of a sample after suffering the contact with ternary mixture after 1500 hours. (note: *solid lines show the pore size distribution curves, principal axis, and dashed lines cumulative intrusion curve, secondary axis*)

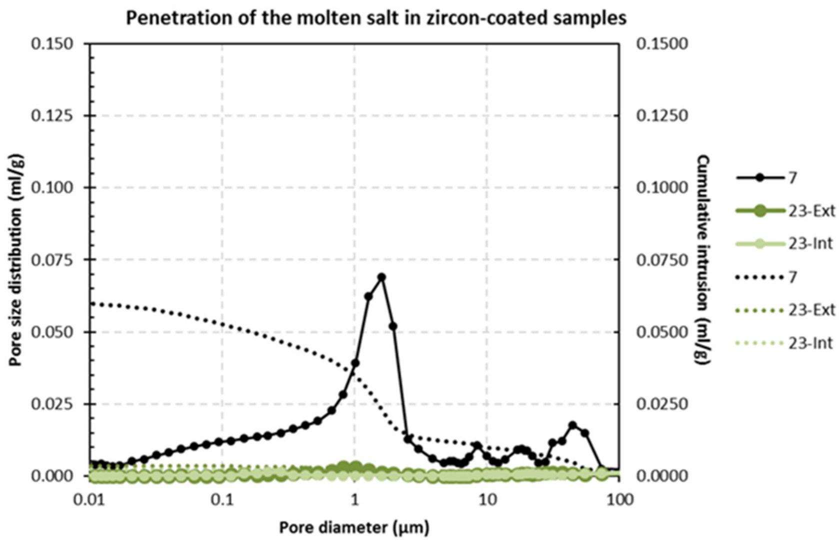


FIGURE 9. Pore size distribution for a reference concrete sample (7) and two zones of a sample coated with zircon paint after interacting with Ternary mixture under thermal cycles for 1500 hours. (note: solid lines show the pore size distribution curves, principal axis, and dashed lines cumulative intrusion curve, secondary axis)

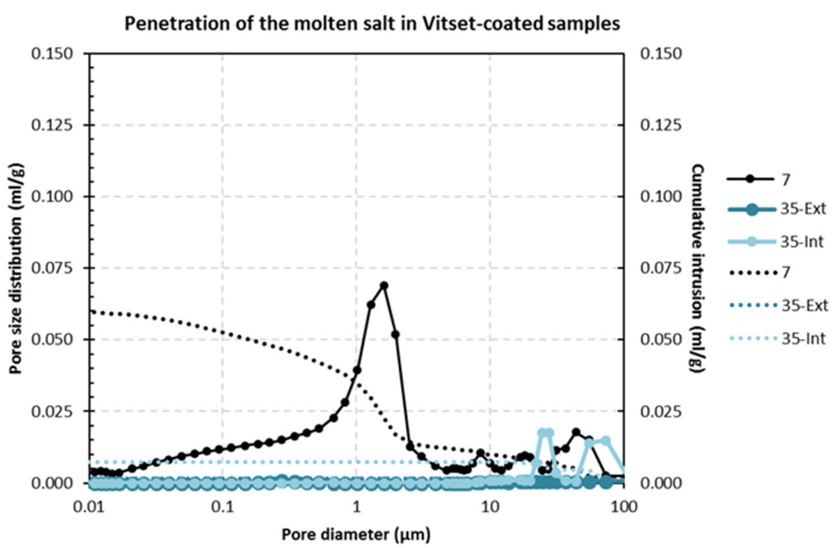


FIGURE 10. Pore size distribution for a reference concrete sample (7) and two zones of a sample coated with vitset mortar after interacting with Ternary mixture under thermal cycles for 1500 hours. (note: solid lines show the pore size distribution curves, principal axis, and dashed lines cumulative intrusion curve, secondary axis)

Table 4 shows the values of total pore area and porosity values obtained for the reference sample, showing the characteristic porosity of this concrete mix and the values obtained after the interaction with the molten salt, either for uncoated or coated samples. The porosity values obtained show that the external points have very low porosity after the interaction with the salt, demonstrating its penetration. However, when analyzing points at 2 cm of the surface ("Internal points"), the results indicate that the vitset mortar is able to reduce and delay the penetration of the molten salt to the interior of the concrete.

TABLE 4. Total pore area and porosity values obtained for the different samples after the interaction with the molten salts for uncoated and coated samples at external and internal points.

Sample type	Total Pore Area (m^2/g)	Porosity (%)		
Reference	1.416	14.9		
	External point		Internal point	
	Total Pore Area (m^2/g)	Porosity (%)	Total Pore Area (m^2/g)	Porosity (%)
Uncoated	0.008	1.3	0.043	1.0
Zircon coated	0.016	1.0	0.011	0.7
Vitset coated	0.003	0.5	0.001	2.1

Results presented indicate that the alumina mortar showed better resistance (2.1% of porosity) than the zircon paint, being able to delay the penetration of the molten salts to the interior of concrete. However, in accordance to the analysis performed in [3], since the salt was able to penetrate inside the concrete to some extent, to guarantee concrete durability for a long-term direct contact, it will be necessary to protect it with a different coating or another protection method, such as a steel liner. These are preliminary results of on-going work within an extensive Project on Materials for Energy Storage [5] and thus further results are expected in the framework of the project.

CONCLUSIONS

These are preliminary results of on-going work within the NewSol Project on Materials for Energy Storage. From the results, it is possible to conclude that the concrete samples analyzed have a slight change (less than 10%) in their thermal properties after being in contact for 1500 h with molten salts. Up to now, concrete shows a good resistance to thermal cycles and is stable when in contact with molten-salts. The thermal measurements result show that the decrease in thermal conductivity produced in those samples coated with the refractory mortar are higher than in the uncoated and coated samples with the paint. Heat capacity shows very little changes after the interaction tests, meaning there are no significant changes on the thermal performance of the samples. Along to this investigation made to the samples with and without coating a first conclusion is that to guarantee a long-term durability of the concrete in direct contact with the salts, it needs to be protected with a coating or another protection method. The sample without coating after the thermal cycles only shows a slight degradation of the surface, however with time it is expected that crack formation will increase. The coated sample with alumina mortar showed better resistance than the zircon paint, which was demonstrated by the absence of surface degradation of the vitset mortar, and the reduction of the penetration of molten salts in the interior of the concrete sample as seen in the increase of porosity values for depths of around 2 centimeters. Even though these protective layers would improve the long-term behavior and durability of the system, in both cases the molten salt is able to penetrate inside the concrete matrix. For this reason, further research is needed to find a completely effective protective layer. For the time being, an alternative (steel lining) is a possible option.

ACKNOWLEDGEMENTS

Research work supported by the European Commission, program H2020, Project Newsol (Project ID: 720985)[5].

REFERENCES

1. H. L. Zhang, J. Baeyens, J. Degrève and G. Cacères, "Concentrated solar power plants: Review and design methodology," *Renewable and Sustainable Energy Reviews,* vol. 22, pp. 466-481, 2013.
2. G. Angelini, A. Lucchini and G. Manzolini, "Comparison of thermocline molten salt storage performances to commercial two-tank configuration," *Energy Procedia,* vol. 49, pp. 694-704, 2014.
3. M. Alonso, J. V. Agullob, L. Guerreiro, V. F. Laguna, M. Sanchez and M. C. Pereira, "Calcium aluminate based cement for concrete to be used as thermal energy storage in solar thermal electricity plants," *Cement and Concrete Research,* vol. 82, pp. 74-86, 2016.
4. J. Emerson, H. Micah and S. Panner, "Concrete as a thermal energy storage medium for thermocline solar energy storage systems," *Solar Energy,* vol. 96, pp. 194-204, 2013.
5. Website, Project Newsol, "www.newsol.uevora.pt," [Online]. [Accessed August 2018].