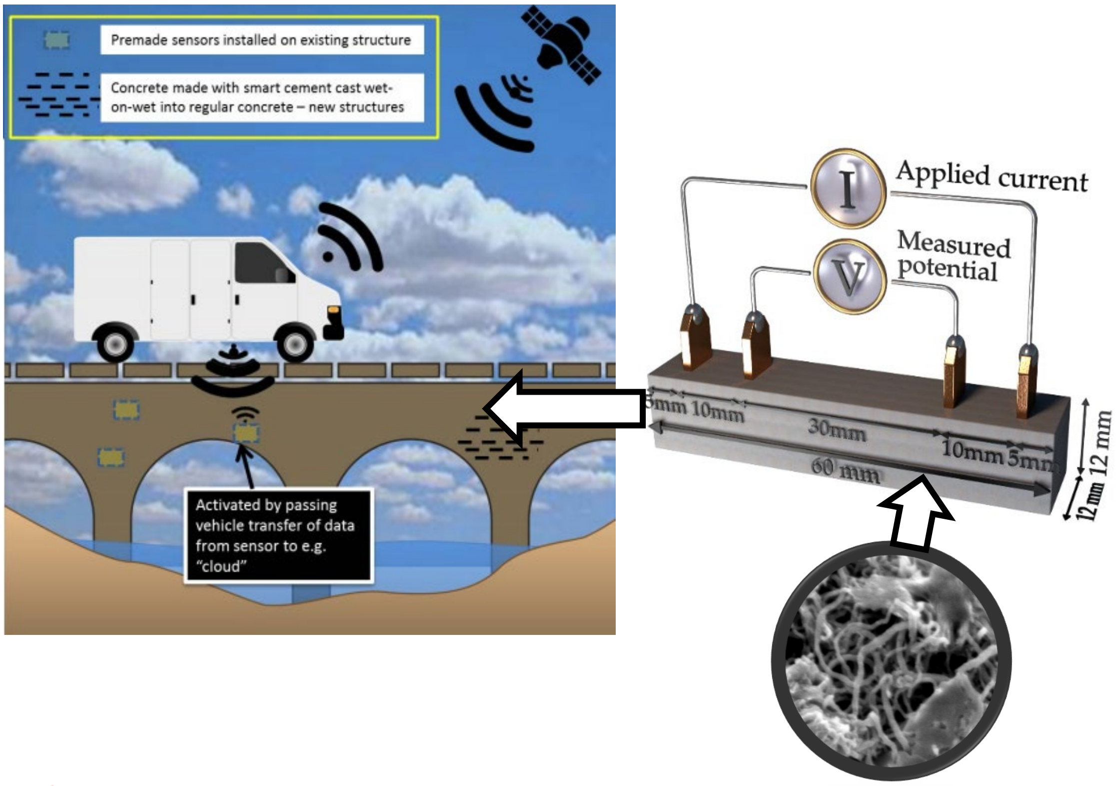
“SmartCem” research project –

Final project report for Vinnova

2016-03285 Smart cement för nya övervakningssystem



Med stöd från:

Contents

1 Project summary

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There is a need for a new generation of efficient and reliable method for monitoring of concrete structures. Present solutions are mostly based on metallic sensors “somehow connected” with concrete surface, which result in their short lifetime and questionable reliability. These aspects are especially significant for concrete structures exposed to harsh environmental conditions; e.g. bridges or marine structures. The ideal solution is to develop a conductive concrete with self-monitoring capability.

The SmartCem project developed a novel modified cementitious binder, which after solidifying has high electrical conductivity and strong piezoelectric properties. These properties enabled to transform stresses and strains into electricity response which were used to develop a prototype of a new monitoring system for monitoring strains, temperature, crack formation and moisture.

The project was led by Lulea University of Technology in cooperation with various industrial partners and end users through reference and steering groups. The project was co-financed by Vinnova, Trafikverket and LTU.

2 Purpose and objectives

Concrete is a well-established and not only the most used building material in the world, but also well-characterized. However, many old and new-build structures suffer from premature failures due to extensive deterioration and decreased load-bearing capacity. Consequently, structural monitoring systems are essential to ensure safe usage of concrete structures within and beyond the designed life. Traditional monitoring systems are based on metallic sensors installed in crucial locations throughout the structure. Unfortunately, most have a relatively low reliability and very short life span when exposed to often very harsh environments. The ideal solution is to develop a smart concrete having itself self-sensing capability. A number of studies show that conductive cementitious matrixes are able to change their electrical resistivity with variations of stresses, strains or, developing microcracking. The project purpose was to develop a novel type of cementitious binder based on Portland cement, which after hydration will produce solid matrix having very high electrical conductivity and some piezoelectric properties. These properties in connection with very good mechanical properties will enable to build in the future smart self-monitoring concrete structures. The project aimed to develop a novel type of sensors suitable for new and existing structures and being fully compatible with the surrounding materials, (the same water-cement ratio, microstructure, strength, shrinkage, creep etc.). The full materials compatibility between the self-monitoring concrete and the surrounding normal concrete will enable extremely reliable and accurate measurements. Since the self-monitoring concrete will be an integral part of the structure, its sensing/detecting performance would not deteriorate with time but rather will follow the actual state of the surrounding material enabling early identification of overloading or internal damage. Piezoelectric property could also enable energy harvesting and creation of fully autonomous systems

The following main objectives of the project were formulated as:

1. Synthesis of smart cement enabling solidification into conductive matrixes
2. Development of monitoring system based on application of the developed smart cement
3. Determining effects of synthesis parameters on electrical properties
4. Determination of the dependency between various loading conditions (deterioration mechanism) and electrical and piezoelectric response of the solidified matrixes
5. Full scale pilot application and verification of laboratory test results

3 Implementation of the project and obtained results

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The following section will describe every work package of the project with short information what was planned and what was actually achieved during the implementation of the project. The project was divided into 5 work packages as shown in Figure 1. The planned time schedule is shown in Table 1.

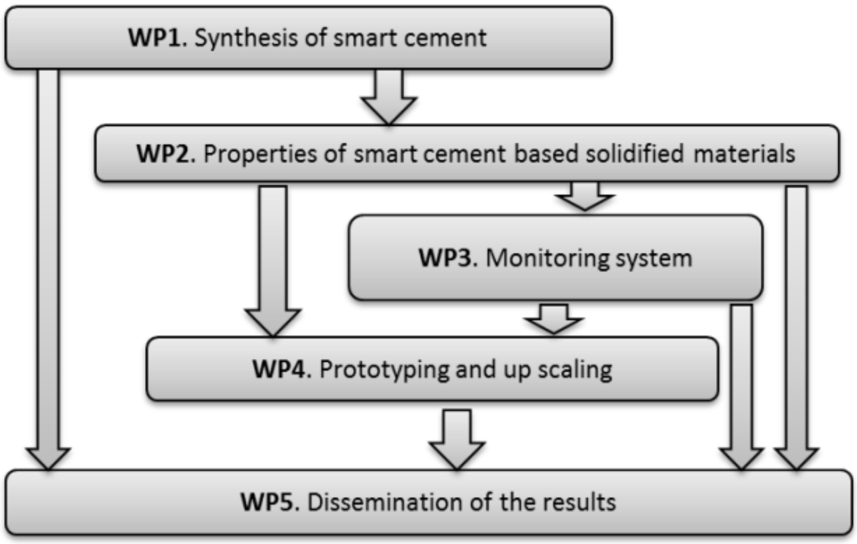

Figure 1. Work packages contained within the SmartCem project as presented in the original project application

Table 1. Time schedule as planned

Work package	Wp description	1-st year	2-nd year	3-rd year
WP1	*Synthesis of smart cement*			
WP2	*Properties of smart cement - nased solidified materials*			
WP3	*Monitoring system*			
WP4	*Prototyping and upscaling*			
WP5	*Dessemination of the results*			
	Milestones		M1 M2	M3 M4
	Dissemination of results			
	scientific papers	1	2	3
	Reference group meetings	1 2	3	4 5
	Workshops		1	2

3.1 WP1 – Synthesis of smart cement

The main scientific objective of this part of the project was to optimize the production method of the nanomodified smart cement, which later was used to develop smart concrete and related nove sensors for monitoring of concrete structures. The used technology was based on earlier development of the project application and project leader Prof. Andrzej Cwirzen, (Nasibulin *et al.*, 2009)(Cwirzen *et al.*, 2009). In the process, Portland cement was treated in Chemical Vapor Deposition reactor (CVD) to synthesize Carbon Nano Fibers (CNFs) directly in its surfaces, Figure 2.

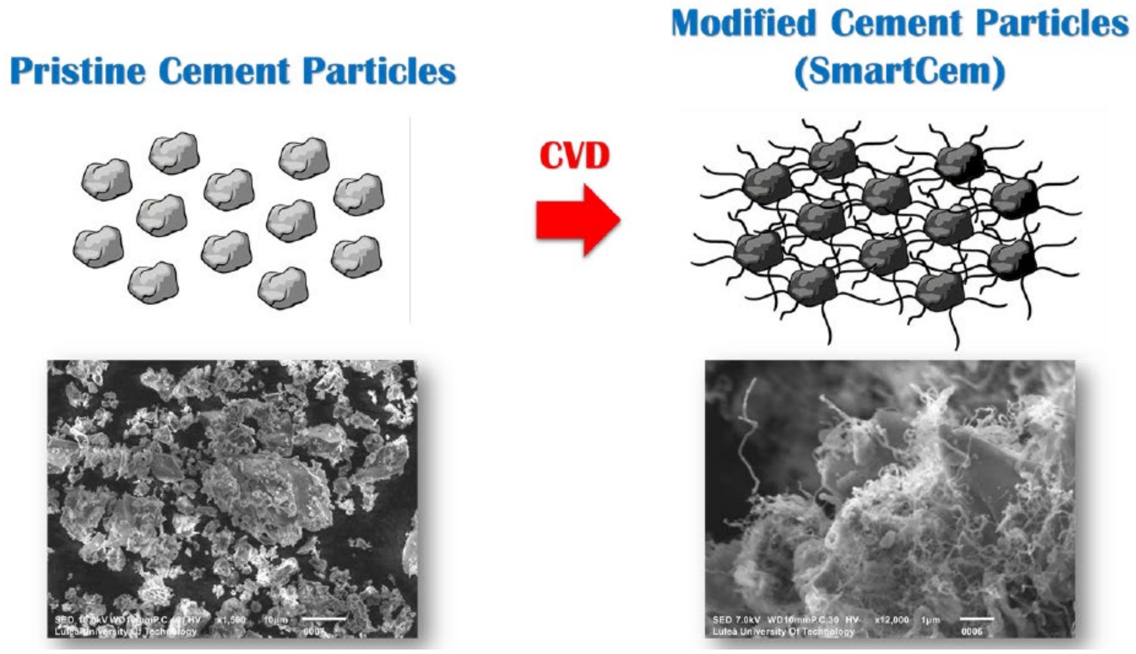

Figure 2. Synthesis of the SmartCem as planned in eth application

The CVD reactor was purchased at the beginning of the project but complicated certification and installation procedure unable to fully utilize its capability within the planned project schedule, Figure 3. Consequently, a cooperation with Silesian University of Technology from Gliwice in Poland was established to synthesize the SmartCem for the project, Figure 4. All test results presented in this final project report were obtained from materials produced by that academic partner.

Figure 3. The CVD reactor which was installed for the project but which did not reach a full operational capacity during the project.

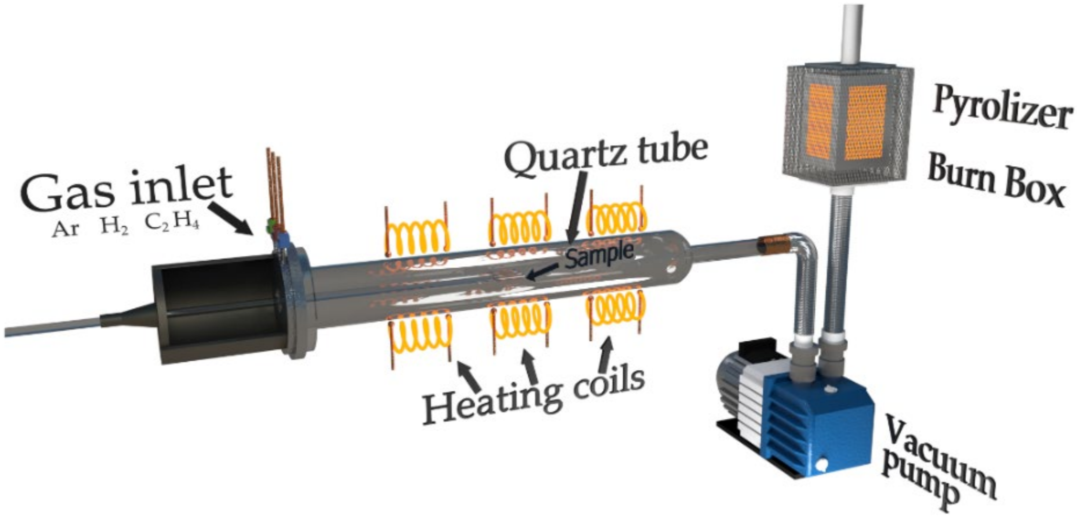

Figure 4. The CVD reactor of a cooperating laboratory from Silesian University of Technology which produced materials used in this project.

Two types of SmartCem were produced using different process parameters. The best results were obtained with parameters listed in Table 1.

Table 2. Synthesis parameters.

Named	Argon (sccm)	Ethylene (sccm)	Hydrogen (sccm)	Synthesis Temperature (°C)	Duration (min)
SmartCem I	600	100	400	750	120
SmartCem II	600	100	500	750	120

The synthesis process used Ethylene (99.999%) was used as the precursor, hydrogen (99.99999%) as the reducer and argon as the transporting media. A total of 10 g of an ordinary Portland cement (CEM I 42.5) was used as a substrate for the synthesis of the carbon phase. The cement powder was placed in four parallel-arranged holders made of quartz having a length of 30 mm and a diameter of 8 mm. The holders were arranged according to the gas flow direction to enhance the reaction efficiency and to remove impurities, Figure 5, Figure 7.

The quartz tube of the CVD reactor had a diameter of 70 mm and a length of 50 cm. The synthesis procedure included degassing at a low pressure (0.001 mbar) at 90 °C for 60 min. Subsequently, the temperature was raised to 110 °C and was kept at that level for 20 min to remove gaseous pollutants and moisture. In the next step, samples were heated to 740 °C in argon atmosphere. After stabilizing of the temperature, the samples were subjected for 15 min to the reduction reaction in an atmosphere of a mixture of hydrogen and argon with flow rate of 500 sccm and 200 sccm, respectively. After the reduction of the catalyst surface, the reactor temperature was stabilized to 750 °C under 1 SLM argon flow, followed by releasing a mixture of reactive gases for the synthesis: 100 sccm ethylene, 400 sccm or 500 sccm of hydrogen (SmartCem I and SmartCem II respectively) and 600 sccm argon for 120 min. Later all samples were purified from amorphous carbon using a mixture of hydrogen and argon with a flow rate of 100 sccm and 1000 sccm, respectively. After the cleaning process, the samples were cooled down to 200 °C at a rate of 12 °C/min under an inert atmosphere, degassed under vacuum and cooled down to 20 °C in an argon atmosphere, (T. Buasiri *et al.*, 2019).

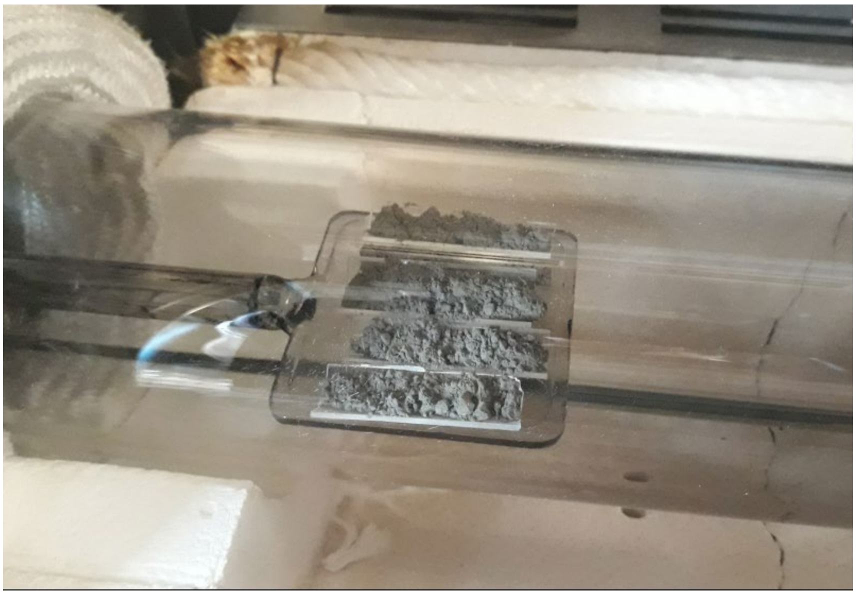

Figure 5. Pristine Portland cement samples placed in the CVD reactor.

Figure 6. Arrangement of the holders for the synthesis of CNF on cement in the CVD reactor. The darker visible powder is cement covered with CNFs.

Cements with synthesized CNFs are shown in Figure 7. The CNFs dimeters varied between 10 and 50 nm and lengths reached up to 20 µm, Figure 8. The CNFs had curly shape.

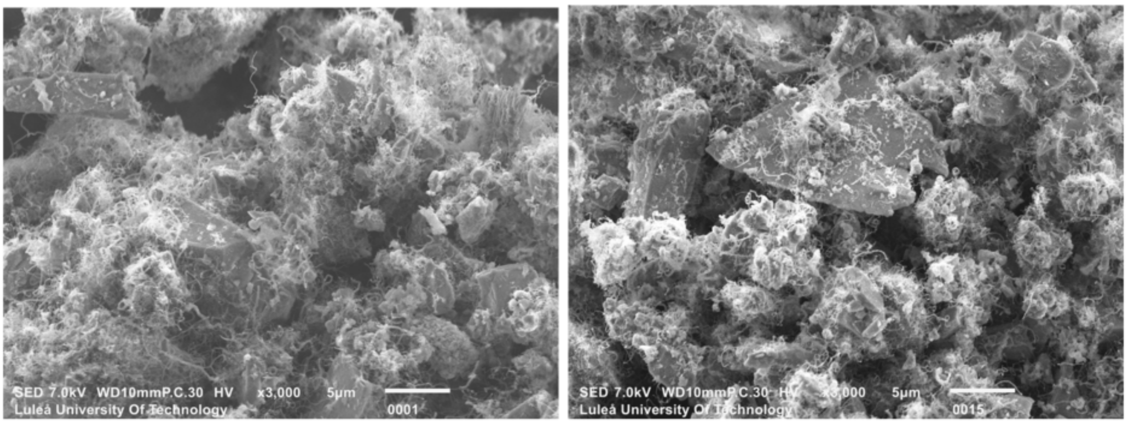

Figure 7. Synthesized SmartCem, SEM images, SmartCemI and SmartCemII, (T. Buasiri et al.*, 2019)*

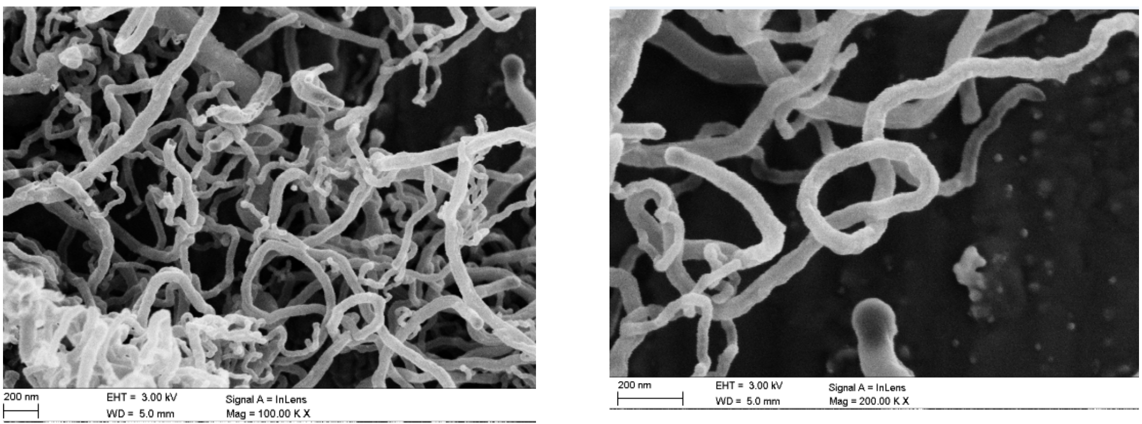

Figure 8. Morphology of the synthesized CNFs

The amount of formed CNFs was estimated based on the results obtained from thermogravimetry, Figure 9. Two peaks formed at around 500 °C and 750 °C were related to the decomposition of CNFs. The estimated quantities were approximately 2.71 wt% and 2.51 wt% for the SmartCem I and SmartCem II, respectively. The SmartCem I was chosen for all further tests and development of sensors and smart self-monitoring concrete due to a slightly higher amount of the formed CNFs.

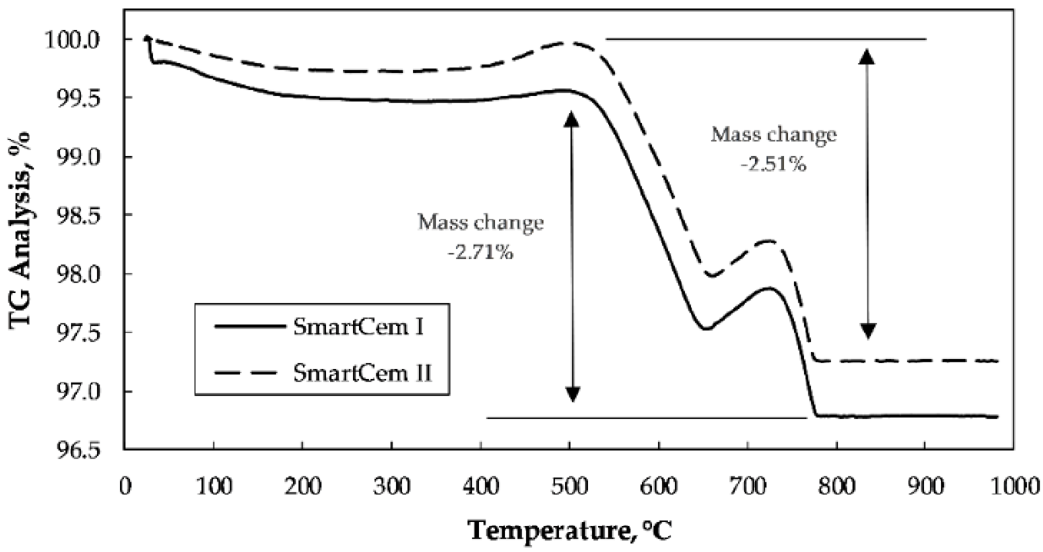

Figure 9. TG Analysis of SmartCem I and SmartCem II, (T. Buasiri et al.*, 2019)*

3.2 WP2 - Properties of smart cement based solidified materials

This work package focused on studying properties of the produced pastes, mortars and concretes, which were incorporating various amounts of the SmartCemI. It included the determination of piezoelectric behavior triggered by property due to various loads. Furthermore, the chemical composition and microstructure of solidified systems were studied by scanning electron microscope (SEM) coupled with the EDX analyser.

Sensors were produced using Portland cement type CEM I 42.5 produced by Cementa-Sweden. The same cement was to synthesize the SmartCem and to produce sensors. Sensors were made as mortars incorporating between 0 and 10 wt% of the SmartCem and fine quartz sand. The workability of the fresh mixes was controlled by the super plasticizing admixture type Glenium produced by Grace Chemicals. All mortar mixes had a water–cement ratio (w/c) of 0.35 and a sand to cement ratio (s/c) of 1. The mix proportions are shown in Table 2. The mortars were mixed using a Bredent vacuum mixer, cast into Teflon molds without the application of any demolding oil and cured at 20 ± 2 °C and a relative humidity of 65 ± 5%.

Table 3. Mix proportions used for test mortars, (Buasiri et al.*, 2019).*

Mix	w/c	s/c	SP (wt% of Cement)	Cement (kg/m³)	SmartCem (wt% of Cement)
Ref	0.35	1.0	0.8	1157	0
S2	0.35	1.0	0.8	1134	2
S4	0.35	1.0	0.8	1111	4
S6	0.35	1.0	0.8	1088	6
S8	0.35	1.0	0.8	1065	8
S10	0.35	1.0	0.8	1042	10

The hydrated SmartCem created matrix have good mechanical and electrical properties, The incorporated CNF created well dispersed and interconnected conductive network, Figure 10.

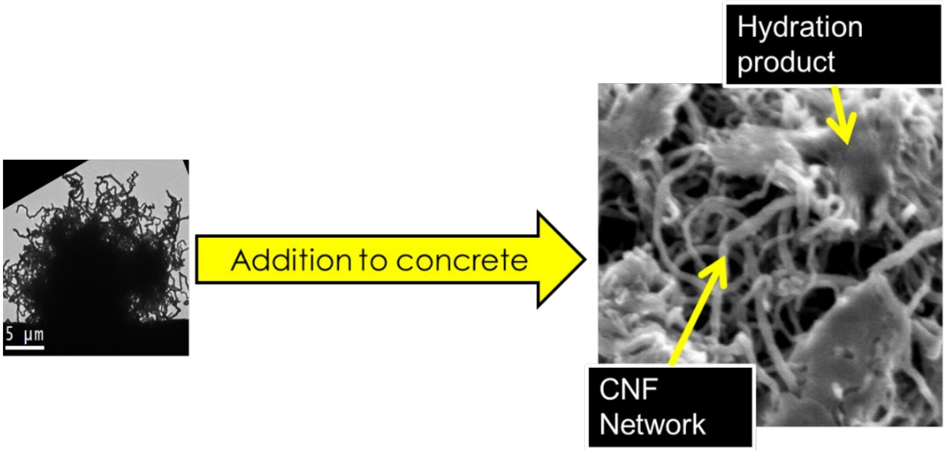

Figure 10. SmartCem is added to pastes, mortars or concrete in various amounts replacing Portland cement. The matrix solidifies through regular hydration reactions.

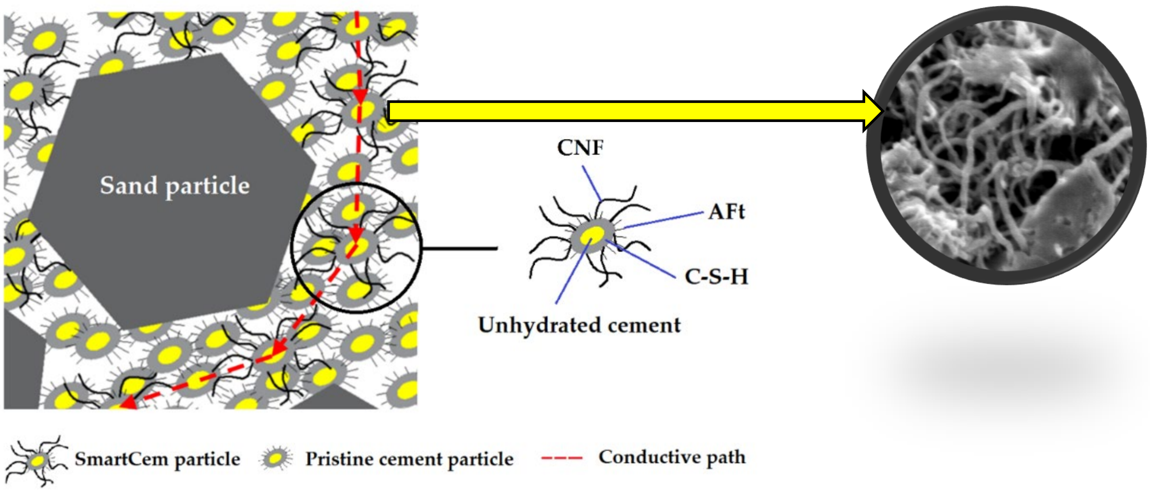

Figure 11. Schematic representation of SmartCem after hydration/solidification and creation of the conductive path though interconnected CNFs (Carbon nanofibers), modified (T. Buasiri *et al.*, 2019).

The electrical properties were determined by means of measuring the electrical resistance. The four-probe method with a digital multimeter type Keysight 34465A was used. Direct current (DC) was applied between the two outer electrodes and the potential was measured between the two inner electrodes, Figure 12. The electrical conductivity was calculated using the Equation (1):

$$\sigma = 1/\rho = L/R \cdot A \qquad (1)$$

where: is electrical resistivity,   is the internal electrode distance,   is the electrode area, =V/I is the measured resistance determined by measuring the voltage drop across the specimen, V is the applied current, I.

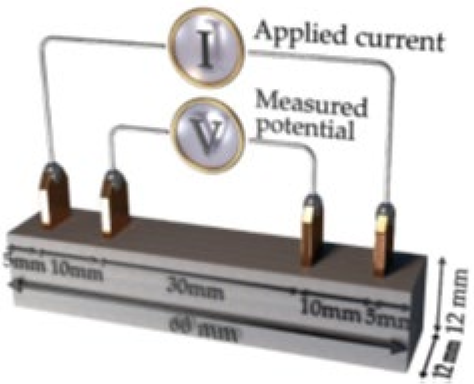

Figure 12. Four-probe method was used to determine electrical resistance of the developed sensors. The same methods was used later while

The measured electrical conductivity decreased with age due to the ongoing hydration process, which decreased the amount of conductive pore water. Replacement of the Portland cement with SmartCem I altered the measured electrical conductivity depending on the age of the sample, Figure 13, Figure 14. The observed percolation threshold values varied between 4 and 10 wt% depending on the sample age. These values corresponded to the presence of 0.271, 0.189, 0.135 and 0.108 wt.% of CNFs s. The CNFs morphology, their distribution within the binder matrix, distance between fibers as well as the microstructure and composition of the isolative binder matrix resulted in good obtained values.

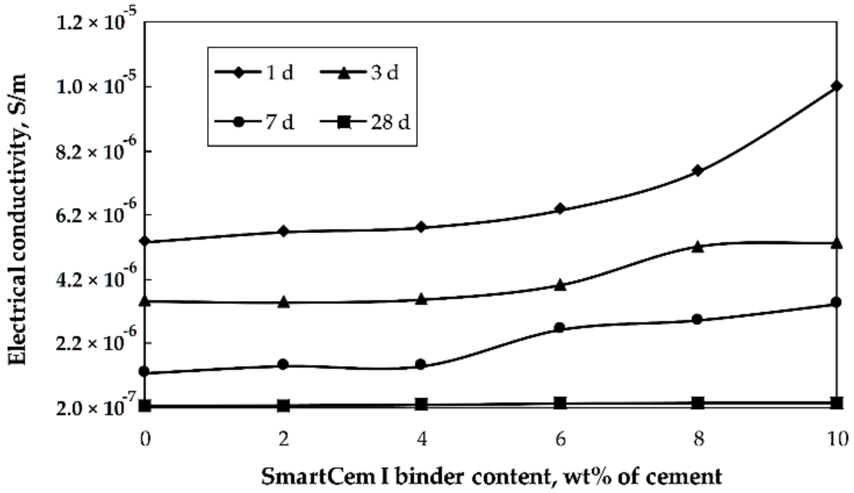

Figure 13. Effects of age and amount of SmartCem I content on the measured electrical conductivity, (T. Buasiri et al.*, 2019).*

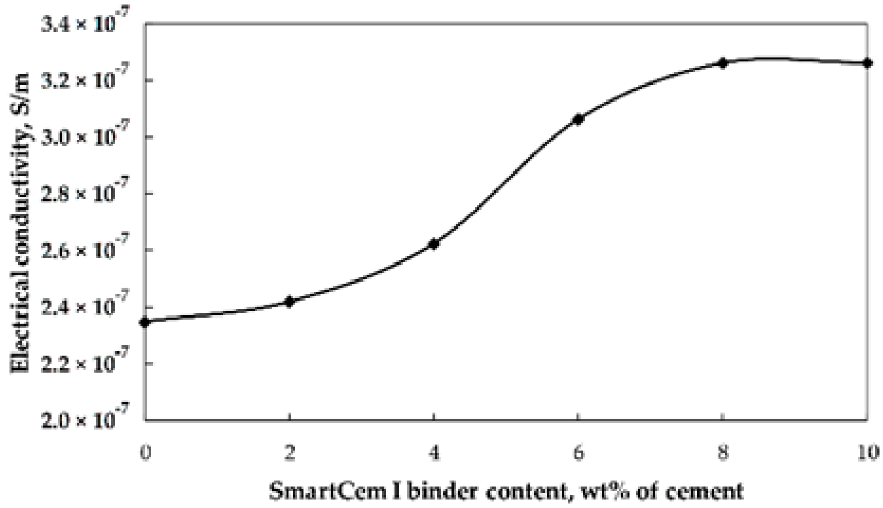

Figure 14. Effects of the SmartCem I content on electrical resistivity of 28 days old samples, (T. Buasiri et al.*, 2019).*

- **Strain and stress**

The used setup for determination of the electrical response of the developed sensor to the applied compression load is shown in Figure 15 and Figure 16. The compression load was applied to the vertically placed beam specimens with the loading rate of 0.05 cm/min. Tests were performed on two sensors containing either 8 or 10 wt.% of the SmartCem. Both showed a strong piezoresistive response within the two stages of nearly linear relationships. In the first stage up to 3.5 MPa of the compressive load, the fractional change of the electrical resistivity reached around 17% for sensor containing 8 wt.% of the SmartCem and 32% for sensor containing 10 wt% of the SmartCem. Between 3.5 and 26 MPa of the compression loading the change reached 90% for both sensors.

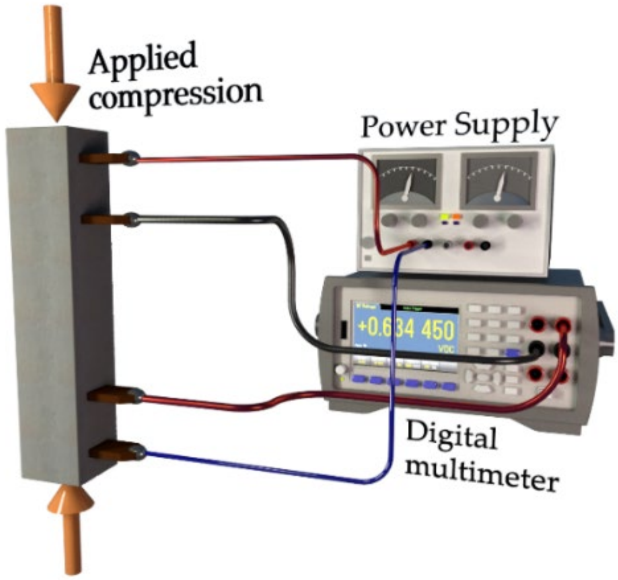

Figure 15. Schematic representation of a setup used to determine the sensitivity to applied compressive loads, (T. Buasiri et al.*, 2019)*

Figure 16. The actual used experimental setup to determine the sensitivity of the produced mortars incorporating various amount of the smart cement to the applied strain and stresses.

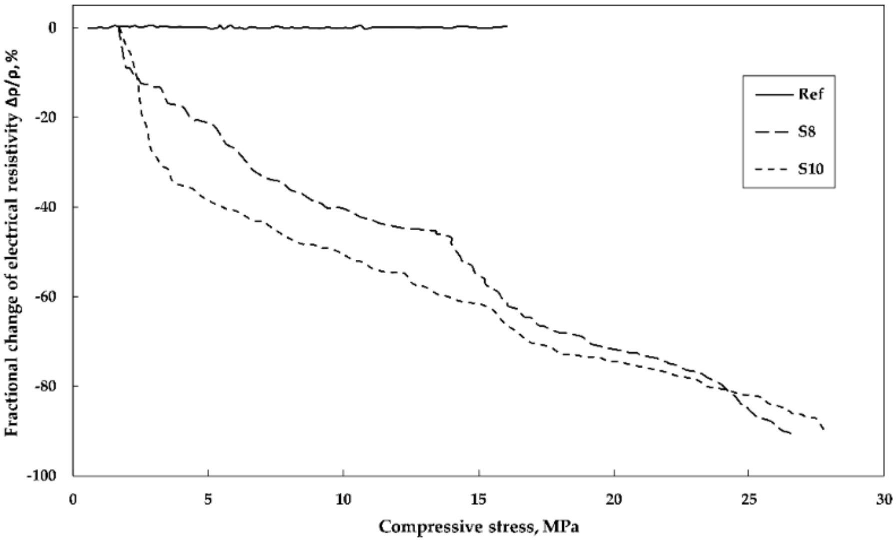

Figure 17. Relationship between fractional change in electrical resistivity and compressive stress, (T. Buasiri et al.*, 2019).*

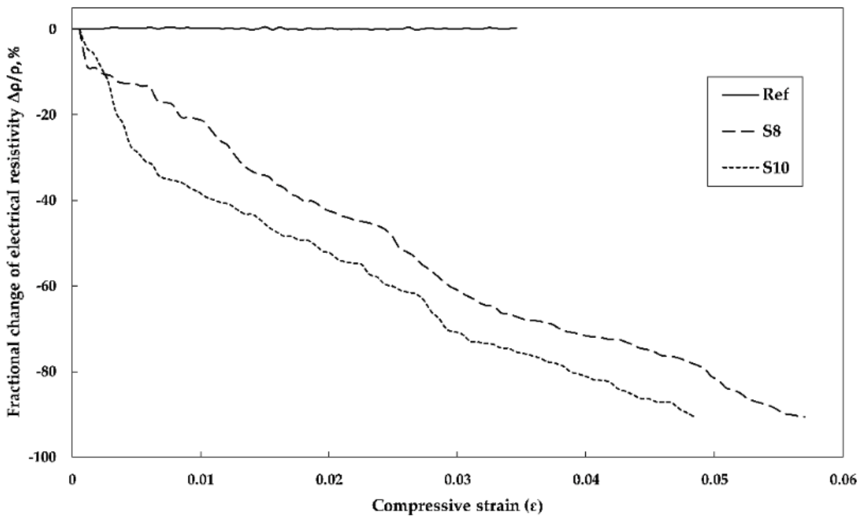

Figure 18. Relationship between fractional change in electrical resistivity and compressive strain, (T. Buasiri et al.*, 2019).*

Other known solutions showed significantly a lower sensitivity in comparison with the SmartCem sensors. A comparison of sensitivity values obtained by others using multi walled carbon nanotubes (MWCNTs) added as a water suspension to the cement in amounts between 0.06 and 2.14 wt% of the cement is shown in Table 4.

The significantly better sensitivity of the developed sensors is related to a number of factors but the most crucial is a better dispersion of the CNFs within the hydrated binder matrix due it their attachment to cement particles. Incorporation of CNFs in traditional way as a water dispersion faces problem of an increased agglomeration in higher pH after mixing with Portland cement.

The piezoresistive response can be related to the intrinsic piezoresistive property of the CNFs, (Dharap *et al.*, 2004). Secondly, the piezoresistive response is related to changes of the electrical resistance of the contact points between fibers due to compression of the binder matrix.

The obtained excellent results for samples containing only 8 wt% of the SmartCem make this technology even more attractive for full scale applications. Future tests will also include lower amounts of the SmartCem to extend the sensor detection range to enable measurement of larger load changes.

Table 4. Comparison of load sensitivity of cement/CNT composites, adapted from (T. Buasiri et al.*, 2019).*

Publication	Amount of Carbon-Based Materials	(Load MPa) Resistance Change, %	(Load, MPa) Resistance Change, %
(Yu and Kwon, 2009)	0	(5.2)	(8.6)
		0.0	0.0
(Yu and Kwon, 2009)	0.06 wt% MWCNT	(5.2)	(8.6)
		8.8	10.3
(Yu and Kwon, 2009)	0.10 wt% MWCNT	(52)	(8.6)
		8.4	11.4
(Zhang *et al.*, 2017)	2.14 vol% MWCNT	(4)	-
		6.8	
Present result S8	0.20 wt% CNF	(3.5)	(26)
		~17	**~90**

- **Humidity**

The mortar specimens containing 4% of SmartCem binder was produced to determine the effect of humidity on the electrical responses. Humidity chambers were created by using close glass containers with salt solutions, Figure 19. Lithium chloride (LiCl), Potassium carbonate (K_2CO_3), Sodium chloride (NaCl) and Potassium sulphate (K_2SO_4) were used. The obtained humidity values included 11%, 43%, 75% and 97%. The commercial humidity sensor was installed in each containers to check the internal humidity. Mortar samples contained 0, 2, 4, 6, 8 and 10 wt% of the SmartCem.

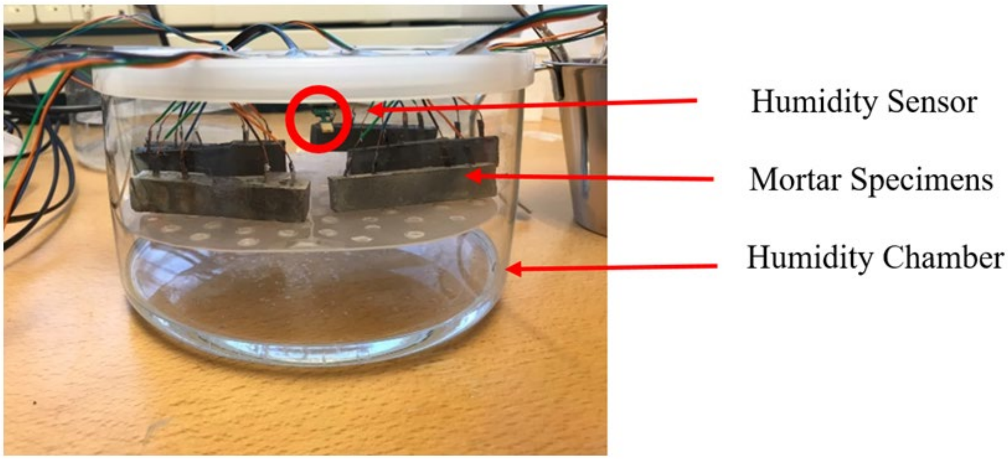

Figure 19. Setup used for determination of the electric response to varying humidity

The nearly linear relationship between the electrical resistivity and the percentage of relative humidity is shown in Figure 20. In general, higher humidity decreased the electrical resistivity of all produced sensors. However, the sensitivity to the humidity variations was significantly increased when the amount of the SmartCem was higher at 8 and 10 wt% of the total amount of cement. A percolation threshold value 8w% of the SmartCem for applications as humidity sensors was established. The obtained results enabled also to determine the effect of humidity on the other measured parameters including temperature and strain stress sensing, Figure 22

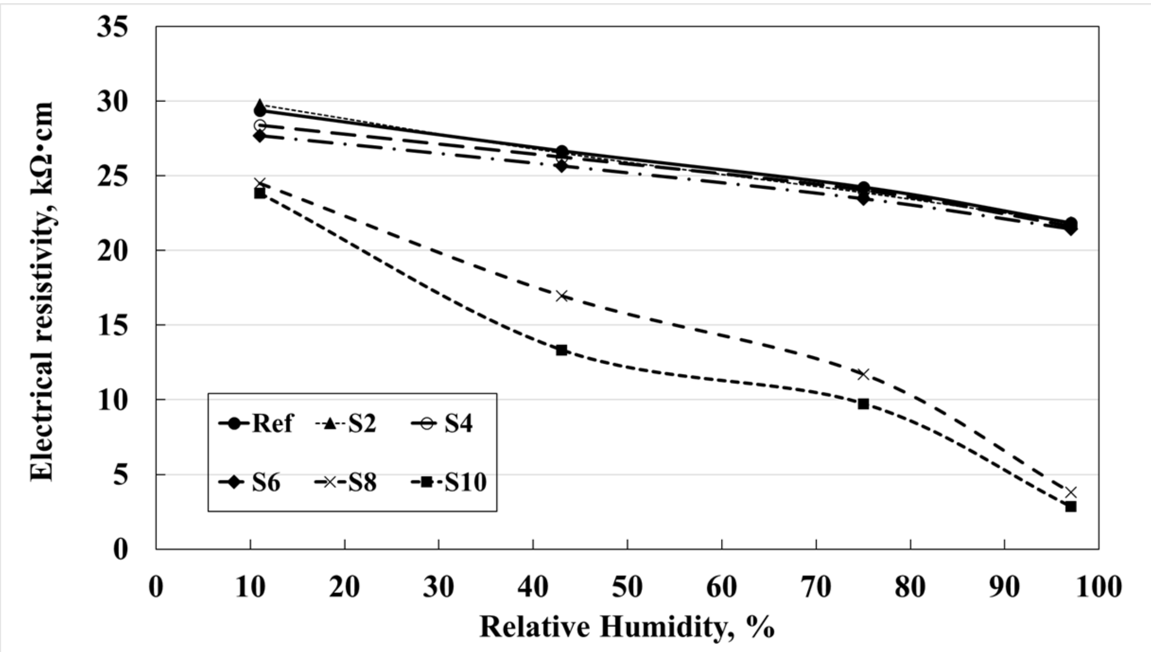

Figure 20. Effects of humidity on the electrical resistivity of the developed sensors containing various amounts of the SmartCem.

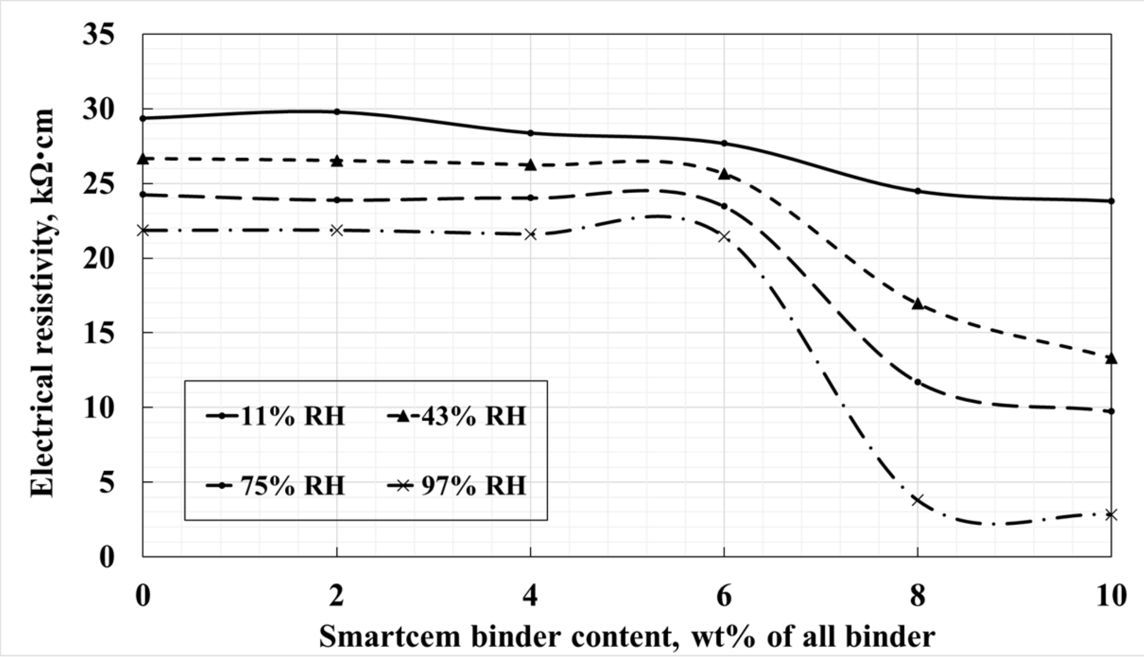

Figure 21. Effects of SmartCem amount on the electrical resistivity of the developed sensors exposed to various humilities.

- **Temperature**

The effects of various temperatures on the electrical resistivity was verified by storing calibrated sensors at various temperatures ranging from -20 to 40ºC. Sensors were sealed with plastic foil to prevent moisture variations, Figure 22. Several mortars containing 0% (Ref), 2% (S2), 4% (S4), 6% (S6), 8% (S8) and 10% (S10) of SmartCem were produced. After water curing for 25 days and air-cured for another 3 days, all samples were placed in the chamber, which maintained the temperature at -20 ˚C, 0˚C, 20 ˚C, and 40 ˚C. Change of the electrical resistivity were measured 24 hours later. All samples were wrapped sealed using an expandable plastic foil to prevent in influence of other factors including for example moisture variations.

At the time of writing this report only measurements performed on SmartCem sensors stored at 0 and 20 degrees were completed and are presented in Figure 23.

The temperature sensing of the SmartCem sensor can be related to the expansion caused by the increased temperature. The expansion results in a longer tunnelling distance leading to the increased electrical resistivity. The threshold value for the effective temperature sensing capability was established to be in the ranges between 2 and 6 wt%.

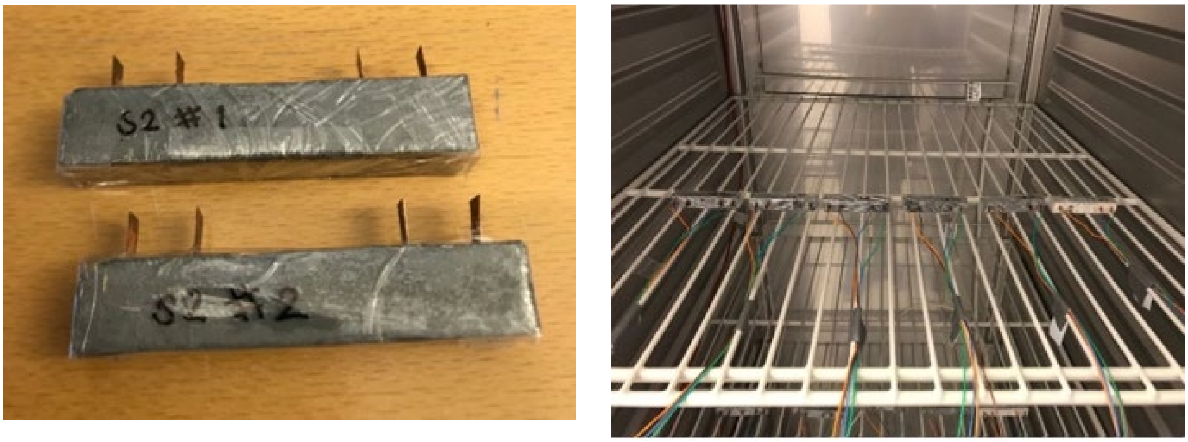

Figure 22. Setup used to determine the effects of temperature on variations of the electrical resistivity of the developed SmartCem sensors, a) sealing of sensors, b) placement in climate chamber.

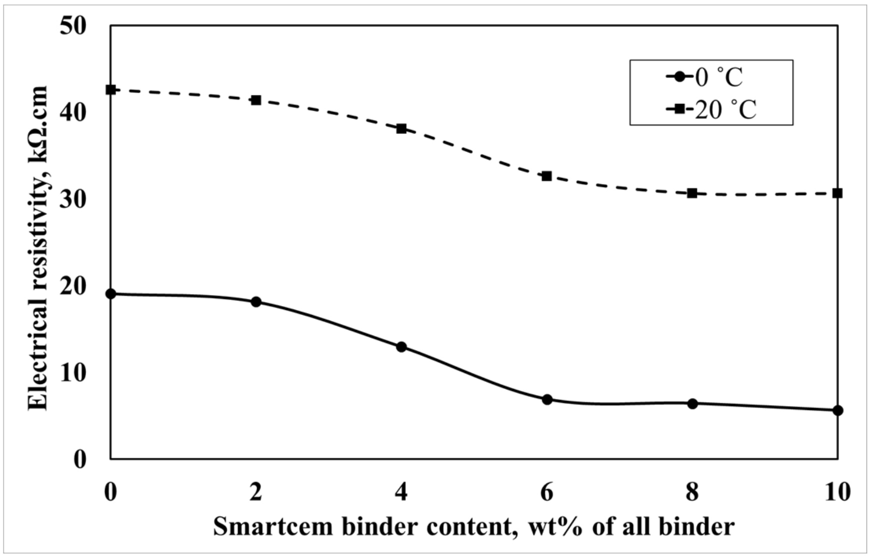

Figure 23. Effects of low temperature and amount of SmartCem on electrical resistivity of the developed sensors.

3.3 WP3 and WP4 – Development of monitoring system and its upscaling

The main objective of the package was to develop a prototype of the monitoring system based on the utilization of changes of the electrical resistivity of matrixes made of nano-modified Portland cement subjected to various types of loading. This will include structural loads as well as environmental impact, including for example internal cracking caused by freeze-thaw cycles. The basic principle of the system is shown in Figure 24. The

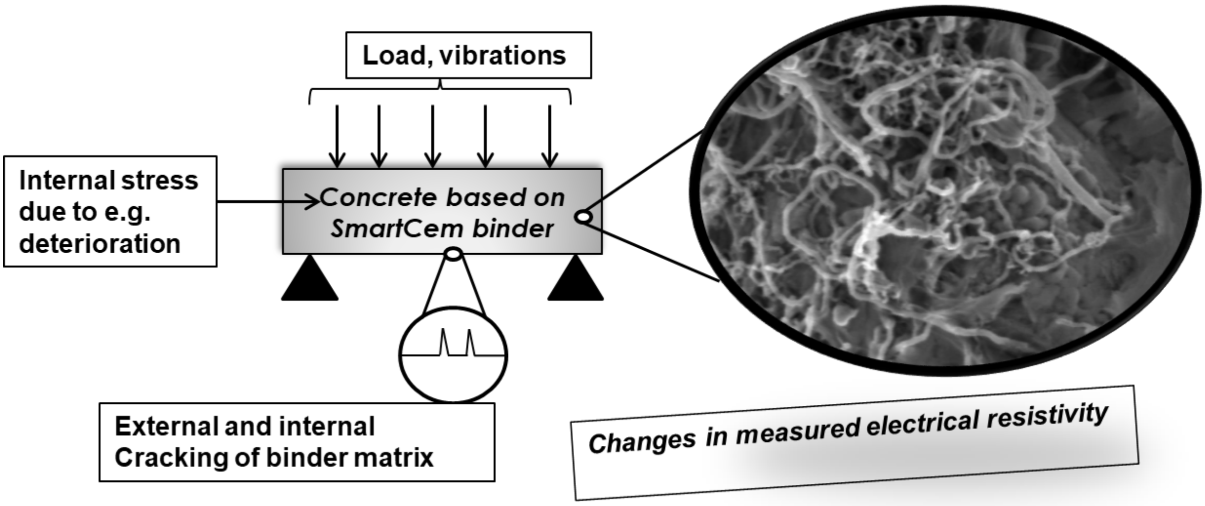

Figure 24. Basic principle of the developed monitoring system.

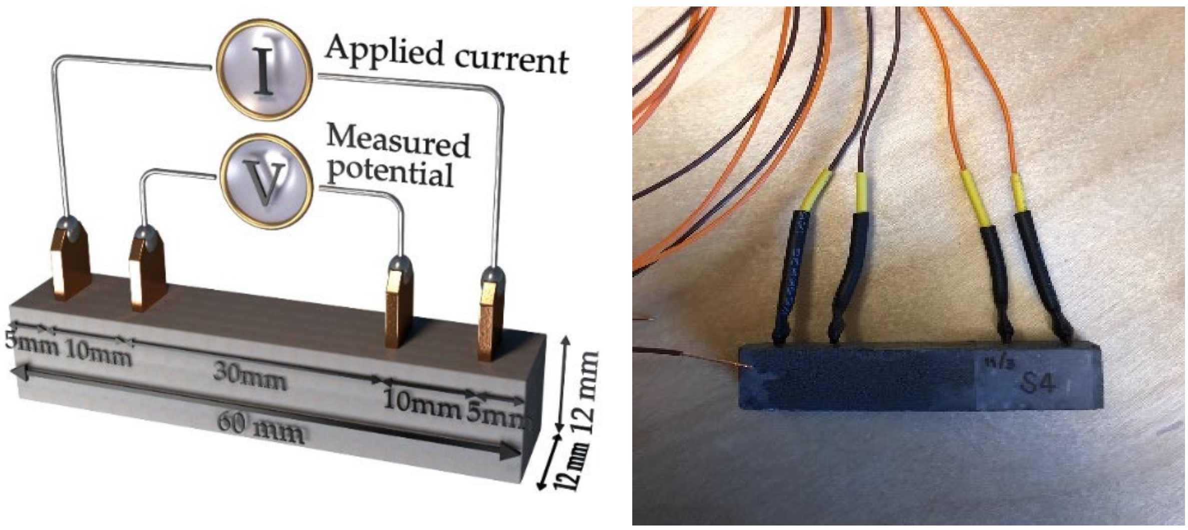

Figure 25. Sensors developed within the SmarCem project.

In this part of the project, the developed prototype monitoring system was installed on a full-scale reinforced concrete column, Figure 26. The produced and calibrated earlier SmartCem sensor was put into the castes concrete alone with regular sensors measuring temperature and humidity. The measured temperature developing within the concrete column was in line with the temperature profile measured by the installed thermocouple, Figure 27. After submission of the report, the element will be subjected to flexural loading and the installed SmartCem sensor will be used to monitor the stress development. Additional, regular strain sensors will be installed for this test for calibration proposes.

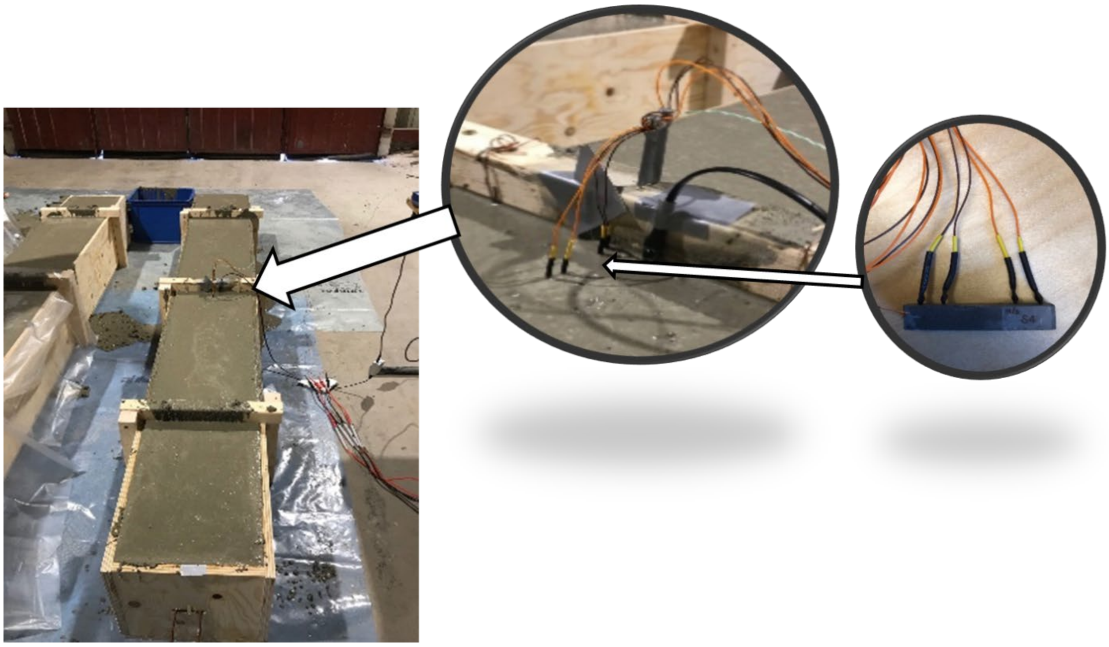

Figure 26. Monitoring of full scale reinforced concrete elements

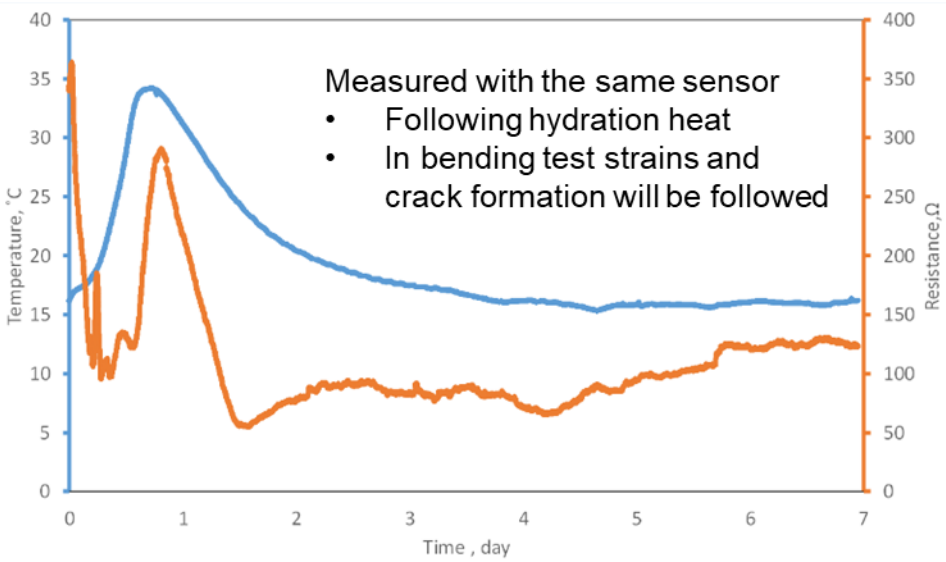

Figure 27. Monitoring temperature development of a full-scale concrete column shown in Figure 26. The blue line represent readings from the reference regular temperature sensor installed in the measured element close to the SmartCem sensor. The orange line shows variations of the electrical resistance recorded by the SmartCem sensor.

4 Dissemination and exploitation of results

The following articles were published:

- The review article title **"State of the Art on Sensing Capability of Poorly or Nonconductive Matrixes with a Special Focus on Portland Cement-Based Materials"** was accepted in Journal of Materials in Civil Engineering on 28th March 2019**.**

- The initial results of load sensing of nanomodified cement **(**SmartCem**)** have presented in the article title **"Piezoresistive Load Sensing and Percolation Phenomena in Portland Cement Composite Modified with In-Situ Synthesized Carbon Nanofibers".** This article was published in Nanomaterials on 10th April 2019**.** **(**https://www.mdpi.com/2079-4991/9/4/594**)**

The following publications are being prepared and planned for the year 2020

- Publication focusing on **humidity sensing and temperature sensing** of SmartCem binder will be finished by winter 2019 and make submission to journal in January/February 2020.

- Publication describing monitoring of full scale concrte column using teh developem SmartCem sensors is planned to by punlished in 2020.

Project will be presented in the following conferences where abstracts/publications were already accepted:

- Luleå SMASCO19 - 1st International Conference On Smart Materials for Sustainable Construction. The coneference will be also combined with workshop on Smart materials for sensing, December 2019, Luleå, Sweden.

- The results of compression load sensing of SmartCem binder will have presented in 2nd International Conference on Nanotechnology of Cement and Concrete (2NCC20) on 20-22 May 2020, in Irvine, CA, USA.

The following conferences/workshops organized with the InfraSweden 2030 program were attended during (or just after finalization) of the project.

InfraSweden 2030 Project conference 2018

Date: 25 October 2018, **Location:** Stockholm Waterfront Congress, Stockholm


The innovation workshop with InfraSweden2030 and KTH Innovation

Date: 18 June 2019, Location: Klarabergsviadukten 90, Stockholm

InfraSweden 2030 Project conference 2019

Date: 24 October 2019, **Location:** Built Fest and Conference, Norrlandsgatan 11 Stockholm

5 Future actions

The project will be still continued until the end of 2020 based on the financing obtained from TRV-BBT. The focus during the additional year will be more on full-scale testing using the developed monitoring system. Additional tests related to the frost attack and to the chloride penetration will be performed. The CVD reactor purchased with in the project will be further modified to enable a better operational efficiently enabling synthesis of larger amounts of the SmartCem.

The results obtained within this project will be disseminated during several planned for 2020 events. One international conference on nanomaterials in concrete materials in the USA in may 2020. Furthermore, an international workshop will be organized in Lulea in autumn 2020 focusing on self-sensing concrete materials. The results will be also presented to the industry during Betong seminar in autumn 2020 in Stockholm.

A possible spin off company might be established in 2021 to utilized the developed technology and to commercialize the findings.

6 References

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