

Initial proposal of a novel voltammetric sensor system for the detection of concrete carbonation by means of PCA model

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Abstract. The monitoring of concrete carbonation takes an important role in the structures maintenance, considering that corrosion induced by this phenomenon is one of the mainly failure causes in the Reinforcement Concrete Structures (RCS) located in industrial zones, roads and cities. Carbonation of concrete is produced by the penetration of the CO₂ inside of the porous net, which is mainly combined with the Ca(OH)₂ contained in the concrete pore solution producing carbonates with low solubility and eventually causing a pH drop until neutral levels. The pH drop produces the instability and final generalised destruction of the rebars passive layers, which is the step that precedes generalized corrosion. The current existing systems to detect concrete carbonation are based on potentiometric sensors to detect the pH of concrete pore solution. These have some limitations such as the interference of different reactions on the sensor surface. Considering these limitations, in this study a novel system of voltammetric Au sensors embedded in concrete for the detection of concrete carbonation was presented. In the voltammetric sensor, the potential sweep signal applied comprises the potential range where the effect of the pH variations has more influence in the sensor response. Then the response processing by means of the multivariate analysis PCA (principal component analysis) allows to manage a huge quantity of variables and to reduce the effect of the interference with other analytes, increasing the importance of the pH changes effect in the obtained data. Thus, increasing the reliability of the system to detect the concrete carbonation.

1 Introduction

The monitoring of the carbonation processes is a challenge in the Reinforcement Concrete Structures (RCS) durability control yet. The main systems to control concrete carbonation, based on pH sensors, are traditionally made by potentiometric sensors which have problems of durability and reactions overlapping [1,2]. Other recently technologies used in pH sensors for RCS are fiber optic sensors for instance, the developed by Fei Lu et al. [3]. But in this type of sensors also exist some limitations, for example the signal is not only changed by the pH variations and the detection range most times do not cover all the pHs that occur in the pore solution during the carbonation [4].

This study presents the bases of novel sensor system for concrete carbonation detection, trying to reduce the existing problems in the current sensors technologies.

The system is novel due to the use of voltammetric sensors, which are virtually never used in RCS. Their efficiency is widely verified in industries such as food or wastewater [5,6]. In these sensors an excitation potential sweep is applied, as response the sensors emit an electric current at each potential which is associated with a specific reaction. Analysing the response in the potential range where the interest reaction takes place by Principal Components Analysis allows to develop a more robust and reliable detection models than with other sensors technologies [7].

Furthermore, the system is configured by Au voltammetric sensor, being the use of gold as voltammetric sensor for the RCS monitoring very interesting because:

- Over the metal surface is favoured the O₂ reduction without overlapping of the reaction stages [8–11],
- and the potential peaks related to the adsorption/desorption of OH⁻ and O₂ change with the variations in pH [12,13].

These aspects could be used to detect and forecast the corrosion processes in RCS, since O₂ is one of the major reducers in the rebars corrosion mechanisms [14–17] and the pH drop of the concrete pore solution due to carbonation is one of the main causes of passive layer destruction [18–21].

With this purpose the results obtained with concrete samples at different carbonation levels were analysed by PCA analysis, an initial detection model was calibrated and validated.

2 Experimental

2.1 Sensor

2.1.1 Au electrode

To manufacture the Au electrode, Au thread was used (99% purity and 1 mm diameter). The electric connection was made employing multifilar cable with Teflon casing. The connection between the cable and the metal was protected by a heat-shrink tube and epoxy resin (Fig. 1).

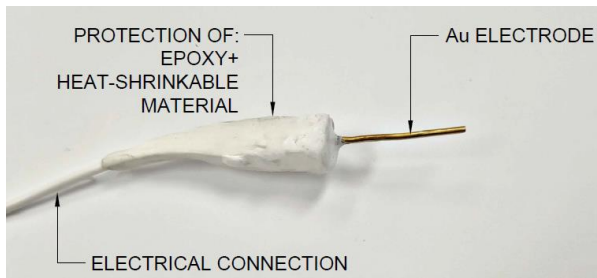


Fig. 1. Au electrode picture

2.1.2 Electrochemical techniques

The cyclic voltammetry (CV)[22] technique was applied with Autolab PGSTAT10. Data were collected by the Nova 1.11 software.

The CV was applied using the 3-electrode configuration, where the working electrode (WE) was the Au sensor and stainless steel (SS) plates were used as the counterelectrode (CE). A saturated calomel electrode (SCE) was employed as the reference electrode (REF). The CV technique was applied in the potential range between the oxygen and hydrogen generation curves (pH=13) and without reaching potentials above 1.1 V vs. SCE, since the passive oxide layer is formed (1,2,29,30). The formation of this stable passive oxide layer can produce the electrical/ionic isolation between electrode and electrolyte.

2.2 Samples

The Au sensors were embedded in 4 x 4 x 16 cm³ samples of 3 different types of concrete (Fig. 2).

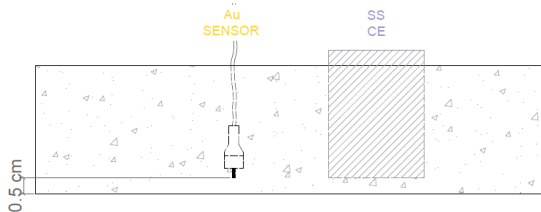


Fig. 2. Scheme of the sample with the embedded sensors

As a counter electrode (CE), an SS sheet (Fig. 2) 3 cm wide and 4 cm high was used, which is left unembedded in the concrete for a depth of 0.5 cm to make the electrical connection to the potentiostat. The surface of the CE was more than 20 times greater than the surface of the working electrodes [23]. Table 1 shows the average surfaces of the sensors and counter electrodes, as well as the surface ratio.

Table 1. Resume of the WE y CE areas

Electrode	Areas (cm ²)	Areas ratio (S _{CE} /S _{WE})
WE Au	0.07 ± 0.02	≈ 357.12
CE SS sheet	24.8 ± 0.7

The concretes employed to manufacture samples were those specified in Table 2.

Table 2 Quantities per m³ of concrete

MATERIALS	kg/m ³ of concrete		
	w/c=0.6	w/c=0.5	w/c=0.4
Cement I 42.5 R-SR5	315	385	490
Water	189	193	196
Superplastifier	2.2	2.7	34
Silica sand	1212	1179	1115
Gravel	653	635	601

For the study to offer statistical reliability for each concrete composition, three batches were made. From each batch, two samples with sensors were manufactured. This totalled 18 samples. Therefore, 18 sensors were manufactured and 18 SS CEs were prepared.

2.3 Concrete characterisation tests

Characterisation tests were performed for each of the concrete compositions studied. The results of these standard tests were used to support the results obtained with the sensors.

The following tests were performed:

- **Hardened concrete tests. Part 3. Determining samples' strength resistance (UNE 12390-3:2009).** Compressive strength was determined at 28 days (fc). Two cylindrical specimens were prepared (10 cm diameter, 20 cm high) for each batch at each dose. Total number of specimens: 12.
- **Determining water absorption, density and accessible porosity for water (UNE 83980:2014).** One cylindrical specimen (10 cm diameter, 5 cm high) was prepared for each batch at each dose. Total number of specimens: 9.

2.4 Study variables and scenarios

The samples were conditioned to three states:

- Non-carbonated water saturated concrete (NCS). The samples non-carbonated were saturated with water.
- Non-carbonated “dry” concrete conditions (NCD). The samples were conditioned under laboratory conditions (T≈ 25°C y HR≈ 50%)
- Carbonated concrete, “dry” conditions (CD): The samples were exposed to a 3.5% CO₂ concentration during 60 days.

2.4.1 Study under CARBONATION CONDITIONS

After performing the study under H₂O saturation conditions and ambient conditions, samples were left inside a carbonation chamber at 3.5% (T=23 ± 2 °C; HR≈60%). They remained inside the carbonation chamber 60 days and different degrees of carbonation according to concrete quality were obtained.

Bearing in mind the relation expressed in (1) and the test data, the carbonation constant (K_{CO2}, mm/year^{1/2}) was calculated for the 3.5% CO₂ concentration in samples without sensors.

$$x = K * \sqrt{t} \tag{1}$$

where:

- x: penetration depth of the carbonation front (mm)
- K_{CO_2} : carbonation constant (mm/year^{1/2})
- t: time in which the carbonation front had advanced (years)

Table 3 shows the K_{CO_2} values. According to these values, it was possible to evaluate the speed at which the studied concretes carbonated. That with the slowest velocity was the concrete with the lowest water/cement ratio, while that with the fastest velocity had the highest water/cement ratio.

Table 3 Carbonation constant (K_{CO_2})

	w/c=0.6	w/c=0.5	w/c=0.4
Average	47.48	32.08	18.87
Standard deviation	4.24	1.44	0.21

2.5 PCA analysis

The statistical PCA method was applied [24–29]. It allowed to simplify the complexity of the sample space so that it became a two-dimensional space to conserve the largest possible amount of information about the initial sample. Both these new variables are known as a principal component (PC)[30,31]. The first PC (PC1) is selected in such a way that it contains maximum data variance. The second principal component (PC2) must contain the maximum of the remaining variance and be orthogonal to PC1. The representation on two axes allows samples to be easily grouped and classified.

This data processing protocol was applied by means of the Solo 9.0 computing tool (2022) (Eigenvector Research, Inc., Manson, WA USA 98831; this software is available at <http://www.eigenvector.com>).

The matrix built by means of the CV results that was entered in the PCA tool is that which appears in Table 4.

Table 4 Data table or matrix used in the PCA

SAMPLES	STATE	Variable 1	...	Variable j
S1
.
.
.
S _n

To develop the model, it was necessary to follow calibration, fit and validation processes. During the fit process, any measurements that proved erroneous due to perturbations occurring while testing were removed. Even so, the size of samples and their variability were suitable to ensure the model's sufficient statistical reliability.

The sample size for calibration was 124 and for validation 38.

3 Analysis of the results

3.1 Results of the characterisation tests

Table 5 shows the average values obtained in the characterisation tests. It also shows the average coefficient of variation (Avrg Coef.V). Coef. V is defined as the quotient between standard deviation and the average value.

Table 5 Average values of the characterisation tests done with the concrete used in Phase 2.

	$f_{c28days}$ (MPa)	% A.P.W.	% W.A.
w/c=0.6	34.5	19.19%	7.59%
w/c=0.5	42.9	17.21%	7.47%
w/c=0.4	56.8	14.85%	6.65%
Avrg Coef.V	5.49%	7.47%	6.27%

Compression resistance at 28 days ($f_{ck28das}$) (UNE 12390-3:2009), % accessible porosity for water (A.P.W.) and % water absorption (W.A.) (UNE 83980).

Bearing in mind the results of the characterisation tests, the indicators established by the French Civil Engineering Association (AFGC) [32] and concrete type according to EN 1992-1-1:2004 (EUROCODE2), we classify the employed concretes according to their potential durability as:

- Concretes with a low potential durability: w/c=0.6 and w/c=0.5.
- Concrete with a medium potential durability: w/c=0.4.

3.2 PCA model for concrete carbonation detection

Fig. 3 includes the graph of the PCA scores, where PC1 is on the X axis and explain the 99.73% of data variance, and PC2 is on the Y axis accounting for 0.18% of data variance. The total data variance explained by both axes is 99.91%. Therefore, the PCA model well represents the information provided by the samples in calibration.

The sensor is capable to distinguish between saturated and non-saturated conditions, it is showed in the graph, since the NCD and CD clusters are on the left and NCS points are on the right.

The clusters associated with carbonated state (CD) can be distinguished from those corresponding to the other states. The sensor is capable of detecting the variations caused by carbonation in the capillary network, by the concrete pore dissolution and its evolution with time. This claim is based on:

- The CD clusters are displaced from their corresponding NCD cluster, regarding to the concrete type. By means of colorimetric test was identified how in all the concretes at least was beginning the carbonation (Fig. 4). Total carbonation does not occur in concrete w/c=0.4 in the zone where the sensor is found. However, the Au sensor is capable of detecting the change that takes place around it when carbonation begins, and dots are displaced upwardly and to the right in relation to the corresponding dots in NCDw/c=0.4.

- Bearing in mind concretes' carbonation constant (Table 3), the degree of carbonation for concrete w/c=0.6 is higher than for concretes w/c=0.5 and w/c=0.4 during the studied period. This is confirmed by the images in Fig. 4 where, after 60 carbonation days, the carbonation front in concrete w/c=0.4 still does not reach the sensor. The clusters are arranged in the direction indicated by the arrow A-CO₂, shown on the PCA graph (Fig. 3). So the last cluster appearing in the A-CO₂ direction is that of the concrete w/c=0.6. Considering the above, the displacement of a sample in the direction A-CO₂ means that its degree of carbonation is higher.
- Furthermore, the system is capable of detecting the advance of the carbonation front over time in the same concrete. The points associated with the w/c=0.6 concrete and the CO₂ conditions were distributed in the A-CO₂ direction, the last points in this direction being those of the samples taken after 60 days, when the concrete was completely carbonated.

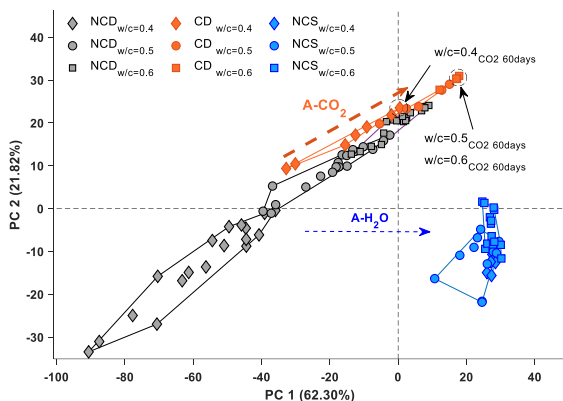


Fig. 3 PCA analysis graph for all the studied concretes and in all the tested states. Grey: Non-carbonated “dry” conditions (NCD); Orange: carbonated samples in “dry” conditions (CD); Blue: Non-carbonated water saturated conditions (NCS).

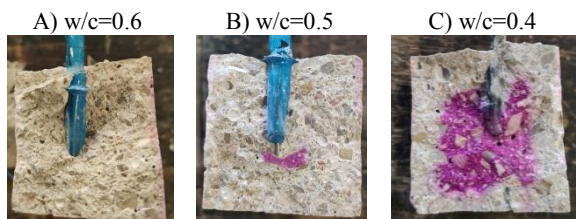


Fig. 4. Photographs taken of the samples sprayed with phenolphthalein after tests. A) w/c=0.6. B) w/c=0.5. C) w/c=0.4. Phenofstaleinen turns pink when the pH > 8.5 conversely the surface is carbonated and keep uncoloured.

3.2.1 Model validation

In Fig. 5, the validation data about the PCA model are represented (V-NCD, V-CD, and V-NCS). The graph shows how most of the samples employed in the validation are represented in the zone that corresponds to the state in which the measurement was taken.

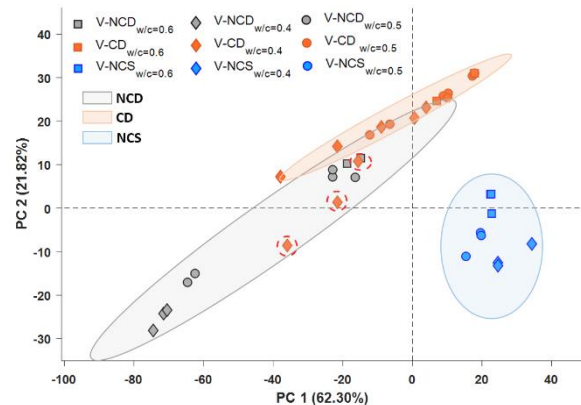


Fig. 5 Validation of PCA model. Grey: Non-carbonated “dry” conditions (NCD); Orange: carbonated samples in “dry” conditions (CD); Blue: Non-carbonated water saturated conditions (NCD). The red circles on the dashed line indicate the values whose position is not coherent with the measurement conditions they belong to.

To assess the frequency of failure of the PCA model was used the data recollected in the confusion matrix showed in Table 6. Considering the number of samples in the validation were 38 and only the model committed 3 errors in the classification, the failure frequency at this point was 7.89 % whereas the success frequency was 92.11 %.

Table 6 Confusion matrix

		PREDICTED		
		NCD	CD	NCS
REA	NCD	10	0	0
	CD	3	15	0
	NCS	0	0	10

4 Conclusions

Taking into account the previously presented analysis, the following conclusions are drawn:

- The sensor detects the carbonation front. The response of the sensor changes as the carbonation front advances in the concrete matrix. This allows high degrees of carbonation to be detected coherently with concrete type
- The success frequency (92.11%) obtained during the PCA model validation verified the high potential of this system to detect the carbonation in RCS.

Based on the study carried out, the following future works have been defined:

- The intention is to increase the robustness and the application range of the model. In order to do this, experiments in concretes with additions and high-performing concretes and non-cracking and cracking samples will be planned.
- The electronic devices which allow the implementation and autonomy of the system in the RCS are currently under development. Work on both, the development of a miniaturized potentiostat and the autonomy of the system by supplying the required energy

with photovoltaic systems is being done. This way, the installation of the system in the reinforcement concrete structures will be simplified.

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