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In situ Monitoring of pH Changes in Concrete and Lime Mortars

G.L. Pesce, R.J. Ball
BRE Centre of Innovative Construction Materials, Department of Architecture and Civil Engineering, University of Bath, Bath, BA2 7AY

M. Serrapede, G. Denuault
Department of Chemistry, University of Southampton, Southampton, SO17 1BJ

ABSTRACT

This paper describes how a new type of solid state microelectrode based on nanostructured palladium-hydride (PdH) can be used to monitor pH variations during carbonation of calcium hydroxide ($Ca(OH)_2$). The experiments described were carried out under conditions similar to those typical of common porous substrates such as cement and lime mortars. In these tests PdH microelectrodes were employed to record pH transients during the carbonation within a humid fibrous mesh that simulated the porous substrate. To control the carbonation rate, experiments were carried out at different carbon dioxide partial pressures (p_{CO2}) and in each case the experimental results were compared to theoretical calculations obtained using PHREEQC (pH-REdox-EQuilibrium) software. Scanning electron microscopy (SEM) observations and X-ray diffraction (XRD) analysis of the calcium carbonate ($CaCO_3$) crystals deposited on the fibrous mesh were used to evaluate characteristics of the solid phases precipitated during the reaction. Results demonstrate that these pH microsensors can operate reliably in very alkaline environments (pH>12) such as those produced by the dissolution of $Ca(OH)_2$.

1. INTRODUCTION

One of the most important electrochemical measurements is that of the acidity or basicity of aqueous solutions. Numerous chemical reactions involve pH changes that can highlight processes otherwise difficult to monitor such as the corrosion of steel bars in reinforced concrete.

The steel reinforcement in concrete is normally in a passive state with respect to corrosion due to a thin iron oxide layer produced by the highly alkaline environment (pH>12) of the concrete pore solution. This alkaline environment is mainly produced by the $Ca(OH)_2$ contained in the cement as well as by the smaller amount of other alkaline species such as sodium and potassium hydroxides (NaOH and KOH, respectively) [1].

Because of the reduced porosity of concrete, these hydroxides do not fully carbonate during the hardening process and this guarantees an almost constant alkaline environment that maintains the protective layer around the steel reinforcement preventing corrosion [2]. However, over time CO_2 may penetrate within the concrete and cause carbonation of alkali and alkaline-earth elements. This eventually produces a more acidic environment which reduces the passive iron oxide layer and increases the risk of corrosion of the underlying steel. For this reason monitoring the pH of pore waters in steel reinforced concrete structures is key to assessing the state of the structures [3].

Despite its importance pH remains a difficult parameter to determine in many applications, including those in the construction industry. In this specific case, two of the main factors affecting pH measurements are: (1) pHs above 11 cannot be measured reliably with most of the currently used pH sensitive devices including the conventional glass electrode, because of the alkaline error; (2) pH is hard to measure in confined places. The alkaline error is due to the fact that in high pH solutions (>11) the hydrogen ion activity is so low and the activity of alkali or alkaline-earth metal ions (mainly contained in the glass of the membrane) is so high that the ordinary pH electrode begins to respond to these ions rather than to the hydrogen ions. To take this effect into account correction tables are available as well as special electrodes (although the correction tables are preferred, [3, p.126]). These special electrodes use alkali-glass membranes that are less sensitive to ions such as Na^+ and Li^+. However, none of the glass membranes currently available has zero alkaline error [4]. For instance, the Sentek P11-PB (PH0043) combination type electrode, sold as suitable for measurements within the pH range 0-14 and, in particular, for measuring the pH in cement, returned a pH of 12.8 in a pure $Ca(OH)_2$ aqueous solution whose pH at 20ºC, according to theoretical calculations and to some measurements carried out with a solid state electrode, had to be 12.56.

2. A NEW WAY OF MONITORING pH IN BUILDING MATERIALS: THE NANO-STRUCTURED PdH MICROELECTRODES

In order to overcome limitations of traditional pH electrodes, a new type of electrode can be exploited for monitoring pH variations in cement and lime mortars: *the nano-structured PdH microelectrode.*

This solid state electrode operates by exploiting the insertion of hydrogen in the palladium (Pd) structure. This absorption leads to a phase change by forming palladium hydride (PdH).

The maximum amount of hydrogen that can be absorbed within the Pd film is relatively large (up to 0.6 H per Pd atom). The crystalline structure formed is dictated by the quantity of H absorbed. Two phases are obtained: the α phase, when the H:Pd ratio is below 0.02, and the β phase when the ratio is above 0.6 In between these limits, the PdH consists of a mixture of the two phases [5, p.8341]. Under these latter conditions, the PdH behaves as a hydrogen electrode yielding a Nernstian dependence of potential on pH, independent of the Pd:H ratio.

Despite the publication of extensive studies of H insertion / extraction in Pd, only one report was published in 2006 regarding a PdH micro-pH sensor [6, p.266]. This was probably due to the fact that the potentiometric response of PdH microelectrodes is generally worse than that of large PdH electrodes. Generally the smaller the electrode, the more unstable is its potentiometric response.

However, the nanostructure introduced in 2006 by Imokawa and colleagues avoids these problems [6, p.266] and allows the PdH micro-electrodes to be successfully used in a number of applications. The nanostructure, in fact, increases the H absorption rate and allows a rapid, stable, reproducible and almost theoretical potentiometric pH response in de-aerated solutions. Furthermore, thanks to these characteristics, the electrode can be reloaded with hydrogen quickly, thereby allowing repeated pH measurements [6, p.271].

3. MONITORING pH IN BUILDING MATERIALS WITH NANOSTRUCTURED PdH MICROELECTRODES

To demonstrate the reliability of these electrodes in monitoring pH variation in porous building materials some tests were carried out in a joint research project between the University of Southampton and University of Bath (UK).

In this research, carbonation was studied within a thin film of water to simulate the conditions existing in a porous media such as concrete once most of the liquid water has evaporated. Experiments were carried out in a specifically constructed PMMA cell under thermostatic conditions (23°C) with different $Ar:CO_2$ gas mixtures. The saturated solution of $Ca(OH)_2$ used for the tests was absorbed onto small strips of cotton lint (3mm wide, 10mm in length) wrapped around the reference electrode. This cotton mesh was used to trap a thin film of solution and simulate carbonation in the confinement of a porous medium, as well as provide an ionic path between the electrodes and capture the solid phases formed during the carbonation for subsequent analysis.

To control the carbonation, the experiments were carried out at different p_{CO2} and in each case the experimental results were compared to theoretical calculations using PHREEQC. The micro-morphology and crystalline structure of solid phases precipitated on the mesh fibres during the tests were studied using a field emission scanning electron microscope (model FESEM6301F from JEOL) and an X-ray diffractometer (Rigaku Smartlab with a 9 kW source and CuK_α X-rays).

Tests were carried out using a three-electrode configuration consisting of the PdH micro-electrode (a 250μm diameter, 2μm thick disc of nanostructured Pd electrodeposited on a Pt disc as reported in [6]), a platinum mesh counter electrode and a saturated calomel reference electrode. The microelectrode was held by a translation stage and inserted in the cell through a specifically made hole in the cell lid. The Pt mesh was clamped at the bottom of the cell by the cell lid and the reference electrode was clamped outside the cell and connected to the solution by means of a salt bridge. The latter was terminated by a capillary tip attached to the microelectrode and held circa 2mm away.

In order to evaluate the Pd microelectrode response, the pHs obtained at the beginning and end of the tests were compared with theoretical values calculated following previously reported PHREEQC (a program for simulating homogeneous and heterogeneous geochemical reactions) protocols [7]. The initial condition was for a solution consisting of 1 kg of pure water with the addition of sufficient Ca^{2+} ions to simulate saturation with lime at temperatures of 20, 23 and 25°C. The equilibrium phases considered for evaluating the final pH were: gaseous CO_2 at different partial pressures and one of the solid polymorphs of $CaCO_3$. The partial pressure of CO_2 considered was the same used during all the experiments. The number of moles of CO_2 was set to 1000 in order to model the equilibrium with an effectively infinite reservoir. Solid $CaCO_3$ phases introduced into the simulation were: monohydrocalcite, vaterite, aragonite and calcite. These were introduced using a saturation index of zero. Simulations were performed with the thermodynamic data contained in the Lawrence Livermore National Laboratory database which was modified by adding data for vaterite taken from the SIT database, developed for the French National Radioactive Waste Management Agency.

Table 1. Initial and final pH values calculated with PHREEQC for the carbonation of a saturated $Ca(OH)_2$ solution at different temperatures and p_{CO2} (In pH=initial pH; Mon=monohydrocalcite; Vater= vaterite; Arago=aragonite; Calc=calcite)

T (°C)	In. pH	p_{CO2} (atm)	Final pH			
			Mon	Vater	Arago	Calc
20	12.56	0.750	6.389	6.317	6.139	6.087
		0.167	6.805	6.734	6.559	6.508
		0.039	7.215	7.154	6.972	6.921
23	12.45	0.750	6.338	6.310	6.135	6.083
		0.167	6.805	6.728	6.555	6.504
		0.039	7.214	7.139	6.968	6.917
25	12.37	0.750	6.388	6.306	6.132	6.080
		0.167	6.805	6.724	6.553	6.501
		0.039	7.214	7.135	6.996	6.915

4. EXPERIMENTAL RESULTS

Table 1 reports the initial (second column) and final pH (last four columns) of a saturated $Ca(OH)_2$ solution before and after carbonation at different temperatures and p_{CO2} as calculated by PHREEQC.

Figure 1 shows the potential transient (left axis) measured by the electrode during carbonation of the solution at 23°C and 0.167atm p_{CO2}. The pH values reported on the right axis were calculated from the potential transient using the potential-pH calibration curve published in [8] where the slope, 58.7±0.5 mV/pH, was in good agreement with the slope found previously by Imokawa and colleagues [6].

For the first 27 min, figure 1, the cell was full of solution and the microelectrode measured the potential in the bulk solution. During this time an inert atmosphere of Ar was introduced into the cell to prevent carbonation. A rise in potential within the first 20 minutes reflected the loss of hydrogen from the β phase of the PdH. Between 20 and 45 minutes a plateau appeared when the α phase started to form. This effect lasted while the two phases coexisted. Under this condition the electrode potential was only determined by the pH allowing the microelectrode to act as a pH electrode.

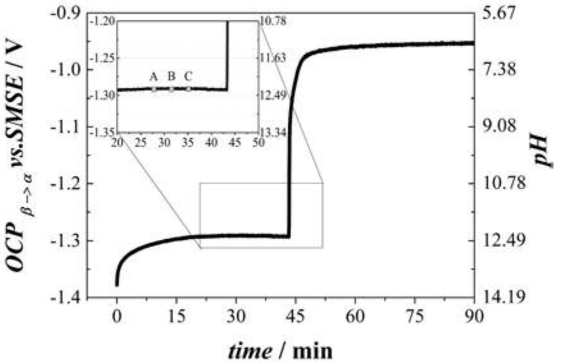

Figure 1. Potential transient (left axis) and corresponding pH (right axis) recorded with a 250 µm diameter nano-structured PdH microelectrode during the carbonation of a saturated $Ca(OH)_2$ solution at 23°C and 0.167 atm p_{CO2}.

After about 27 minutes from the beginning of the experiment, when the bulk measurement was considered stable, the microelectrode was moved down toward the cotton lint (point A in the inset in figure 1). Once in contact, the signal stability was checked and, then, the solution was removed using a syringe connected to a capillary tube (point B in figure 1). After having checked once again the stability of the potential transient, a mixture of Ar and CO_2 with a p_{CO2} of 0.167atm was introduced into the cell (point C). Soon after, the potential began to rise steeply until it reached a second plateau. This steep increase reflected the change in pH due to the carbonation reaction within the solution trapped in the mesh. A new plateau was reached after approximately 60 minutes from the beginning of the experiment. This reflected the potential (i.e. the pH) of a theoretical water solution with no free Ca^{2+} ions, in equilibrium with two phases: a $CaCO_3$ solid phase and CO_2 gaseous phase. At this stage all Ca^{2+} ions initially in solution were bonded to CO_3^{2-} ions in the $CaCO_3$ structure and the pH was mainly influenced by the solubility of the solid phases formed and by the p_{CO2} (table 1).

According to the calibration curve in [8], the initial pH of the solution was 12.45 (between points A and C in figure 1). A value in perfect agreement with the results of the PHREEQC calculation (table 1) and quite different from the values measured with the glass electrodes in a similar solution (about 12.7). In comparison, the pH of the plateau formed at the end of carbonation was 6.34. The theoretical pH of a similar system calculated by PHREEQC, assuming formation of calcite, was 6.50 (table 1). Repetitions of the same test (table 2) led to a mean experimental value of 6.46±0.06. The difference between this mean and the theoretical value (-0.04) suggests that calcite is the most likely phase formed. To ascertain which phase had precipitated, the mesh was observed using a SEM.

Table 2. Experimental pH values recorded at the end of the carbonation tests of a saturated $Ca(OH)_2$ water solution at different p_{CO2} and at 23°C.

p_{CO2} (atm)	1st test	2nd test	3rd test	average	St. Error
0.750	6.13	6.06	6.17	6.12	0.03
0.167	6.34	6.56	6.47	6.46	0.06
0.039	6.95	6.78	6.85	6.86	0.05

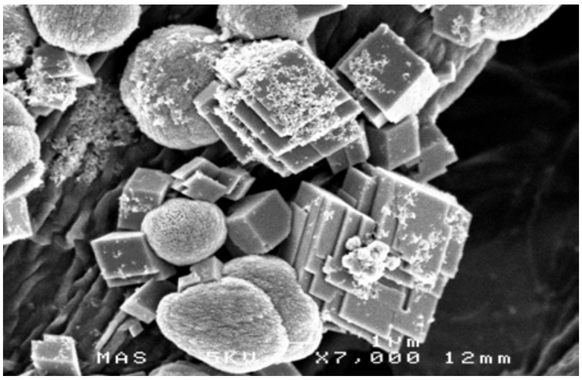

Figure 2. FE-SEM images of the cellulose mesh with calcite. The sample was previously coated with chromium to avoid charging in the SEM chamber.

Figure 2 shows the morphologies of the main solid phase found on the cotton lint. The rhombohedral crystals are characteristic of calcite formations while the round particles among some of the rhombohedra are characteristic of vaterite. Results of the SEM analysis were confirmed by X-ray diffraction. More details on these tests and the results obtained are reported in [8].

5. CONCLUSIONS

This study demonstrates that pH micro-sensors manufactured from nano-structured PdH can operate reliably in very alkaline environments such as those produced by the dissolution of $Ca(OH)_2$. The electrodes were successfully employed to monitor the pH changes during carbonation in a porous substrate exposed to different p_{CO2} and the pH detected in situ was found to be in perfect agreement with the theoretical calculations made with PHREEQC. To our knowledge, these microelectrodes are currently the only analytical tool capable of monitoring high pH in confined places. For this reason these electrodes can be considered very valuable for the study of reactions involving building materials.

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