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Nano-pH Sensor for the Study of Reactive Materials

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We report the development of a new iridium oxide nano-pH sensor designed to work in the range of pH 3–14. The fabrication process of reproducible iridium nanotips is described. The nanotips are covered by an insulating layer of parylene to ensure a chemical insulation. The use of a gallium focused ion beam enables the opening of the apex, leading to a sensing area of 100 nm diameter. A 12 h oxidation of the iridium tip in an oxygen atmosphere gives in a stable pH response. The calibration curve in buffer solutions exhibited a Nernstian behavior (slope 59.2 mV/pH). The distance control between the sample and the nanosensor is performed by atomic force microscopy (AFM), using either a shear force control or an inverted AFM configuration. The results of the hydration of two reactive samples, tricalcium silicate and tricalcium aluminate, having a size of 50 μm only, are presented.

The pH measurement of reactive materials or cells at a micro- or nanoscale is still a challenging issue. In biology, the knowledge of the pH variations at the surface of cells, or from samples of a few microliters only could help in better understanding biological processes. In chemistry, in the case of multiphase samples (like cement), it is currently impossible to study the local hydration of the different phases at a microscale. Here, we aim at developing a micro- or nano-pH sensor stable at pH up to 14, since the cement hydration is highly alkaline (pH \sim 12.5). As regards the pH microsensors found in the literature, glass micropipettes with H-ionophores have been widely used for years in biology to study the pH of samples with a resolution of a few micrometers.¹ The main problem of the ionophores is their chemical stability, limited to a pH range between 4 and 11, since they usually are derived from amino or pyridine compounds.² Many groups tried to use a dye sensitive to the pH, fixed at the end of an optical fiber.³ Usually the tip has a diameter of a few tens of micrometers⁴ and a limited spatial resolution. Some other groups tried to improve this approach by the use of SNOM (scanning near-field optical

microscopy) fibers, having a diameter of a few tens of nanometers.⁵ The main problem encountered in the use of optical fibers is a “memory” effect of the dye, making it rather difficult to follow fast pH changes. Moreover, the fluorescence signal is usually sensitive to temperature variations, as already observed in the case of calcium-sensing dyes.⁶ In the case of SNOM fibers, another problem is the lack of optical signal due to the size of the apex. Other groups tried to functionalize AFM (atomic force microscopy) cantilevers,⁷ by the deposition of layers of Al_2O_3 or NH_2 -silanes. But, in this case, the whole cantilever reacts over a few hundreds of micrometers, making it impossible to localize the signal. Another interesting approach is the chemical pH mapping^{8,9} in which an array of pH sensors is used to collect information from a sample (usually cells) spread over it. Unfortunately, either the spatial resolution is a few hundreds of micrometers⁸ or the optical fibers array used has the same aforementioned problems of dye stability.⁹ Moreover, in both cases, the pH range is limited from 4 to 8. Another approach is the deposition of a metal-oxide pH-sensitive layer on a microelectrode. Pd deposited on Pt microdisks¹⁰ has unfortunately a rather short lifetime (a few hours) because of its sensitivity to the oxygen in the air. WO_3 deposited on a tungsten nanotip¹¹ (diameter of about 800 nm) led to a rather stable pH sensor, but the signal comes from the whole tip (not covered). Nevertheless, this nanotip shape is very interesting for local sensing. Some other groups tried the deposition of iridium oxide on carbon microelectrodes¹² or glass micropipettes.¹³ Iridium oxide seems to be the most promising material for pH sensing.¹⁴ It has been used since the mid-1980s and is known to have a rather low sensitivity to redox interferences due to other ions.^{15–17} There are many ways of

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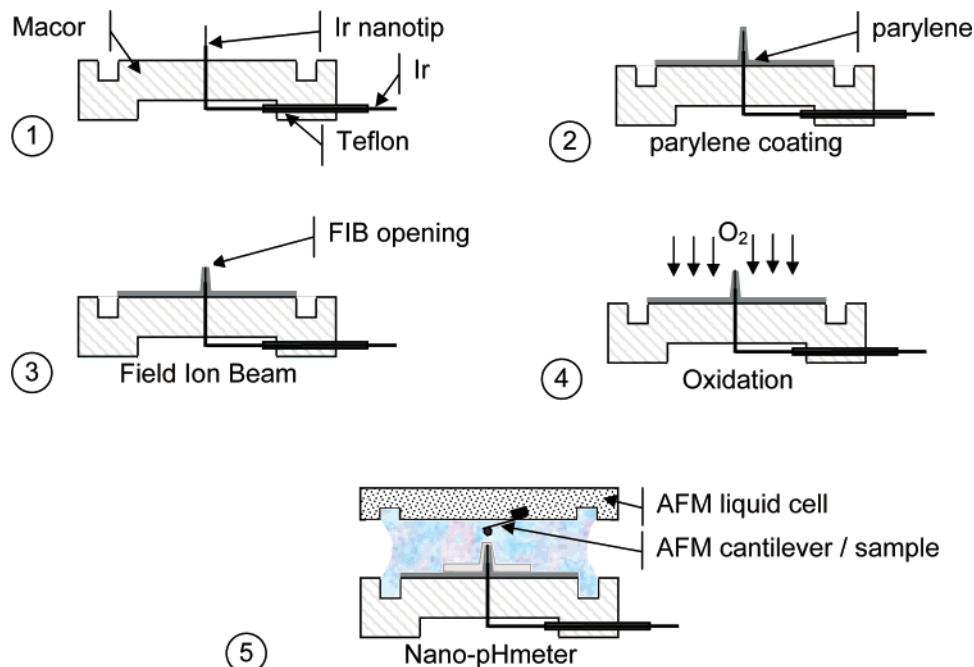


Figure 1. Fabrication steps of the nano-pH-meter.

depositing iridium oxide: electrochemical growth by anodic deposition,^{18,19} sputtered coating,²⁰ or thermal oxidation.²¹ An excellent review has been written on the subject by Yao et al.²² The main problem of the iridium oxide films is their stability, especially in the case of anodic deposition:¹⁸ the iridium oxide tends to dissolve in water, inducing long-term drifts of the signals. Yao et al.²² proposed a new synthesis of iridium oxide from the thermal oxidation of an iridium wire in the presence of lithium carbonate. The resulting thick layer is very stable even after a few years.²³ We have tested this synthesis, and it works fine. The main problem comes from the thickness of the iridium oxide layer (about 20 μm or more), not dedicated to pH sensing at a nanoscale. We nevertheless decide to use iridium oxide as a pH sensor, since it seems to be the most stable of all the metal oxides, even at pH values near 14 (pH of the cement hydration).

In the present work, the synthesis of a new pH sensor from an iridium nanotip, dedicated for measurements of pH at a nanoscale, is presented. Even if there are many papers on the synthesis of Pt/Ir nanotips for STM (scanning tunneling microscopy),²⁴ there is no publication on the synthesis of pure iridium nanotips. With our pH nanosensor, we characterize the surface reactivity of cementitious materials and their hydration kinetics as a function of time.

EXPERIMENTAL SECTION

Synthesis of Iridium Nanotips. Iridium wire (150 μm diameter, Goodfellow, purity 99.9%) was chemically etched in a solution made of 6 g of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 11 mL of bidistilled water at 18 M Ω . This solution was placed on 25 mL of chloroform (99.9%, VWR) in a dish of 4.5 cm diameter and 2.5 cm high. The chloroform is used for its insulating property. The height of the etching solution was limited to 5 mm. The cathode is composed of four graphite electrodes, ensuring a homogeneous field around the wire. A copper mass of about 50 mg is fixed at the end of the iridium wire in the chloroform to ensure that the wire remains straight during the whole etching. The etching is made with an ac current (400 mA, 50 Hz) and manually stopped when the copper mass falls. The fabrication of an iridium nanotip takes approximately 30 min. The reproducibility of the nanotips is controlled by a field-emission gun scanning electron microscope (FEG-SEM) (JEOL 6500, Japan), as in Figure 2, and by optical microscopy.

Preparation of the pH Nanosensor. The fabrication steps of the nano-pH-meter are described in Figure 1. An iridium nanotip is bent with a pair of tweezers at about 1 cm from the tip and fixed in a ceramic holder by fresh epoxy resin designed for vacuum applications (Varian Torr Seal). This glue is very stable under water at any pH with no detectable thermal drift. A Teflon sleeve is used to protect the longer part of the iridium nanotip (opposite to the tip) during the other steps of the fabrication. Once the epoxy resin dried, a parylene coating (200 nm thick, SCS Cookson Electronics, U.K.) is deposited over the whole nanotip. The thickness of the layer has been determined to be the minimum one ensuring a good electrical insulation: after the deposition of parylene, we checked that the potential of the iridium electrode versus a Ag/AgCl electrode remained the same whatever the pH of the buffer solution (from 3 to 14), meaning no sensitivity to the pH. In this way, we are sure that the whole tip does not give any signal, except the apex opened in the next step.

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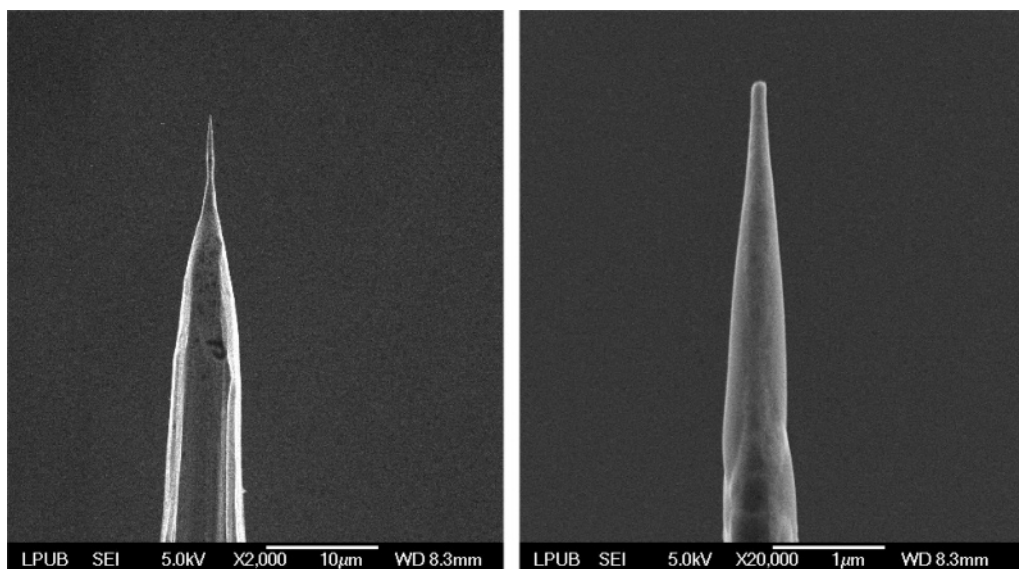


Figure 2. Example of iridium nanotip. Bars: left 10 μm , right 1 μm .

This opening is done by a gallium focused ion beam (FIB, from FEI, Hillsboro, OR, XP Dual Beam). The last step is the oxidation by oxygen during 12 h. The distance control between the sample and the nanotip is described elsewhere²⁴ and summarized here. We use an atomic force microscope (AFM Nanoscope III, Veeco, CA). The samples (tricalcium silicate and tricalcium aluminate, Lafarge Research Center, France) are stuck on AFM cantilevers (DNP Si_3N_4 probes with a spring constant of $0.12 \text{ N}\cdot\text{m}^{-1}$, Veeco, CA) with some epoxy glue (Varian Torr Seal). An approach is done in the air to locate the sample. Once the contact found, the sample is lifted up to 50 μm to avoid any alteration of the nanotip during the injection of water. The acquisition is started a few seconds before the injection of water. Once the water is injected, the signal from the laser on the AFM tip is manually recovered (since air and water do not have the same optical indexes) and the approach is done in solution. This phase takes approximately 40 s during which the tip/sample distance is about 50 μm . Then, the contact between the sample and the sensor is found at a nanoscale and the measurement goes on.

The pH signal is measured by a digital multimeter (Keithley 2701, Keithley Instruments) at a rate of 4 points/s, after impedance adaptation (AD549JH, Analog Devices). The reference electrode is obtained by the oxidation of a pure silver wire (99.99%, diameter 250 μm , Goodfellow) in a 4 M KCl solution (99.0%, Acros). The potential difference between the silver wire and the graphite counter electrodes was kept at 1.5 V during 10 min, leading to a thick stable layer of AgCl on the Ag wire. This wire was then placed in a small tube of 2 mm diameter with a KCl solution at 1 M, separated from the solution under study by the use of a frit glass. The pH buffer solutions for the calibration are provided by VWR (pH 4, 7, 9, 12, and 13) and kept in a refrigerator to avoid their alteration. These solutions are equilibrated at the temperature of the lab during 1 h before any experiment. All the measurements are performed in less than 6 months after the opening of the buffer solutions bottles.

RESULTS AND DISCUSSION

Synthesis of the Nanosensors. The synthesis of the iridium nanotips is highly reproducible. The average tip diameter is 100

nm (standard deviation of 10 nm over 33 nanotips). The length of the tip was 1 mm, with a diameter of 500 nm over the last 10 μm (Figure 2). This very thin shape avoids the perturbation of the fluid flows in solution at a nanoscale. In order to make a pH sensor from these iridium nanotips, we first tried the oxidation described by Yao et al.,²² in the presence of lithium carbonate. As expected, the iridium oxide layer obtained was much too large for nanosensor use (about 20 μm). We tried to decrease the oxidation time, but it led to a decrease of the stability of the pH signal. Moreover, the coating of such a surface was rather difficult to control at a nanoscale, since a large amount of insulating layer was required. We tried to use a Nafion coating as suggested by Kinlen et al.²⁶ on iridium oxide samples, but it only led to drifts and a large increase of the response time (more than 20 min). Therefore, we tried here to use a softer oxidation for our iridium nanotips. By measuring the pH response of the latter without any oxidation, we noticed that they are sensitive to the pH, even if the signal was unstable (Figure 3a). We tried an oxidation by the use of an oxygen plasma (5 min at 0.1 mtorr, 150 W), which led to a much more stable signal (Figure 3b). Note that the acquisition time was about 3 h, meaning a really stable signal, especially for pH 7 and 9. SEM observations showed that the nanotips were etched over a few hundreds of nanometers but kept their very thin shape with a tip diameter of about 100 nm (isotropic etching). The main problem of the use of a plasma was the destruction of the parylene coating. Therefore we tried to let the oxygen of the air oxidize the nanotips after cutting the end of the tip with an FIB.

The parylene deposition on nonoxidized iridium nanotips led to a uniform and smooth surface. The opening with an FIB led to nanosensors having a diameter of less than 100 nm (Figure 4). The oxidation of the iridium nanotips was done by the oxygen in the air. It was enough to oxidize such a small surface and to lead to a stable pH response, contrarily to Figure 3a, in which the whole wire over 2 cm was tested. The pH response was Nernstian (slope 59.2 mV/pH), and the confidence interval at 95% showed that the pH can be determined with a precision of about ± 0.2 pH unit.

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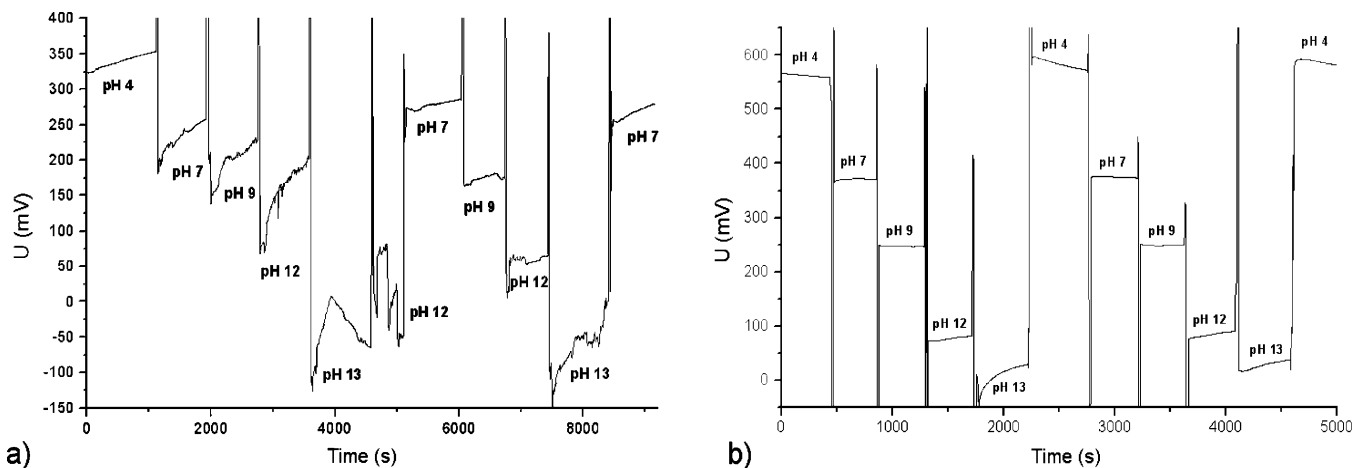


Figure 3. pH response as a function of time of the iridium nanotips before (a) and after (b) O₂ plasma oxidation.

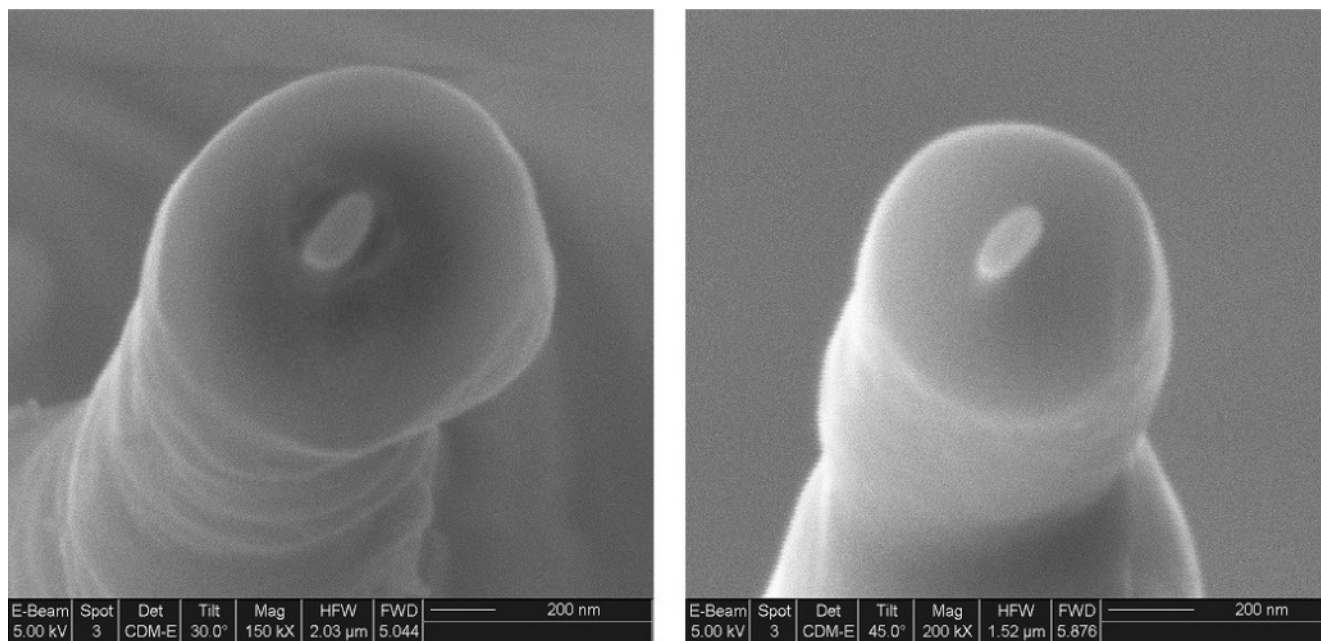
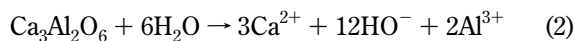
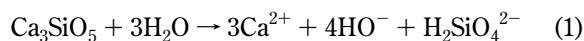


Figure 4. Two iridium nanotips after oxidation (nano-pH-meters). The iridium appears clearly in the middle by contrast. Bars: 200 nm.

Measurements at a Microscale of the Hydration of Tricalcium Silicate and Aluminate. We studied the hydration in distilled water of tricalcium silicate (referred as “C₃S”) and aluminate (referred as “C₃A”), two widely used components of cements:



The names “C₃S” and “C₃A” correspond to international abbreviations in the cement industry. The samples (average size of about 50 μm) were glued on AFM tips. As shown in Figure 5, the dissolution of C₃S led to a short increase of the pH during the first 5 min, and then the presence of distilled water decreased the pH from 8 to 6.5 (CO₂ from the air). The size of the sample was only 50 μm. To our knowledge, it was the first time that the pH evolution of a reactive sample during its hydration was followed at a nanoscale. We expected a much higher pH (near 13 or 14)

because of the large amount of OH[−] ions liberated during the hydration (eq 1). Since the distance between the sample and the nanosensor was about 50 μm during the first 40 s of the experiment (before the contact), the distilled water at pH 6.5 may have had enough time to react with OH[−] ions at a nanoscale near the sample. We know indeed that the hydration of reactive samples can lead to very high thermal peaks (up to a few hundreds of degrees Celsius) at a nanoscale,²⁵ thus inducing large fluid flows. The hydration of C₃A led to another phenomenon: the pH increased to 8 and decreased very slowly. It was still at about pH 8 even after 20 min (Figure 6). From eq 2, the hydration of C₃A leads to more OH[−] ions in solution than C₃S, which could explain this behavior. We performed other experiments with other C₃S and C₃A samples in the same conditions and observed the same phenomena. We checked that the pH response during the hydration of C₃A was not an artifact: after the previously described measurement, we washed the nanosensor with distilled water and injected a pH 7 buffer solution. The pH measured by the sensor in this buffer solution was 7 and not 8. There are two possible

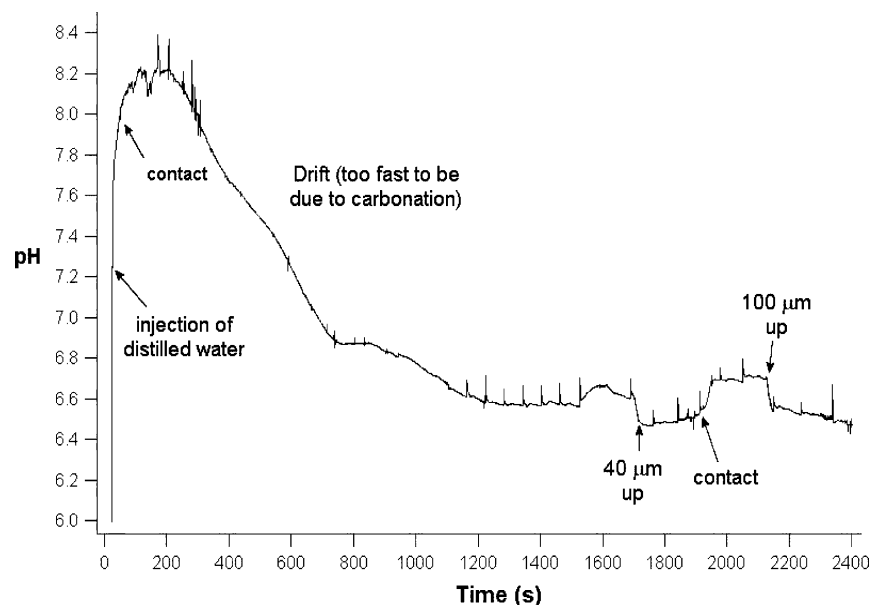


Figure 5. pH response as a function of time of an iridium nano-pH-meter during the dissolution of a tricalcium silicate (C_3S) sample in distilled water.

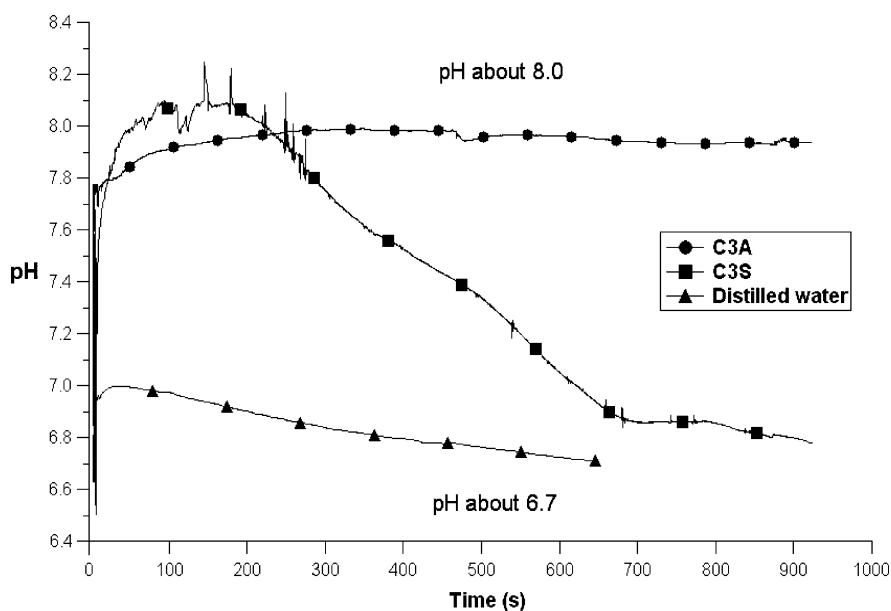


Figure 6. Comparison of the pH responses as a function of time for distilled water alone and for C_3A and C_3S samples hydrated in distilled water.

explanations: a piece of C_3A stuck on the sensor at each experiment, or the dissolution of C_3A is slow enough to lead to an equilibrium between the OH^- ions from the sample and the surrounding distilled water at pH 6.5. Nevertheless, our pH nanosensor could clearly distinguish the behaviors of two different samples of $50\ \mu m$ only, which was impossible to study in any other way.

CONCLUSIONS

We have presented a new nano-pH sensor which enables for the first time the measurement of pH variations during the first minutes of the hydration of reactive materials in solution. This nanosensor is made of an iridium nanotip having a diameter of about $100\ nm$, covered by a parylene layer of $200\ nm$, and an active surface of less than $100\ nm$. The calibration curve showed that the pH signal in buffer solutions is stable over a few hours without any drift at pH 7 and 9 and a limited one at pH 4 and 13.

The hydration of tricalcium silicate and aluminate samples, having a size of only $50\ \mu m$, led to OH^- ions that could be detected at a nanoscale, with a pH increase at about 8. Since samples down to a few micrometers or of a few microliters only can be easily studied, the potentialities of this new nanosensor in biology are under study.

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