

FIBEROPTICAL SENSORS IN CONCRETE

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Abstract. Buildings of reinforced concrete are exposed to a variety of damaging influences. In particular, moisture has an important influence on the lifetime of concrete structures. This is caused by the involvement of free water in corrosion of the steel and the fact that water acts as a transport medium for damaging ions such as chloride, sulfate, carbonate and ammonium. Thus, we have developed fiberoptical moisture sensors, which allow an in-situ non-destructive long-term monitoring of concrete structures. As indicator we use a pyridinium-N-phenolat betain (Reichardt's dye), which shows a high solvatochromic behavior. The dye is embedded in a polyacrylonitrile polymer matrix whose polarity is enhanced by free water diffusing into the sensor. This leads to a continuously hypsochromic shift of the absorption spectrum in dependency on the water concentration. Without moisture the sensor shows a peak-wavelength in the absorption spectrum at 602 nm. The wavelength is shifted about 40 nm to 562 nm by a maximum relative concentration of water in the matrix (28 wt%). This behavior is fully reversible. We use the same sensor concept to measure the pH-value in the concrete by using an azo-dye as pH-indicator. So we applied fiberoptical moisture sensors as well as pH sensors to observe chemical attack at a concrete testing structure. The structure has been developed in a cooperation with different research groups of chemists, electrical engineers and civil engineers in a collaborative research project to study the damaging influences of moisture and different ions on concrete.

Keywords: Fiberoptical Sensor, Moisture Sensor, pH Sensor, Polymer, Concrete.

1 INTRODUCTION

Buildings have an enormous economic importance. While investments in new buildings decrease rapidly, the maintenance costs increase in like manner. The overall value of all buildings in Germany amounts to approximately 25 billion Dollars. Assuming a mean life cycle of about 100 years (optimistically), 2.5 billion Dollars are needed year by year for reinvestment. Using appropriate monitoring procedures, the service life of structures can be extended considerably, or they can be rehabilitated and put to new use in a way conventional standards would never permit.

Concrete is one of the important building materials. It is an inhomogeneous porous material which pH-value is normally in the range of 11 to 13. The high pH-value is caused by the dissolution of calcium-hydroxide in the pore-liquid. In reinforced concrete this basic environment produces an inert surface and protects the steel against corrosion. Exhaust fumes like CO₂ and SO₂, which are soluble in the pore-water, react to carbonic acid and sulfuric acid, respectively. This leads to a decrease in the pH-value during the lifetime of concrete structures. Thus, both the calciumsilicate hydrate crystals of the concrete and the protecting oxide layer on the reinforcement steel are converted such that a concrete structure might fail. In special cases other chemical specimens like ammonium can reduce the pH-value in concrete as well. All these chemical damaging processes require the presence of water. To judge the condition of a concrete structure it is therefore necessary to observe the moisture content and the pH-value in the material [1].

For this purpose we developed fiberoptical sensors to facilitate non-destructive long-term in-situ monitoring of the moisture content and the pH-value in concrete structures.

2 FIBEROPTICAL SENSORS

Fiberoptical sensors are well known since more than twenty years [2-5]. Generally, the probe of an optical sensor consists of an indicator whose optical properties, e.g. refraction, fluorescence or absorption are influenced by the environmental condition. In consequence light will be changed in intensity, phase or polarity. The change of the optical signal can be used to monitor the state of the surroundings.

Some properties of fiberoptical sensors are listed below:

- no interference with electromagnetic fields
- no galvanic connection between sensor and analytical unit
- durability in extreme environmental conditions and high resistance against chemical attack
- low optical loss of the fiber allows long distance measurements
- low-priced

Hence, high flexibility, environmental stability, trouble-free behavior and low costs are the basic advantages of fiberoptical moisture sensors designed for non-destructive in-situ monitoring of concrete structures.

2.1 Measurement Setup

Figure 1 shows the measurement setup for the developed sensors. The light of a lamp with a continuous spectrum in the visible range is focused on the facet of a fiber. As source we use a combined Deuterium-Halogen lamp with an integrated lens system. As an alternative for short distances a white light LED can be used. The light is guided to the probe that is designed as an extrinsic sensor. A sensitive thin polymer film with a characteristic extinction is illuminated. The light is reflected back into the same fiber by an integrated mirror. The resulting absorption spectrum is coupled through a 3dB-coupler and analyzed with a Microspectrometer. This spectrometer includes a grating that splits the light into its spectral components and, simultaneously, focuses these onto a single line CCD chip. This measurement principle yields a complete spectrum almost instantaneously, thus, avoiding time consuming measurements.

To monitor a variety of sensors we use a fiberoptical switch (not shown in the figure). The control of the spectrometer and the switch as well as the analysis of the recorded spectra is done by a PC.

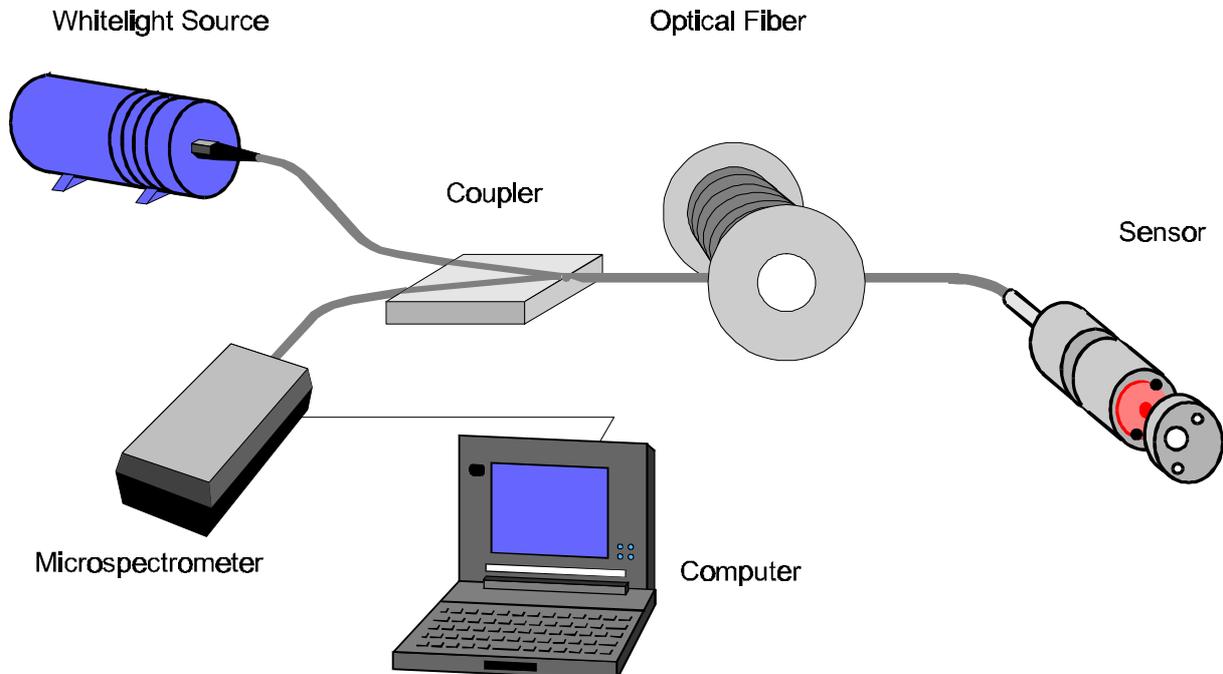


Figure 1. Scheme of the fiberoptical sensor measurement setup.

2.2 Moisture Sensor

To measure the moisture content of concrete, i.e. the free movable water in the pores, it is necessary to create reproducible moisture dependent proportions within the probe. Therefore the optode consists of a polymer matrix made of polymethacrylonitrile (PMAN). When the concrete is in direct contact with the polymer, water diffuses through the materials until an equilibrium of diffusion is reached.

The water-content in the polymer matrix was determined by a solvatochromic dye. We use a pyridinium phenolate betaine. The absorption spectra of the dye, dissolved in acetonitrile at various water concentrations are shown in Figure 2 [6]. An increase in water content leads to a continuous hypsochromic shift in the absorption spectrum. Different water concentrations show definite spectra, so the moisture content can be extracted from the peak wavelength of the absorption spectrum.

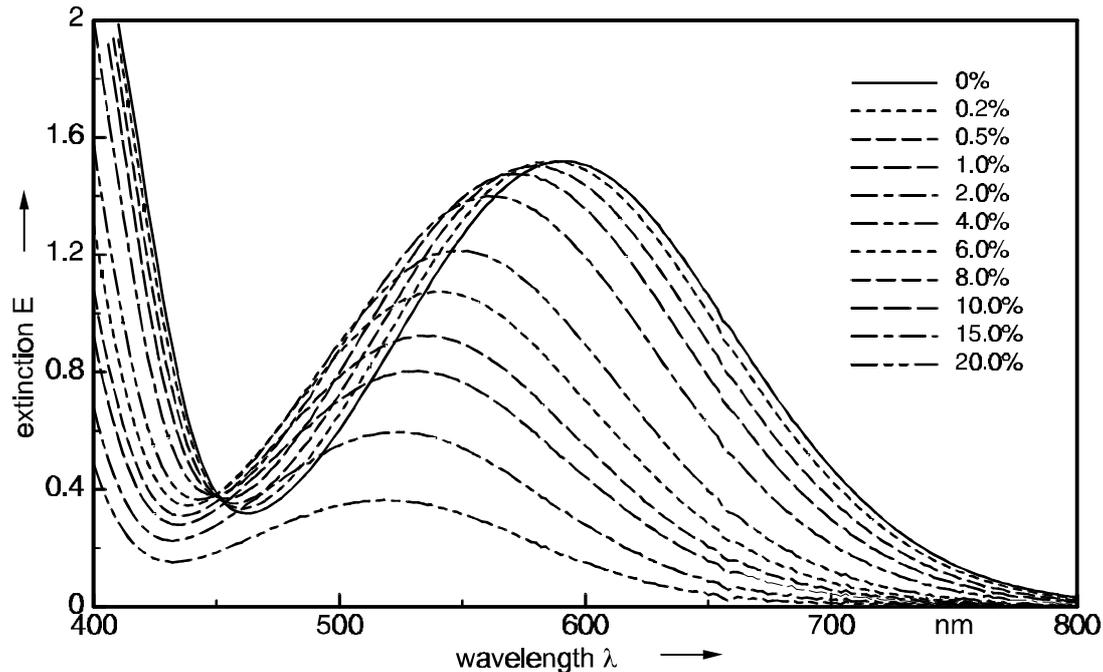


Figure 2. Absorption spectra of the indicator dye in acetonitrile at various water concentrations.

The polymeric matrix in a moisture sensor must possess a moderate hydrophilicity in order to absorb a limited amount of water. The water content of the polymer shall adequately represent the water content of the surrounding building material. Furthermore, the polarity of the polymer has to be carefully chosen, because the matrix has to be insoluble in aqueous media and the polarity should still be increased by the presence of water in order to cause a spectral shift of absorption. The polymer has to be soluble in common organic solvents with fairly low boiling points, as the sensor matrix has to be processed and conditioned in order to ensure transparency as required for optical measurements. Therefore, polymers have been examined which showed limited swelling ability. In this respect polymethacrylonitrile (PMAN) was found to be a promising candidate for sensor applications.

For the sensor calibration, climate boxes for various definite humidity levels were used. The dye and the polymer were dissolved in acetone and dropped onto a thin glass substrate. After evaporation of the solvent and drying at 70°C, the probe was placed into the boxes and the absorption spectra were successively recorded until no further changes occurred. The peak-wavelength of the spectrum was determined by Mathias rule [7,8]. This geometrical procedure is very suitable for the determination of the maximum of a broad absorption band. A number of equidistant horizontal lines are drawn within a region of 10 to 15% from the maximum extinction. The half-radii of this secants are then connected by a straight line. The point of intersection of this line with the data gives a very good approximation of the maximum wavelength.

The relative water concentration was measured by a standard weight-procedure. The calibration curve of PMAN is depicted in Figure 3. When dry, the sensor shows a peak-wavelength in the absorption spectrum at 602 nm. The wavelength is shifted about 40 nm to 562 nm by a maximum relative concentration of water in the matrix (28 wt%).

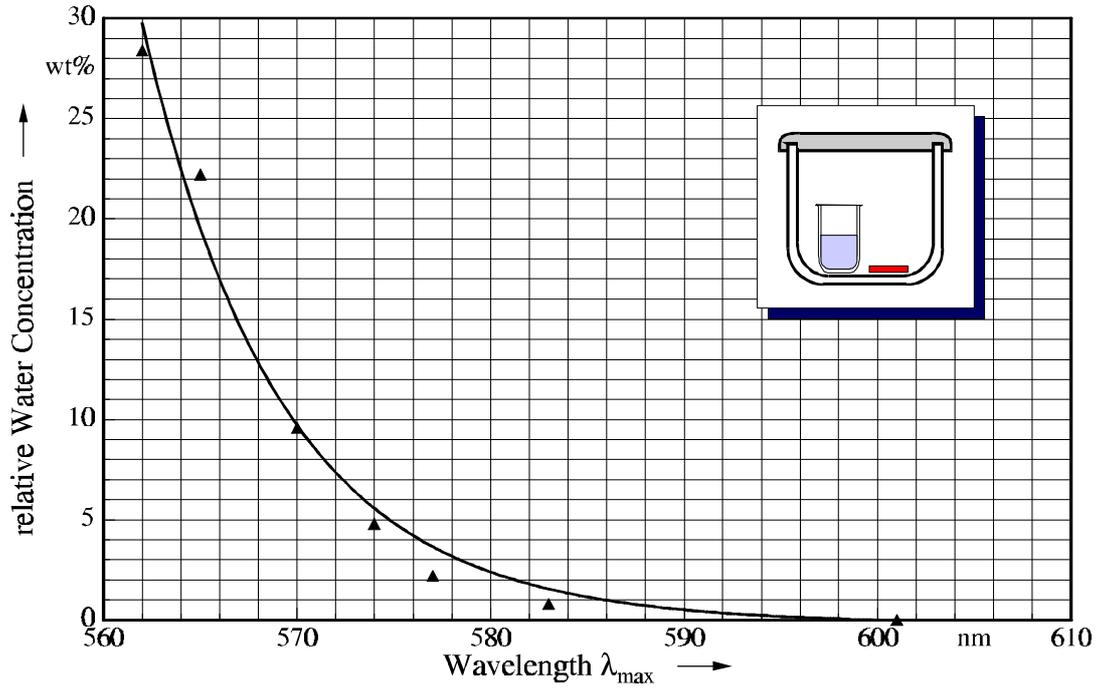


Figure 3. Calibration curve of PMAN.

The wavelength λ_{max} of the maximum of the absorption spectrum represents the polarity of the surroundings, which can be described by the empirical polarity parameter $E_T(30)$ [6,7]. The correlation between the polarity and the maximum wavelength is shown in equation (1).

$$E_T(30) / kcal \cdot mol^{-1} = \frac{28590}{\lambda_{max} / nm} \quad (1)$$

The polarity parameter $E_T(30)$ of a binary mixture can be calculated using equation (2). $E_T^0(30)$ is the polarity parameter of the component with the lower polarity, i.e. the polymer, and c is the concentration of the more polar component, i.e. the water content in the polymer. $c^\#$ and $E^\# = 28590 [kcal \cdot nm] / E_D$ are the two parameters of the equation to be calculated from the measured data.

$$E_T(30) = E_D \cdot \ln \left(\frac{c}{c^\#} + 1 \right) + E_T^0(30) \quad (2)$$

Using equation (1) and (2), one can derive an expression for the dependency of the maximum wavelength on the water content (3), with λ_{max}^0 as the maximum wavelength of the dry polymer/dye system.

$$c = c^\# \cdot \left(\exp \left(E^\# \left(\frac{1}{\lambda_{max}} - \frac{1}{\lambda_{max}^0} \right) \right) - 1 \right) \quad (3)$$

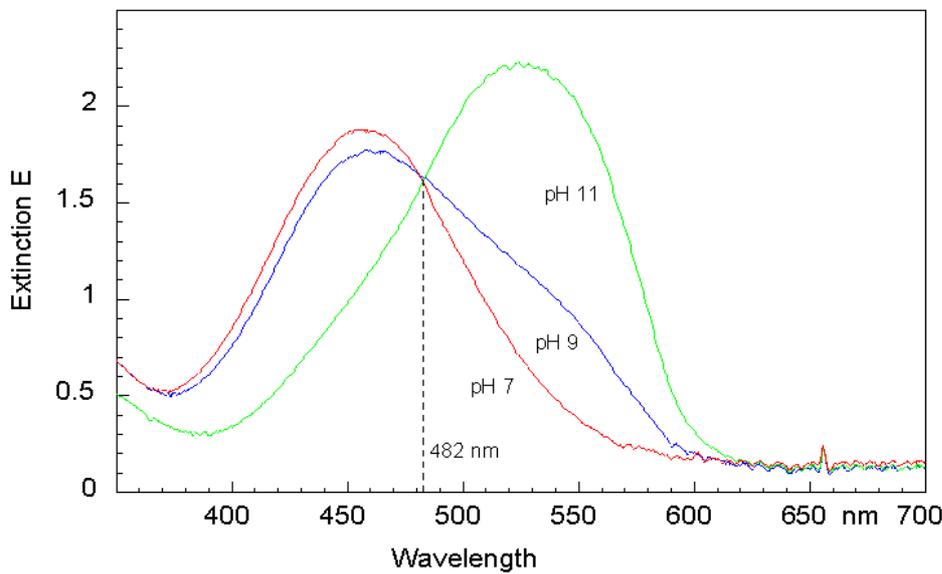
To fit our measured data (triangle in figure 3) we use equation (3). The parameters are calculated to be $E^\# = 44.260,14 \text{ nm}$ and $c^\# = 0,204$. The results are shown in figure 3 (solid line).

2.3 pH-Sensor

The measurement of pH-values in wet concrete is very important for a comprehensive evaluation of stability and corrosive damage in reinforced concrete. It is usually assumed that pH-values less than 9 lead to premature corrosive damage of reinforcement steel. It is therefore of great interest to develop a pH-sensor that is capable of indicating a decrease of basicity in the pore solution. In order to use an all-optical setup we synthesized an indicator dye that covers the relevant pH-range from 7 to 11. It shows a pH-dependent colour change from red (λ_{max} 535 nm, pH 11) to yellow (λ_{max} 452 nm, pH 7), due to the deprotonation of a phenolic OH-group in the conjugation pathway of the chromophore. The pH-values are determined by measuring the dye's absorption at 535 nm where maximum changes occur (see figure 4). The absorption value is related to the constant absorption of the system at 482 nm, i.e. the isosbestic point of the dye. This internal reference made it possible to

determine the pH-value quantitatively by using only one indicator dye.

To prevent loss of dye, the indicator was covalently attached to a hydrophilic polymer host using a reactive functional group (vinylsulfone). The polymer, consisting of a carbohydrate material, is supported by a polyester foil that provides improved handling properties and stability for technical sensor

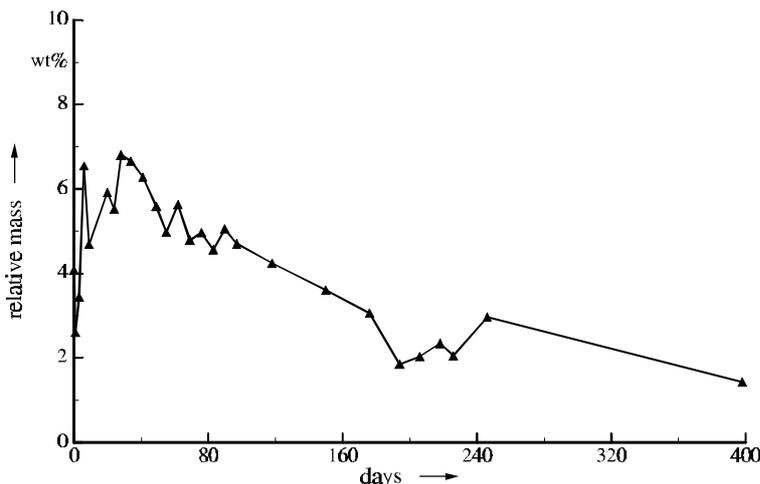


applications.

Figure 4. pH dependence of the absorption spectrum of a carbohydrate foil.

3 RESULTS

To test the functionality and the long term stability of the moisture sensors we installed them in a small concrete structure with dimensions of about 30 x 30 x 60 cm³. We stored this cubic testing structure under room conditions at a temperature of 22°C and a relative humidity of about 40% in the laboratory. The results of the first year are depicted in figure 5.



The moisture content can be determined by using the principle of balanced moisture. The salt solution in the concrete, i.e. the pore liquid, causes a relative humidity level in the pores of the material. Thus, we get a definite moisture content within the sensor. The relation between the relative humidity and the water content of a material is described by the sorption-isotherm. To calculate the relative mass of the moisture

content from the measured data we used the sorption-isotherm of concrete given in [9].

Figure 5. Drying process of a cuboid concrete testing structure.

A larger concrete test structure, shown in figure 6, was developed and built in May 1999. The outer surface of the structure is subdivided into four areas, which were exposed to solutions of NaCl, Na₂SO₄, NH₄NO₃ and CH₃COOH. A further area was only exposed to the weather. The test structure, formed like a "C", was prestressed to produce cracks in the outer surface, leading to an increased transport velocity of the damaging chemicals.



In this structure, a number of different sensor-types for the detection of corrosion activity or the measurement of the temperature have been installed as well as fiberoptical sensors for the measurement of the pH-value. Since the last 6 month, the sensors, mounted in a depth of 4 cm, haven't show any changes, since the velocity of the acid front is very low in spite of the cracks.

As a further test we are planning to install fiberoptical moisture sensors. They shall be included additionally in the test structure to investigate the possibility of a later instrumentation of buildings.

Figure 6. Concrete testing structure.

4 ACKNOWLEDGEMENT

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