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Assessment of the effectiveness of potentiometric sensors for measuring the pH of concrete

Ocena skuteczności działania czujników potencjometrycznych do pomiaru pH betonu

The paper presents the results of long-term tests of pH-metric potentiometric sensors containing metal oxides in concrete, using the example of manganese oxide. Unfortunately, their long-term effectiveness in natural conditions is not known. These tests showed their poor effectiveness in determining the pH value under variable moisture conditions of concrete. The jumps in the potential of the pH sensors resulting from changes in humidity significantly exceeded the so-called theoretical Nernst response (59.16 mV per pH unit), which disqualifies them from monitoring changes in the pH of liquids in concrete pores in natural conditions.

Keywords: corrosion, carbonation, pH

W pracy przedstawiono wyniki długotrwałych badań pH-metrycznych czujników potencjometrycznych w betonie zawierających tlenki metali, w tym wypadku tlenek manganu. Nie ustalono dotychczas, czy działają prawidłowo po długim czasie w warunkach naturalnych. Badania wykazały ich słabą skuteczność w określaniu wartości pH przy zmiennych warunkach wilgotnościowych betonu. Wynikające ze zmiany wilgotności skoki potencjału czujników pH znacznie przekraczały tzw. teoretyczną odpowiedź Nernsta (59,16 mV na jednostkę pH), nie mogą być więc stosowane w monitorowaniu zmian pH cieczy w porach betonu w warunkach naturalnych.

*Słowa kluczowe: korozja, karbonatyzacja, pH*

1. Introduction

The development of systems for the recording and time control of physical and chemical parameters is increasingly being used to monitor building structures. This solution is particularly desirable for monitoring reinforced concrete structures in very aggressive environments that can cause corrosion of the reinforcement. One of the factors causing reinforcement corrosion is a reduction in the pH value of concrete to a level that causes depassivation of steel. Glass electrodes (commonly used to test the pH of solutions) may appear to be the natural choice for pH measurement, but due to great difficulties in their miniaturisation, the lack of long-term stability of the electrodes, their calibration capability, as well as their high brittleness, they are completely unsuitable for placement in concrete [1]. For this reason, potentiometric sensors are beginning to attract great interest and are now being successfully used to measure water quality, as well as in food processing, agriculture, pharmaceuticals and medicine [2].

This paper examines the behaviour of potentiometric sensors placed in concrete elements during several months of tests in which the moisture conditions of the concrete were significantly varied. The purpose of the tests was to verify the effectiveness of this type of sensor in continuously monitoring the pH of concrete.

2. Principle of pH measurement by potentiometric methods

The operating principle of potentiometric sensors is based on that of classical reference electrodes of the second type using a metallic conductor coated with an oxide of that metal. An example of such a half-cell is the antimony electrode. It consists of an antimony rod coated with a thin layer of antimony oxide Sb_2O_3 and immersed in a solution containing H^+ ions. The following reaction takes place at the H^+/Sb_2O_3, Sb electrode [3]:

$$Sb_2O_3 + 6H^+ + 6e^- = 2Sb + 3H_2O. \tag{1}$$
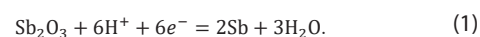
The potential of the above electrode in a solution containing H^+ ions can be expressed by the following formula and, after taking into account the definition of pH and converting the constants, the potential of the antimony electrode can be presented as:

$$E_{H^+/Sb_2O_3,Sb} = E^0_{H^+/Sb_2O_3,Sb} - \frac{RT}{6F}\ln\frac{1}{a^6_{H^+}} = E^0_{H^+/Sb_2O_3,Sb} - 0.05916\,pH, \tag{2}$$

where $E_{H^+/Sb_2O_3,Sb}$ is the standard potential of this electrode. In most cases, metal-oxide electrodes are hydrogen electrodes whose

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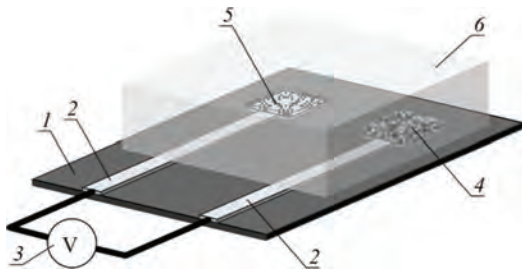
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Fig. 1. Structural scheme of metal oxide-based potentiometric sensor for measuring pH of a solution (description in the text)

Rys. 1. Schemat konstrukcji czujnika potencjometrycznego na bazie tlenków metali do pomiaru pH roztworu (opis w tekście)
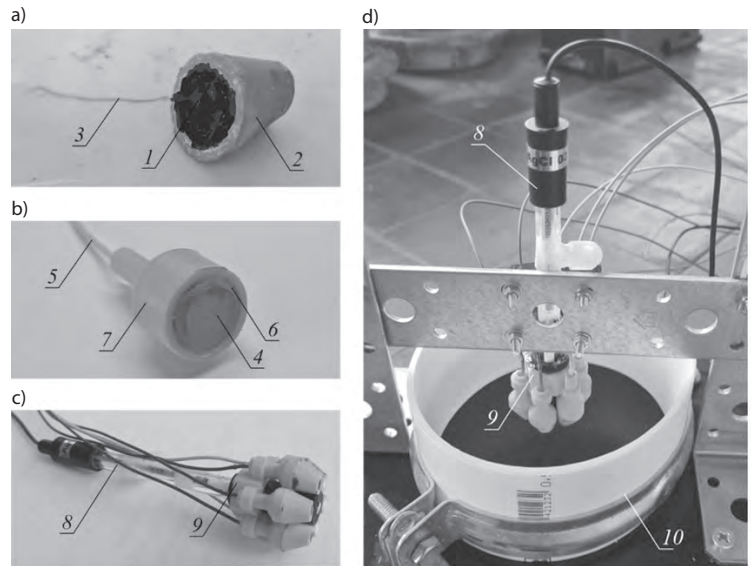

Fig. 2. Design of electrodes used in the tests (description in the text)

Rys. 2. Budowa elektrod wykorzystanych w badaniach (opis w tekście)

potential depends linearly on pH with a slope of −59.16 mV per pH unit, as shown in equation (2). The potential of a metal-oxide electrode can therefore be written as a function of pH according to the more general relationship of

$$E = E^0 - 0.05916\,pH, \tag{3}$$

where 59.16 mV per pH unit is defined as the so-called theoretical Nernst response.

Not only antimony oxide, but also many insoluble metal oxides placed in aqueous solutions can be used to determine pH. The following oxides are most commonly used to measure pH: IrO_2, RuO_2, PtO_2, TiO_2, SnO_2, CeO_2, PbO_2, Ta_2O_5 or mixed oxides Bi_2O_3–Nb_2O_5, IrO_2–TiO_2, RuO_2–TiO_2 [2]. Iridium oxide has the most common application due to its extreme sensitivity to hydrogen ions and high measurement accuracy. However, due to its extremely high price, it is mainly used in laboratories. Fig. 1 shows schematically the construction of a typical potentiometric sensor, where conductive layer 2 is applied on the same substrate 1, allowing the sensor electrodes to be connected to voltmeter 3. In contact with or on the surface of layer 2, metal oxide 4 and a substance forming solid reference electrode 5, e.g. Ag/AgCl, graphite, are applied. The closing of the system and the electrical contact of the two electrodes is provided by test solution 6 (liquid in the pores of the concrete). In principle, two techniques are used for the production of metal oxide substances, i.e. thin film application – by sputtering, electro-deposition, sol-gel [4] or a microelectronic fabrication technique called thick-layer screen printing, where oxides are added to a coating [5].

The use of metal oxide-based potentiometric sensors for pH measurement appears to be a good solution, mainly due to the simplicity of the measurements and the ease of application in monitoring systems. The main problem, apart from the lack of possibility to calibrate and check the sensors after installation in the concrete, is the stability of the potential with changing thermal and moisture conditions in the concrete. The effect of drying of concrete containing pH sensors and solid reference quasi-electrodes on the stability of their potential is presented in the following tests.

3. Experimental

Among the potentiometric sensor applications described in the literature, iridium oxide and ruthenium oxide are the most commonly used for measuring pH in concrete [5]. Their advantage is their high sensitivity, while a significant disadvantage is their price, which ranges from several hundred to several thousand PLN per 1 g. The use of these sensors in construction practice is therefore often not economically justified. In order to determine the effect of changes in concrete moisture on the pH sensors, tests were carried out on previously unproven inexpensive manganese oxide as a pH sensor (manganese oxide was normally used as a quasi-reference electrode [6]) and compressed graphite acting as a quasi-reference electrode [7]. Testing the graphite electrode for its potential stability with changes in concrete moisture is also necessary, as quasi-reference electrodes are also an important component of potentiometric sensors, as shown in Fig. 1.

As mentioned in point 2, thick-layer screen-printing techniques that utilise coatings are used for the application of powder substances. In the present study, a bonding substance made by dissolving polystyrene granules in toluene was used, which has been successfully applied to conductive coatings based on silver powder [8]. MnO_2 was added until paste 1 was obtained (Fig. 2a). Paste 1 was added in layers into housing 2 made of ABS plastic by 3D printing, and a silver plate with silver wire 3 was placed between the layers. A copper lead was connected to the wire, and the entire electrode was sealed and insulated with epoxy resin.

Graphite rod 4 without specified purity of 6 mm diameter was wrapped with silver wire, which was connected to copper wire 5 and then encapsulated in epoxy resin 6 in ABS plastic housing 7 (Fig. 2b). The front surface was mechanically aligned and polished with water paper.

Finally, three electrodes each were made and attached to glass-bodied chlorosilver electrodes 8 using printed dies 9 containing six electrode slots (Fig. 2c). The systems were concreted in circular moulds 10, a view of which before placing the concrete mixture is shown in Fig. 2d. The concrete in the moulds was de-
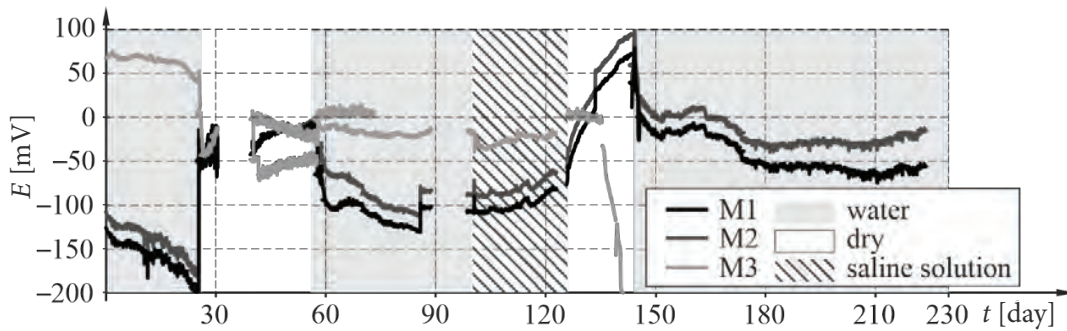
Fig. 3. Changes in the potential of pH sensors made of paste MnO₂ (M1–M3 – sensor symbols)

Rys. 3. Zmiany potencjału czujników pH z pasty MnO₂ (M1–M3 – symbole czujników)
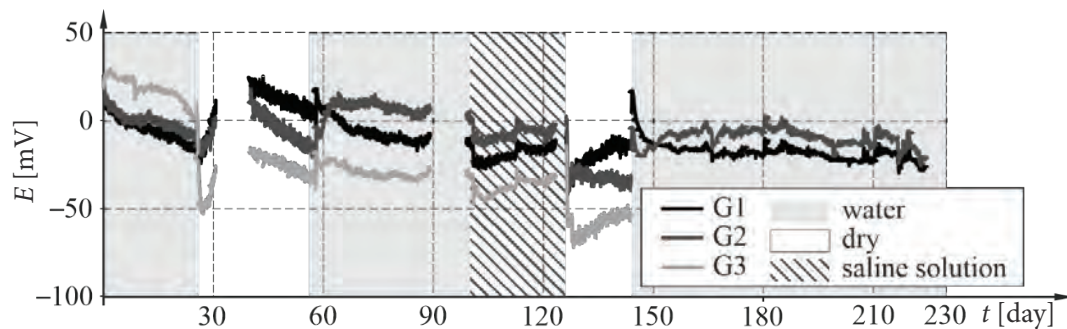

Fig. 4. Changes in the potential of graphite reference quasi-electrodes (G1–G3 – sensor symbols)

Rys. 4. Zmiany potencjału grafitowych quasi-elektrod odniesienia (G1–G3 – symbole czujników)

signed as class C20/25 using CEM I 42.5 R cement (at 324 kg/m^3) and natural aggregate up to 8 mm diameter (at 1931 kg/m^3) at a *w/c* ratio of 0.4 without additives or admixtures.

In order to monitor potential changes over a long period of 230 days, National Instruments DAQ data acquisition cards were used, which allow for measurements of e.g. potential difference. Readings were programmed at hourly intervals. All electrodes were connected to the corresponding connectors on the DAQ card at the same time, and potential changes were measured relative to the corresponding reference electrode concreted into the sample.

The overarching aim of the study was to test the effect of changing concrete moisture content on the potential values of the electrodes described above. The cycling of soaking in water and drying under laboratory conditions was not followed in replicating random near-natural conditions. Therefore, the samples were kept half immersed in tap water for an initial period of 26 days. The samples were then left under air-dry conditions in the laboratory for 30 days. Then again, for a period of 44 days, the samples were immersed half in tap water, and then in a period of 26 days the water was changed to a 3% saline solution. For a further 18 days the samples were left in air-dry conditions in the laboratory, and in the final step the samples were submerged halfway in tap water for a period of 86 days. The results of the paste pH sensors are shown in Fig. 3 and the graphite quasi-electrodes in Fig. 4.

4. Analysis

Long-term testing of the potentiometric sensors in concrete highlighted the clear effect of concrete moisture on the potential val-

ues. The breaks in the graphs in the figures shown were due to the failure of the recording devices (Fig. 3, 4).

In all the sensors, the potential decreased during the first stage of the tests when the samples were immersed in water, which may be related to the so-called potential drift, i.e. a long-lasting movement towards a certain constant value. Such a phenomenon is common in potentiometric sensors. On the other hand, pulling the samples out of the water caused a rapid change in potential and there was a tendency for the potential to rise in most sensors. The surge reached dozens of millivolts, followed by a stabilisation of the potential or even a decrease under the same conditions, similar to that with samples immersed in water. When placed back in water, the potential again gradually decreased.

Placing the samples in a 3% saline solution (to simulate a contaminated environment with high conductivity) slightly altered the trend to a slight increase in potential or stabilisation. Removing the samples from the wet environment (saline solution) caused a rapid change in the potential of the reference quasi-electrodes. Reintroduction of the samples into water induced a third potential drift, characteristic of immersion in water. This drift was less pronounced in the graphite electrodes.

The largest changes in sensor values were recorded for manganese oxide, which were around 300 mV (Fig. 3). When taking into account the so-called theoretical Nernst sensitivity of the electrodes (59.15 mV/pH), the error in pH values can be as much as 5 units. The potential differences of the graphite electrodes were smaller and amounted to about 100 mV.

The observed changes in potential with varying concrete moisture content are primarily related to the amount of water present

in the concrete pores. With the loss of water, the flow of ions is reduced and consequently the electrical resistance increases. A correct measurement of the *emf* of a cell is possible when there is a free flow of electrical charges between the electrodes (half-cells). A high resistance of the medium causes an incorrect voltmeter reading. In addition, the loss of water changes the concentrations of the ions involved in the reactions at the electrodes, which directly affects their activity and the change in potential. The above trends will have an effect on any type of potentiometric pH electrode based on metal oxides, including those already tested and found to be satisfactorily effective [5], as fluctuations in the amount of water in the concrete pores will cause the same type of measurement errors.

5. Conclusion

Long-term testing of potentiometric sensors in concrete has shown their poor performance in determining pH values under varying concrete moisture conditions.

The potential spikes of the pH sensors, resulting from changes in moisture content, significantly exceeded (by as much as several times) the so-called theoretical Nernst response (59.16 mV per pH unit), which disqualifies them for monitoring changes in the pH of liquids in concrete pores. Graphite electrodes showed a smaller amplitude of change.

The direct cause of the instability of the potentials of the electrodes tested was the changing moisture content of the concrete, which directly translated into fluctuations in the conductivity of the concrete. This in turn led to erroneous measurements of the potential difference of the electrodes due to the insufficient conductivity of the concrete. In addition, changes in the moisture content of the concrete affected the ionic activity on which the potential of the electrodes under test depended.

It cannot be ruled out that potentiometric sensors in concrete may prove their worth under constant humidity conditions, e.g. in internal liquid tanks, etc., but their measurement stability over a long period would need to be confirmed experimentally.

CRediT authorship contribution statement
Tomasz Jaśniok: Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

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