Title: MEASUREMENT OF ENVIRONMENTAL PARAMETERS IN CONCRETE

A combination of electrodes to be moulded into concrete with purpose of measuring environmental parameters in concrete. The combination comprises a plurality of sensor electrodes (1), each of which being comprised of substantially one material. The materials are chosen in such a way that the electrode potentials of the sensor electrodes as measured in relation to a reversible reference electrode (2), vary in a mutually divergent manner in relation to the environmental changes in concrete. By utilising this electrode combination values of the environmental parameters are calculated, and thus the corrosive environment for the reinforcement in the concrete is determined.
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MEASUREMENT OF ENVIRONMENTAL PARAMETERS IN CONCRETE

The present invention relates to the determination of the corrosive environment for reinforcement in concrete, and concerns in particular a combination of electrodes to be moulded into the concrete for the purpose of measuring environmental parameters in the concrete, such as the content of oxygen, the pH value and the content of chloride in the concrete pore water, and a device and method wherein such a combination of electrodes is used to determine said corrosive environment.

The corrosion of steel reinforcement in concrete creates problems of great importance for the society. If possible damage which may be caused by the corrosion of the reinforcements is discovered on the surface of a concrete structure, the damaging process has often gone so far that the concrete, and possibly also the reinforcement itself, must be removed and replaced. However, a concrete structure can also be weakened due to the corrosion of the reinforcements without being directly evident by inspection of the surface of the structure. The rate of attenuation may be so large that breakdown of the structure may result in the worst case without any clear warning in advance.

In this connection various technics have been developed for the purpose of asserting the corrosive environment of the reinforcement in a concrete structure. One way is to strip the reinforcement and by inspection obtain an opinion of the corrosive environment of the reinforcement. Also, so called none destructive methods have been developed which do not require that parts of the concrete are removed, whereby certain parameters which are characteristic for the corrosion of the reinforcement, are determined depending on the method employed.

A common method of this kind comprises that a probe consisting of one or more electrodes is placed on a concrete surface, a measuring device being electrically connected to the electrodes of the probe as well as to a reinforcement iron bar in the concrete. Then, measurements may be carried out in different modes such as with different excitation voltages and with equalizing voltages applied by the measuring device onto the electrodes and/or the reinforcement iron bar. Thus, by means of the surface probe a current conducting electro chemical cell is artificially established and from the measured polarisation resistance a.o. the corrosion rate can be calculated for a restricted art of the reinforcement. Such a surface probe is disclosed e.g. in US Patent No. 5,259,944.
Similar prior art methods are known whereby in addition to the polarisation resistance, the corrosion potential (i.e. the electrode potential of the corroding materials) and the concrete resistance (or liquid resistance) are also determined to estimate the corrosion condition of the reinforcement. For example, US Patent No. 4,958,130 describes such a method whereby surface electrodes are used and power is fed from the outside to carry out the measurements. By the measurement and comparison of a plurality of parameters more reliable results are obtained for the valuation of the corrosion environment.

However, to examine a structure of a certain size the probe must be moved from one place to another all across the surface of the structure, which, particularly in the case of a free standing structure, such as e.g. the arch or span of a bridge, can be very expensive to accomplish, i.e. because of the erection of the scaffolding required, and the like.

The purpose of these known methods is to find the corrosion of the reinforcements which reoccurs and possibly obtain an indication as to how far it has advanced. Such corrosion measurement technics, however, provides little information, or no information at all, about the environmental conditions which causes the corrosion. Therefore, to discover the conditions which prevail in the concrete itself, it is usual to take samples of concrete which then are analysed with respect to the content of damaging a matter of different kinds, e.g. such as the concentration of chloride. It goes without saying that such a process of removing and analysing concrete samples is expensive as well as time consuming, not at least in the case of larger constructions by which it is necessary to obtain a large number of such samples to achieve a satisfactory mapping of the corrosive environment.

Therefore, it is desirable to bring about a non destructive method which makes it possible to detect that with conditions in the concrete a development is in progress which can create corrosion problems, if it continues. With the possibility of continuously or at certain intervals carrying out such examinations without huge expenditure, and which are able to give a warning in advance, it will be possible to be more foresighted and early enough implement preventive measures e.g., aiming at limiting the amount of corrosive matter present in the concrete, and which later can cause corrosion of the reinforcement.
With respect to the corrosive environment in concrete it is found that the alkalinity or acidity of the pore water, which usually is specified in pH value, as well as the content of chloride and oxygen, to be the most significant parameters. At the same time available equipment for measuring these parameters, such as oxygen sensors and ion selective electrodes, did not exhibit such sturdiness and working life which would make them suitable for being moulded into concrete. Therefore, there is a need for equipments adapted to the measurement of these parameters, and having a long life when being moulded into concrete, and being useful in a method the purpose of which being to determine the corrosive environment in the concrete.

Hence, the present invention concerns a combination of electrodes to be moulded into concrete for the purpose of measuring enviremental parameters in the concrete, such as content of oxygen, pH value and chloride content in the pore water of the concrete. According to the invention this combination is characterised by comprising a plurality of sensor electrodes, each mainly consisting of one material selected from a group of electric conducting materials which are mutually different so that the electrode potentials of the sensor electrodes as measured relatively to a reversible reference electrode at a known temperature, vary in a mutually divergent manner in relation to the environmental changes in concrete, thereby enabling the calculation of the values of the environmental parameters from measured variations in said electrode potentials.

In this way, the invention relies on the principle that the electrode potential of the different electric conducting materials varies in a non equal manner in the case of a variation of oxygen content, pH value and chloride content in water. So, by using a plurality of mutually different electrodes which are moulded into the concrete the corrosive environment can be determined as a whole from the potential difference between each of this dissimilar electrodes and a reference electrode.

According to the invention, said group of electric conducting materials preferably comprises silver (Ag), lead (Pb), copper (Cu), carbon (C), nickel (Ni), palladium (Pd) and electric conducting ceramic or organic materials, the reversible reference electrode advantageously being made of a material which is insensitive as to those environmental parameters which are to be measured, such as silver-silverchloride-potassiumchloride (Ag-AgCl-KCl).
In a preferred embodiment the combination of electrodes according to the invention comprises three center electrodes, the first one of which being made of metallic silver (Ag), the second of metallic lead (Pb) and the third of copper (Cu), or possibly carbon (C), nickel (Ni), or palladium (Pd) in the place of copper. Besides, in addition to a reference electrode, each combination of electrodes may also comprise a temperature sensor for the measurement of the temperature in the concrete adjacent the electrodes of the combination.

The invention also concerns a device and a method whereby one or more combinations of electrodes are used to determine the corrosive environment for the reinforcements in concrete. Thus, according to the invention the values of the environmental parameters are preferably calculated by:

- determining the oxygen content mainly from the difference of the electrode potential variation measured for a copper sensor electrode and a metallic lead sensor electrode, respectively,
- determining the chloride content mainly from the difference of the electrode potential variation measured for a metallic silver sensor electrode and a metallic lead or copper sensor electrode, respectively, and
- determining the pH value mainly from the difference of the electrode potential variation measured for a metallic lead electrode in relation to the reference electrode.

A more detailed explanation of the invention will now be given by way of an embodiment of a probe or electrode assembly comprising the combination of electrodes according to the invention, and by reference to the accompanying drawings, where:

Fig. 1 shows a side view of such a probe where the electrodes are partly moulded into a housing which for purpose of illustration, consists of a transparent material,

Fig. 2 shows a view of the probe of fig. 1, as seen from below, and

Fig. 3 is a sketch showing a section through a portion of a reinforced concrete structure, three probes of the type depicted in fig. 1 and 2, being moulded into the structure.

Referring to fig. 1 and 2, the probe comprises three sensor electrodes 1, one reference electrode 2 and a temperature sensor 3, about half of each of these being moulded into a compact plastic material, preferably an alkali resistant polymer, such as a epoxy.
Within the plastic material an electric conductor 4 from each electrode 1, 2, and from the temperature sensor 3 passes collectively through a cable 5 which extends to the outside of the housing 6 to be connected to a measuring apparatus (not shown) or any other suitable equipment (not shown) for the further processing of the values to be measured. The conductors 4 may be isolated copper wires and preferably the cable 5 is provided with a sheath made of a material which is resistant to such environmental stress which the cable is exposed to during using.

In fig. 1 and 2 the probe is drawn about double the actual size, the probe housing 6 having a height of about 30 mm (as viewed from the side, such as in fig. 1) and a diameter of about 35 mm, and the electrodes 1, 2, 3 being about 25 mm in length and having a diameter of about 5 mm.

Although the example shown is an embodiment having three sensor electrodes 1, one reference electrode 2 and one temperature sensor 3 arranged with relatively uniform spacing, the number of electrodes and their mutual location may be different in other embodiments, as long as the desired total effect according to the invention, is achieved. Usually is then required that there are at least three different sensor electrodes. In some special embodiments of the probe, however, the reference electrode 2 and/or the temperature sensor 3 may be omitted. Such omission may be possible in case a plurality of probes is to be moulded into the concrete, as a common reference electrode and/or common temperature sensor can be utilized, such as discussed below. In any case each sensor electrode 1 will be comprised of an electric conducting material which is different from the electric conducting material in the other sensor electrodes 1 in the same probe, the materials exhibiting mutually different properties relating to the electrode potential.

In fig. 3 an example is given of how probes 6 according to the invention may be arranged at various distances from the surface 8 of the concrete and at the same time away from the reinforcement 9. As shown in fig. 3, the cable 5 from each probe can extend directly to the surface of the concrete, where the cables are terminated in contact points 7, such as of the multiple type, for the connection of external cables leading to the measuring equipment. When a plurality of probes are moulded in the concrete, such as shown in fig. 3, their sensor electrodes can make use of a common reference electrode and/or common temperature sensor, i.e. just one of the probes in such a group needs to be furnished therewith, and the other probes may then be of a simpler kind having
sensor electrode 1. Alternatively, a separate reference electrode and/or temperature sensor may be moulded into the concrete together only with probes of the simpler kind.

Instead of letting the cables from the probes take the shortest route out of the concrete, they may, of course, extend through the concrete to a common output location (not shown) provided with contacts having indications for the unambiguous identification of the probes and their position in the concrete. This is particularly useful in cases where the contacts 7 for the cables 5 which extend directly out of the concrete are hard to access or impossible to gain admission to when the construction in question is finished. Measuring equipments may then be placed at such common output locations, as desired.

It is to be understood that probes having the electrode combination according to the invention are best suited for being moulded into concrete during the initial erection of a building. However, installation at a later time is also possible by drilling holes of a suitable size in the concrete to accommodate a probe. To keep an inserted probe in place in the hole, it should be filled with a suitable filler. Then if, the electrodes are not in contact with the concrete directly, but surrounded by the filler material, the latter should be of such a kind that pore water in the concrete is allowed to arrive at and preferably surround the electrodes. Furthermore, the filler must be inert and not alter the pH value, oxygen content or chloride content of the pore water.

The measuring equipment which is used is adapted to measure the electrode potentials of one or more electrode combinations and output corresponding measurement signals, and the means for the further processing of the measurement signals is adapted to calculate the values of the environmental parameters from the measured variations or differences in said electrode potentialss, thereby determining the corrosive environment for the reinforcement in the concrete. As the calculations are somewhat complicated and at best are carried out by means of a computer programme, the processing means preferably comprises a computer programmed for this purpose.

As regards the materials which advantageously should be employed in the sensor electrodes 1, it is referred to the following table 1 which demonstrates the potential sensitivity of different electrode materials as to the environmental parameters in concrete. Actually, experiments have shown that the electrode potential of metallic lead is unaffected of the chloride content, relatively modestly influenced by the oxygen content,
and relatively heavy influenced by the pH value. The electrode potential of metallic silver is very much influenced by the chloride content. Even more so this is the case for silver coated with Ag₂O. By conditions where the oxygen content and pH value of the pore water is unaltered, the potential difference between lead and silver may be used to determine the chloride content of the water phase. The potential difference of lead and copper does not depend on the chloride content, but depends on the concentration of oxygen, and therefore can be used to determine the oxygen content, if the pH value is known.

The pH value of the pore water will influence the electrode potential of all materials tested, except for Ag-AgCl-KCl (such as indicated in table 1). It will then be possible to determine the pH value by measuring the potential between lead and a reversible reference electrode, of a kind just as the silver-silverchloride-potassiumchloride electrode, if the oxygen content is the same. The presence of chloride does not influence these measurements. By measuring the potential between a reference electrode and all of lead, silver and copper, respectively, the oxygen content, pH value and chloride content in the pore water can be calculated at a known temperature measure by means of the temperature sensor.

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<tr>
<td>8</td>
<td>Pd</td>
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*) 0 = no sensitivity
1 = modest sensitivity
2 = large sensitivity
The Ag-AgCl-KCl electrode (type No. 1) is a well known thermo dynamic reversible reference electrode (or reference half cell) having an electrolyte (saturated potassium oxide) included. It is not influenced by the environmental parameter listed in the table. The potential of the other electrodes (type Nos. 2-8) is measured against this Ag-AGCl-KCl electrode (type No. 1) and is recorded typically in terms of millivolts in relation thereto. Alternatively, instead, a reference electrode made of manganese dioxide (MgO₂) be used, but such an electrode does not possess as good properties.

The Ag-AgCl electrode (type No. 2) is composed of a silver thread coated with silver chloride by anodic coating in 0.1 M (mols/l) HCl for 30 min. at another current of 1 mA/cm² and the Ag-Ag²O electrode (type No. 3) is constituted by a silver thread coated with silver oxide by anodic oxidation in 1 M (mols/l) NaOH for 30 min. at approximately +0.5 V in relation to the standard hydrogen electrode. These coated silver electrodes (type Nos. 2 and 3) are thermo dynamically reversible and satisfy Nernst's equation which specifies the relationship between potential and concentration of chloride (Cl⁻) and hydroxyl (OH⁻):

\[ E(2) = E^* (2) - \frac{RT}{F} \ln [Cl^-] \]

\[ E(3) = E^* (3) - \frac{RT}{F} \ln [OH^-] \]

where:
- \( E \) = potential (V),
- \( E^* \) = standard reduction potential at 25°C (V),
- \( R \) = the gas constant,
- \( T \) = temperature (K),
- \( F \) = Faraday's constant.

This means that the potential falls by 59 mV with an increase of a factor of 10 in concentration (at 25°C), the pH value been given by \( pH = -\log K_w/[OH^-] \), where \( K_w \) which denotes the ione product of the water equals \( 1x10^{-14} \) at 25°C.

The electrode of the type Nos. 4-9 made of carbon (C), lead (Pb), copper (Cu), nickel (Ni) or palladium (Pd), are not reversible, i.e. they do not satisfy Nernst's equation with respect of the relation between potential and concentration. The change in potential as a result of the change in concentration will normally be less for reversible electrodes, typically in the range 20-50 mV for a change in the concentration having a factor of 10.
All of the electrodes (type Nos. 1-8) have some sensibility as to the changes in temperature, in the order of 0.1 - 1 mV/°C. This sensitivity as to temperature is compensated by the recording of the temperature simultaneously with the carrying out of the potential measurement and is included in the calculation which preferably is done by means of a computer programme, as discussed above.

To determine the corrosive environment for the reinforcements in a concrete structure a probe is moulded into the concrete which comprises a reference electrode 2 (electrode type No. 1 i table 1) and a selection of electrodes 1 of the types Nos. 2-8 (in table 1) and usually a temperature sensor 3. The probe is moulded into the concrete at the location where it is desired to monitor the environmental parameters and the measurement cable 5 is extended out of the concrete e.g. to suitable contents 7 for conductive terminals on the surface 8 of the concrete, so that the conductor links from the probe optionally may be coupled to a voltage measuring apparatus, e.g. an MV meter, or some other adequate measuring equipment, such as already discussed.

Having such an arrangement pH, chloride and oxygen can be detected by measuring the potential between electrodes of a different material, such as indicated below, the Nos. 1-8 referring to the types of electrodes listed in table 1:
- pH between electrode type No. 1 and types Nos. 3-8,
- chloride between electrode type No. 1 and types No. 2, and
- oxygen between electrode type No. 1 and type Nos. 4, 6 or 8.

The electrode materials mentioned above constitute one only of many possibilities. In addition to the materials already mentioned, experiments performed have pointed out platina (Pt) as an interesting material for this usage. Electric conducting ceramics and organic materials have so far not been subjected to experiments, but there is reason to believe that also some of these may have the ability to be employed in equipment according to the invention.

Electrodes made of silver (Ag), carbon (C), lead (Pb), copper (Cu), nickel (Ni) and possible other materials can, as discussed above, be of a relatively small size, and since there really is need only for one real reference electrode a number of sets comprising the other electrodes can be located at various distances away from the surface to record the differences in a direction inwards.
In addition to the measurement of the environmental parameters the probe can be used to measure the corrosion potential of the steel reinforcements by measuring the potential difference between one electrode of type No. 1 (in table 1) and the steel reinforcement itself. Such a measurement requires electrical contacts with the reinforcement through an electric conductor from the measuring apparatus being connected to the reinforcement. As mentioned above, corrosion potential of the reinforcement is often used to judge the corrosion condition of the reinforcement, as a low corrosion potential indicates corrosive activity.

It may also be of interest to combine the probe with the steel electrodes to carry out measurements of the corrosion potential and/or linear polarisations. Thus, in a possible embodiment the probe according to the invention may also be provided with one or more steel electrodes for this purpose. Simultaneous measurements of environmental parameters and the corrosion of steel at the same location provide in many cases interesting possibilities and will be of great value.
PATENT CLAIMS

1. A combination of electrodes to be moulded into concrete with the purpose of measuring environmental parameters in the concrete, such as the content of oxygen, pH value and content of chloride in the pore water of the concrete, characterised in that by the combination comprising a plurality of sensor electrodes (1), each of which mainly consisting of one material chosen from a group of electric conducting materials which are mutually different so that the electrode potentials of the sensor electrodes as measured relatively to a reversible reference electrode (2) at known temperature, vary in a mutually divergent manner in relation to the environmental changes in the concrete, thereby enabling the calculation of the values of the environmental parameters from measured variations in said electrode potentials.

2. A combination of electrodes according to claim 1, characterised in that said group of electric conducting materials comprises silver (Ag), lead (Pb), copper (Cu), carbon (C), nickel (Ni), palladium (Pd) and electric conducting ceramic or organic materials, said reversible reference electrode (2) preferably being made of a material without sensitivity as to the environmental parameters to be measured, e.g. silver-silver chloride-potassium chloride (Ag-AgCl-KCl).

3. A combination of electrodes according to claim 1 or 2, characterised in that it comprises three sensor electrodes (1), a first one of which being made in metallic silver (Ag), a second of metallic lead (Pb) and a third in copper (Cu); or possibly carbon (C), nickel (Ni) or palladium (Pd) in the place of copper.

4. A combination of electrodes according to any preceding claim, characterised in that said sensor electrodes (1) are assembled with the reference electrode (2) and/or a temperature sensor (3) to measure the temperature of the concrete in the vicinity of the sensor electrodes (1) and to produce a corresponding measurement signal.

5. A combination of electrodes according to any preceding claim, characterised in that it is assembled with a steel electrode with the same, or nearly equal, composition as the present reinforcement and a counter electrode preferably made of stainless steel, for thereby measuring the corrosion potential and/or
rate of the steel electrode in an electro chemical way, such as by linear polarisation resistance.

6. A device for determination of the corrosion environment for the reinforcement in concrete, comprising a combination of electrode according to one the claims 1-4, characterised in that the device further comprises:
- measurement means for measuring the electrode potentials of said combination of electrodes and deliver corresponding measurement signals, and
- processing means for receiving said measurement signals and from measured variations in said electrode potentials at the temperature measured, calculating the values of the environmental parameters, and thereby determine the corrosion environment for the reinforcement in the concrete.

7. A Device according to claim 6, characterised in that the processing mean is adapted to:
- calculate said oxygen contents mainly from the difference in the measured electrode potential variation for a copper sensor electrode and a metallic lead sensor electrode, respectively,
- calculate said chloride content mainly from the difference in the measured electrode potential variation for a metallic silver sensor electrode and a metallic lead or copper sensor electrode, respectively, and
- calculate said pH value mainly from the difference in measured electrode potential variation for a metallic lead electrode relative to the reference electrode.

8. A method of determining the corrosion environment for the reinforcement in concrete comprising locating one or preferably more combinations of electrodes according to one the claims 1-4 in the concrete, characterised in that the method comprises:
- measuring the temperature of the concrete in the vicinity of each electrode combination by means of a temperature sensor which produces a corresponding measurement signal,
- measuring the electrode potentials of said electrode combinations by means of measuring equipment which produces corresponding measurement signals, and
- receiving said measurement signals by processing means which from the variation measured in the electrode potentials of each electrode combination at respective
measure temperature, calculates the value of the environmental parameters, thereby
determining the corrosion environments for the reinforcements in the concrete.

9. A method according to claim 8,
characterised in that the combinations of electrodes are arranged at
different distances from the surface of the concrete.

10. A method according to claim 8 or 9,
characterised in that, in said calculation of the values of the environmental
parameters,
- determining the oxygen content mainly from the difference in the electrode potential
  variation measured for a copper sensor electrode and a metallic lead sensor
  electrode, respectively,
- determining the chloride content from the difference in the electrode potential
  variation measured for a metallic silver sensor electrode and a metallic lead or
  copper sensor electrode, respectively, and
- determining the pH value mainly from the difference in the electrode potential
  variation measured for a metallic lead electrode in relation to the reference
  electrode.

11. A method according to one of the claims 8-10,
characterised in that at least one electrode combination is used to
determine the corrosion potential and/or rates for a piece of steel placed in the concrete,
by means of measurements of linear polarisation resistance.

12. A method according to one of the claims 8-11,
characterised in that a sensor of steel assembled with the electrode
combination is used to register corrosion by measuring and increase in electrical
resistance which is caused by a reduction of the sectional area due to corrosion.
Fig. 3
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: GOIN 17/00 // GOIN 33/38
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: GOIN

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG: WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>A</td>
<td>US 5015355 A (SCHIESSL), 14 May 1991 (14.05.91), figure 5, abstract</td>
<td>1-12</td>
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<tr>
<td>A</td>
<td>EP 0100813 A1 (PETROLITE CORPORATION),</td>
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<td></td>
<td>22 February 1984 (22.02.84), page 3, line 20 - line 34, figure 2, abstract</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search 30 May 1996

Date of mailing of the international search report 15-07-1996

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