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CORROSION 97

LONG TERM PERFORMANCE OF

MnO$_2$-REFERENCE ELECTRODES IN CONCRETE

Hans Arup
Hans Arup Consult
Dyreborgskovvej 16
DK-5600 Faaborg

Oskar Klinghoffer
FORCE Institute
Park Alle 345
DK-2605 Brøndby

Jürgen Mietz
Bundesanstalt für Materialprüfung (BAM)
Unter den Eichen 87
D-12205 Berlin

ABSTRACT

The embeddable MnO$_2$-electrode for use in concrete has been tested and used in the field since 1986. The present paper supplements earlier publications and presents new data on short and long term stability, temperature response, polarization behaviour and performance in concrete with cathodically protected steel subjected to climatic cycling. Results compare favorably with published data for other embeddable electrodes.

Keywords: Concrete, embeddable electrode, potential measurements, long term stability, polarization.

INTRODUCTION

Embeddable reference electrodes for use in concrete are needed in connection with long-term monitoring and potentiostatically controlled cathodic protection of reinforcement in concrete. Their use in laboratory work and field exposure tests is advisable for the purpose of ensuring a valid exchange of data between lab and field work. As pointed out in [1-4] they should be stable, invariant to chemical changes of the concrete, tolerant to climatic variations and have the ability to pass small currents with a minimum of polarization and hysteris effects.

The embeddable MnO₂-electrode for use in concrete was developed during a BRITE-programme in 1986. It is, together with the Ag/AgCl-electrode, the only embeddable true reference electrode which has found widespread use in the construction industry.

A description of the electrode and its performance was published first in Scandinavia [1] and later in CORROSION/92 [2]. The purpose of this paper is to present results of additional laboratory tests and to document its long term performance. For the convenience of the reader a brief description of the electrode is given below.

The MnO₂-electrode is a half-cell consisting of a compacted mass of MnO₂ inside a metal thimble, since 1992 made of stainless steel (Fig.1). This electrode[1] has been used in all the experiments described in this paper. The half cell potential is a complex function of the reduction state of the MnO₂ [5] - the statement in [2] about the potential being determined by an MnO₂/Mn₂O₃-equilibrium was an oversimplification. With any given composition of the MnO₂ the potential is a linear, 59mV/decade function of the hydrogen ion activity from pH 3.5 to over 14.

The inner electrolyte is a buffered solution with a pH of appr. 13.5 corresponding to normal porewater. It is therefore in chemical balance with the surrounding concrete and differs from the Ag/AgCl-electrode by being chloride-free.

The electrolytic contact to the concrete is through a diffusion barrier made of fibre reinforced cement paste, which protrudes from the insulation sheath, which protects the metal thimble and the cable connection. This ensures a very good bond to the concrete and it also means that the all-important interface between the electrode and the concrete is contained within the electrode. The junction potential across this interface is minimal because the pH is nearly the same in the barrier plug and in the cell interior. Also, when the electrode is embedded in concrete, no significant junction potential develops at the plug/concrete interface.

If a user wishes to compare the potential of an "as-delivered" MnO₂-electrode with that of a Ag/AgCl-electrode (or any other type of embeddable electrode), it will be found that the observed potential difference varies with the pH of the contact solution by as much as 30 mV/pH-unit [2,3,6]. A fair comparison should be made with both electrodes embedded in concrete or with the comparison electrode mounted in a precast mortar block.

EXPERIMENTAL

In a series of laboratory tests, which are described below, the new type of MnO₂-electrodes (with stainless steel thimble) have been tested for uniformity, long term stability, temperature response, polarization characteristics and behaviour in specimens with impressed current cathodic protection with simultaneus exposure to climatic cycles. Some of these tests were done at the FORCE Institute, others at BAM under contract with FORCE.

Uniformity of MnO₂-electrodes.

Before delivery, the potential of every electrode is measured against SCE (Saturated Calomel Electrode) in a thermostatted solution of saturated Ca(OH)₂, which is maintained by daily additions of fresh Ca(OH)₂. The SCE is connected via a saltbridge with KNO₃, because prolonged contact with the alkaline solutions destroys the glass fritte of the SCE.
Figure 2 shows the distribution of measured potentials in a delivery of 172 MnO₂-electrodes.

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[1]Embeddable reference electrode ERE 20 from FORCE Institute.

Short-term stability of embedded electrodes.

The potential difference between two MnO_2-electrodes, which had been embedded in the same cement mortar block for over a year in an indoor climate was measured with a 6½ digit system voltmeter with 0.1 μV resolution and >10 $G\Omega$ input resistance. Readings were recorded every minute for about 3.5 hours as shown in the curve in Fig.3. There was a steady trend of appr 6 $\mu V/h$ and a ripple of about ± 2 μV.

Long-term stability of embedded electrodes.

Ten blocks of mortar, prepared with OPC and Quartz sand, W/C ratio 0.50 and with dimensions 15x15x15 cm were cast in July 1992. Each block contained a rod of 8mm diam smooth mild steel and 4 or 5 MnO_2-electrodes, 44 electrodes in total. Blocks 1-5 were stored in chambers with different relative humidities, from 32 to 100 % RH. Block 6 was exposed in air with 1.5% CO_2 and 60% RH. Blocks 7-10 contained additional chloride (from 0.25 - 1.5% Cl of cement weight), added as NaCl to the mixing water, and these were stored at 100% RH. All blocks were stored at room temperature.

With increasing intervals the potential of a randomly chosen "master-electrode" in each block was measured against a SCE in contact with the surface via a sponge wetted with tap water. The potentials of the other 3 or 4 electrodes were measured relative to the master electrode.

In all blocks except no 9, the potential difference between embedded electrodes did not exceed 12 mV. In block 9, which contained 0.75% Cl, there were some unexplained aberrations, but these could be contained within a scatterband of 30 mV.

As expected from other investigations [2,6], the measurements with the external SCE were marred by the variable contributions of the junction potential. The apparent potential of the masterelectrodes varied from +150 to +230 mV with occasional higher readings. This will of course make it difficult to register any trends in the potential of the embedded electrodes, and no such trends have in fact been detected during the first 4 years, except for the effect of carbonation in block 6. Figs. 4a-c illustrate the results from the carbonated block 6 and typical sets of curves from two of the other blocks.

Temperature response.

There are two aspects regarding the temperature response of a reference electrode. One is the recovery of an electrode after temperature excursions, the other is the temperature coefficient of the electrode, i.e. the variation of potential with temperature. The temperature coefficient is difficult to define and to apply. The potential of the electrode under test has to be measured against a laboratory reference, e.g. a SCE, and one is often left in doubt whether the laboratory reference shall be kept at constant temperature or follow the temperature of the electrode under test. In the last case, should the readings be adjusted using the literature values for the temperature coefficient of the laboratory reference?

The tests described below serve primarily to document the ability of the MnO_2-electrode to recover after thermal cycling.

In one test, 10 MnO_2-electrodes were placed in a thermostatted solution of saturated $Ca(OH)_2$ and measured against a SCE, which was immersed in the solution for 1 minute before each series of 10 readings. The time was probably too short for the SCE to reach a steady potential. As shown in Table 1, the 10 electrodes respond very uniformly to a four day heating cycle up to a temperature of 70°C and they revert to very nearly the same potential as before heating, especially if correction is made for the small difference in temperature before and after, using the "temperature coefficient" of -0.77 mV/°C found in this particular test.

In another temperature test, performed at BAM, 3 MnO_2-electrodes and 3 Ag/AgCl-electrodes[2], the latter delivered precast in cement mortar by the supplier, were placed in a thermostatted bath of stirred, saturated $Ca(OH)_2$. Potentials were measured against a calibrated saturated Ag/AgCl-electrode, which was placed in the bath for one minute before each measurement. From the initial temperature of +5°C the temperature was raised to +10°C and then in 10°C steps to +80°C. At each step the temperature was kept constant for 4 days before the potentials were measured. Up to about 40°C the potential of the MnO_2-electrodes was nearly constant. At higher temperature a decreasing tendency can be observed. The potential of the Ag/AgCl electrodes showed much more scatter. After completion of the test all 3 Ag/AgCl cells showed cracks in the mortar surrounding the cell itself, and this may have affected the measurements (Fig.5).

Note also that thermal cycling forms part of the dynamic tests to be described later.

Polarization behaviour.

Polarization is the offset in potential caused by a current flow to or from the electrode. Normal use of the electrode only gives rise to very small currents, in the order of 0.1 µA if the voltmeter has an input resistance of 10 MΩ. Inadvertent shortcircuiting of the electrode to the steel, e.g. through an instrument used in the amp-range, results in currents only limited by the resistance in the electrode and in the concrete, possibly as high as 1 mA. Part of the polarization is caused by the IxR drop within the electrode and will disappear when the current is interrupted, but permanent changes of the potential may result if the total charge passed is large enough.

The polarization behaviour of the MnO_2-electrode was investigated by placing two electrodes in a saturated solution of $Ca(OH)_2$ and measure their potential relative to a SCE. They were connected in series with a 9V battery and a 1 MΩ resistor, thus passing a current between the two electrodes of approximately 9 µA. The current was maintained for 80 hours. The total charge passed is 0.71 mAh or 2.6 coulomb.

Fig. 6 shows the potentials of the two electrodes as a function of time during the experiment. The IxR drop in each electrode is 8 mV, corresponding to an internal resistance in the electrode (mainly in the cement plug) of 900 Ω. This figure is typical for a newly made electrode; it will rise as the cement plug continues to hydrate and will attain a value of about 2 kΩ in older electrodes.

The persistent part of the polarization after switching off the current is approximately 1.5 mV for the cathodic curve, which corresponds to loading through an instrument.

If an electrode is permanently connected through a 10 MΩ instrument to cathodically protected steel at a potential of minus 1 Volt, the charge passed in 1 year will be 88 mAh, which may be expected to result in a permanent change of minus 2 mV in the potential of the electrode. In the worst case a similar charge will have passed if the electrode is shortcircuited to the steel during three quarters of an hour.

Dynamic tests

A special dynamic test was designed, in which the electrodes were close to cathodically protected steel in concrete, while the concrete blocks went through climatic variations.

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[2]Type WE50 from Silvion

A total of 6 blocks with dimensions and electrode arrangements as shown i Fig. 7 were cast from concrete with 325 kg/m³ Portland cement and a W/C ratio of 0.6. Two of the blocks contained 2% (by weight of cement) of chloride added as $CaCl_2$. These two blocks also contained Ag/AgCl-electrodes of the types mentioned earlier. The impressed current cathodic protection was with a constant current density of 80 mA/m² steel surface. Of the 4 blocks with chloride-free concrete, two were exposed weekly to a NaCl-solution.

The six blocks thus formed two sets of three blocks with three different levels of chloride exposure. One set of blocks was exposed to cycles of 12 hrs in a 40°C condensing atmosphere shifting with 12 hours drying in the laboratory air. The other set went through 80 hour cycles of shifting temperatures from minus 10°C to plus 80°C.

During exposure the "On"-potentials were measured in 4-hour intervals. Once per week the "Off"-potential of the steel was measured relative to all embedded electrodes and a surface held $Cu/CuSO_4$-electrode 1s after switching off the current. The measurements were made simultaneously using 3 or 4 voltmeters as required. A separate measurement of the potential difference between the two embedded MnO_2-electrodes was also made.

The "On"-potentials are affected by strong IxR-drops and need not be discussed. The "Off"-potentials are indicative of the level of CP achieved, but are also sensitive to the exact timing of the measurement, because the potentials are still changing 1 second after interrupting the current. The curves for all 6 test conditions are shown in Fig. 8 a-f. Some of the early measurements were unreliable due to technical difficulties and have been omitted.

The curves show that the pairs of installed MnO_2-electrodes are in good mutual agreement, except in Fig. 8a, where there is a 30-60 mV difference, which cannot be explained, and Fig. 8f, where the results seem to be influenced by local corrosion which has occurred in spite of the CP under the rather extreme experimental conditions. Note that the generel level of the off-potentials is higher than in the other curves. Note also that one of the MnO_2-electrodes is placed very near to the Ag/AgCl-electrode and stays in agreement with this, while the other is farther away and apparently picks up the IxR-drop from a local anode.

FIELD EXPERIENCE

The MnO_2-electrode has found wide acceptance in the industry, and thousands of electrodes are installed in bridges, tunnels, docks and swimming pools in Europe, in the Middle and Far East and elsewhere. Most are part of monitoring systems, and some are sensors in potentiostatically controlled current supplies for CP installations. A few reported failures seem to have been of a mechanical nature, probably broken electrical cables. Requested by the manufacturer, some users have reported attempts to calibrate embedded electrodes ag   inst surface-held reference electrodes, but it is in practice impossible to calibrate single embedded electrodes against surface-held electrodes, due to the great variability of the surface junction potential. In the few cases, where MnO_2-electrodes have been installed in pairs, they have shown parallel behaviour [4].

The best way to calibrate an embedded electrode is to insert the external reference in a drilled hole through the climate-affected surface layer of the concrete (near to the embedded electrode) and use a saturated solution of either KCl [2] or KNO_3 for wetting the sponge used for making the electrolytic contact with the external electrode (SCE or Ag/AgCl). Needless to say, any installed impressed current CP should be swithed off during the measurement.

DISCUSSION

As fabricated, MnO_2-electrodes exhibit slightly different calibration potentials within a reasonably narrow scatterband ($\pm$ 10 mV). Individual electrodes have maintained their relative potential differences with even less variation under a variety of climatic conditions in ongoing tests for periods of up to 4 years so far. The exceptionally good short term stability, in the order of 10 μV/h, make them ideally suited for electrochemical noise measurements and Electrochemical Impedance Spectroscopi, where such measurements are considered.

The polarization behaviour is characterised by an internal resistance of 1-2 kΩ and an ability to deliver (or receive) small currents for prolonged time. The change in potential after such polarization was found to be less than 1mV per coulomb.

The MnO_2electrodes were able to survive cyclic temperature excursions from -10°C to +80°C in laboratory tests. Attempts to measure the temperature coefficient must be considered as tentative in view of the ambiguity of such tests. Besides, there are good reasons for not using temperature coefficients - regardless of their pedigree - for "normalizing" field or laboratory measurements. Firstly, it will always be good laboratory practice to store the actual measured value with information on the reference electrode used and its temperature, if different from that of the object. Secondly, information on the temperature dependence of protection potential, pitting potential and hydrogen evolution potential for steel in concrete is close to non-existing. Thirdly, the chemistry of porewater in concrete is strongly temperature dependent, but also insufficiently documented.

The most important stumble block for the interpretation of potentials of metals in concrete is the existence of strong junction potentials at surfaces and probably also internally in the concrete. This problem was discussed in [2] and [3]. At CORROSION/96 Myrdal [6] discussed the diffusion potentials at liquid junctions and compared calculations with experimental data. His experiments were limited to liquids making contact through opening valves and joining of wet sponges. The contact between an electrolyte and a cement-based capillary system has added problems stemming from the double-layer effects in the fine pores, especially in semidry concrete. Two of the authors are presently engaged in work on this subject, and it is hoped that results from this work can be published in the near future.

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Date	16-05-94	16-05-94	17-05-94	17-05-94	18-05-94	20-05-94	20-05-94	20-05-94	24-05-94
Time	13.00	13.50	12.00	15.00	15.00	08.30	11.30	11.30	09.00
Temp.	23°C	70°C	70°C	70°C	70°C	70°C	40°C	40°C	21°C
	mV	mV	mV	mV	mV	mV	mV	mV	mV
1	168	147	149	141	129	130	162	169	163
2	168	149	150	143	131	129	158	168	172
3	168	147	144	140	129	131	159	167	173
4	169	148	147	141	129	131	163	168	174
5	170	149	150	145	133	133	160	169	173
6	167	144	146	142	130	130	156	165	170
7	168	145	148	146	132	131	159	169	173
8	165	146	148	146	133	132	160	169	173
9	164	144	141	141	132	132	160	169	173
10	167	144	141	140	132	132	160	169	173

TABLE 1. Change of potential measured against a saturated calomel electrode of 10 MnO_2-electrodes kept in a thermostatted bath of saturated $Ca(OH)_2$. The temperature was cycled from room temperature to 70°C, kept for 4 days and returned to RT.
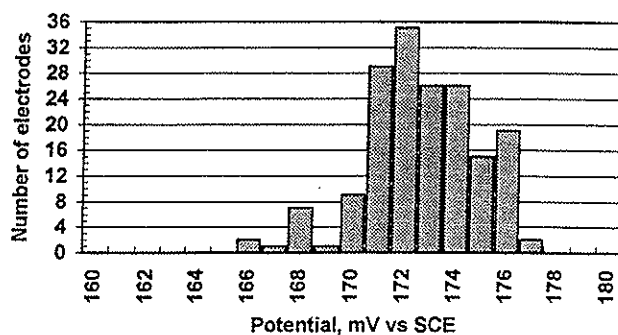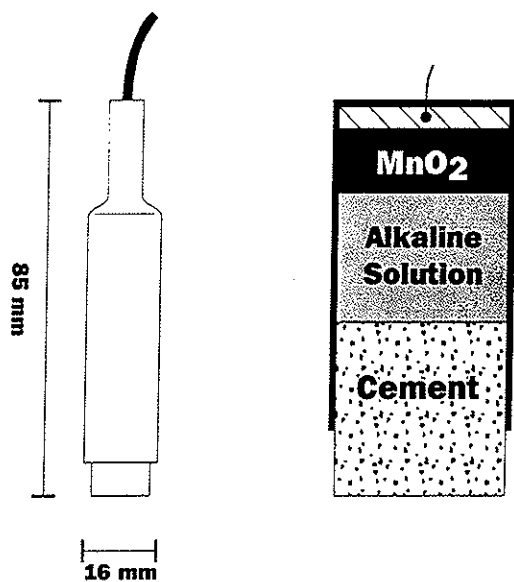
Fig. 1. Dimensions and construction of MnO_2-electrode used in this work.

Fig. 2. Distribution of measured potentials of 172 MnO_2-electrodes in a saturated solution of $Ca(OH)_2$.
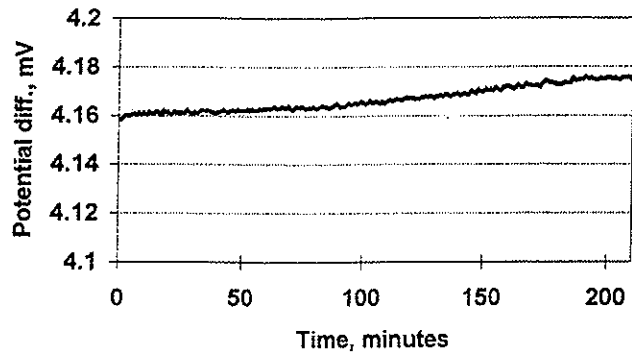
Fig. 3. Difference in potential of two MnO₂-electrodes in the same block of mortar as a function of time.
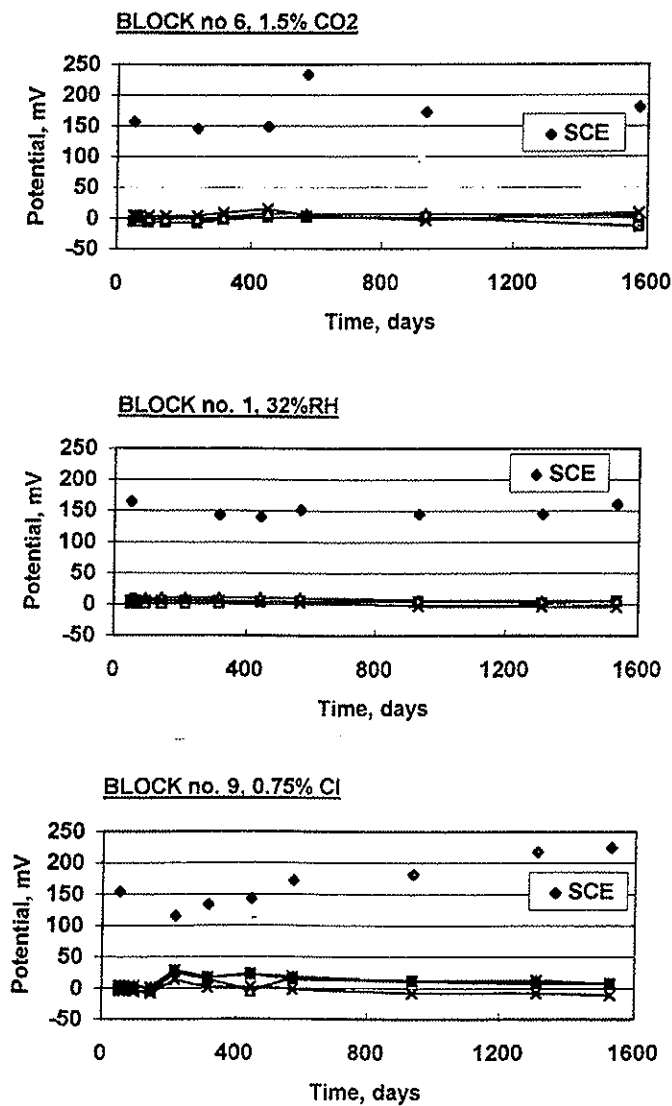

Fig. 4a-c. Long-term relative stability of MnO₂-electrodes in mortar blocks at three different storage conditions. a) carbonating atmosphere, b) 32% RH, c) with mortar containing 0.75% chloride. See text for further explanation
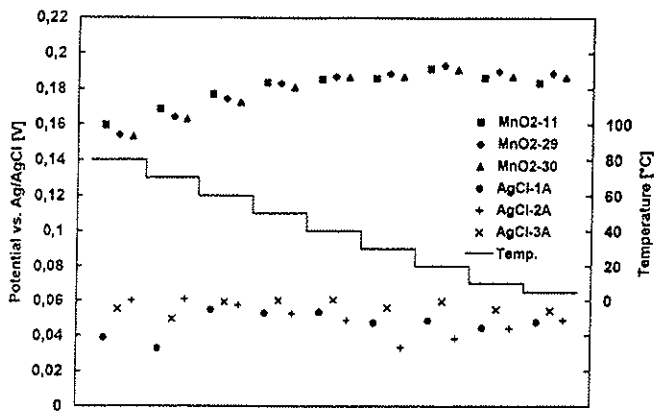
Fig. 5. Change of potential with temperature for 3 MnO$_2$-electrodes and three Ag/AgCl-electrodes. The temperature was kept constant for 4 days at each temperature.
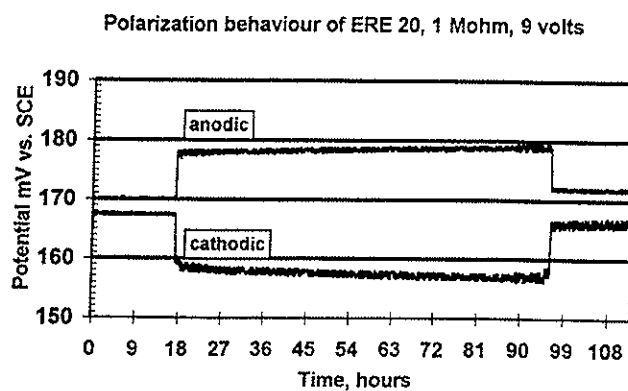

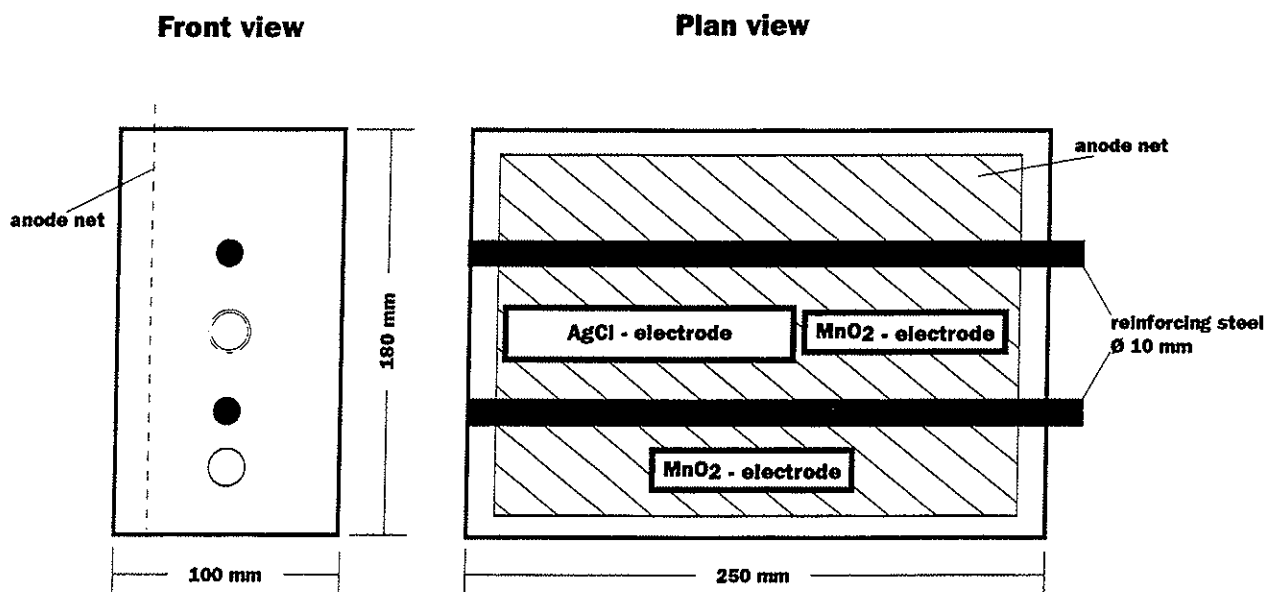Fig. 6. Potential changes of two MnO$_2$-electrodes while a current of approximately 9 μA was passed between them.

Front view   **Plan view**

Fig. 7. Drawing of testblock used for Dynamic tests - see text for further explanation.
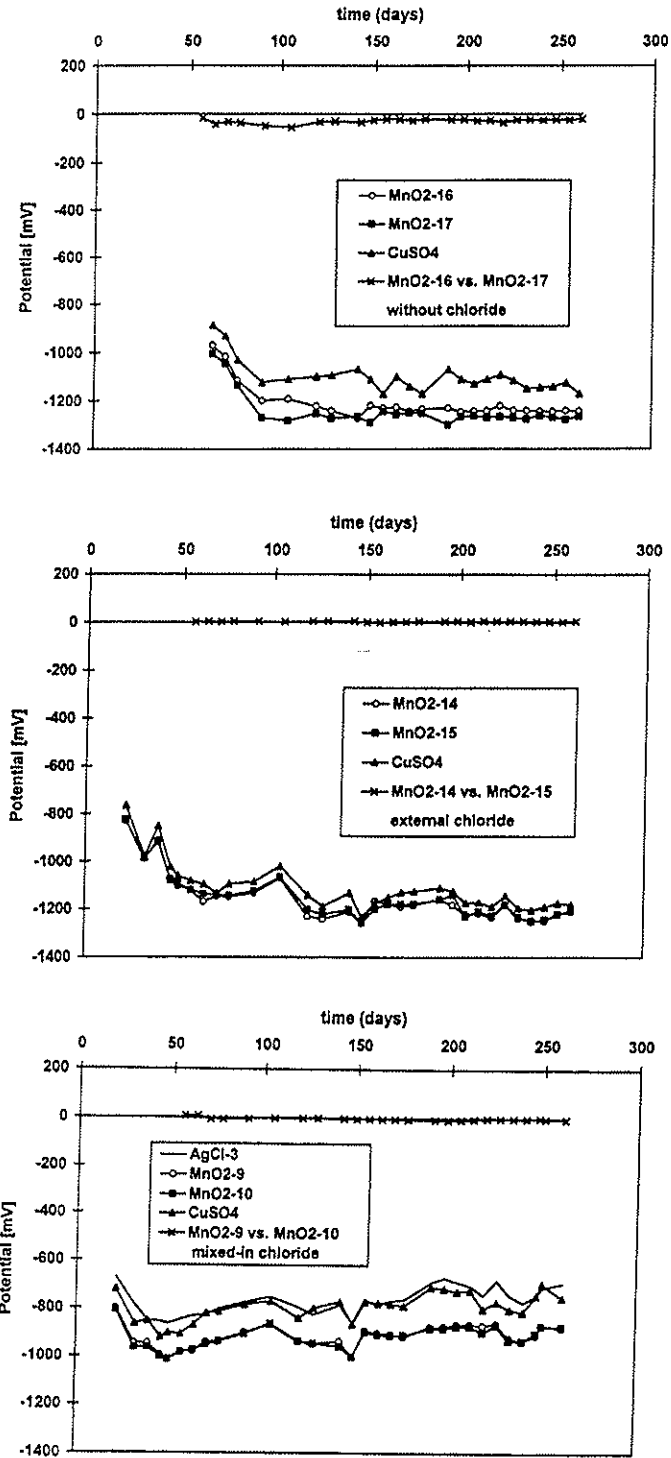
Fig. 8a-c. Results of dynamic tests for test blocks cycled between 40°C condensing atmosphere and laboratory air. See also text.
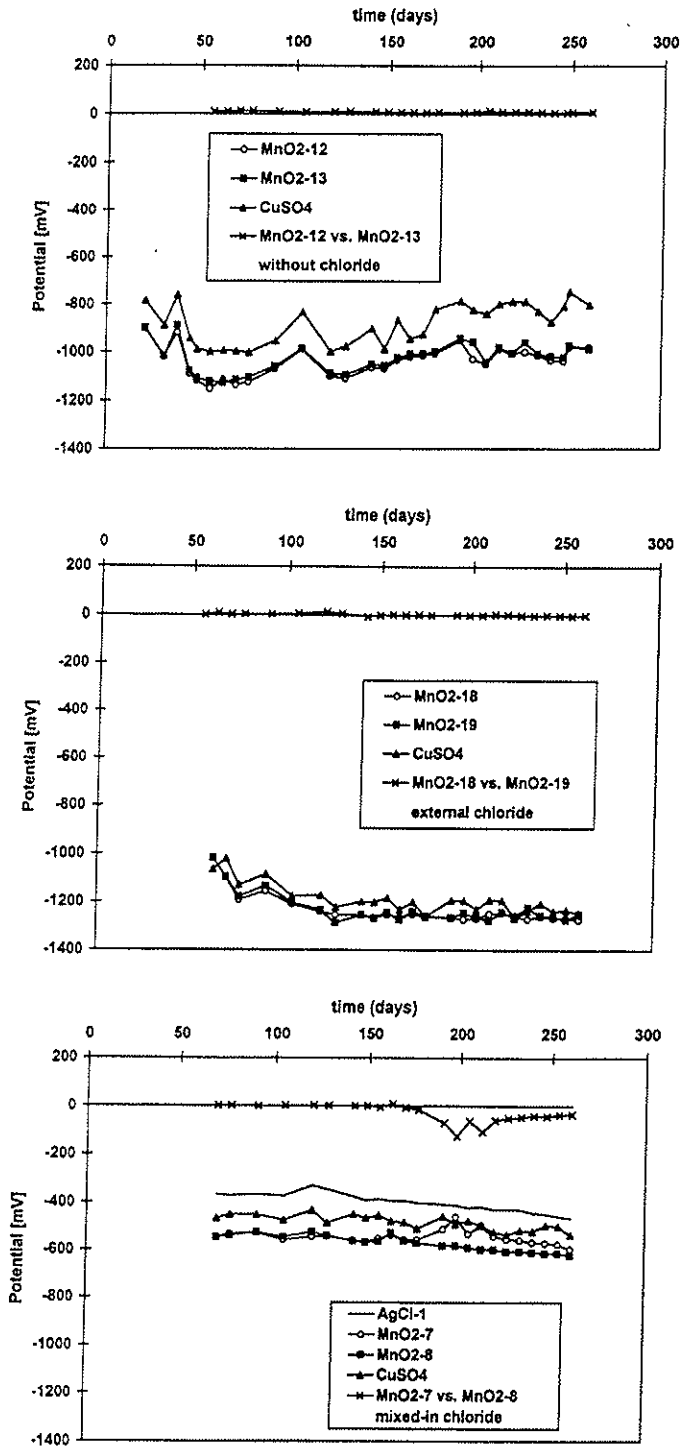
Fig. 8d-f. Results of dynamic tests for test blocks cycled from -10°C to +80°C. See also text.