LONG-TERM FIELD TESTS OF REFERENCE ELECTRODES

FOR CONCRETE - TEN YEAR RESULTS

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ABSTRACT

This paper presents the results from ten years of stability testing of commercial silver/silver chloride, manganese oxide and graphite embedded reference electrodes used in reinforced concrete structures. Tests were performed in chloride-free and chloride-contaminated slabs exposed to the weather in the northeastern United States. Also included is the effect on potential readings of IR drops caused by corrosion of an embedded rebar.

Keywords: Reference Electrodes, Reinforced Concrete, Silver Chloride, Graphite, Manganese Oxide, Stability, Long-term Testing

INTRODUCTION

Stable reference electrodes are required to reliably measure corrosion potential of steel in reinforced concrete structures. Such measurements are important when designing and maintaining cathodic protection systems for these structures. In particular, accurate measurements are mandatory for pre-stressed structures where over-protection can be as deleterious as under-protection. The increasing usage of remote monitoring also requires that reference electrodes be capable of delivering reliable stable performance over an extended period of time.

Silver/silver chloride (Ag/AgCl) reference electrodes are commonly used in concrete structures to measure the potential of reinforcing steel. These electrodes have developed a reputation for being reliable and stable in a variety of underground, aqueous, medical and laboratory applications. Yet, there are occasional reports of their instability when used in reinforced concrete, particularly during cold periods[1], or

in long term applications[2]. Ag/AgCl reference electrodes are true reference electrodes in the thermodynamic sense; the reference potential established at the element/electrolyte interface is only dependent upon the chloride ion activity and the temperature[3]. It would seem likely, therefore, that any erratic behavior of these electrodes must be related to some other cause.

A second type of reference cell which is being used extensively in reinforced concrete is graphite. Some short term testing has shown graphite cells to have performed satisfactorily[1], however they are not thermodynamically true reference electrodes[4]. This means that no reversible reaction has been identified for graphite in this environment. Their long term stability, therefore, is suspect. A third type of reference electrode based on manganese oxide (MnO_2) was developed for concrete use[5]. Initial reports on its behavior show it to be a stable reference.

The primary objective of this project is to demonstrate the long term performance of several embedded reference electrodes under controlled field conditions. All the test electrodes are contained in the same slabs eliminating any differences in the local environment as a variable. A secondary objective of the project is to attempt to determine possible causes for the reported erratic behavior of Ag/AgCl electrodes in some installations. While the test slabs contain both commercially available and experimental electrodes, this paper focuses only on the results of the commercially available ones. An earlier version of this paper presented the results after three years of testing[6]. This paper updates the results to ten years of testing.

PROCEDURE

Two slabs, approximately 3 ft x 6 ft x 6 in. (0.9 m x 1.8 m x 15 cm), were poured in February, 1990. Bridge deck grade concrete was used on both slabs; Slab 1 contained 0 pounds per cubic yard (pcy) chloride added, Slab 2 contained 15 pcy (9 kg/m^3) chloride added as NaCl. These slabs are exposed to the weather in northern Ohio. Each slab contains a single No. 5 deformed rebar located at the mid-thickness and an array of reference electrodes suitable for embedding in concrete. The reference electrodes are also located at mid-thickness about 3 in. (7.5 cm) away from the rebar. All electrodes with the exception of the manganese oxide (MnO_2) electrode were embedded at the time the slabs were originally cast. The slabs were not disturbed in any way for the first full year of tests in order to maintain a consistent environment for all units under test for that time period. The only exception was that for the first three years Slab 2 was salted in the winter by scattering salt on the surface whenever the local roads were salted.

In April, 1991, the MnO_2 electrodes were installed by drilling in from the side. The deeper drill residues from the MnO_2 electrode installation were used for chloride analyses using the method outlined in Federal Highway Report FHWA-RD-77-85, "Sampling and Testing for Chloride Ion in Concrete. Slab 1, which had 0 pcy added, contained 21.3 ppm or 0.084 pcy Cl (0.049 kg/m^3). Slab 2, which had 15 pcy added, contained 1,260 ppm or 4.93 pcy (2.92 kg/m^3). This is likely due to salt leaching out of Slab 2. After the MnO_2 electrodes were installed, the side walls of the slabs and the extended portion of the rebar were coated with a latex rubber coating formulated for concrete applications. This was done to prevent further leaching of salt from the edges of the slab and better simulate a large concrete structure.

A cross section and plan view of the slabs is shown in Figure 1. The silver/silver chloride reference electrodes are standard commercial units in which the element housing is completely encased in a cotton bag containing backfill to ensure good ionic contact with the concrete. All the Ag/AgCl electrodes were modified by the addition of a small access tube running from the backfill bag up to the surface of the slab (see Figure 1, cross section). The access tube permits direct measurement of the potential of an embedded

reference electrode with a laboratory reference electrode which is inserted into the tube to make direct contact with the backfill. This procedure minimizes errors associated with taking potential measurements through concrete. The graphite and MnO_2 electrodes are also standard commercial products. The graphite rod in contact with the concrete measures 5/8" dia. x 2" long (1.6 cm x 5 cm). The MnO_2 electrode makes contact with the concrete through a porous cement plug 1.6 cm dia. x 1 cm long.

In May 1993, each slab was fitted with an array of commercially available potential wells in preparation for additional experimentation on the slabs (see Figure 1). A potential well is an access port to an embedded bag containing a backfill mix. It permits the use of an external reference electrode to make potential measurements of an embedded reference electrode or rebar without having the measuring circuit pass through a concrete surface. Attempting to make potential measurements through a concrete surface can introduce uncontrolled junction potential errors[2]. Potential wells are also advantageous because a series of measurements can be made over an extended period at the exact same location.

RESULTS

Data demonstrating the long term stability of embedded reference electrodes is shown in Figures 2 through 5. In each of these figures, the left graph is data from the low chloride slab (#1) while the right graph shows the corresponding data from the high chloride slab (#2). Figure 2 shows the potential of the individual embedded silver/silver chloride electrodes as measured by a laboratory silver/silver chloride electrode inserted through the access tube. The three embedded silver/silver chloride electrodes in Slab 1 have maintained reference potentials within 20 mV of both a laboratory grade electrode and each other through-out the ten year duration of the test program. The potentials of two of the three embedded silver/silver chloride electrodes in Slab 2 have remained clustered for the test duration while the third one, AGG5, shows an apparent 50 mV deviation.

Electrodes AGG1 and AGG4 were selected as the "master" electrodes in slabs 1 and 2 respectively. This means that they are the ones used to measure the potential of all other embedded electrodes. Measurements made between the master electrode and the remaining embedded silver and graphite electrodes are shown in Figure 3. Potentials of the graphite electrodes (solid lines) had remained closely clustered to each other and steady for only about three months after installation. After that, both the clustering and consistency was lost as the potentials of the individual cells deviated rather widely from each other. The spread of readings between the three individual cells at any one point in time is as high as 100 mV. This behavior is in sharp contrast to that of the embedded silver/silver chloride electrodes (dashed lines) which show much smaller spreads for the duration of the test.

This behavior is best understood by considering the nature of the two types of electrodes. A silver/silver chloride reference electrode is considered a true reference electrode in the thermodynamic sense. Its reference potential is established in accordance with the Nernst Equation and, as such, is affected only by chloride concentration and temperature at the element surface[3]. The graphite electrode, on the other hand, is what is often termed a "pseudo-reference" electrode[4]. The potential of such electrodes is not established in accordance with the Nernst Equation but rather by some other interaction with its environment. As long as its environment remains constant, its reference potential will likely remain constant.

In the case of graphite, the potential established is partly dependent on the oxygen level in the surrounding concrete. After 100 days or so, the homogeneity in the original concrete is lost and local

environmental differences begin to appear which affect the reference potential. The local environment changes over time leading to a continuous variation of the reference potential. Because of this, graphite electrodes are usually only considered suitable for measuring relative potential variations over a period of hours, such as for potential decay tests. Where absolute or long term measurements are required, a thermo-dynamically stable reference electrode such as Ag/AgCl must be used.

Figure 4 shows the rebar potential as measured against each of the embedded Ag/AgCl (dashed lines) and graphite (solid lines) electrodes. The potential of the Slab 1 rebar is relatively constant and the Ag/AgCl electrodes track it closely. The data from the three individual electrodes is virtually identical. As discussed previously, when measurements are made using the graphite cells, the shifting potential of the rebar is not clearly established due to the independent shifting of the reference potential of the graphite cells. The Slab 2 rebar potential is showing a continuous negative shift when measured against the three Ag/AgCl electrodes. As is the case for Slab 1, the independent movement of reference potential of the three graphite cells masks this behavior. The potential of the manganese oxide reference electrodes, as measured against both the embedded master Ag/AgCl (solid lines) electrodes and the rebars (dashed lines), is shown in Figure 5. The potential variations, both between the individual electrodes and over time, is minimal in the chloride free slab. Similar behavior was initially observed in the chloride contaminated slab, but continued testing shows that the potentials of the three MnO cells have deviated widely.

DISCUSSION

The data presented in Figure 2 demonstrates that embedded Ag/AgCl electrodes do exhibit stable reference potentials over extended periods of time. Yet, as stated earlier, there are reports that such electrodes either operate intermittently, the reference potential changes over time, or the cell resistance increases over time. These are separate phenomena: intermittent operation is related to the design and construction of the reference electrode, changing potential is a function of both the design and construction as well as the environment in which it must operate, and resistance increases are an environmental effect.

Intermittent Operation.

Concrete consists of an aggregate, typically stone and sand, bound together in a porous cementatious matrix. The electrolyte permitting ionic conductivity through concrete is water which is contained in the interconnected pores. If concrete becomes extremely dry or if the pore water freezes, the ionic part of the measuring circuit becomes interrupted. This makes it appear as though the electrode has quit working. The electrode is still establishing a reference potential; it is the open circuit condition which is preventing measurements from being made. This phenomena affects all embedded reference electrodes, regardless of element type or housing construction.

Some embedded reference electrodes for concrete consist of a laboratory grade reference electrode placed directly into concrete. Typically, these electrodes have a polymer body for durability and a gelled electrolyte to minimize electrolyte leakage. Such electrodes are usually about 1/2 in. (1.3 cm) dia. by 6 in. (15 cm) long. On the membrane end, they taper to a blunt point about 1/8 in. (3 mm) dia. containing a frit membrane. On the wire end, the diameter of the housing is somewhat enlarged. Electrodes of this construction work quite well in aqueous media in a laboratory, but their use in the field for concrete can result in two possible problems: 1) high resistance contact at the membrane, or 2) loss of contact at the membrane from differential thermal expansion.

If a piece of aggregate in the concrete rests against the membrane, the higher resistance of the aggregate results in a high resistance contact. It is not possible to predict in advance whether or not this will occur. One way to avoid this is to pre-encase the electrode in a fine sand mortar in order to ensure that the membrane does not become occluded. While pre-encasing a laboratory electrode can reduce the contact resistance at the membrane, it does not solve the problem of differential thermal expansion.

Polymer bodied electrodes are commonly made of epoxy which has a coefficient of thermal expansion of about 33 µin./in./F. The coefficient for concrete is about 8 µin./in./F which means there is a differential expansion coefficient of 25 µin./in./F. The relative length change between a typical 6" laboratory electrode and the adjacent concrete would therefore be about 150 µin./F. Ambient temperature ranges of 100F are not unusual for many exterior concrete structures which means that the length of an embedded laboratory electrode would change by 15,000 µin. (0.015 in. or 0.4 mm) relative to the adjacent concrete. Since the electrode is enlarged at the wire end, it is effectively locked in place at that point. Any thermally induced length changes have the effect of either driving the membrane more firmly into the concrete on heating or causing it to withdraw which would leave a gap between the membrane and the concrete on cooling. An electrode embedded in concrete poured and allowed to set at the upper end of the ambient temperature range would be in geometric equilibrium at the warmer temperatures. Contractions, even at temperatures well above freezing, may result in open circuits.

The solution to the problem of intermittent operation of embedded reference electrodes is in the design and construction of the device. One successful approach is to encase the electrode in a cloth bag containing a conductive backfill. The entire surface of the bag is the contact area with concrete, ensuring a low resistance path. In addition, the relative thermal expansion between the backfill and concrete is quite low which minimizes the problem of differential thermal expansion at this interface. There still remains the problem of maintaining a stable ionic contact across the membrane between the gel and the backfill through the full range of expected service temperatures. This has been solved by manufacturers who have addressed this issue through proprietary techniques.

Changing Reference Potential.

One would expect consistency between the potentials of the embedded Ag/AgCl electrodes as individually measured against a laboratory electrode inserted through the embedded electrode's access tube and those measured against an adjacent embedded electrode. When making measurements through the access tube, the ionic portion of the measuring circuit does not pass through concrete (refer to cross-section drawing in Figure 2). The ionic portion of this circuit does pass through concrete when measuring potentials between adjacent electrodes. A significant offset appears between the two sets of measurements as shown below in data collected around day 800:

Slab 2	Measured	Expected	Difference
AGG4 vs. Lab1	-3.6		
AGG5 vs. Lab1	+1.9		
AGG6 vs. Lab1	-3.5		
AGG5 vs. AGG4	+33.7	+5.5	+28.2
AGG6 vs. AGG4	-20.1	+0.1	+20.0

Due to the chloride content of the slab and potential measurements of the rebar embedded therein, it is believed that active corrosion is occurring in Slab 2. These observed measurement offsets can likely be attributed to an IR drop potential from corrosion currents flowing between anodic and cathodic areas of the rebar. To verify this, the above measurements were repeated by using a pair of calibrated Ag/AgCl laboratory electrodes inserted through the access tubes rather than with the embedded electrodes:

Slab 2	Measured	Expected	Difference
Lab2 (beaker) vs. Lab1 (beaker)	-1.6		
Lab2 (AGG5) vs. Lab1 (AGG4)	+26.5	-1.6	+28.1
Lab2 (AGG6) vs. Lab1 (AGG4)	+19.3	-1.6	-20.9

The very close agreement in the magnitude and direction of the offset when independently measured by two different sets of reference electrodes indicates that the voltage drop is not an artifact but is, in fact, real. AGG5 is located about 1 foot away from AGG4 while AGG6 is about 2 1/2 feet away in the opposite direction (refer to Figure 2, plan view). There appears to be no correlation between either the magnitude or the sign of the offset and the cell location. This suggests that the pattern of the potential drop within the slab is quite complex.

As stated earlier, potential wells were later installed at several locations on the slabs (See Figure 2). A laboratory grade Ag/AgCl electrode was inserted into a well near the center of the slab. A second similar electrode was moved to all the remaining potential wells and access tubes and the potential between the two laboratory electrodes was measured. The resulting data was plotted as isopotential diagrams which show the nature of the potential field existing within the slabs. Slab 1 (Figure 6) had a relatively flat profile in the first three years with all three embedded Ag/AgCl electrodes located on the plateau in areas within 5 mV of each other. By 2000, the magnitude of this profile had increased significantly.   The magnitude of the isopotential pattern in Slab 2 (Figure 7) did not change significantly over the past seven years. The three embedded Ag/AgCl electrodes are located at sites in different isopotential bands; they appear to have shifted their reference potentials by tens of millivolts. Apparently, the in-service changes in the reference potential which have been reported in the past may be due to a form of corrosion current induced IR drop in the concrete which is incorporated into the calibration measurement.

Resistance Changes

On occasion, the resistance between an embedded reference electrode and the rebar is used as a means of determining whether the electrode is still operating properly. The following data shows why this criteria can be very misleading.

Slab 1, (September, 2000)	AGG1	AGG2	AGG3
Pot'l, Emb. Vs. Lab thru access tube, mV	0.2	0.4	0.7
Cell resistance measured through access tube	16k	33k	38k
Cell resistance measured to rebar	13k	32k	31k

Slab 2, (September, 2000)	AGG4	AGG5	AGG6
Pot'l, Emb. Vs. Lab thru access tube, mV	-7.0	-22.0	-7.6

Cell resistance measured through access tube	6.4k	8.0k	7.5k
Cell resistance measured to rebar	6.3k	7.5k	7.4k

Resistance measurements made with a Nillson meter.

The potentials of the embedded references in Slab 1, which has had no chloride additions, are very close to that of the laboratory reference used for calibration. The resistance of these references is extremely high and is about the same whether the measurement is made between the reference and a probe contacting the backfill or the reference and the rebar. The situation in Slab 2, which has had chloride added, is just the opposite. The potential difference between the embedded and the laboratory references is greater but the resistances are much lower. The measured resistance on an embedded reference electrode is determined primarily by the resistivity of the concrete or backfill through which the measurement is made and is not a good indicator of the condition of the embedded reference.

CONCLUSIONS

1. Embedded silver/silver chloride reference electrodes which are designed to be compatible with a concrete environment show excellent long term stability in both chloride-free and chloride-contaminated slabs

2. The reference potential of the graphite cells remained stable for about three months after initial installation after which they began to deviate. Because of this behavior, these cells are only suitable for short term relative measurements. Graphite cells should not be used for long term or absolute measurements.

3. Manganese oxide reference electrodes show good stability in chloride-free concrete but demonstrate long term deviations in chloride contaminated concrete.

4. Differential thermal expansion between the electrode body and the adjacent concrete can lead to an open circuit condition at cooler temperatures. To avoid this, it is necessary to use reference electrodes specifically designed for use in concrete.

5. Corrosion currents resulting from corrosion of embedded rebars can set up a complex IR drop field within concrete which can affect potential readings. When calibrating embedded reference electrodes, this effect makes it appear that the reference potential has shifted when, in fact, the shift is simply a measurement error.

6. There is no correlation between the resistance of an embedded reference electrode and whether or not it is providing reliable potential readings.

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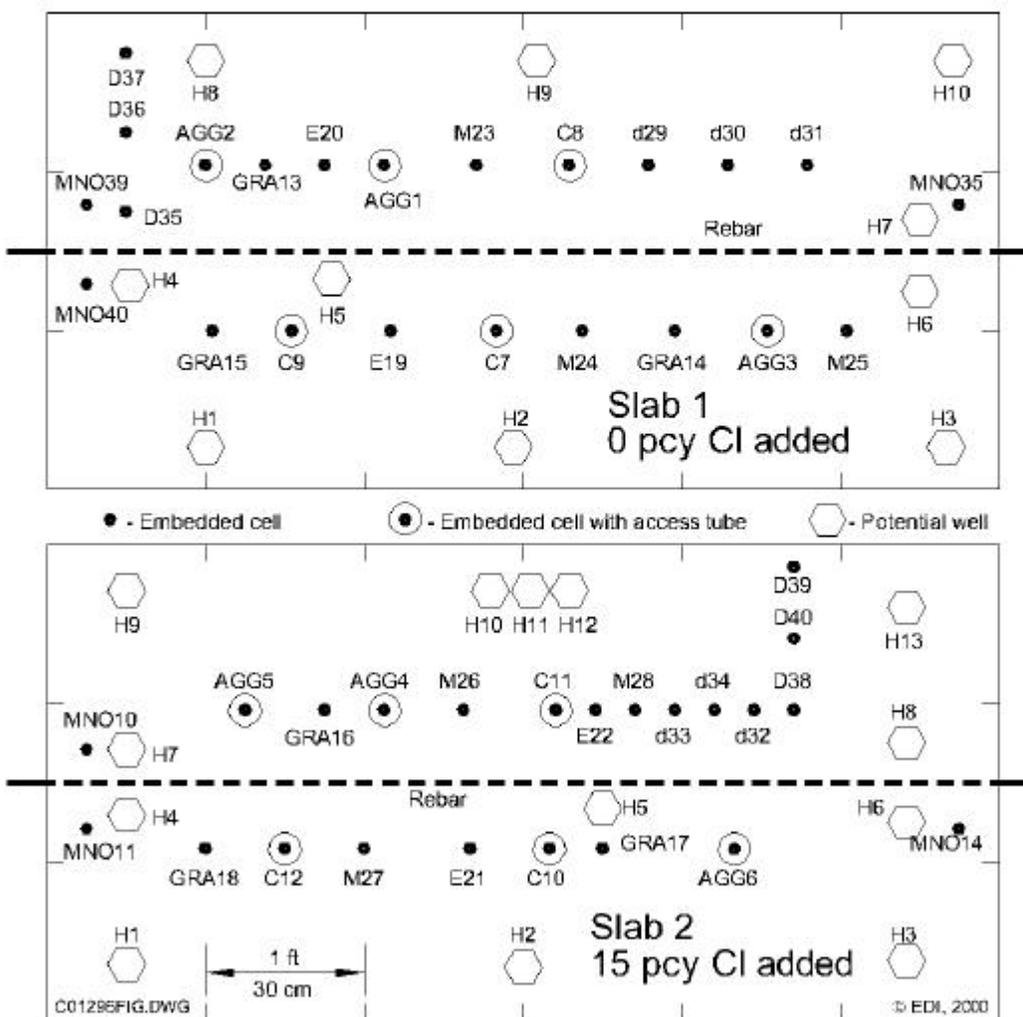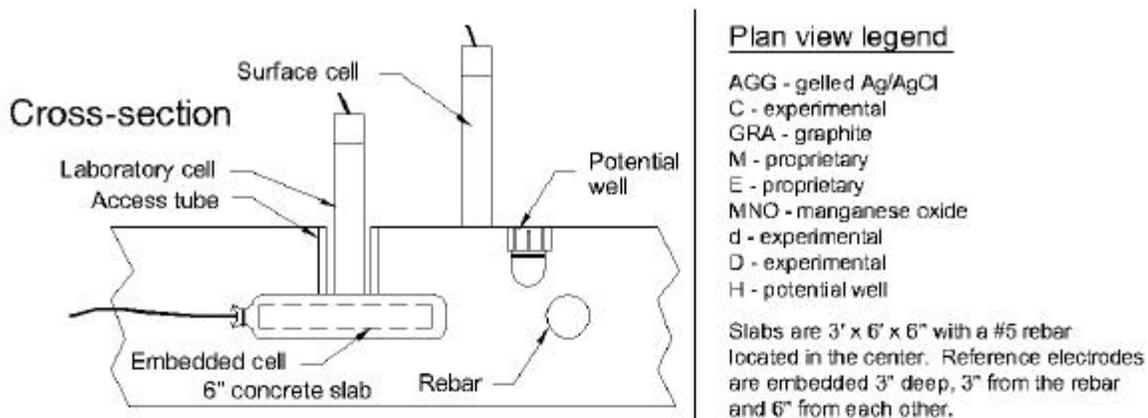
Figure 1   Top: Test slab cross section showing the location of an access tube
relative to its embedded reference electrode.
Bottom: Plan view of the test slabs showing positions of the
embedded reference electrodes and potential wells.
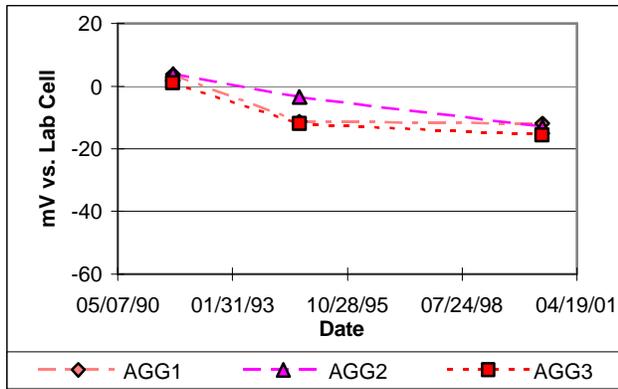
Slab 1
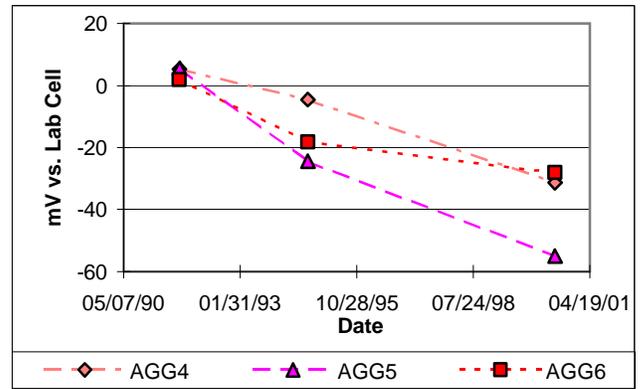
Slab 2

Figure 2   Potentials of embedded permanent Ag/AgCl references vs. laboratory references inserted through the access tubes.
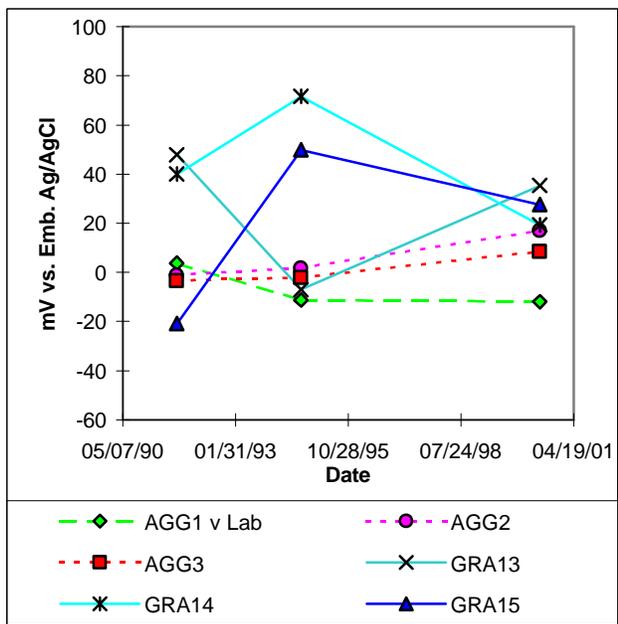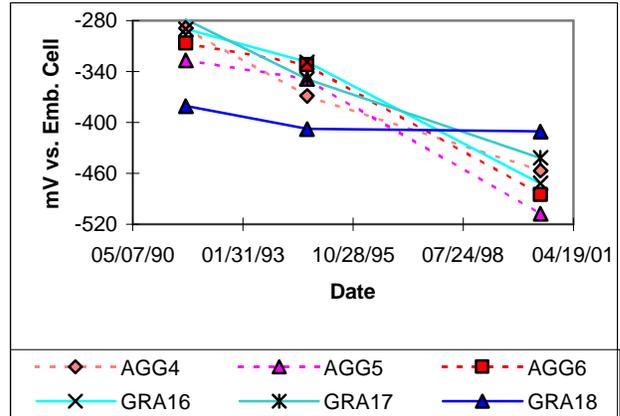

Slab 1
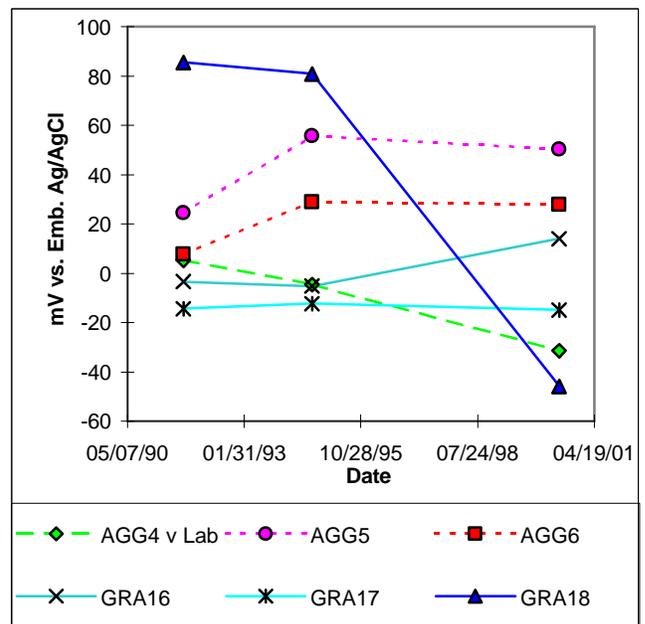
Slab 2

Figure 3   Potentials of embedded permanent Ag/AgCl references and graphite probes vs. the "master" embedded Ag/AgCl reference (AGG1 or AGG4). Potentials of the master references vs. a laboratory electrode are repeated from Figure 2 for comparison.
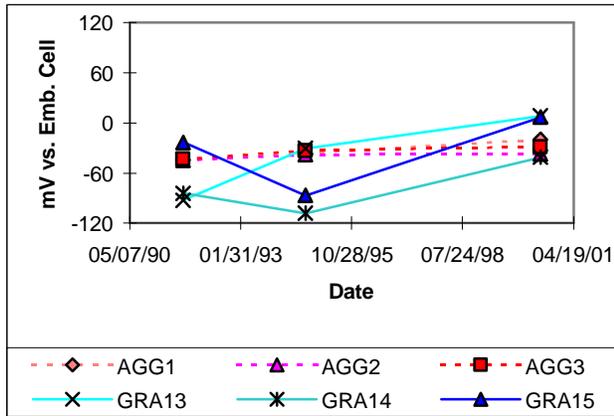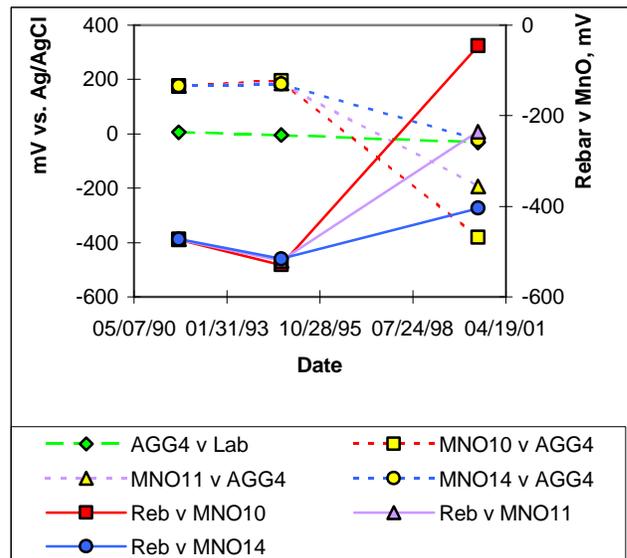
Slab 1   Slab 2

Figure 4   Potentials of rebar as measured against embedded Ag/AgCl reference electrodes
              (dashed lines) and graphite probes (solid lines).
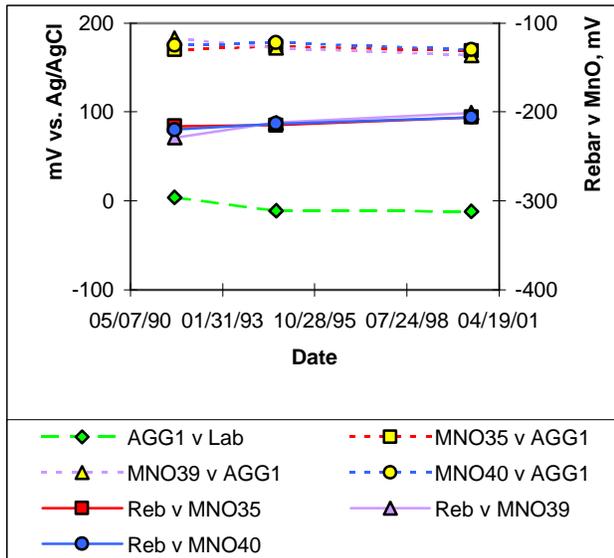
Slab 1   Slab 2

Figure 5   Left axis: Potentials of MnO electrodes vs. the "master" embedded Ag/AgCl electrode
              (AGG1 or AGG4) and the "master" electrode vs. a laboratory reference electrode
              repeated from Figure 2 (dashed lines).
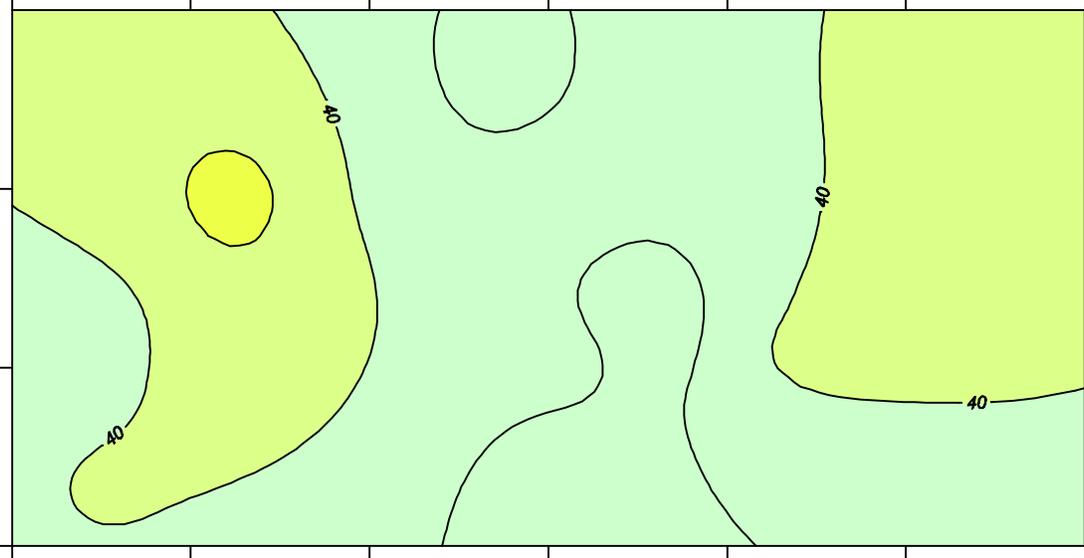   Right axis: Potentials of rebar vs. MnO electrodes (solid lines).
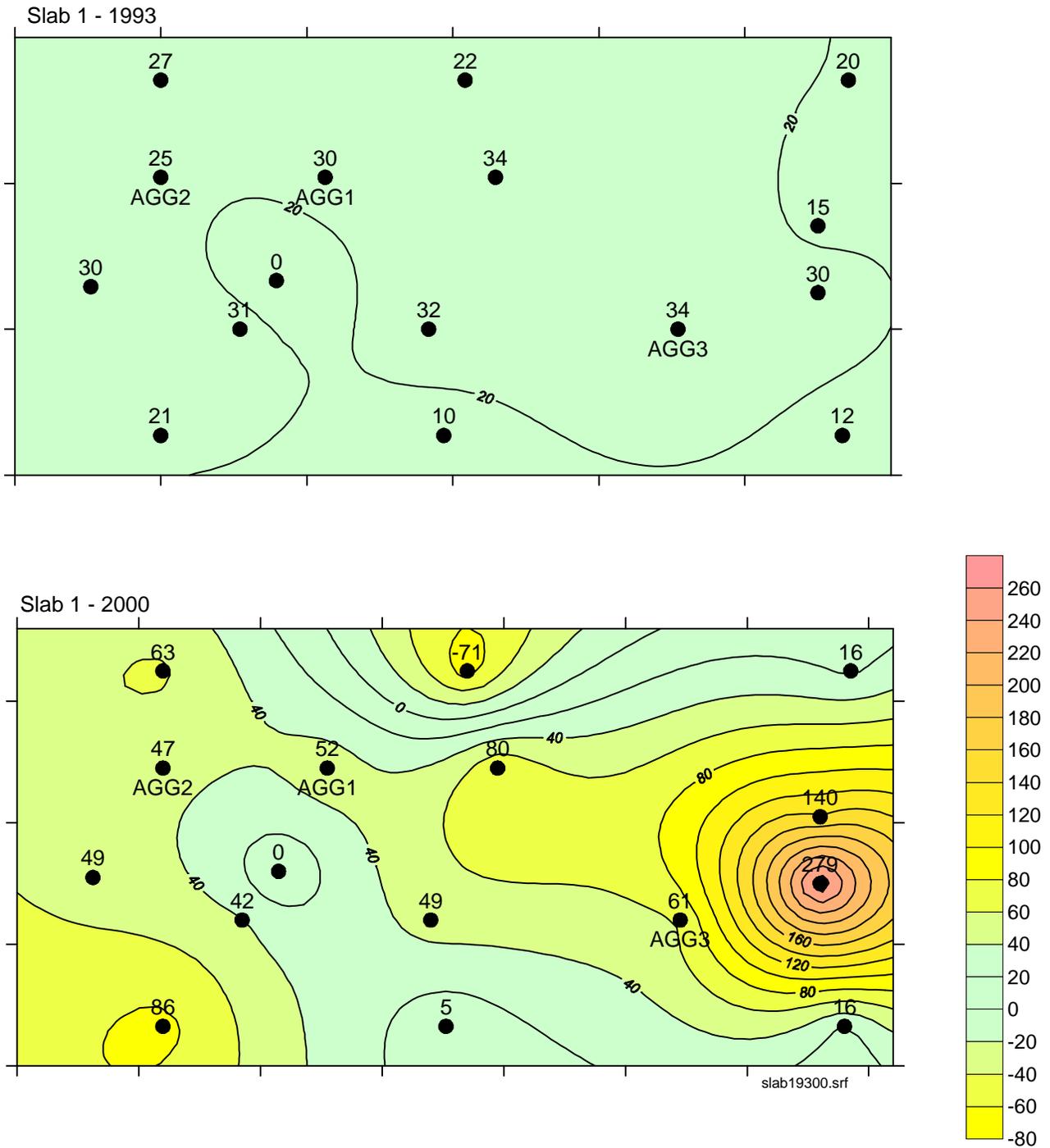
Figure 6 - Isopotential plots of the IR drop field in Slab 1 in 1993 and 2000.
The magnitude of the field increased over the seven year interval but this was not noticable on the three Ag/AgCl cells which were located in a similar iso-potential band.
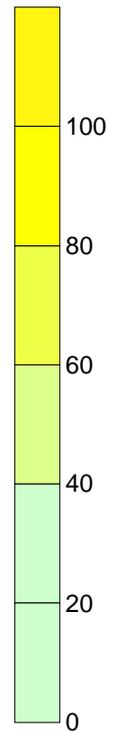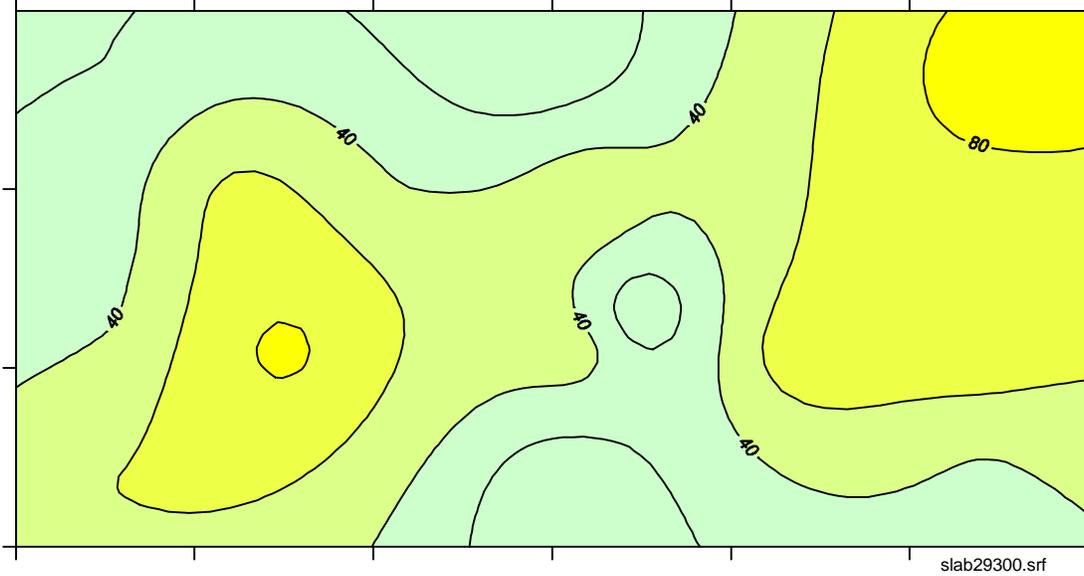
Figure 7 - Isopotential plots of the IR drop field in Slab 2 in 1993 and 2000.
The magnitude of the field did not change significantly over the seven year
interval but the cells were located in different isopotential bands which makes
it appear as though they had drifted apart.