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NEUTRALIZATION OF CHLORIDE IN CONCRETE

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16. Abstract

This study was concerned with one solution to the problem of deterioration of bridge decks due to corrosion of reinforcing steel caused by chloride from deicing salts. Flushing of salts by application of water to the underside of the concrete and electrochemical removal of the chlorides were investigated. Flushing was found to be ineffective and work on it was abandoned early. However, the electrochemical removal technique showed promise of success first in the laboratory and later in a small scale field trial. In the latter chloride present at the level of the top rebar mat was reduced to below the concentration that is known to cause corrosion in 24 hours of treatment, and active corrosion of the steel that was going on was completely stopped.

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SUMMARY

Deterioration of portland cement concrete (PCC) bridge decks is a serious problem in many parts of the U. S. resulting in high maintenance costs to keep the decks in a safe and serviceable condition. Although deck deterioration can take several forms, such as scaling, cracking, or spalling, it is the spalling problem that has become predominant within the last 10 years or so as the major contributor to the bridge deck maintenance situation. The increased frequency of spalling of PCC bridge decks appears to be directly related to the increased use of deicing salts (primarily NaCl and $CaCl_2$) in recent years. Chloride ion in water in the concrete accelerates the rate of corrosion of the reinforcing steel in the concrete. The formation of corrosion products on the steel results in a buildup of stresses in the concrete which is manifested as spalling of concrete on the deck surface.

Assuming that the use of deicing salts will be continued for the foreseeable future, it is obvious that remedial steps must be taken if the problem is not to worsen. Recognizing this, the FHWA and other highway agencies have initiated research and field programs to investigate the feasibility of a number of potential solutions to the problem, including (1) polymer impregnation of bridge decks, (2) cathodic protection of reinforcing steel, (3) protection of the reinforcing steel through the use of various coatings, (4) application of impermeable membranes or coatings to the concrete, and (5) sophisticated rehabilitation procedures involving removal of chloride-contaminated concrete to below-steel levels with subsequent protection of the steel (e.g., with epoxy coatings) prior to the placement of new concrete. One means of providing extended service life to existing chloride-contaminated PCC decks that has not yet been adequately researched is the actual removal of the chloride from the concrete or in-place passivation of the chloride ion. The current program was intended to fill this need.

The research undertaken on this project was done under Contract No. DOT-FH-11-8133 for the Federal Highway Administration. The scope of the program as originally defined by FHWA was "to develop a practical treatment for the neutralization of chlorides that can be applied to existing bridge decks that will neutralize or immobilize chlorides already present in the concrete and, thus, prevent or eventually arrest corrosion of the reinforcing steel". A two-phase program was begun at Battelle's Columbus Laboratories during July, 1973, and was completed in September, 1975.

The laboratory phase (Phase I) was designed to identify practical treatments for neutralizing chloride ions in concrete. This work was followed up by a second phase in which the treatment concept developed in the laboratory was successfully applied to an existing bridge deck in the State of Ohio.

The laboratory phase involved studies of flushing and electrochemical removal as a means of neutralizing the chloride ion. In this sense, "neutralization" is somewhat of a misnomer inasmuch as the intent was to physically remove the chloride ion from the concrete.

An additional task of the laboratory phase was to evaluate techniques for rapid, in-situ measurements of chloride ion in concrete. Although considerable effort was devoted to this task, the work was not carried to fruition by mutual agreement of Battelle and FHWA personnel. For this reason the work involved in this effort is not discussed in the text of this report but is described in some detail in Appendix A.

The flushing concept, as originally envisioned, was intended to move ion-free water from the bottom to the top of a section of concrete with solution and transport of chloride ion to near the top surface of the concrete. Following this step, the chloride ions would be removed from the concrete using an electrochemical technique which was conceptualized as the migration of chloride ions in concrete under the influence of an electrical potential gradient through the concrete and an electrolyte contained above it.

Laboratory work on the flushing concept was discontinued when it was learned that, under the constraints of actual field conditions, the technique could not produce the desired redistribution of chloride ion in the concrete. In contrast to this result, the laboratory work on electrochemical removal was very encouraging. Initial laboratory work on small (3 x 6-in.) chloride contaminated concrete cylinders was followed by work on 4 x 5 ft x 9-in.-thick slabs from which substantial quantities of chloride ion were electrochemically removed down to the level of top reinforcement (2 in.).

The final effort in the program involved the electrochemical treatment of 400 ft^2 of an existing (8-year-old) bridge deck in Ohio during April, 1975. The effectiveness of the procedure was monitored through pre- and posttreatment measurements of rebar corrosion potentials and chloride analysis of bridge deck cores.

This report describes the procedures and findings of the research program and discusses needed areas of additional work en route to full implementation of the chloride-removal technique.

CONCRETE FLUSHING EXPERIMENTS

Prior to the initiation of the current program, laboratory studies at the FHWA Fairbank Highway Research Station had indicated that ion-free water, transported by capillary forces through chloride-containing cement paste, provided a redistribution of chloride in the paste (a reduction of chloride behind the moving water front and an increase ahead of the front). Moisture movement was achieved by the passage of dry air (0 percent relative humidity) across the evaporating surface of the cement paste specimens.

On the basis of this work, it was reasoned that ion-free water supplied to the bottom surface of a PCC bridge deck could move upwards through the concrete if moisture in the upper portion of the deck was removed via normal evaporation processes. Solution and transport of chloride then could produce a concentration of chloride in the upper few inches of the deck which then could be completely removed from the concrete using the electrochemical technique.

In the current program experiments were carried out on 4 x 8 in. concrete cylinders to which chloride ion had been added via the mixing water. The initial experiments were conducted on specimens whose sides were sealed with epoxy to restrict moisture movement to a uniaxial direction. The bottom surface of the specimens was immersed in deionized water and the top surface was subjected to an air flow of 60 ft/min as shown in Figure 1. The humidity was maintained constant at 50 percent and the temperature at 74 F. Dry air was not used in these experiments due to the inability to achieve this condition in the field.

As these experiments progressed, it became obvious that no redistribution of chloride ion was occurring. At this point, additional experiments were initiated in an effort to identify methods for increasing the rate of ion-free water movement through the concrete to the evaporating surface. Methods that were studied included

(1) Pressurizing the deionized water supply
(2) Vacuum applied to the evaporating surface combined with (1)
(3) Increasing the air flow rate over the evaporating surface of the concrete by an order of magnitude
(4) Heating the bottom of the concrete.

None of these attempts were successful in producing the desired redistribution of chloride ion in the concrete.

In view of these results, a decision was made to terminate the experiments on the flushing concept. Prior to this decision, however, a number of additional experiments were conducted to learn why the results achieved by FHWA on cement paste could not be achieved on concretes.

The procedures and findings of all of the flushing experiments are summarized below.

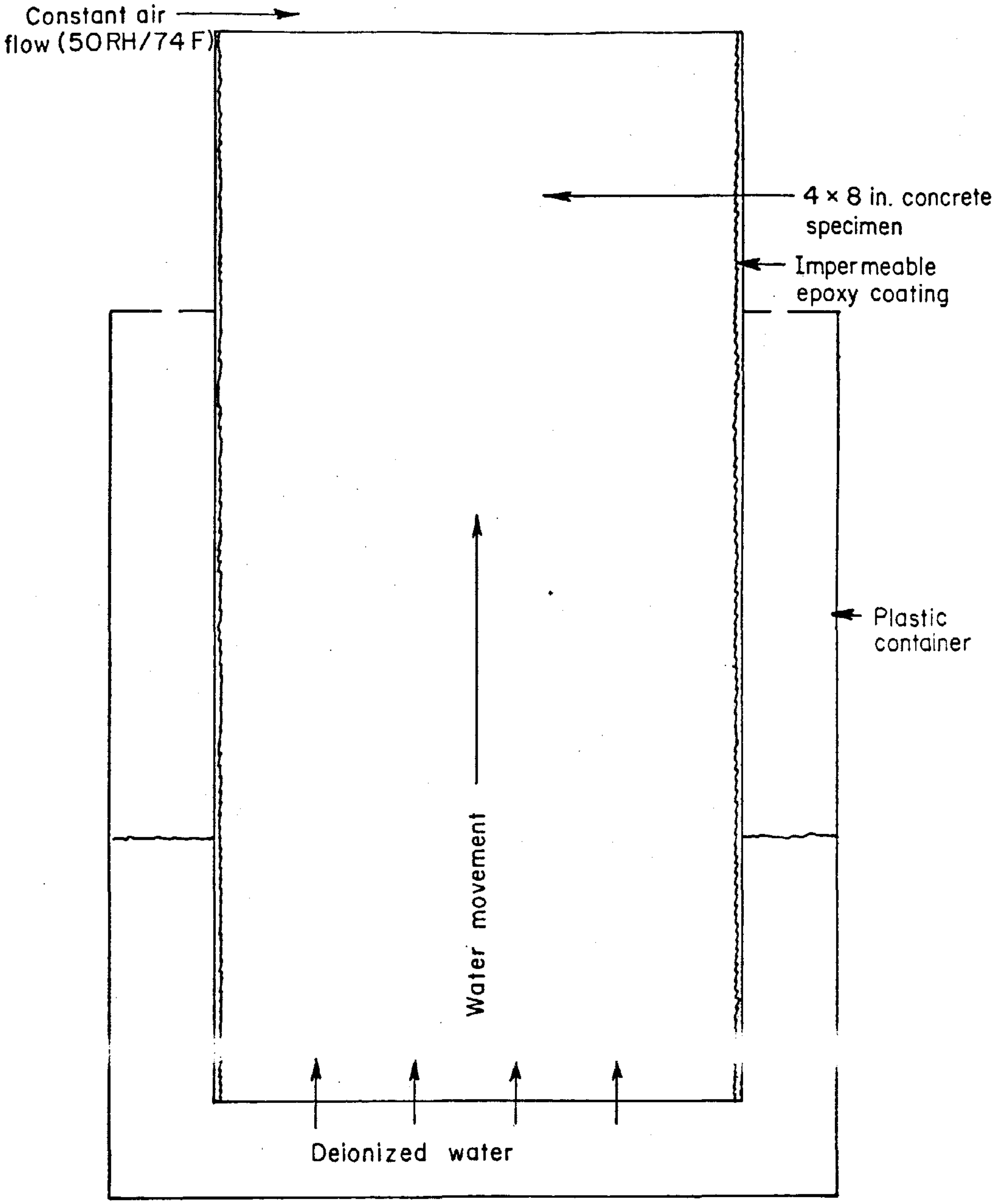

FIGURE I. SCHEMATIC REPRESENTATION OF TEST PROCEDURE USED TO PROVIDE UNIDIRECTIONAL MOVEMENT OF DEIONIZED WATER IN CONCRETE

Specimen Preparation and Treatment

The 4 x 8 in. concrete cylinders used in the flushing experiments were prepared using the Ohio Department of Transportation Class C gravel concrete which is currently in use for bridge deck construction. The specimens were prepared in three lifts with the middle and top lift containing preselected amounts of chloride ion. Chloride was added as NaCl to the mix water.

The selection of chloride levels for the concretes was based on data reported by Spellman et al.(1)* on the chloride content of concrete from 16 California bridges. These data are shown below.

Depth of Surface Below Surface, in.	Chloride Content at Indicated Depth, lb/yd^3		
	High	Low	Average
1.0	12.50	1.80	5.10
2.0	4.80	0.85	2.30
3.0	1.70	0.25	0.90
4.0	0.82	0.23	0.37
5.0	0.51	0.23	0.30
6.0	0.44	0.18	0.38

The bridges received an average of 0.2 lb of salt/ft^2/year.

The median chloride level of concretes in the present study was calculated by taking an average value of the Spellman data for the first 3.0 in. (5.10 + 2.30 + 0.90 ÷ 3 = 2.77), as the chloride concentration of the top third of the specimens, and values for 3.0 to 5.0 in. (0.90 + 0.37 + 0.30 ÷ 0.52), as the chloride level of the middle third of the specimens. No chloride was added to the bottom third of the specimens.

The high chloride level (5.54, 1.04, and 0 lb/yd^3 (for top, middle, and bottom thirds, respectively) is simply a twofold increase in the median level. The low chloride level (1.38, 0.26, 0 lb/yd^3 for top, middle, and bottom thirds, respectively) is simply half the median values.

A summary of the chloride ion distribution in the specimens is reported in Table 1. Details of the concrete mix design and the specimen preparation procedure are given in Appendix B.

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* References are listed on Page 106.

TABLE 1. IDENTIFICATION OF CHLORIDE CONCENTRATION AND DISTRIBUTION IN 4 X 8 IN. CONCRETE CYLINDERS USED IN FLUSHING EXPERIMENTS

Qualitative Descriptor For Chloride Content	Amount of Chloride in Fresh Concrete (lbs. chloride ion per cu yd of concrete) in Indicated Portion of 4 x 8 in. Cylindrical Specimen		
	Top Third	Middle Third	Bottom Third
High	5.54	1.04	0
Median	2.77	0.52	0
Low	1.38	0.26	0

The demolded specimens were sealed in polyethylene bags and placed in a fog room for 28 days. At that time, they were removed from the fog room and the sides of most of the specimens were sealed with an epoxy sealer* prior to their use in the flushing experiments.

A total of 12 concrete series (17 specimens per series) were prepared to permit investigation of the following variables as to their influence on redistribution of chloride ion.

(1) The initial chloride content of the concrete
(2) The initial moisture content of the concrete
(3) The surface treatment of the concrete
(4) The water/cement ratio of the concrete
(5) The frequency of change of deionized water supply
(6) The influence of surface wetting.

The series are identified in Table 2.

Initial Experiments

The initial experiments were conducted in a controlled temperature/humidity room on specimens subjected to an air flow (50 percent relative humidity/74 F) of 60 ft/min over the evaporating surface (see Figure 1).

It was intended originally to analyze all of the specimens for chloride content as a function of depth from the evaporation surface after (1) demolding (24-hr cure), (2) a 28-day fog cure just prior to initiating flushing, and (3) flushing periods of 1 week, 1 month, 2 months, 4 months, and 6 months. Chloride analyses were made using a technique described by Berman(2), details of which are given in Appendix C. The technique provides a measurement of the total chloride content of the concrete.

As the data were accumulated, it soon became obvious that no redistribution of the chloride was occurring in the concrete. This situation is revealed in the data presented in Table 3 which gives chloride ion distribution in the cylinders under various treatments for flushing times up to 6 months. The variables of initial chloride content and concrete permeability (as influenced by water/ cement ratio of the concrete) did not appear to affect this result.

At this point, additional experiments were carried out to investigate methods for increasing the flow rate of deionized water through the concrete.

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* Sika-Guard, Aqua Top. Sika Chemical Corporation, Lyndhurst, New Jersey.

TABLE 2. DESCRIPTION OF CONCRETE FLUSHING EXPERIMENTS

Concrete Series Number	Variable Investigated	Chloride Content[(a)]	Concrete Mix Design	Deionized Water Supply Replenished or Changed	Moisture Condition of Concrete at Start of Flushing Trials
C2	Chloride Concentration	High	Standard OHD Class C Concrete W/C = 0.45[(b)]	Replenished	Mass concrete cure.
C3	Chloride Concentration	Median	"	"	"
C4	Chloride Concentration	Low	"	"	"
C5	Frequency of Water Supply Change	Median	"	Deionized Water Supply Changed at Weekly Intervals	"
C6	Surface Coating on Concrete	Median	"	Replenished	Mass Concrete Cure. Linseed Oil Coating on Concrete Drying Surface Prior to Flushing Trials
C7	Moisture Content of Concrete	Median	"	"	Specimens Dried at 50 RH (74 F) Prior to Use in Flushing Trials
C8	Moisture Content of Concrete	Median	"	"	Specimens with Sides Sealed Dried From the Ends Only at 50 RH (74 F)
C9	Concrete Permeability	Median	Modified Class C Concrete W/C = 0.4	"	Mass Concrete Cure
C10	Concrete Permeability	Median	Modified Class C Concrete W/C = 0.5	"	Mass Concrete Cure
C11	Concrete Permeability	Median	Modified Class C Concrete W/C = 0.6	"	Mass Concrete Cure
C12	Rainwater Effect	Median	Standard OHD Class C Concrete W/C = 0.45	"	Mass Concrete Cure. Deionized Water Placed on Drying Surface of Specimens at Bi-Weekly Intervals to Simulate Rainfall
C13	Method of Chloride Addition	Standard ODH Class C Concrete Prepared with no Chloride in Fresh Mix. Specimens Cured in Fog for 14 Days. Chloride Solution then Ponded on Top Surface of Side-Sealed Specimen. Moisture Free to Evaporate from Bottom Surface.			

(a) See Table 1 for quantitative meaning of descriptors.

(b) See Table 33.

TABLE 3. CHLORIDE ION ANALYSES OF CONCRETES SUBJECTED TO FLUSHING WITH DEIONIZED WATER AIR (50 RH/74 F) FLOW OVER EVAPORATING SURFACE OF 60 FT/MIN

Concrete Series	Chloride Content[(a)]	Component or Treatment Variable	Depth of Sample From Top of Evaporating Surface, in.	Chloride Content, gms per 100 gm of Dry Concrete After Indicated Treatment						
				Demolded	28-Day Fog Cure	Flushed 1 Week	Flushed 1 Month	Flushed 2 Months	Flushed 4 Months	Flushed 6 Months
C2	High	Air (50 RH/74 F) at 60 ft/min	0 to 1.0	0.139	0.135	0.146	0.142	0.135	0.134	-----
			1.0 to 2.0	0.117	0.124	0.119	0.124	0.117	0.119	-----
			2.0 to 3.0	0.059	0.064	0.061	0.071	0.055	0.061	-----
			3.0 to 4.0	0.025	0.026	0.025	0.025	0.026	0.024	-----
			4.0 to 5.0	0.018	0.019	0.017	0.018	0.016	0.018	-----
C3	Median	Air (50 RH/74 F) at 60 ft/min	0 to 1.0	0.068	0.065	0.073	0.069	0.071	0.071	0.071
			1.0 to 2.0	0.058	0.060	0.062	0.062	0.061	0.060	0.054
			2.0 to 3.0	0.043	0.026	0.040	0.036	0.034	0.034	0.030
			3.0 to 4.0	0.017	0.014	0.015	0.016	0.014	0.015	0.016
			4.0 to 5.0	0.017	0.011	0.012	0.012	0.011	0.013	0.012
C4	Low	Air (50 RH/74 F) at 60 ft/min	0 to 1.0	0.038	-----	0.036	0.037	0.035	0.037	-----
			1.0 to 2.0	0.030	-----	0.032	0.032	0.031	0.031	-----
			2.0 to 3.0	0.024	-----	0.020	0.018	0.019	0.020	-----
			3.0 to 4.0	0.010	-----	0.010	0.009	0.009	0.011	-----
			4.0 to 5.0	0.010	-----	0.009	0.007	0.007	0.009	-----
C9	Median	w/c ratio 0.4 Air (50 RH/74 F) at 60 ft/min	0 to 1.0	-----	-----	-----	-----	0.066	-----	-----
			1.0 to 2.0	-----	-----	-----	-----	0.050	-----	-----
			2.0 to 3.0	-----	-----	-----	-----	0.037	-----	-----
			3.0 to 4.0	-----	-----	-----	-----	0.020	-----	-----
			4.0 to 5.0	-----	-----	-----	-----	0.011	-----	-----
C10	Median	w/c ratio 0.5 Air (50 RH/74 F) at 60 ft/min	0 to 1.0	-----	-----	-----	-----	0.084	-----	-----
			1.0 to 2.0	-----	-----	-----	-----	0.064	-----	-----
			2.0 to 3.0	-----	-----	-----	-----	0.041	-----	-----
			3.0 to 4.0	-----	-----	-----	-----	0.015	-----	-----
			4.0 to 5.0	-----	-----	-----	-----	0.012	-----	-----
C11	Median	w/c ratio 0.6 Air (50 RH/74 F) at 60 ft/min	0 to 1.0	-----	-----	-----	-----	0.088	-----	-----
			1.0 to 2.0	-----	-----	-----	-----	0.061	-----	-----
			2.0 to 3.0	-----	-----	-----	-----	0.039	-----	-----
			3.0 to 4.0	-----	-----	-----	-----	0.017	-----	-----
			4.0 to 5.0	-----	-----	-----	-----	0.011	-----	-----

(a) See Table 1 for Quantitative Description of Chloride Contents.

Pressurized Supply Water Experiments

Specimens used in these experiments contained the median chloride level (Series C-3). The specimens were sealed in a Lucite water reservoir on the bottom surface, and overpressures of 5 and 15 psi were applied to the flushing water. Calibrated water columns formed a part of the reservoir water supply so that water movement into the specimens could be monitored.

The water movement into these specimens over a 90-day period is shown in Figure 2. For comparative purposes, data are included which show the moisture loss from the evaporating (top) surface of side-sealed specimens (no pressure on flushing water) over the same time period.

The total water movement into the bottom surface of the specimens ranged from 6 to 14 cm^3 over the 90-day period. The use of pressure (5 and 15 psi) on the supply water did not have any beneficial effect on the amount of deionized water which entered the specimens. The moisture movement of 6 to 14 cm^3 obtained by pressurizing the flush water for 90 days represents replacement of only 3 to 8 percent of the total free water in the specimens.

Pressure Plus Vacuum Experiment

In one of the pressurized supply water experiments, a Lucite chamber was attached to the top of the specimen so that a vacuum (29 in.) could be applied over the evaporating surface while a 15 psi overpressure was maintained on the flushing water. The results of this effort (also shown in Figure 2) showed that the application of vacuum at the evaporating surface, while maintaining 15-psi pressure on the flushing water, resulted in movement of 17.5 cm^3 of water in a period of 55 days. Extrapolated to 90 days, the total water movement under these conditions would be about 23 cm^3, or about 2-1/2 times the combined average movement under the influence of 5 and 15-psi overpressure.

Although the application of vacuum increased the moisture movement (12 percent free water replacement in 90 days), the use of a vacuum for this time period on a bridge deck in service is not practical nor would it be cost/effective.

Increased Air Flow Rate Experiment

In this experiment, specimens from the C-3 series (median chloride content) were placed (as shown in Figure 1) in a wind tunnel with an air flow of 600 ft/min over the evaporating surface. Ambient temperature was 74 F and the relative humidity 50 percent. Specimens were analyzed for chloride distribution following flushing periods of

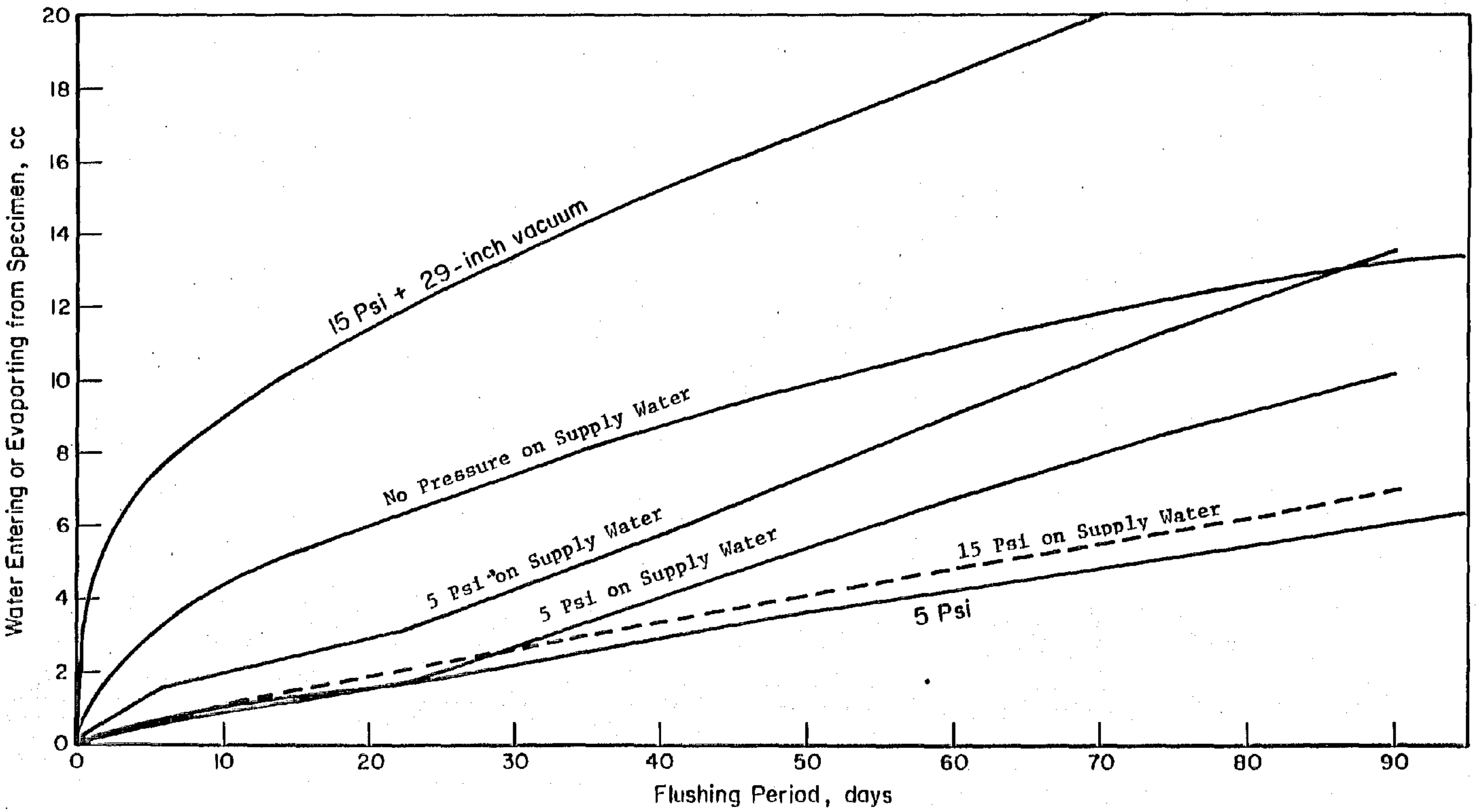


FIGURE 2. MOVEMENT OF WATER THROUGH AND FROM 4 x 8-IN. CONCRETE CYLINDERS (SIDES SEALED; BOTTOM SURFACE IMMERSED IN ION-FREE WATER; EVAPORATION FROM TOP SURFACE)

2 weeks, and 1 and 2 months. These results, shown in Table 4, indicate that an order of magnitude increase in the air flow rate over the evaporating surface had no effect on chloride distribution in the concrete in the 2 month period. The tests were discontinued at this time.

Heated Concrete Experiment

A concluding experiment involved the heating of the bottom of a sealed chloride-containing concrete cylinder in an effort to increase the driving force for the unidirectional movement of water upwards through the specimen. A potential twofold benefit was expected from the heating assuming that all of the water lost was from the evaporating (top) surface. First, movement of in situ free water from near the bottom (low chloride) to the top could, in itself, cause solution and transport of chloride ions toward the top. Second, subsequent immersion of the bottom of the previously heated specimen in ion free water should result in relatively rapid movement of water through the dried concrete to effect an additional flushing action.

The specimen used in this experiment was also from the C-3 series with the median chloride level. The bottom surface of the specimen was sealed to a 1/8-in.-thick aluminum plate, placed on a hot plate, and heated to 200-250 F (hot face temperature). Thermocouples were inserted at a depth of 1/2 in. into the specimen at intervals of 1, 2, and 3 in. from the bottom. The evaporating surface of the concrete specimen was subjected to an air (50 RH/74 F) flow of 60 ft/min.

Heating was carried out over an 80-day period during which time over 50 percent of the free water was removed from the specimen. Following this treatment, the bottom of the specimen was reimmersed in ion-free water until 90 percent of the water lost during heating was regained. A chloride analysis was then performed on the specimen. The results of this analysis are compared with the initial chloride distribution in the concrete below.

Depth of Sample From Top of Evaporating Surface, in.	Chloride Content, percent of dry concrete weight after indicated treatment	
	As-Cured	Heated and Flushed
0 - 1	0.068	0.072
1 - 2	0.058	0.056
2 - 3	0.043	0.038
3 - 4	0.017	0.018
4 - 5	0.017	0.014

It is obvious that the treatment of the concrete by heating and flushing did not produce the desired result of concentrating the chloride in the top portion of the concrete specimen.

TABLE 4. CHLORIDE ION CONTENT OF CONCRETE SPECIMENS (MEDIAN CHLORIDE CONTENT) FLUSHED WITH DEIONIZED WATER UNDER INFLUENCE OF 600 FT/MIN AIR (50 RH/74 F) FLOW

Depth of Sample From Top of Evaporating Surface, in.	Chloride Content, percent, After Indicated Flushing Period			
	Before Flushing	2 Weeks	1 Month	2 Months
0 to 1	0.065	0.068	0.070	0.070
1 to 2	0.060	0.063	0.061	0.058
2 to 3	0.026	0.038	0.028	0.035
3 to 4	0.014	0.015	0.009	0.015
4 to 5	0.011	0.013	0.007	0.012

The failure of the flushing concept to provide the desired redistribution of chloride is directly related to the relatively low rate of evaporation of water from the evaporating surface of the sealed specimens. This is illustrated in Figure 3 which shows the free water lost from 4 x 8-in. concrete cylinders exposed to 50 RH/74 F air for up to 30 weeks (air flow = 60 ft/min). In one case, the sides of the specimens were sealed so that evaporation took place only from the top and bottom of the cylinders (evaporating surface = 25.1 in.^{2}, maximum diffusion path = 4 in.). In the other case, the specimens were not sealed so that evaporation took place from the top, bottom, and sides of the specimen (evaporating surface = 125.6 in.^{2}, maximum diffusion path = 2 in.). After 30 weeks of drying, only 20 percent of the free water had been removed from the sealed specimens, compared with over 60 percent for the unsealed. Free water loss from the sealed specimens used in the flushing experiments (bottom immersed in ion-free water) was from the top surface only (maximum diffusion path = 8 in.), which means that less than 10 percent of the free water was removed from these specimens in a 6-month period. The depletion of free water in the capillaries of the concrete near the evaporating surface provides the driving force for upward movement of free water lower down in the specimens. For the flushing conditions used, this depletion was not enough to cause any significant movement of water from the lower portions of the specimens.

ELECTROCHEMICAL REMOVAL EXPERIMENTS (PHASE I)

The electrochemical removal concept involves the migration of chloride ions in concrete under the influence of an electrical potential gradient through the bridge deck concrete and an electrolyte contained above it. The potential gradient is produced by applying a direct current potential source between the reinforcing steel and an electrode contained in the electrolyte above the bridge deck. An ion-exchange resin contained in the electrolyte captures the chloride ions prior to their reaching the anode which prevents the discharge of chlorine gas and minimizes corrosion of the anode.

The laboratory phase of this work (Phase I) involved studies on 3 x 6-in. concrete cylinders and 46 x 60 x 9 in. concrete slabs. The initial laboratory work was directed at investigations of

(1) The identification of a suitable anode material
(2) The identification of a suitable ion exchange resin
(3) The identification of a suitable electrolyte.

Following this work the effort was directed to a study of the effect of concrete and process variables on the electrochemical removal of chloride ion. The variables studied included

(1) The magnitude of the applied electrical potential gradient
(2) The duration of treatment
(3) The initial chloride content of the concrete.

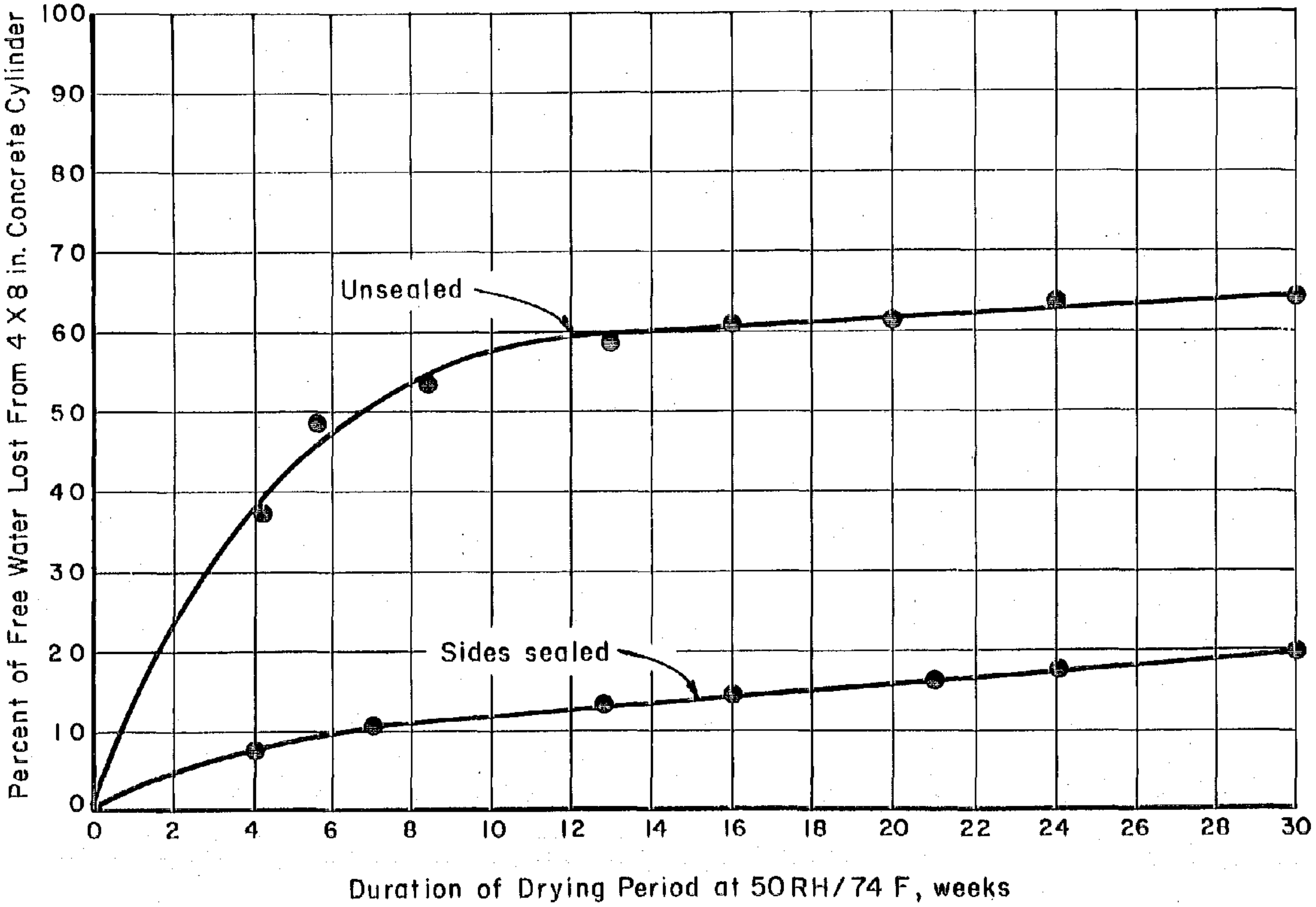


FIGURE 3. FREE WATER LOSS FROM SEALED AND UNSEALED CONCRETE CYLINDERS (4 X 8 IN.) AT 50RH/74 F

Air flow rate of 60 ft/min.

Initial Laboratory Experiments

All of the initial experiments were carried out on 3 x 6 in. standard concrete cylinders. The composition of the standard concrete and the specimen preparation procedure is described in Appendix B. Three levels of chloride ion were incorporated in the concrete (mean, high, and low) in the manner described in Appendix B. The specimens were fog room cured for at least 28 days prior to use in the experiments. On removal from the fog room the specimen sides were sealed with epoxy.

Laboratory experiments were conducted using the procedure illustrated in Figure 4. The concrete cylinder contained a No. 3 conventional reinforcing rod (with 2 in. of concrete cover) which functioned as the cathode in the system. A Lucite cell fitted to the top of the concrete specimen provided containment for the electrolyte and ion exchange resin and positioning for the anode. The top of the specimen was tapered slightly to fit snugly into the cell and sealing was effected by a neoprene O-ring. Lucite spacers in the cell provided control of the depth of electrolyte and resin between the anode and the concrete surface. The anode rested on the top spacer.

Electrical connections were made from the cathode through an Electronic Measurement Company, Inc. Programmable Transistor D-C Power Supply to the anode. Current was measured using a microammeter circuit linked to a Heath/Schlumberger Model SR-255B Strip Chart Recorder. The entire specimen assembly was housed in a plywood/Lucite box for safety purposes. In several of the experiments, specimen temperature was measured by means of copper/constantan thermocouples embedded in the concrete in drilled holes which were subsequently filled with cement paste.

Anode Materials

There are four main requirements for the anode material:

(1) Low anodic polarization characteristics (i.e., good electrocatalytic activity)
(2) Corrosion resistance at high anodic potentials
(3) Adequate mechanical strength
(4) Reasonable economy.

Candidate materials for anodes were titanium and titanium alloys, and also anodes used in industrial chloride production, that is, graphite and noble metals. Platinized titanium mesh was chosen to represent the latter because of its reasonable cost and availability. All of these materials, with the possible exception of the graphite, fulfill the mechanical strength requirement. Tests were devised to ascertain the electrochemical suitability for service.

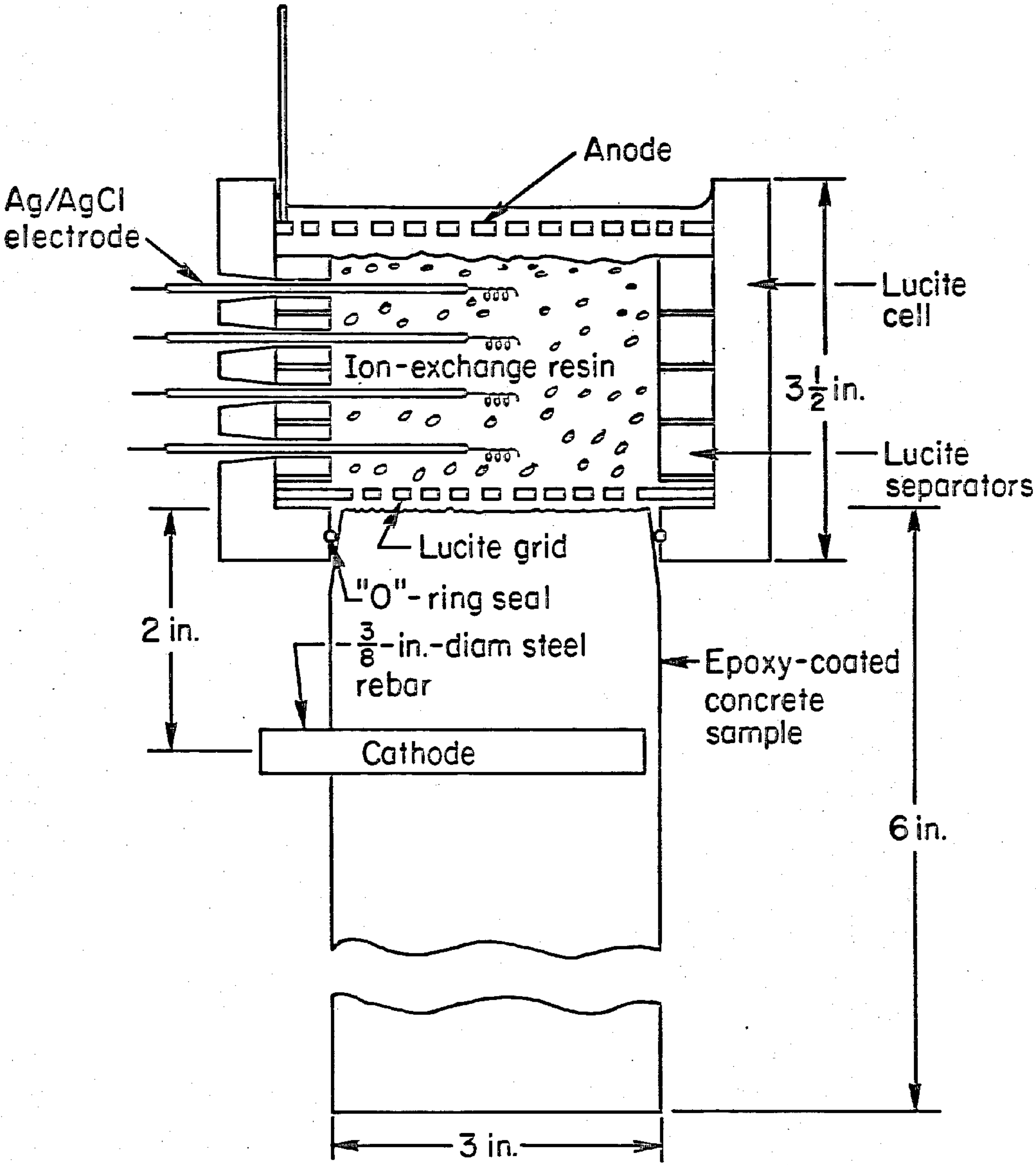


FIGURE 4. LABORATORY SETUP FOR STUDIES OF CHLORIDE REMOVAL

To obtain a fairly rapid evaluation of electrochemical behavior, the materials were subjected to an electrochemical test known as "potentiodynamic scans" in a standard electrochemical cell. Some confirmation experiments were carried out potentiostatically. The specimen was in the form of a sheet of the candidate material, 1 cm^2 in area, mounted in a Teflon holder facing downward towards a platinum counter electrode to simulate service conditions. A Luggin probe eliminated ohmic drops and a solution bridge led to an external saturated Calomel reference electrode. The electrochemical cell which was used is shown in Figure 5. The anode specimen is the disc labeled "A", the specimen holder labeled "H", and the counter electrode (platinum) labeled "C". The saturated Calomel reference electrode "R" and the Luggin probe "P" are also shown.

Experiments were performed in aerated pH 12 $Ca(OH)_2$ containing either 0, 0.1 M, or 1M NaCl to simulate possible service environments.

Figure 6 shows potentiodynamic scans obtained on titanium in the three solutions (direction of scan active to noble, from -1 V to +5 V_{SCE}). Examination of the titanium specimens at the end of each experiment showed a gold finish (anodization--interference colors from oxide film) but no corrosion. There was essentially no effect of Cl^- ion on the electrochemical behavior of this material. However, the current density was low, of the order of 10^{-4} A/cm^2 throughout the scan, and this indicated poor electrocatalytic activity for any anodic process. This was undoubtedly due to the oxide film present on the surface. The film provided good corrosion protection, but effectively stifled electrocatalysis.

The experiments were then repeated on three titanium alloys:

- Ti-0.2Pd (a much-used, corrosion-resistant alloy)
- "β-III" (Ti-11.5Mo-6Zr-4.5Sn; a high-strength corrosion-resistant alloy)
- Ti-6Al-4V (a high-strength, less corrosion-resistant alloy).

Results from scans for these materials in $Ca(OH)_2$ + 1 M NaCl are shown in Figure 7. There was little difference between the materials. Examination of the specimens revealed the gold anodized surface, with some incipient pitting on the Ti-6Al-4V. The electrocatalytic activity was low for all of these materials.

To investigate the pitting of the Ti-6Al-4V material, potentiostatic polarization at +5 V_{SCE} was performed on each alloy in the 1 M Cl^- solution. The resulting current density versus time curves are shown in Figure 8. There is no doubt that the Ti-6Al-4V supported a much greater current density than the other alloys. After the experiments this alloy was found to be extremely heavily pitted whereas the other alloys were anodized and unattacked.

These results suggested that, for one or more reasons, titanium and its alloys were not suitable anode materials. Graphite and platinized titanium were then tested. The results of potentiodynamic curves in $Ca(OH)_2$ + 1 M NaCl on these materials (up to 2 V_{SCE}) are shown in Figure 9.

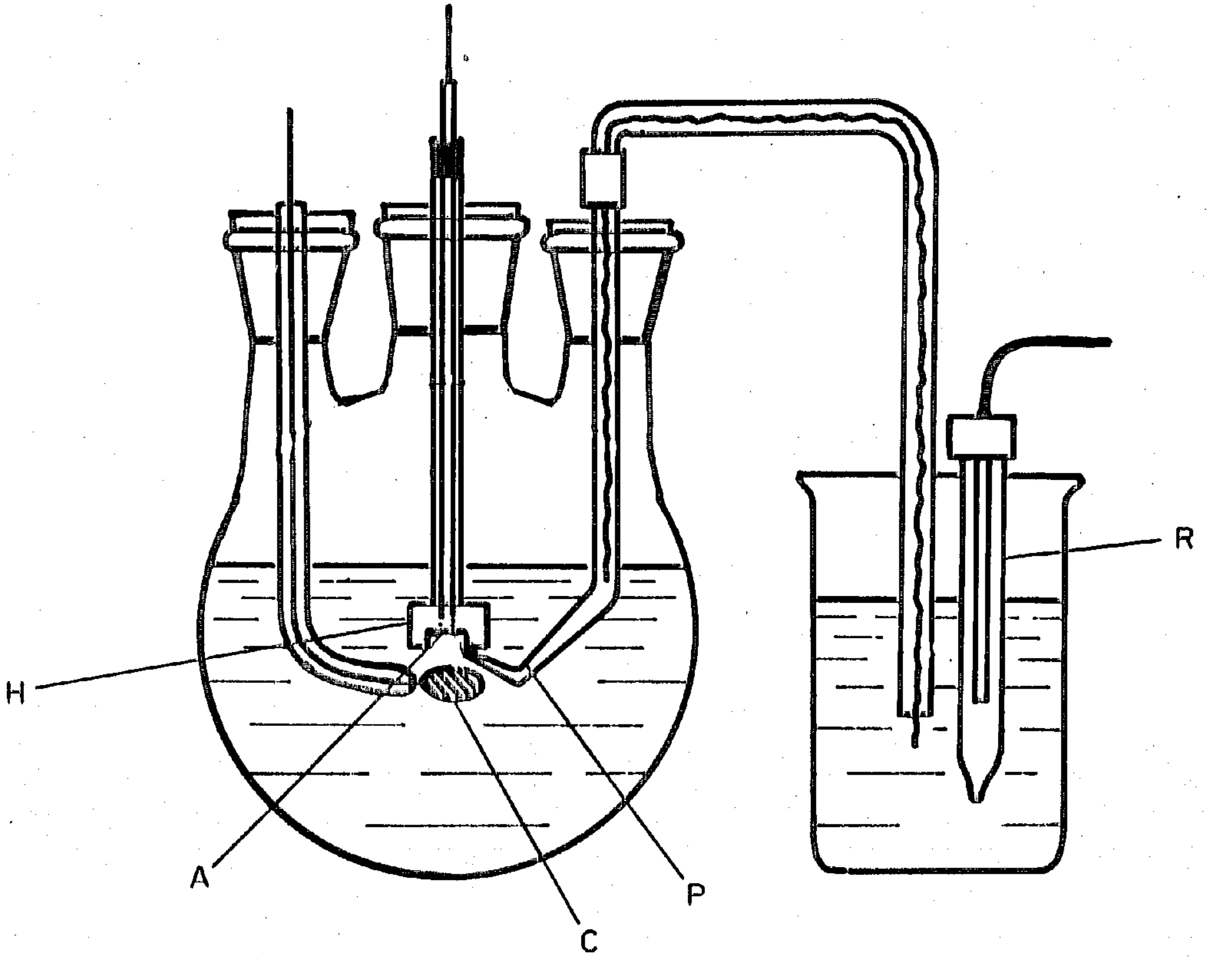


FIGURE 5. ELECTROCHEMICAL CELL FOR ANODE MATERIAL STUDIES

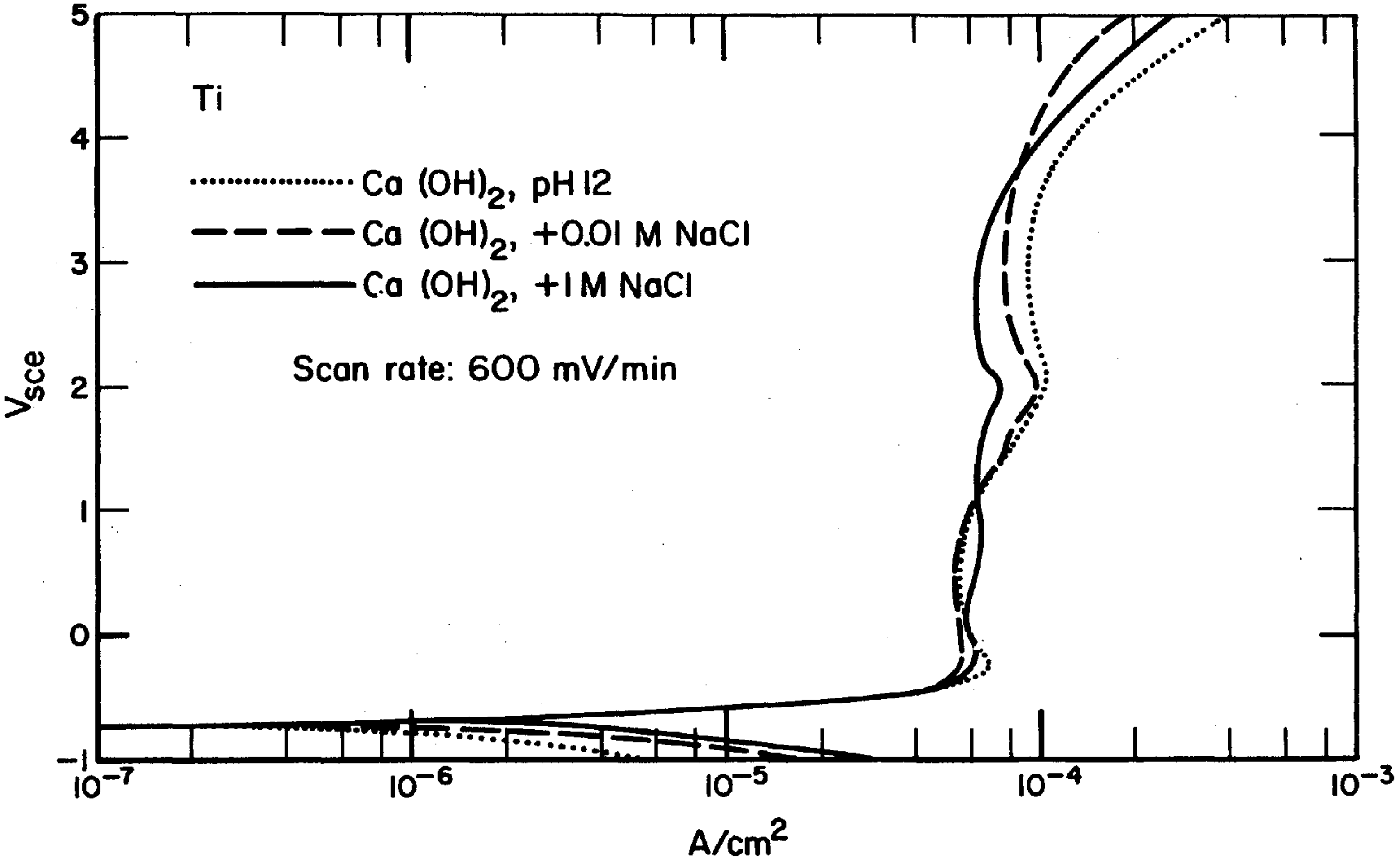


FIGURE 6. POTENTIODYNAMIC POLARIZATION CURVES FOR Ti

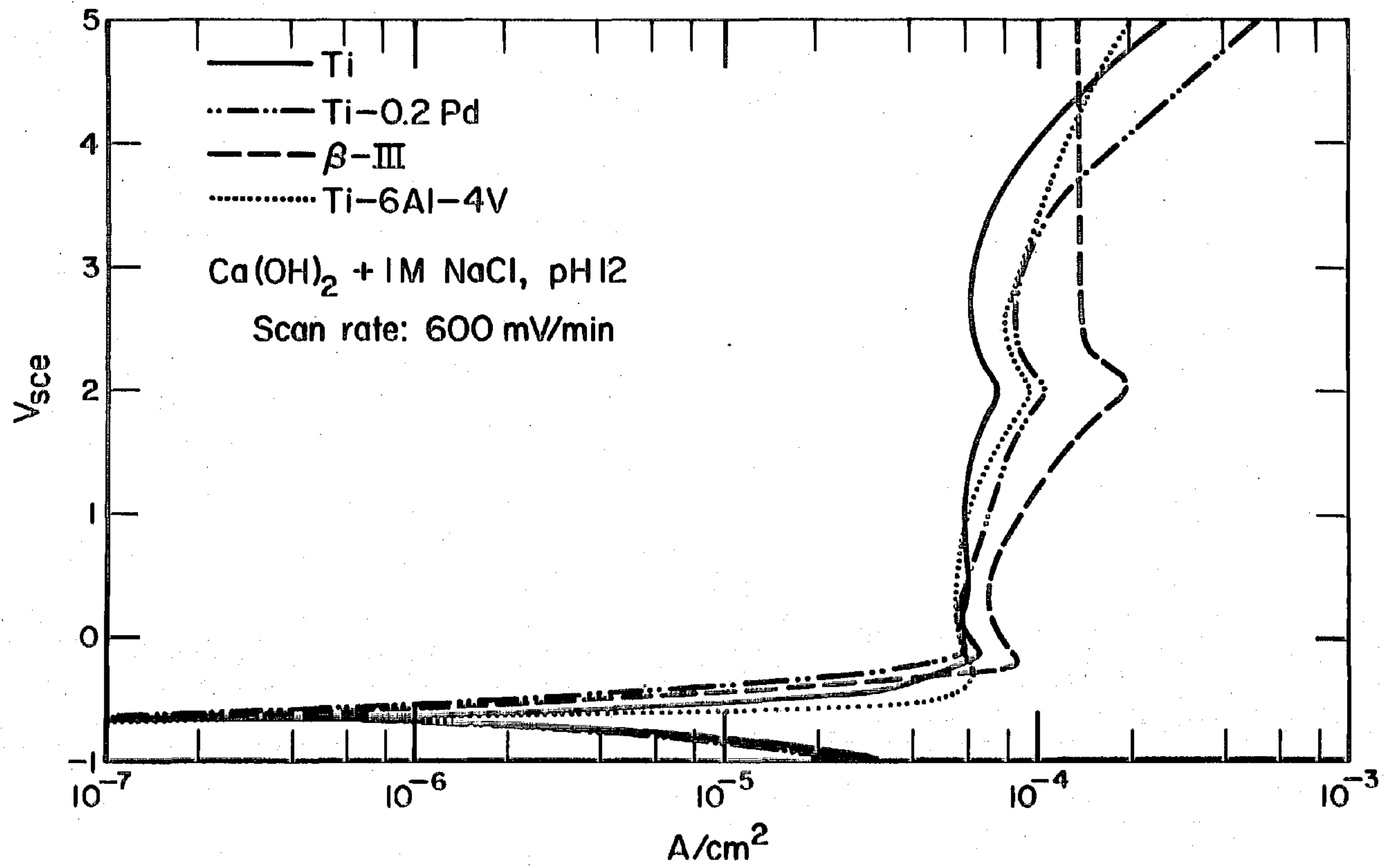


FIGURE 7. COMPARATIVE POTENTIODYNAMIC POLARIZATION CURVES FOR Ti ALLOYS

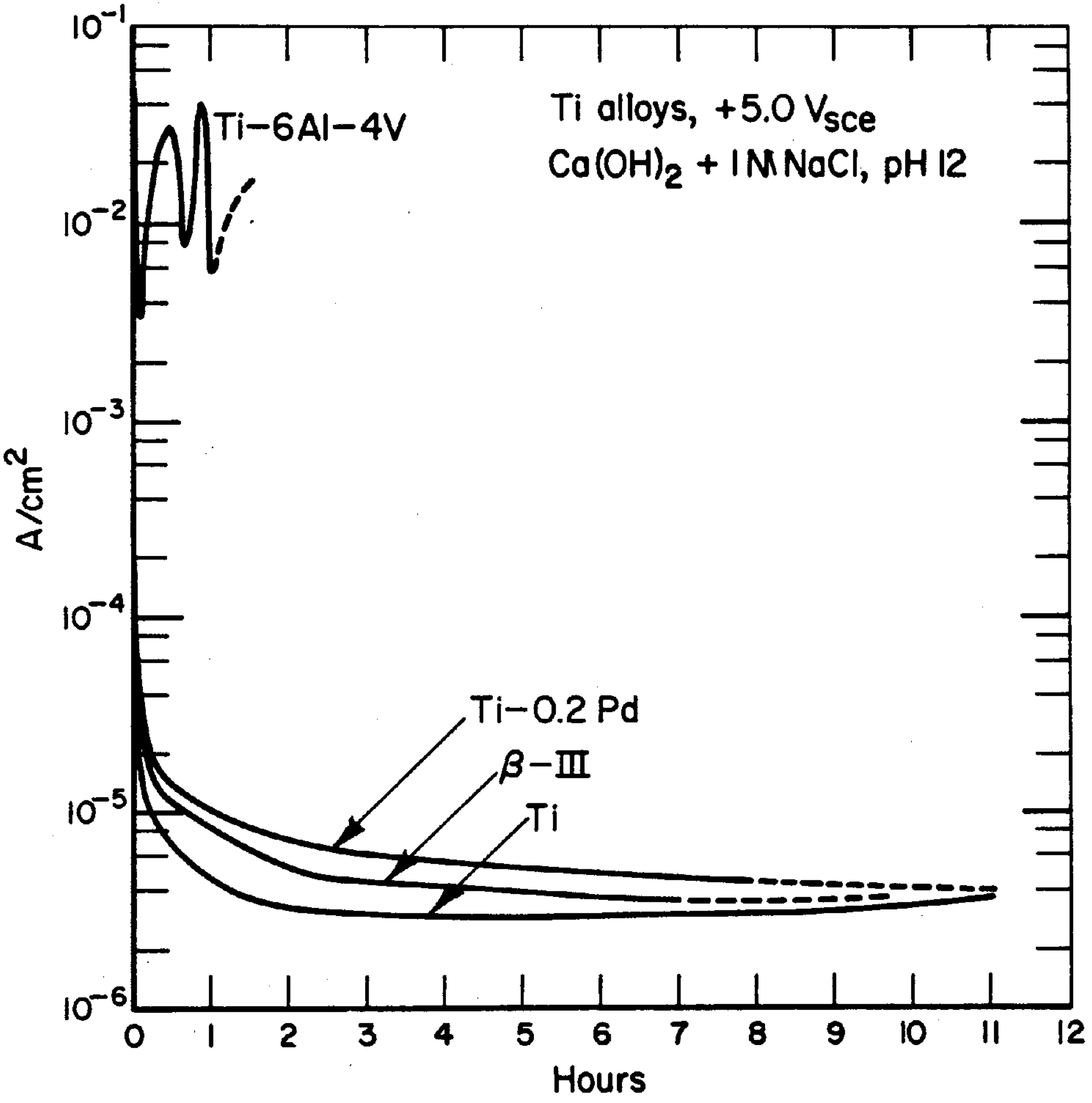


FIGURE 8. POTENTIOSTATIC POLARIZATION OF Ti ALLOYS AT +5 V_{SCE}

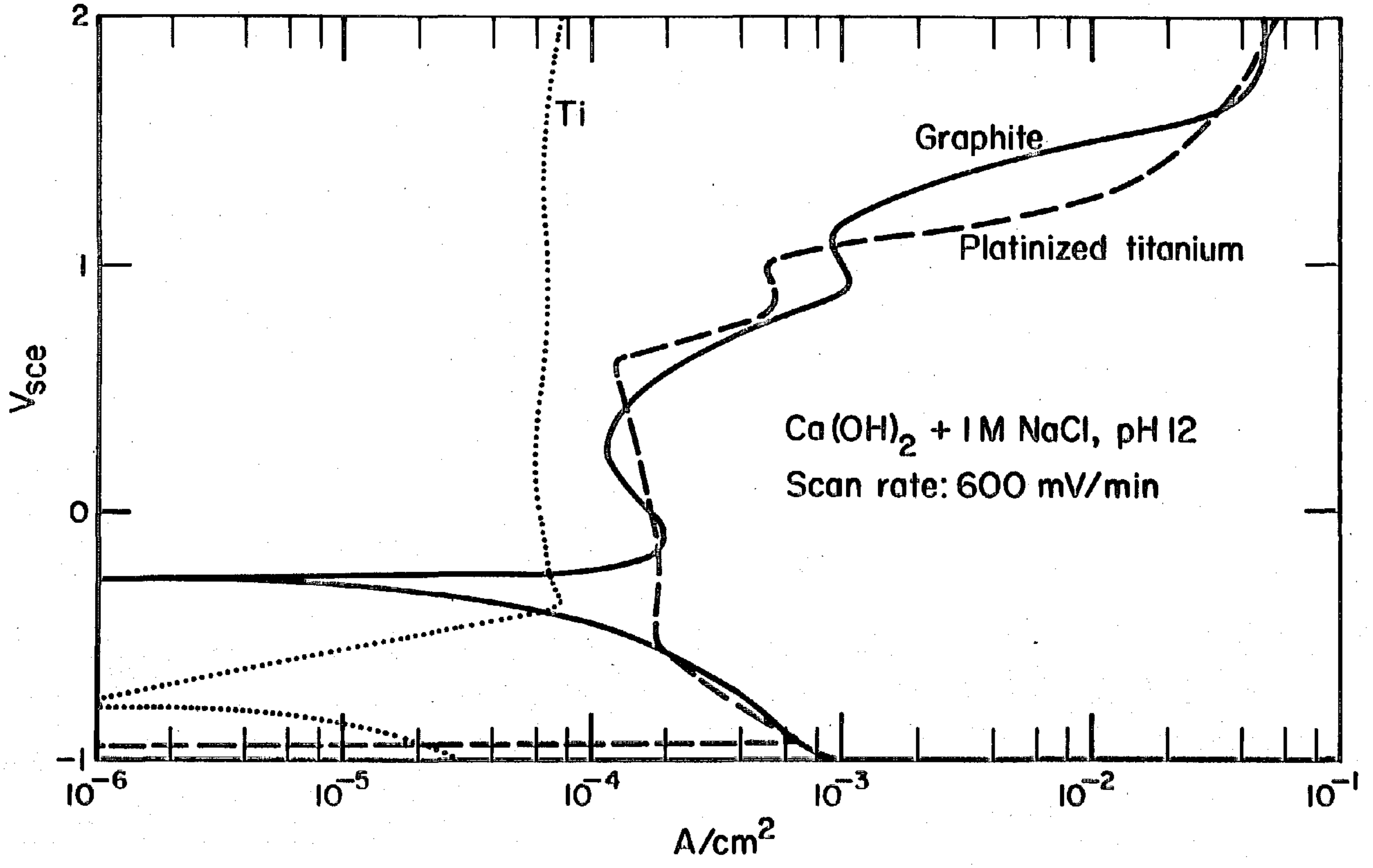


FIGURE 9. POTENTIODYNAMIC POLARIZATION CURVES FOR TITANIUM, GRAPHITE, AND PLATINIZED TITANIUM

The anodic branch of the curves for these materials was very similar. The "bumps" probably correspond to oxygen and chlorine evolution consecutively as the potential is increased. There is no doubt about the electrocatalytic activity of these two materials when compared with the titanium. At +1 V, the current density is an order of magnitude greater than for titanium, and at 2 V it is more than two orders of magnitude greater. As far as corrosion is concerned, the platinized titanium was unaffected at the end of the experiment. The surface of the graphite specimen was slightly disintegrated, probably due to bubble formation ($O_2 + Cl_2$) and/or some oxidation to CO_2.

On the basis of the established performance criteria, platinized titanium appeared to meet all of the requirements of an anode material. This material was used in all of the subsequent laboratory and field work.

Anion Exchange Resins

Chloride ions emerging from the concrete surface under the action of the driving voltage were to be "fixed" by reaction with anion exchange resin in the hydroxide form. The chloride ions exchange with the hydroxyl ions on the resin, and the freed hydroxyl ions move towards the anode to be discharged as oxygen. In this way, the evolution of chlorine at the anode, with its concommitant toxicity and corrosion problems, can be largely avoided.

The requirements for the exchange resin were

(1) Stability to oxidizing conditions in the anolyte
(2) Stability to extremes of pH in the anolyte
(3) Good strength for field use
(4) High exchange capacity
(5) Easy regeneration.

The first three of these requirements were met by a strongly basic resin containing quaternary ammonium groups fixed to a poly styrene-divinylbenzene matrix. High exchange capacity and ease of regeneration are reflected in the "selectivity ratio" for $Cl^-:OH^-$. In general, a high selectivity indicates a low regeneration efficiency, or at least a long regeneration time. Since it was desirable to optimize both removal of Cl^- and regeneration to the OH^- form for field use, these two parameters were studied for several candidate exchange resins.

The two resins studied were Dowex 1-X8 and Dowex 2-X8. Dowex 1 has trimethyl benzyl ammonium as the quaternary ammonium group, and exhibits a high selectivity ratio ($\sim$25) for $Cl^-:OH^-$. Dowex 2 has dimethyl ethanol benzyl ammonium as the quaternary ammonium group, and this gives a much lower selectivity ratio for $Cl^-:OH^-$ ($\sim$1.5). Table 5 gives selected properties of the two resins.

Most anion exchange resins are commercially available in the Cl^- form only. Inasmuch as the chloride-removal technique requires that the hydroxyl form be used, and regeneration also will be required in in the field, regeneration techniques in column and in batch form were evaluated.

A column elution apparatus was set up using a 100-ml burett as the column. Structure of the column is shown in Figure 10. In order to ascertain the progress and efficiency of regeneration, the H_2SO_4 and wash water were analyzed for chloride by electrometric titiation against $N/_{10}$ $AgNO_3$, using either an Ag/AgCl or Cl^--specific electrode as indicator. Typical results obtained on two Dowex 1-X8 Cl^- form columns were:

	Column 1	Column 2
Theoretical Cl^- in 100 ml wet resin	133 mE	133 mE
Cl^- extracted	153 mE	162 mE
Extraction Efficiency	115 %	121 %

This "over-extraction" was probably due to insufficient backwashing of the column, which led to an "effective" resin volume of greater than 100 ml. Nevertheless, it was obvious that the resin is easily regenerated via a sulfate intermediate in the column.

Column regeneration is possible only in the laboratory, as a means of converting Cl^- form to OH^- form and as a means of measuring Cl^- uptake by the OH^- form. Field regeneration requires a batch-type "immersion and mild agitation" regeneration process. In order to investigate this process, 50 g of Dowex 1 and Dowex 2 were treated with successive 50-ml portions of 5 percent NaOH, each extraction employing a 5-min agitation. The resin was filtered off after each treatment, washed, and each extraction plus wash analyzed for Cl^- ion electrometrically. The regeneration efficiency resulting from the batch operation is shown in Table 6.

These results indicated a significant advantage for the Dowex 2-X8 resin with regard to the efficiency of batch regeneration.

The column regeneration procedure for Dowex 1 provided by the manufacturer includes the intermediate step of treatment with H_2SO_4 before elution with NaOH. To investigate this procedure, two experiments were performed:

(1) Column elution without H_2SO_4 (only NaOH)
(2) Batch extraction with H_2SO_4 and then NaOH.

In the column, 100 ml of resin was treated with two consecutive 200-ml portions of 10 percent NaOH at a flow rate of 4.5 ml/min and a 500-cm^3 wash with distilled water followed each extraction. The eluates were analyzed for Cl^-after acidification with H_2SO_4. The results are shown in Table 7. This extraction efficiency (56 percent) after one

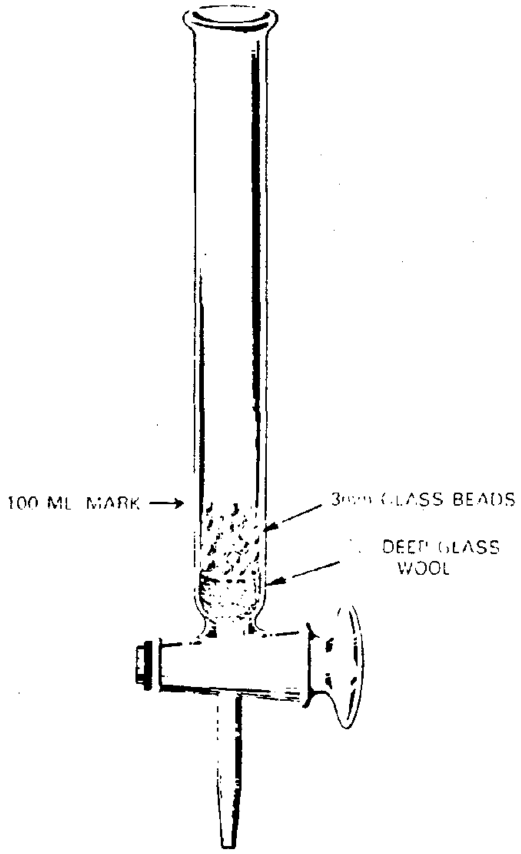


FIGURE 10. CONVERSION OF 100 ml BURETTE TO ION EXCHANGE ELUTION COLUMN

TABLE 5. PROPERTIES OF CANDIDATE ANION EXCHANGE RESINS

	Dowex 1	Dowex 2
Selectivity, $Cl^-:OH^-$	$\sim$25	$\sim$1.5
Moisture Content, %	43-48	38-45
Nominal Exchange Capacity (Cl^- Form)		
mE/g Dry Resin	3.2	3.2
mE/ml Resin in Column	1.4	1.4

TABLE 6. REGENERATION EFFICIENCY OF DOW ANION EXCHANGE RESINS-BATCH PROCESS

Total Available	Dowex 1-X8 88 mE		Dowex 2-X8 93 mE	
Cl⁻/50g	mE Cl⁻	% Efficiency	mE Cl⁻	% Efficiency
Extraction 1	14.2	16	35.4	33
Extraction 2	8.6	10	18.5	17
Extraction 3	6.3	7	10.8	10
Extraction 4	4.9	5	----	--
Total	34.0	38	64.7	60

TABLE 7. EFFECT OF H_2SO_4 INTERMEDIATE TREATMENT OF THE COLUMN REGENERATION EFFICIENCY OF DOWEX 1-X8

	mE Cl^- Extracted	Total Cl^- Available at Start	Percent Efficiency
Extraction 1	75.6	133	56
Extraction 2	22.8	133	17
Total Efficiency	98.4	133	73

extraction, compared with that previously given for the H_2SO_4 column extraction (115 percent) showed the necessity of the H_2SO_4 intermediary.

To investigate the use of H_2SO_4 in the batch extraction process, a 50-g sample of Dowex 1-X8 resin was treated successively with two 50-ml portions of 5 percent H_2SO_4 with a wash and filter after each extraction. Extractions were under agitation for 5 min. The extractant was analyzed for Cl^- with the results shown in Table 8.

After conversion to the sulfate form, the same 50-g resin was treated with two batches of 50-ml (standardized) 5%percent NaOH using the same wash and filtration procedure. The resulting extraction was titrated against N/10 HCl to give the hydroxyl ion exchange. The results are given in Table 9 (all efficiencies are based on total exchange sites available).

Based on SO_4^{2-} sites available of 70 percent, this result corresponds to a complete conversion of SO_4^{2-} to OH^- during this extraction.

It was concluded from this work that the use of Dowex 1-X8 in the field would require an intermediate regeneration step of conversion to the SO_4^{2-}-form. Dowex 2-X8 which had a better than 30 percent exchange efficiency after treatment with one batch of 5 percent NaOH is obviously preferred for field regeneration and was used in most of the subsequent laboratory and field work.

An experiment also was carried out to determine the efficiency of pickup of the migrating Cl^- by the ion-exchange resin during electrochemical treatment of a concrete specimen. Approximately 115 ml of resin bed (Dowex 2-X8) was used. This corresponds to an exchange capacity of 160 milliequivalents (mE) based on earlier experiments. In the experiment, 50 percent of the Cl^- was extracted from the concrete specimen during electrochemical treatment. This corresponds to 7.7 mE of Cl^- passing into the resin. Analysis of the resin after the treatment by eluting with H_2SO_4 in a 100-ml column revealed that 1.5 ml of 0.1N $AgNO_3$ was required to neutralize the eluted chloride; i.e., there was ∿6 mE of Cl^- in 100 ml of resin and ∿7 mE in the total resin volume (115 mE) used in the treatment. This correlated quite well with the calculated 7.7 mE passing into the resin and indicates a very efficient capture capacity for the resin under migration conditions.

Electrolytes

In most of the early experiments, 0.1N $Ca(OH)_2$ was used as the electrolyte solution. Table 10 presents data on four concrete specimens (3 x 6 in. cylinders, median chloride content) subjected to electrochemical treatment in terms of total chloride removed, the theoretical charge density required to remove that quantity of chloride, and the actual charge density used in the experiments. A comparison of the theoretical and actual current

TABLE 8. EFFECT OF H_2SO_4 INTERMEDIATE TREATMENT ON THE BATCH REGENERATION EFFICIENCY OF DOWEX 1-X8

	mE Cl^- Extracted	Total Cl^- Available	Percent Efficiency
Extraction 1	39.6	88	45
Extraction 2	22.4	88	25
Total Efficiency	62.0	88	70

TABLE 9. HYDROXYL ION EXCHANGE EFFICIENCY OF DOWEX 1-X8 RESIN

	mE OH^- Exchanged	mE Available	Percent Efficiency
Extraction 1	49.6	88	56
Extraction 2	16.2	88	18
Total Efficiency	65.8	88	75

TABLE 10. COMPARISON OF THEORETICAL AND ACTUAL CURRENT DENSITY REQUIREMENTS FOR CHLORIDE ION EXTRACTION FROM CONCRETE

Concrete[(a)] Specimen Number	Cl^- Removed, percent[(b)]	Theoretical Charge Necessary, C/cm^2	Actual Charge Necessary, C/cm^2	Efficiency, percent
11	26	8.2	95	9
2	49	15.8	480	3
3	57	18.4	390	5
4	50	16.1	240	7

(a) Concrete cylinders (3 x 6 in.) containing the median chloride content.

(b) Percent of total chloride in the concrete above the reinforcing bar (2 in.).

densities indicated a very low efficiency. That is, the contribution of chloride ion to the total current flow was quite low. This result was attributed to the predominance of hydroxyl ion in the system (from the electrolyte and the concrete free water). The hydroxyl ion is a much more mobile ion than the Cl^- ion. It therefore will move through the concrete faster than the Cl^- and carry a majority of the ionic current; thus the efficiency for Cl^- removal is low.

Several experiments were conducted in an effort to identify electrolytes that would produce a more efficient chloride ion extraction. In this work, magnesium acetate and distilled water were used as the electrolytes.

The investigation of distilled water as the electrolyte solution was prompted by the assumption that the ion source for this solution would be only dissolved hydroxyl and chloride ions from the concrete, which could permit chloride ion to provide a larger contribution to the current flow.

It was also assumed that the contribution of Cl^- to the ionic current flow could be increased through a decrease in the OH^- ion concentration by precipitation. $Mg(OH)_2$ is less soluble than $Ca(OH)_2$; hence the use of a magnesium salt in the electrolyte solution should lead to penetration of Mg^{2+} into the concrete to provide precipitation of $Mg(OH)_2$ and thereby reduce the OH^- concentration. The choice of magnesium salts was limited due to possible exchange of the anion with the ion exchange resin. Magnesium acetate was identified as an acceptable magnesium salt for this work.

In the experiments, concrete cylinders containing the median chloride level were subjected to electrochemical treatment for 24 hr under an applied potential of 100 V. The variation in current density with treatment time for the various electrolyte solutions is shown in Figure 11. The effect of the electrolyte on chloride extraction is shown in Table 11.

The use of distilled water and magnesium acetate as the electrolyte did not result in any significant increase in current density or chloride extraction relative to $Ca(OH)_2$ in the same function. The chloride removal was about the same when $Ca(OH)_2$ and $MgAc_2$ were used as the electrolyte. The use of distilled water as the electrolyte produced anomalous results in that while current densities were relatively high, very little chloride ion extraction took place.

On the basis of these results, no further work was done on electrolyte composition and $Ca(OH)_2$ was used as the electrolyte in all subsequent work.

One other aspect of the electrolyte which was investigated was the residence time of the electrolyte on the concrete prior to the initiation of the electrochemical treatment. The electrical conductivity of partially dried concrete is lower than that of saturated concrete. The shape of the current density versus time curves, with a rapid increase in current density to a maximum and then a gradual "tailing off", suggested that

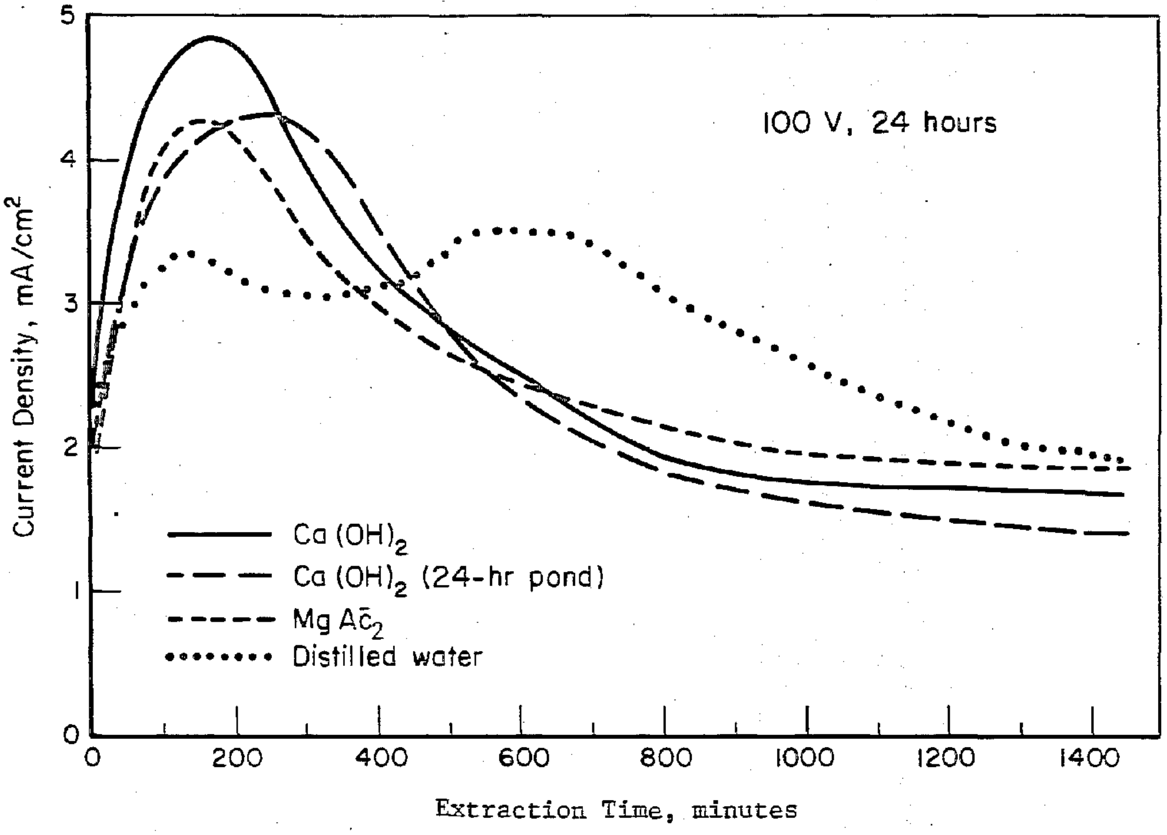


FIGURE 11. CURRENT DENSITY DURING ELECTROMIGRATION TREATMENT AS AFFECTED BY ANOLYTE COMPOSITION

TABLE 11. EFFECT OF ELECTROLYTE ON CHLORIDE EXTRACTION (100 Volts for 24 Hours)

	Chloride Content of Specimen After Electrochemical Treatment, percent		
Electrolyte	Top Slice, 0 to 0.7 in.	Middle Slice, 0.7 to 1.4 in.	Bottom Slice, 1.4 to 2.0 in.
Control Specimen	0.071	0.062	0.054
Dist. H_2O	0.069	0.053	0.046
0.1 N $Ca(OH)_2$	0.027	0.020	0.014
1M $MgA\bar{c}_2$	0.028	0.021	0.014

during the initial period of voltage application, an increase occurs in the conductivity of the concrete. A possibility which was considered here is that water, with or without dissolved ions, penetrates into the concrete during this initial period. In order to decrease the time necessary for extraction, therefore. the electrolyte could be applied for some time prior to application of voltage. In this way, the current density would be at a maximum upon initial voltage application. Inasmuch as the concrete near the surface of a bridge deck is in a partially dried condition, it was of interest to evaluate the effect of this variable on the rate of chloride ion removal.

In the experiment, the electrolyte solution [$Ca(OH)_2$] was ponded on the surface of the 3 x 6-in. concrete cylinder (median chloride content) for 24 hr prior to application of the voltage. This was intended to assure that the concrete above the reinforcing steel was near saturation at the time electromigration was initiated. The results of this work were presented in Figure 11.

Ponding of the electrolyte solution prior to electrochemical treatment did not have any significant beneficial effect on the amount of chloride removed under an applied potential difference of 100 V for a 24-hr removal period. The shape of the current density versus time curve also was essentially unchanged by preponding.

This result prompted the conclusion that electrolyte residence time was not a significant variable relative to chloride extraction and in most of the subsequent experiments, the residence time was 1 hour or less prior to electrochemical treatment.

Concrete and Process Variables

Concrete and process variables investigated relative to electrochemical chloride extraction efficiency included

(1) Duration of the electrochemical treatment
(2) The magnitude of the applied electrical potential
(3) The initial chloride content of the concrete.

In these experiments, the electrolyte solution was $Ca(OH)_2$, the anode was platinized titanium, and the exchange resin was Dowex 2-X8. The resin was slurried with the electrolyte prior to use. The resin depth was 0.5 in.

Applied Voltage Magnitude and Treatment Duration. Experiments were run on concrete containing the median chloride level using potentials of 50 and 100 volts for treatment periods up to 72 hr. The change in current density at 50 and 100 V as a function of treatment time is shown in Figure 12. The current density versus time curves at 50 V were essentially time independent, unlike the behavior at 100 V.

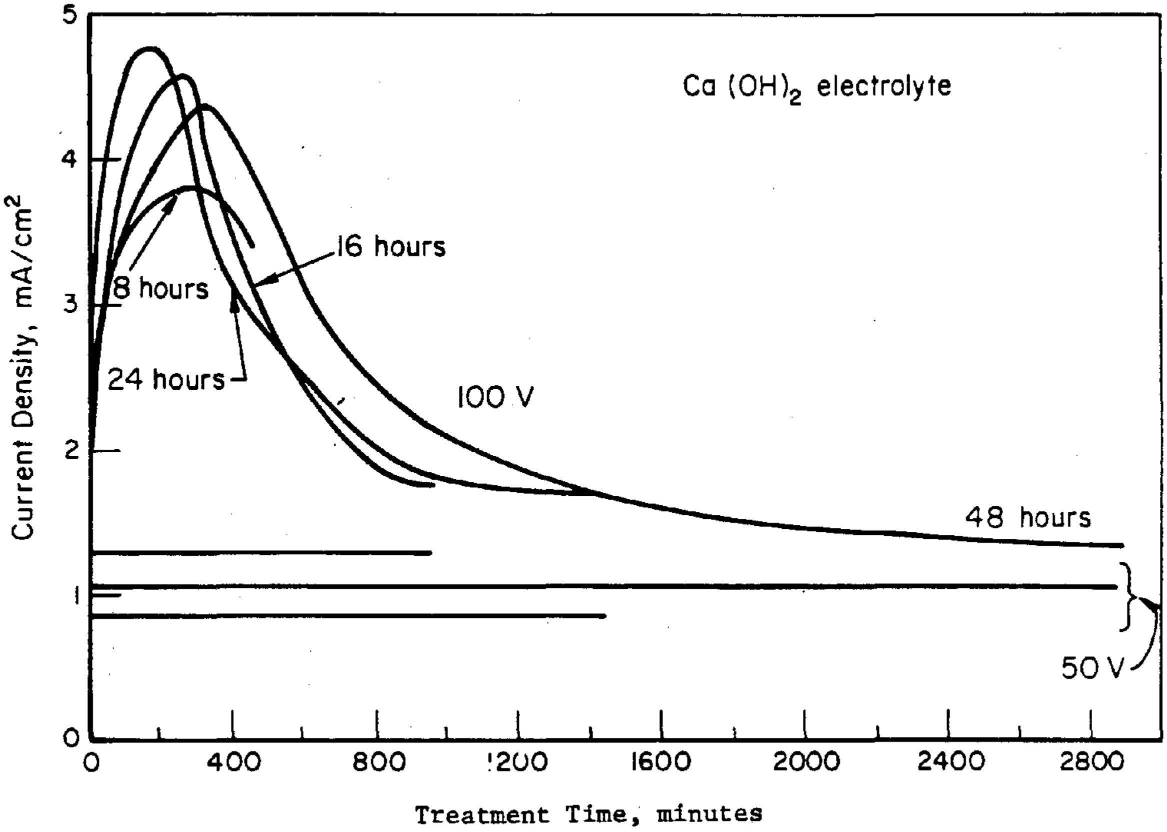


FIGURE 12. CHANGE IN CURRENT DENSITY WITH TIME DURING ELECTROMIGRATION TREATMENT

The effect of the duration of treatment at 100 V on the redistribution of chloride ion in the concrete is shown in Figure 13 and Table 12. At this chloride level, the removal was essentially complete in 24 hrs relative to the total removed after 72 hr treatment. A residual chloride content of 0.02 percent appeared to represent a threshold value for removal.

Figure 14 shows the effect of current passage and treatment time on the total chloride removed from the concrete at 100 V. Anionic currents evident at treatment times in excess of 24 hr are probably due predominantly to OH^- transport. Table 13 shows the efficiencies measured in the experiments. The efficiency fell rapidly after 24 hr due to Cl^- depletion or lack of mobility. Significantly, however, almost 70 percent of the total chloride was removed in just 24 hr of treatment at 100 V.

The use of an applied d-c voltage of 50 V did not produce any substantial reduction in the total chloride ion content of the concrete but did result in a migration of chloride ion from the concrete adjacent to the reinforcing steel to concrete near the top surface of the specimen. Following a 48-hr treatment at 50 V, only 9 percent of the total chloride in the concrete specimen was extracted. Total Cl^- content per cm^2 of surface above the rebar was 2.3 mE; thus, Cl^- removed was 0.21 mE. This should require 2.0 C for complete removal. In fact, 187 C were passed, giving an efficiency of 1 percent, about one-tenth that observed at 100 V. The reason for the lower efficiency at the lower voltage is probably associated with the high $OH^-:Cl^-$ ratio. Under the reduced electric field, the larger Cl^- ion is probably even less mobile than at 100 V. The time-independence of the current density, however, is not fully understood, when compared with the results at 100 V.

The temperature of the concrete during electrochemical treatment was measured through the use of a dial thermometer which was embedded within 1/8 in. of the reinforcing steel in the center of the 3 x 6 in. concrete specimen. Under an applied d-c potential of 100 V, the temperature of the concrete near the rebar rose to a maximum of 125 F over a 24-hr treatment period. At 50 V, the maximum temperature recorded was 85 F.

Concrete Chloride Content. Electrochemical treatment data were also obtained on concretes containing high and low chloride levels. Chloride analyses of the high chloride content concrete before treatment and after 24- and 48-hr treatments are shown in Figure 15 and Table 14. The results indicate that as the chloride content increases it may be necessary to increase the treatment time at a given voltage to reach the minimum residual chloride content. This latter value appears to be about 0.02 percent Cl^- (based on dry concrete weight) which is about 0.8 lb Cl^-/yd^3 of concrete. It is likely that this residual chloride may be complexed chemically with cement hydration products and is, thus, insoluble and not amenable to removal by the electrochemical process. This conjecture is strengthened by chloride analysis data obtained on concrete containing the low chloride content which was subjected to a 24-hr electrochemical treatment at 100 V (see Table 15). The starting chloride ion content varied from 0.012 to 0.010 percent in this concrete (top to 2.0-in. depth). Treatment of this concrete for 24 hr at 100 V had no measurable effect on the chloride content indicating that no Cl^- ion moved out of the concrete.

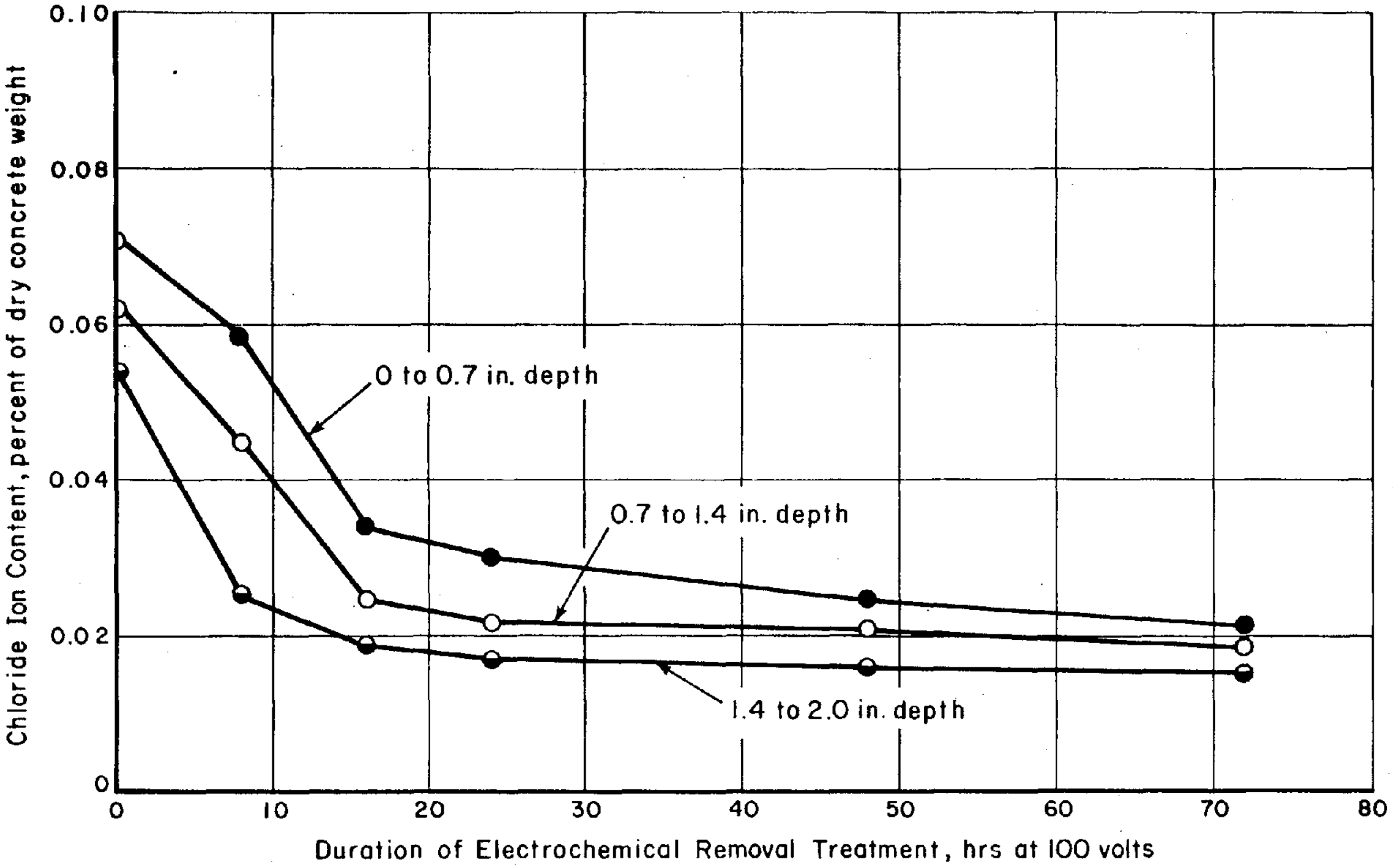


FIGURE 13. EFFECT OF DURATION OF ELECTROCHEMICAL REMOVAL TREATMENT ON THE CHLORIDE ION CONTENT ON CONCRETE CONTAINING THE MEDIAN CHLORIDE LEVEL (100 VOLTS APPLIED POTENTIAL)

TABLE 12. EFFECT OF TREATMENT TIME AND VOLTAGE ON THE ELECTROCHEMICAL REMOVAL OF CHLORIDE FROM CONCRETE

Specimen Identification Number	Applied d-c Voltage	Duration of Voltage Application, hours	Chloride Ion Content at Indicated Depth in Specimen, percent[(a)]		
			0 to 0.7 in.	0.7 to 1.4 in.	1.4 to 2.0 in.
C3 - 2	0	0	0.071	0.062	0.054
C3 - 30	100	8	0.059	0.045	0.025
C3 - 26	100	16	0.034	0.025	0.019
C3 - 44	100	24	0.030	0.022	0.017
C3 - 32	100	48	0.025	0.021	0.016
C3 - 27	100	72	0.021	0.019	0.015
C3 - 37	50	16	0.076	0.066	0.047
C3 - 34	50	24	0.077	0.061	0.040
C3 - 31	50	48	0.073	0.060	0.037

(a) Based on dry concrete weight

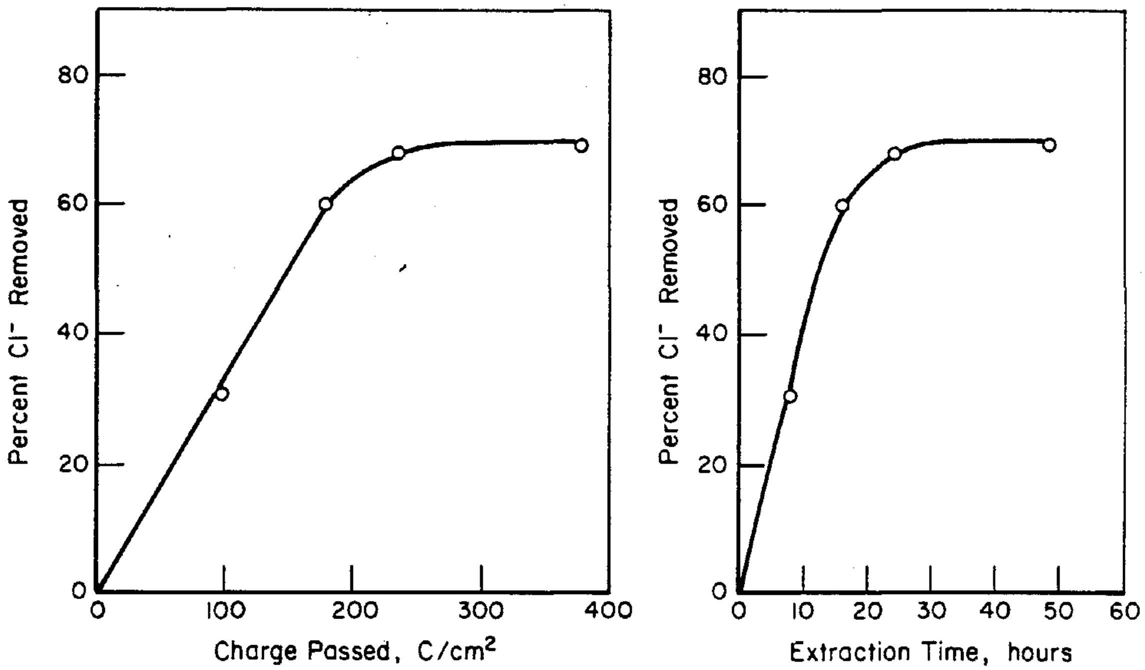


FIGURE 14. REMOVAL OF CHLORIDE ION FROM CONCRETE AS A FUNCTION OF CHARGE PASSED

TABLE 13. CALCULATION OF EFFICIENCY OF CHLORIDE ION REMOVAL DURING ELECTROMIGRATION TREATMENT

Condition	Chloride Content Percent[a/] Top Slice	Middle Slice	Bottom Slice	Percent Cl^- Extracted, total	Cl^- Extracted, mE/cm^2	Charge Needed, C/cm^2	Charge Passed, C/cm^2	Efficiency, percent
Control	0.071	0.062	0.054	----	----	----	----	--
8 Hours, 100 Volts	0.059	0.045	0.025	31%	0.072	6.9	99.5	7
16 Hours, 100 Volts	0.034	0.025	0.019	58%	0.133	12.8	178	7
24 Hours, 100 Volts	0.027	0.020	0.014	68%	0.156	15.1	234	6
48 Hours, 100 Volts	0.025	0.021	0.016	68%	0.156	15.1	378	4

Note: Specimen contains 2.77 lb. Cl^-/cu.yd. above rebar.
Volume above rebar = $1.5^2 \times \pi \times 2$ in. = 14.14 cu.in.
$\therefore$ total Cl^- in specimen = 0.38 g
$\therefore$ total Cl^-/cm^2 of surface = 0.00828 g/cm^2
= 0.23 mE/cm^2.

[a/] Based on dry concrete weight.

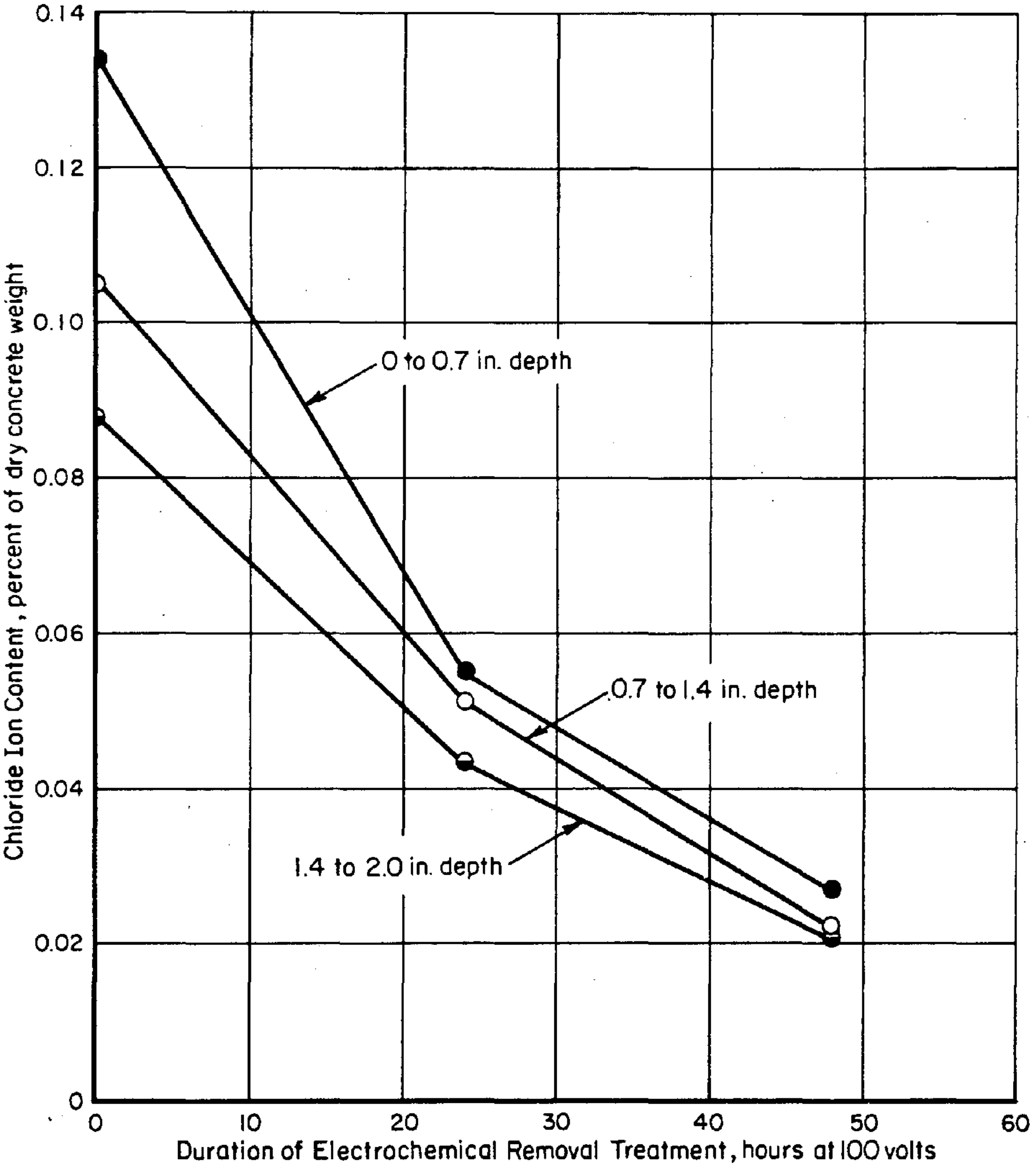


FIGURE 15. EFFECT OF DURATION OF ELECTROCHEMICAL REMOVAL TREATMENT TIME ON THE CHLORIDE ION CONTENT OF CONCRETE CONTAINING THE HIGH CHLORIDE LEVEL (100 VOLTS APPLIED POTENTIAL)

TABLE 14. CHLORIDE ANALYSES OF CONCRETE CONTAINING HIGH CHLORIDE LEVEL BEFORE AND AFTER ELECTROMIGRATION TREATMENT (100 VOLTS FOR 24 HOURS)

Depth of Concrete From Top Surface, inches	Chloride Content, percent[a/]	
	Untreated Concrete	Concrete Treated 24 Hours at 100 Volts
0 to 0.7 (Top Slice)	0.134	0.051
0.7 to 1.4 (Middle Slice)	0.105	0.055
1.4 to 2.0 (Bottom Slice)	0.088	0.043

[a/] Based on dry concrete weight.

The current density (at 100 V) as affected by initial chloride content is shown in Figure 16. The lower current density obtained on the high chloride content concrete remains an unresolved anomaly of the program results.

Results

The initial laboratory experiments demonstrated that the electrochemical technique for removing chloride ions from concrete is indeed feasible. Significant quantities of chloride were removed from 2 in. of concrete (above the top steel reinforcement level) using small laboratory specimens (3 x 6-in. cylinders) and using operating techniques and equipment that should be amenable to scale up to larger specimens and ultimately to bridge decks.

The salient findings of the initial laboratory work were as follows:

(1) Calcium hydroxide solution (0.1N) was identified as a suitable electrolyte.

(2) Platinized titanium was identified as a suitable anode material.

(3) Dowex 2-X8 was identified as a suitable anion exchange resin.

(4) The amount of chloride removed for a given treatment time increased with an increase in applied d-c voltage. At 100 V d-c (the maximum voltage used in the program), treatment times of 16 to 48 hr resulted in significant reductions in the chloride content depending on the initial chloride level and distribution. Treatment at 50 V was not sufficient to provide significant levels of chloride removal within a reasonable time frame.

(5) The treatment time for chloride removal increased as the initial chloride content of the concrete was increased. Substantial reductions in total chloride, however, were achieved in the high chloride content concrete in a 24 hr period.

(6) Although the efficiency of the chloride removal technique was quite low, it was possible to significantly reduce the chloride content of the concrete to below what is now considered a threshold value regarding the corrosion of the reinforcing steel. Attempts to improve the efficiency of the treatment through changes in the composition of the electrolyte solution were not successful.

TABLE 15. CHLORIDE ION CONTENT OF CONCRETE CONTAINING LOW CHLORIDE LEVEL (C4) BEFORE AND AFTER ELECTROCHEMICAL TREATMENT AT 100 VOLTS FOR 24 HOURS

Depth of Concrete From Top Surface, inches	Chloride Content, percent[a]	
	Untreated Concrete, (C4-19)	Treated 24 Hr. at 100 Volts (C4-18)
0 to 0.7	0.012	0.012
0.7 to 1.4	0.011	0.011
1.4 to 2.0	0.010	---

[a] Based on dry concrete weight.

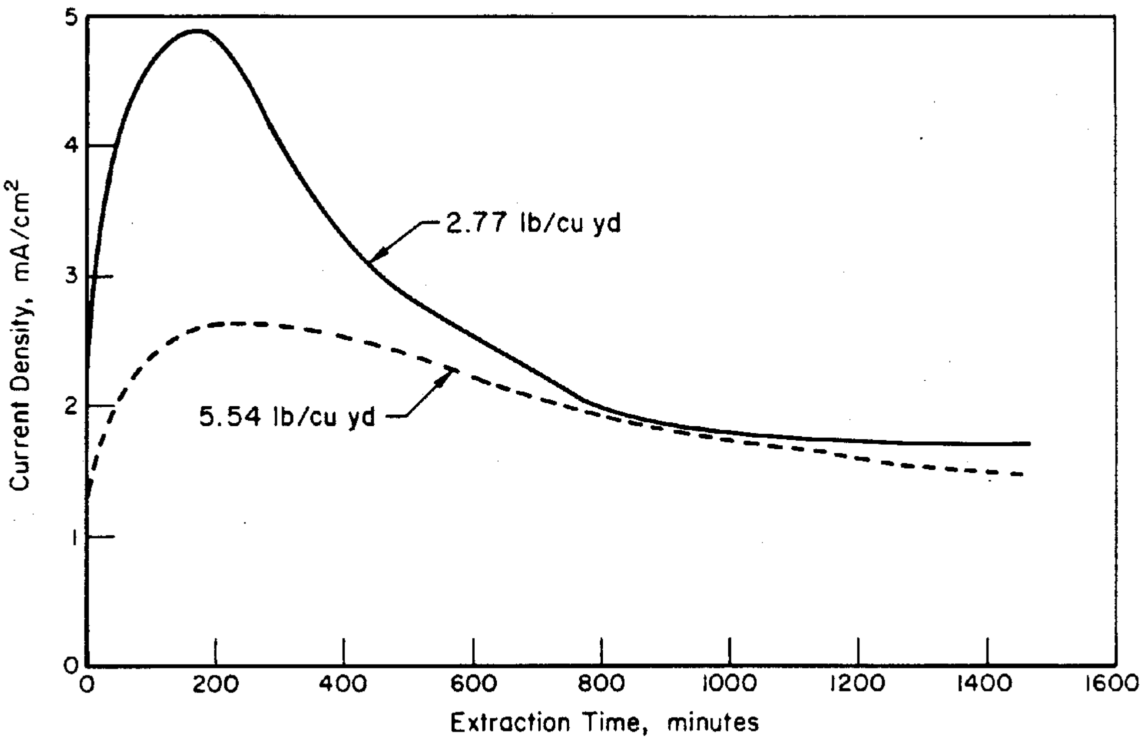


FIGURE 16. CURRENT DENSITY DURING ELECTROMIGRATION TREATMENT (100 V) AS AFFECTED BY INITIAL CHLORIDE CONTENT OF THE CONCRETE

(7) The temperature of the concrete (laboratory specimens) during electromigration treatment increased from 75 to about 125 F at 100 V d-c. The elevated temperature exposure had no obvious adverse affect on the integrity of the concrete.

(8) For the laboratory specimens there appeared to be a threshold value for chloride removal (residual chloride content of 0.02 percent or about 0.8 lb Cl^-/yd^3 of concrete). The fact that no chloride was removed from concretes containing 0.012 percent Cl^- which were electrochemically treated for 24 hr places more credence in the existence of a lower threshold value. These and other laboratory results suggest that a portion of the total chloride in concrete is present in an insoluble form and hence will not be amenable for removal by the electrochemical technique. If the insoluble chloride remaining in the treated concretes stays in that form, it will not be available to influence the steel corrosion process. However, the removal of Cl^- electrochemically could possibly upset an equilibrium between soluble Cl^- and complexed, insoluble Cl^- which could result in dissolution of the latter to reachieve equilibrium.

The positive results obtained in the initial experiments prompted the decision to continue the electrochemical removal investigations on 46 x 90 x 9 in. simulated bridge deck slabs.

EXPERIMENTS ON SIMULATED BRIDGE DECK SLABS

Following laboratory work on 3 x 6 inch cylinders, electrochemical chloride removal experiments were begun on 46 x 90 x 9-in. concrete slabs. The slabs were constructed in several lifts, with concrete containing Cl^-(added as NaCl to the mix water). Concrete composition and rebar placement and size was the same as in the actual bridge deck which was selected for study in the program. A total of five slabs were constructed which are identified in Table 16. Details concerning the construction of the slabs are given in Appendix D.

The slabs were prepared during November, 1973, and were wet burlap cured in the molds for 28 days. On demolding the sides of the slabs were coated with epoxy. This was followed by a 14-day indoor drying period at which time the slabs were placed outdoors on elevated (3-ft) standards. Ponding of the slabs with a 3 percent NaCl solution was begun in April, 1974. The solution was replenished on a daily basis. Electrochemical removal experiments with the slabs were begun during September, 1974. With the obvious exception of scale-up requirements the technique and equipment used was similar to the laboratory experiments on the small 3 x 6-in. cylindrical specimens. The experimental set-up is shown in Figure 17.

TABLE 16. PROPERTIES OF FRESH CONCRETE USED IN SIMULATED BRIDGE DECK SLAB CONSTRUCTION

Slab No.	Mix Designation	Layer in Slab	Chloride Added (Cl^-), lb/yd^3	MBVR Added, cc per batch	Slump, inches	Air Content, v/o	Measured Unit Weight, lb/ft^3
A-1	A	Bottom	0	60	3	4.0	--
	B	Middle	0.52	85	4-1/8	6.6	139.00
	C	Top	2.77	70	4-1/2	6.4	139.25
A-2	A	Bottom	0	70	3-1/8	5.0	144.75
	B	Middle	0.52	70	3-1/16	6.0	143.50
	C	Top	2.77	70	3-1/8	5.6	142.75
B-1	A	Bottom	0	70	3	5.2	142.00
	A	Middle	0	70	3-3/8	5.6	142.75
	D	Top	5.54	70	3-3/4	5.8	142.25
B-2	A	Bottom	0	70	3-1/2	6.0	141.25
	A	Middle	0	70	3-1/8	5.7	141.75
	D	Top	5.54	70	4-1/2	6.2	140.25
C-1	A	Bottom	0	70	3	5.0	144.25
	B	Middle	0.52	70	3	5.2	143.50
	C	Top	2.77	70	3-1/4	6.4	144.25

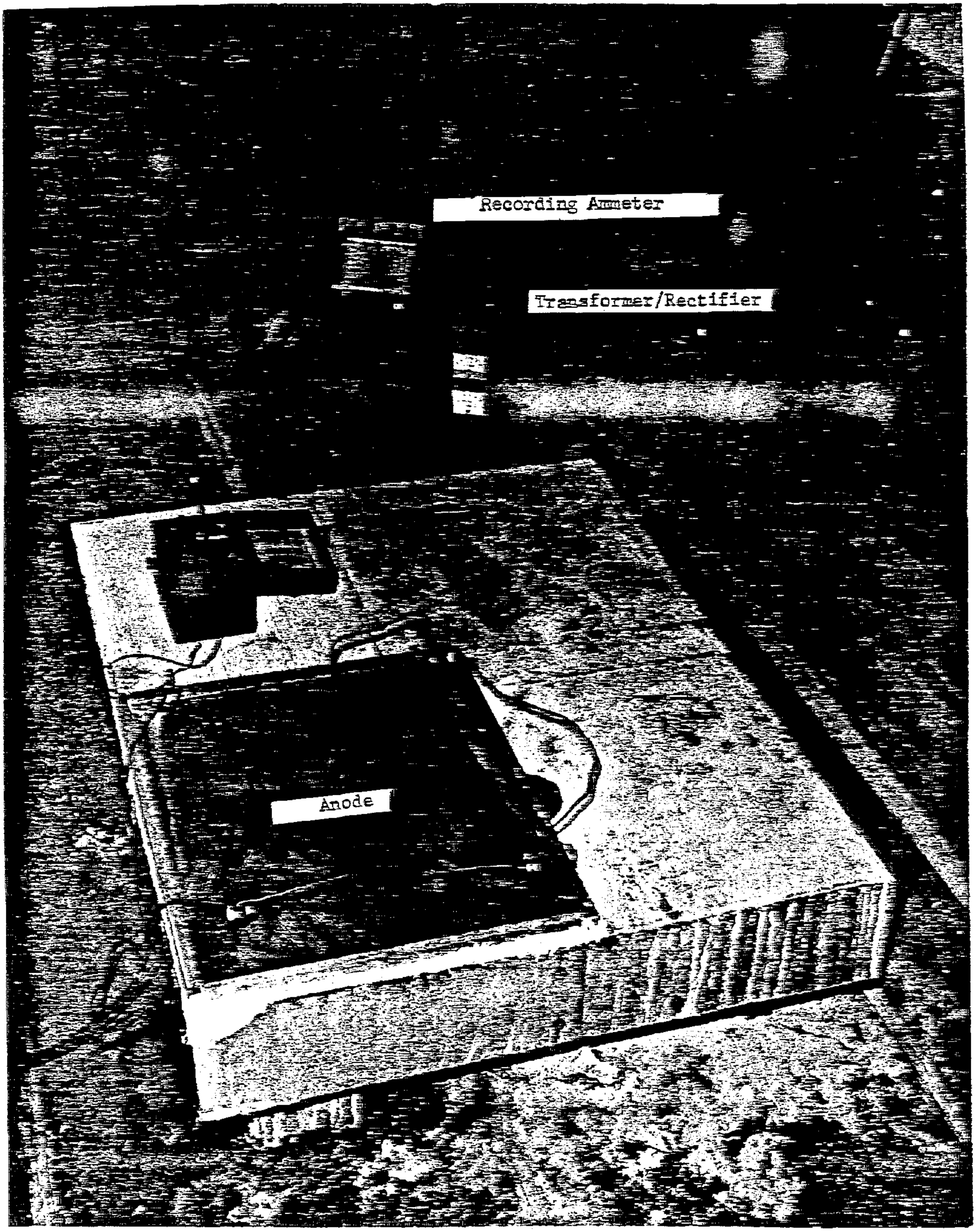


FIGURE 17. EXPERIMENTAL SETUP FOR THE ELECTROCHEMICAL REMOVAL OF CHLORIDE ION FROM (4 X 5 FT) SIMULATED BRIDGE DECK SLABS

Electrical power for the large slab work was supplied by a 5-kW gasoline-driven portable generator. Voltage was controlled by a variable transformer and a full-wave rectifier was used to convert the a-c current to d-c. Electrical connections were made to the reinforcing steel in the concrete (top and bottom mats) and to a 24 x 30-in. platinized titanium electrode (in expanded metal form) on the upper surface of the slab. A wooden dike, sealed with silicone sealant, served to contain the ion exchange resin and the anolyte solution (0.1N calcium hydroxide solution).

A total of three experiments were completed in which the primary variables were the total duration of treatment and the continuity of treatment (intermittent versus continuous treatment). In all cases the applied d-c potential was 100 V.

Data were obtained under the following conditions:

(1) 24-hr intermittent treatment (three 8-hr runs)
(2) 48-hr intermittent treatment (six variable time runs)
(3) 24-hr continuous treatment.

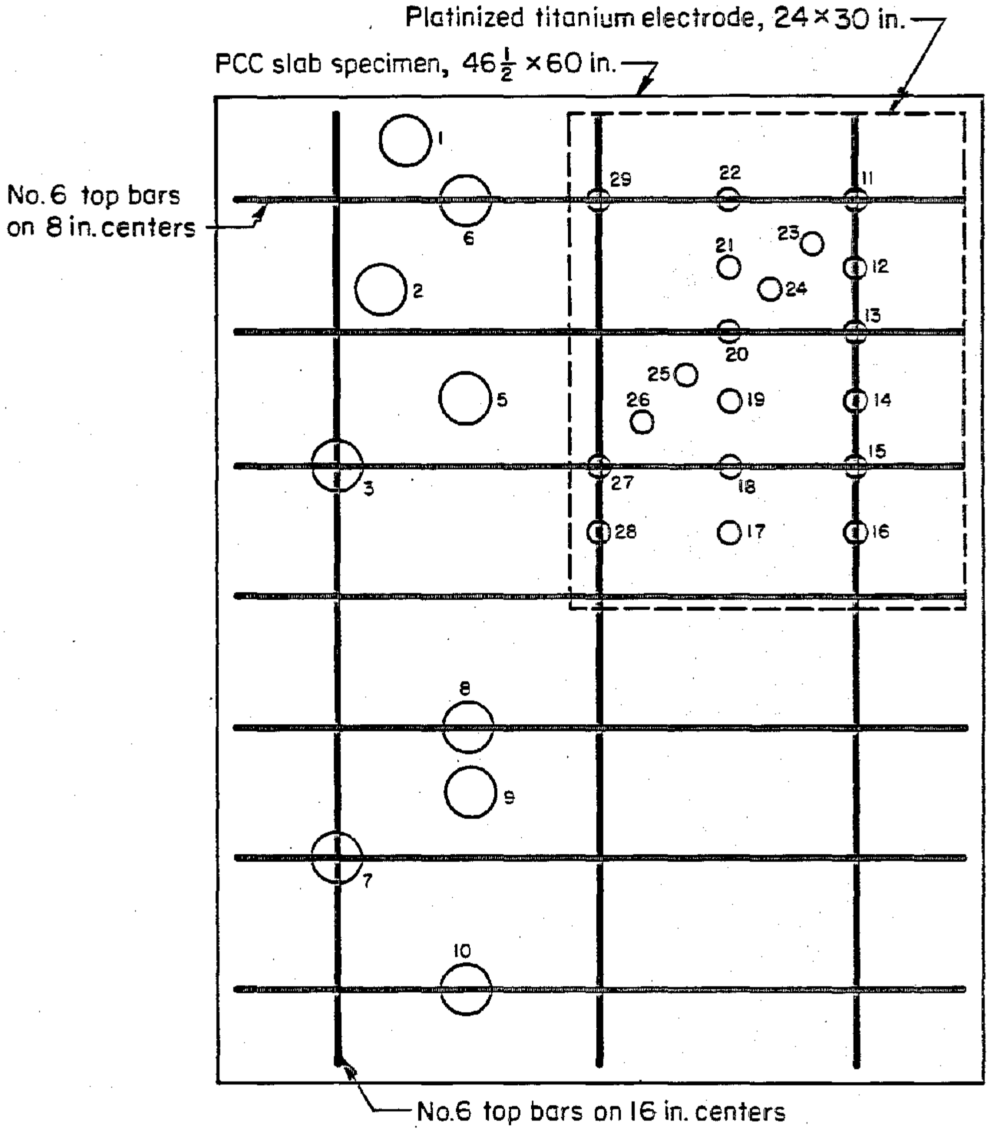
The temperature of the concrete during treatment was monitored in several cases using imbedded copper-constantan thermocouples.

24-hr Intermittent Treatment

The initial experiment was conducted at 100 V d-c potential with a total treatment time of 24 hr (three 8-hr runs). A total of five 3-in.-diam cores were taken from the slab before (two cores) and after (three cores) the electrochemical treatment. The location of the cores taken for chloride analyses and the location of the anode with respect to the slab surface and the top rebar mat is shown in Figure 18. The cores representing post-treatment conditions were taken directly over a longitudinal/transverse rebar crossing, directly over a transverse rebar and in the geometrical center of a transverse/ longitudinal rebar grid (8 x 16-in. section). The latter core represents concrete furthest removed from the cathode.

As was observed with the small laboratory specimens, the current rose slowly as treatment progressed, peaked (at 16 A), then slowly fell for the duration of the treatment period. The temperature of the electrolyte solution increased during treatment from 74 F to about 140 F.

Chloride analysis data obtained on the cores before and after the 24-hr treatment are presented in Table 17. As was expected, chloride removal was greatest in the concrete located directly over the reinforcing steel (Cores 6 and 3) where current flow is undoubtedly highest. At the level of the reinforcing steel, the chloride content was reduced to 0.02 to 0.03 percent, which in previous work was a lower limit threshold value for removal by the technique.



Cores 1-6 quadrant treated 24 hrs intermittent
Cores 7-10 quadrant treated 48 hrs intermittent
Cores 11-29 quadrant treated 24 hrs continuous

FIGURE 18. CORE AND ANODE LOCATIONS ON THE SIMULATED BRIDGE DECK SLAB

TABLE 17. CHLORIDE ION CONTENT OF CORES FROM SIMULATED BRIDGE DECK SLAB NO. B-1, BEFORE AND AFTER 24 HOUR INTERMITTENT ELECTROCHEMICAL TREATMENT

Depth of Core Samples From Slab Surface, inches	Chloride Ion Content, percent (Based on Dry Concrete Weight)						
	Untreated Concrete			Treated Concrete, 24 hr at 100 volts			
	Core 1	Core 2	Average	Core 3	Core 5	Core 6	Average
0 to 1.1	0.32	0.32	0.32	----	----	----	----
1.1 to 2.2	0.14	0.13	0.14	----	----	----	----
2.2 to 3.3	0.07	0.11	0.09	----	----	----	----
3.3 to 4.4	0.01	0.04	0.03	----	----	----	----
4.4 to 5.5	0.01	0.01	0.01	----	----	----	----
0 to 0.8	----	----	----	0.05	0.08	0.03	0.05
0.8 to 1.7	----	----	----	0.04	0.11	0.02	0.06
1.7 to 2.5	----	----	----	0.03	0.09	0.02	0.05
2.5 to 3.0	----	----	----	0.03	0.10	0.02	0.05
3.0 to 4.1	----	----	----	----	0.09	----	----
4.1 to 5.2	----	----	----	----	0.02	----	----

Core Locations:

3 = Above rebar crossing point
5 = Central between transverse rebars, 8-in. spacing
6 = Above transverse rebar

Chloride removal was least in the concrete furthest removed from the reinforcing steel (Core 5). Even in this area, significant reductions in chloride content were achieved. In the top 1 in. of concrete in this area, the chloride content was reduced from 0.32 to about 0.10, a reduction of almost 70 percent. However, the chloride distribution in the top 4 in. of concrete in this area was quite uniform (about 0.10 percent). This indicates an actual increase in the chloride content of concrete located at approximately the 3 to 4-in. level.

On the basis of averaged values, it is estimated that about 65 percent of the total chloride in the concrete in the slab (in the treated area) was removed by the 24-hr treatment. If a threshold removal value of 0.02 percent is assumed, this value increases to imply that approximately 80 percent of the chloride that can be removed by the technique was removed.

One problem that emerged in the experiment was the high temperature created in the concrete (about 140 F). This caused the formation of two cracks in the concrete which were located about 10 in. from the corner of the treated slab area. The cracking is undoubtedly due in part to the asymmetrical nature of the heating in the slab (one quadrant heated, three quadrants at ambient temperature). The cracking situation was discussed with Mr. William Cheatham, Structure Maintenance and Inspection Engineer with the Ohio Department of Transportation. He noted that most, if not all, of the bridge decks in Ohio have numerous transverse cracks already and that if new cracks were created during the treatment, they would have no effect on the structural integrity of the bridge and could probably be tolerated.

48-Hr Intermittent Treatment

Table 18 gives chloride analysis data obtained on 3-in. diam cores before and after the 48-hr intermittent treatment (six individual runs). Extending the duration of treatment from 24 to 48 hr (on an intermittent basis) did not provide any further reduction in the chloride ion content of the concrete.

The current density versus time data for the 48-hr intermittent run are shown in Figure 19. It appears that the serrated nature of the curve is due to the cool down and, hence, decreased conductivity of the concrete between extraction periods.

24-Hr Continuous Treatment

A 720-in.^{2} area of slab B-1 was subjected to a continuous 24-hr treatment at 100 V d-c potential. Following treatment, nineteen 1-1/4-in. diam cores were taken as shown in Figure 18 to establish the effect of cathode location on the removal of chloride ion. The data also permit a comparison of the relative effectiveness of continuous versus intermittent treatment as regards the amount of chloride removed in a 24 hr period.

TABLE 18. CHLORIDE ION CONTENT OF CORES FROM SIMULATED BRIDGE DECK SLAB NO. B-1, BEFORE AND AFTER 48 HOUR INTERMITTENT ELECTROCHEMICAL TREATMENT

Depth of Core Samples From Slab Surface, inches	Chloride Ion Content, percent (Based on Dry Concrete Weight)							
	Untreated Concrete			Treated Concrete, 48 hr at 100 volts				
	Core 1	Core 2	Average	Core 7	Core 9	Core 8	Core 10	Average
0 to 1.1	0.32	0.32	0.32	----	----	----	----	----
1.1 to 2.2	0.14	0.13	0.14	----	----	----	----	----
2.2 to 3.3	0.07	0.11	0.09	----	----	----	----	----
3.3 to 4.4	0.01	0.04	0.03	----	----	----	----	----
4.4 to 5.5	0.01	0.01	0.01	----	----	----	----	----
0 to 1.1	----	----	----	0.05	0.10	0.07	0.06	0.07
1.1 to 2.2	----	----	----	0.04	0.11	0.05	0.04	0.06
2.2 to 3.3	----	----	----	----	0.12	----	----	----

Core Locations:

7 = Above transverse and longitudinal rebar crossing point
9 = Central between transverse rebars, 8-in. spacing
8 and B1-10 = Above transverse rebar, midway between longitudinal rebars

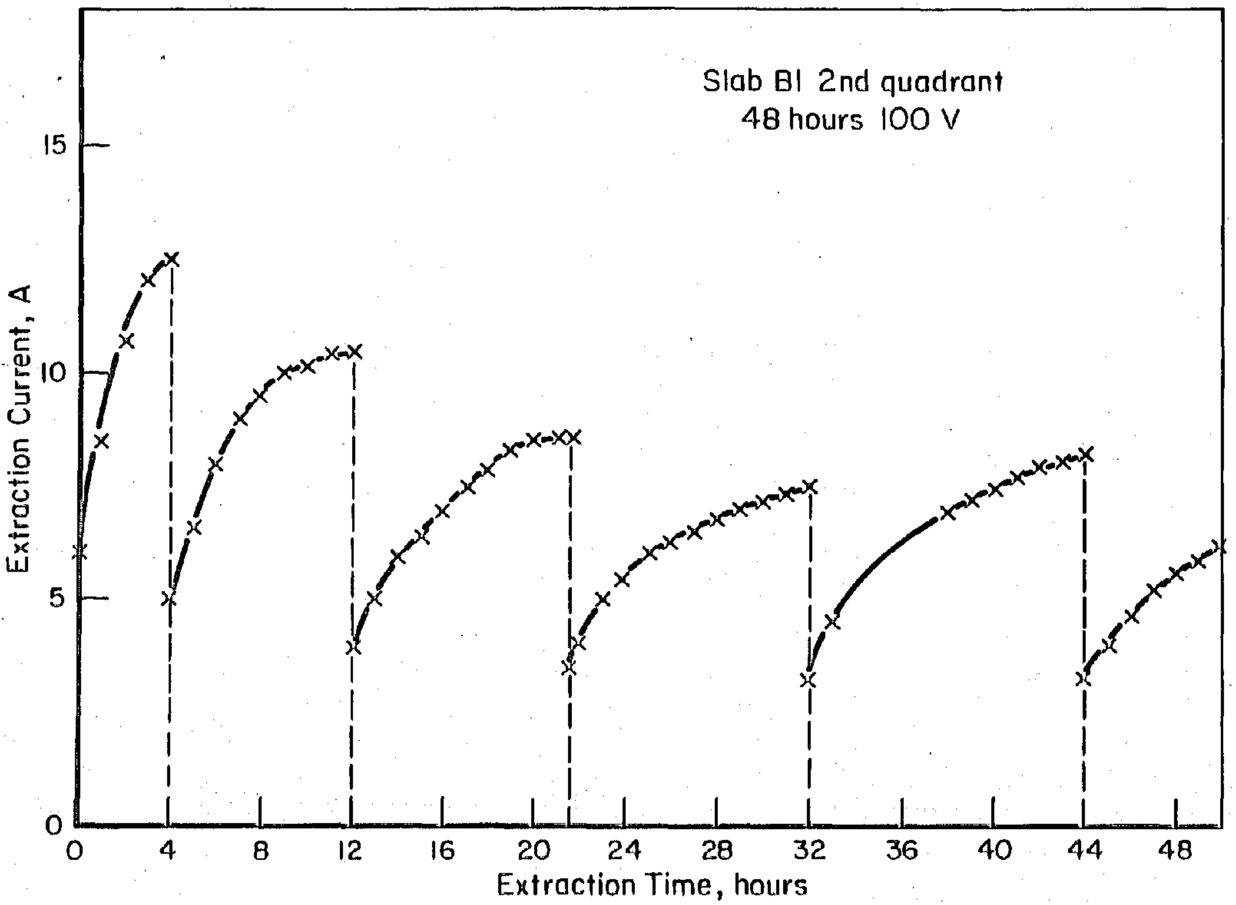


FIGURE 19. CURRENT DENSITY VERSUS EXTRACTION TIME FOR 48-HOUR INTERMITTENT RUN

Figure 20 shows the current density versus time relationship obtained on the 24-hr continuous run. Figure 20 is identical in shape to the current-time curves obtained during extractions on the small laboratory specimens, with a rise to a maximum current and a drop thereafter to a quasi-steady value. Temperatures measured in the concrete by thermocouples embedded just above and between rebars are also given in Figure 20. They indicate that the maximum temperature lags the maximum current. This implies that additional factors other than temperature may affect the current flow in the concrete. The maximum temperature reached was 183 F.

The chloride analyses data from the 24 hour continuous run are presented in Table 19. The average chloride content of the top 0 to 1.1 in. of concrete (based on 19 samples) after treatment was 0.11 percent or about 4.0 lb/yd^3. The initial chloride content of the top 0 to 1.1 in. of concrete was 11.7 lb/yd^3 indicating that the treatment removed about 66 percent of the chloride at this level.

The average chloride content at the 1.1 to 2.1-in. level (based on 18 samples) after treatment was 0.085 percent or 3.2 lb/yd^3. The initial chloride content (before treatment) at this level was 0.14 percent or 5.3 lb/yd^3. The average chloride content of the concrete above the reinforcing steel (Cores 11, 12, 13, 14, 15, 16, 18, 20, 22, 27, and 29) at the 1.1 to 2.1-in. level was 0.063 or 2.4 lb/yd^3.

The results confirm that chloride removal is greatest in the concrete adjacent and overlying the reinforcing steel cathode. The results suggest that there may be an edge effect with respect to the specimen geometry. Cores taken over the longitudinal rebar closest to the side of the specimen (Cores 11 through 16) had relatively higher chloride contents at all levels relative to concrete over reinforcing steel in the interior portions of the slab.

A comparison of Tables 17 and 19 indicate that the amount of chloride removed in a 24-hr period is not dependent upon whether or not the treatment was continuous.

Results

At the conclusion of the third experiment on the large slabs, it was felt that enough information had been gained to permit the planning and design of the experiment on the full size bridge deck. The findings indicated that

(1) Significant quantities of chloride ion can be removed from thick concrete slabs using the electrochemical treatment within a reasonable time period.

(2) Treatment times of 24 hr appeared adequate to achieve a significant reduction in chloride ion content.

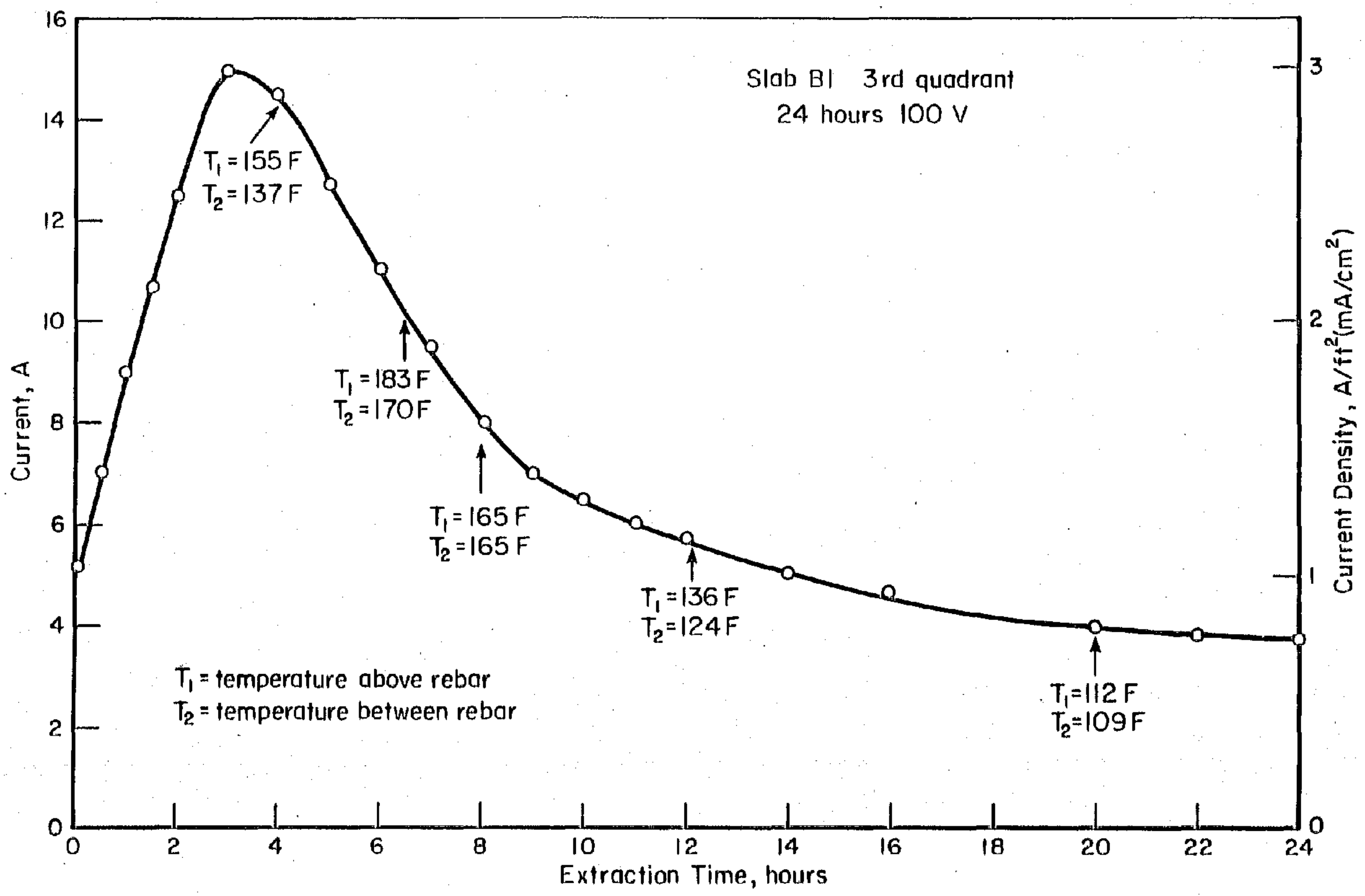


FIGURE 20. CURRENT DENSITY VERSUS EXTRACTION TIME FOR 24-HOUR CONTINUOUS RUN

TABLE 19. CHLORIDE ION CONTENT OF CORES FROM SIMULATED BRIDGE DECK SLAB NO. B-1, AFTER 24 HOUR CONTINUOUS ELECTROCHEMICAL TREATMENT

Depth of Sample From Slab Surface, inch	Chloride Ion Content, percent (Based on Dry Concrete Weight)						
	Traverse Over Longitudinal Rebar						
	Core No. 11	Core No. 12	Core No. 13	Core No. 14	Core No. 15	Core No. 16	
0 to 1.1	0.13	0.11	0.09	0.12	0.09	0.16	
1.1 to 2.1	0.06	0.10	0.09	0.10	0.03	0.15	
2.1 to 3.1	----	----	----	----	----	----	
	Traverse Parallel to Longitudinal Rebar (8 in. From Longitudinal Rebar)						
	Core No. 22	Core No. 21	Core No. 20	Core No. 19	Core No. 18	Core No. 17	
0 to 1.1	0.01	0.10	0.07	0.11	0.06	0.13	
1.1 to 2.1	0.04	0.12	0.02	0.11	0.03	0.12	
2.1 to 3.1	----	0.12	----	----	----	0.10	
	Diagonal Traverse						
	Core No. 11	Core No. 23	Core No. 24	Core No. 20	Core No. 25	Core No. 26	Core No. 27
0 to 1.1	0.13	0.12	0.14	0.07	0.13	0.13	0.04
1.1 to 2.1	0.06	0.10	0.10	0.02	0.11	0.08	----
2.1 to 3.1	----	----	0.11	----	----	0.09	----
	Traverse Along Transverse Rebar						
	Core No. 29	Core No. 22	Core No. 11		Core No. 27	Core No. 18	Core No. 15
0 to 1.1	0.08	0.10	0.14		0.04	0.06	0.09
1.1 to 2.1	0.05	0.04	0.06		----	0.03	0.03
2.1 to 3.1	----	----	----		----	----	----
	Traverse Parallel to Transverse Rebar (4 in. From Transverse Rebar)						
					Core No. 28	Core No. 17	Core No. 16
0 to 1.1					0.11	0.13	0.16
1.1 to 2.1					0.10	0.12	0.15
2.1 to 3.1					----	0.10	----

(3) The removal of chloride ion was greatest in the concrete overlying the cathode (rebar). Significant, but lesser reductions in chloride content were also achieved in concrete adjacent to the cathode areas.

(4) Current densities of at least 5 A/ft^2 were required for electrochemical treatment

(5) Scale-up problems with the treatment were minimal.

BRIDGE DECK EXPERIMENTS

The requirements for a bridge deck for the electrochemical chloride removal experiments were that it have substantial quantities of chloride but no evidence of surface spalling. With the cooperation of the Ohio Department of Transportation, a number of candidate bridges were identified and visited in the fall of 1973. The bridges were examined visually for spalling and electrical potential scans were run to assess corrosion activity of the reinforcing steel.

The bridge selected for study was an 8-yr-old, two-lane, steel girder bridge on the southbound lane of U. S. Route No. 33 near Marysville, Ohio (No. UNI-33.1138R). The deck was completely free of surface spalls. As a matter of interest, a similar deck less than 100 yd away, constructed at the same time by the same contractor, had about 60 percent of the surface repaired due to spalling. A 10 x 20-ft area of the selected bridge deck on the west side lane was chosen for evaluation.

Pretreatment Electrochemical Potential Measurements

Potential Scans

Prior to electrochemical treatment of the selected area, a number of electrical potential scans were made of the deck (in November, 1973, August, 1974, and April, 1975). Measurements were made on a 1-ft grid in general accordance with the technique described by Stratfull(3) using $Cu/CuSO_4$ as the reference cell. In this technique, it has been established that steel showing potentials more negative than about -0.35 V is undergoing active corrosion. The potential contours taken over the 17 month period are shown in Figures 21, 22, and 23.

The increase in area of deck showing active potentials (more active than -0.35 V) is obvious. As a rough attempt to quantify this behavior, the areas showing such active potentials were measured for the contour maps. The results were:

Scan Date	Percent Active
November, 1973	18
April, 1975	55

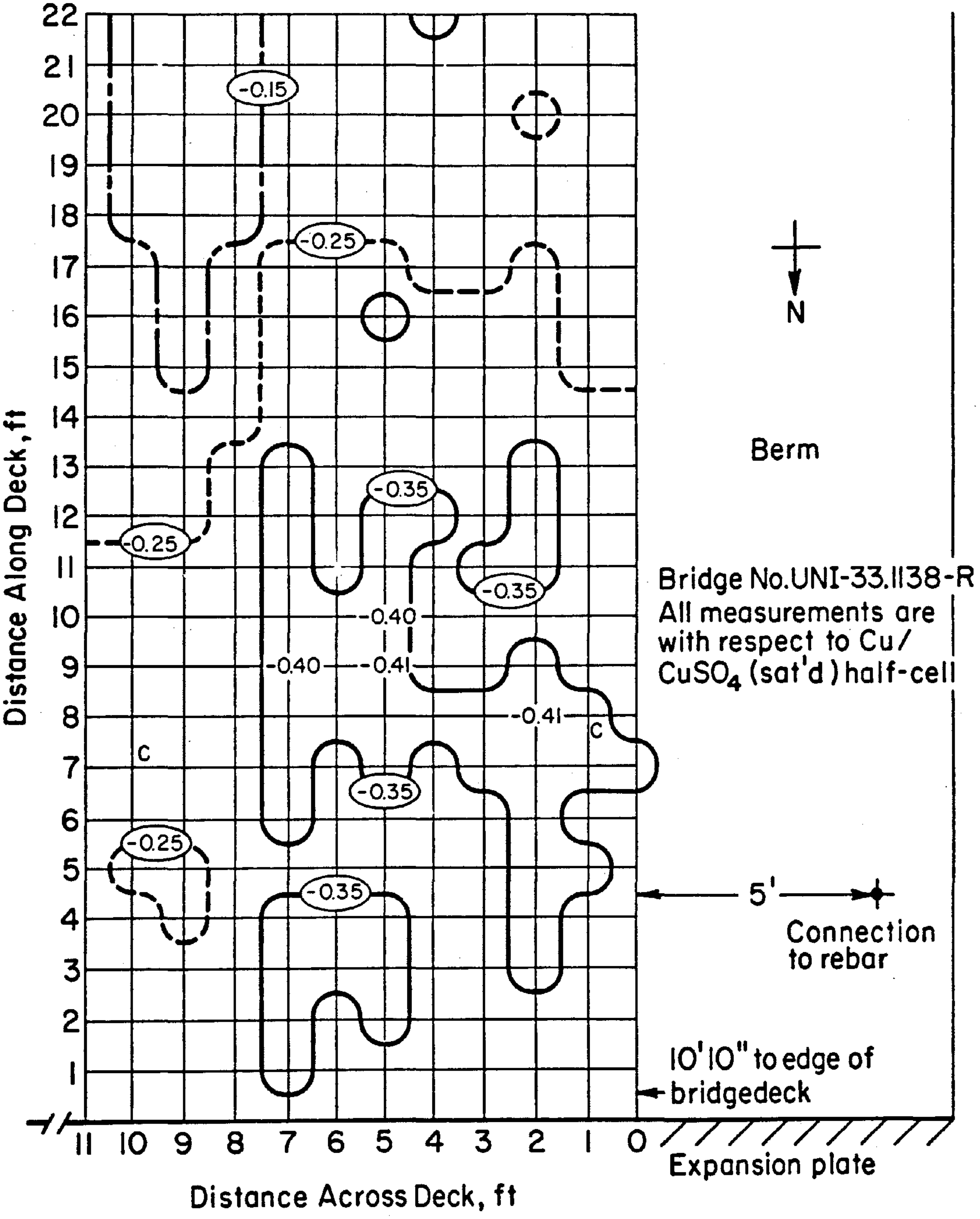


FIGURE 21. POTENTIAL PROFILE OF THE SELECTED 10 X 20 FT SECTION OF BRIDGE NO. UNI-33.1138R (MARYSVILLE, OHIO) TAKEN DURING NOVEMBER, 1973

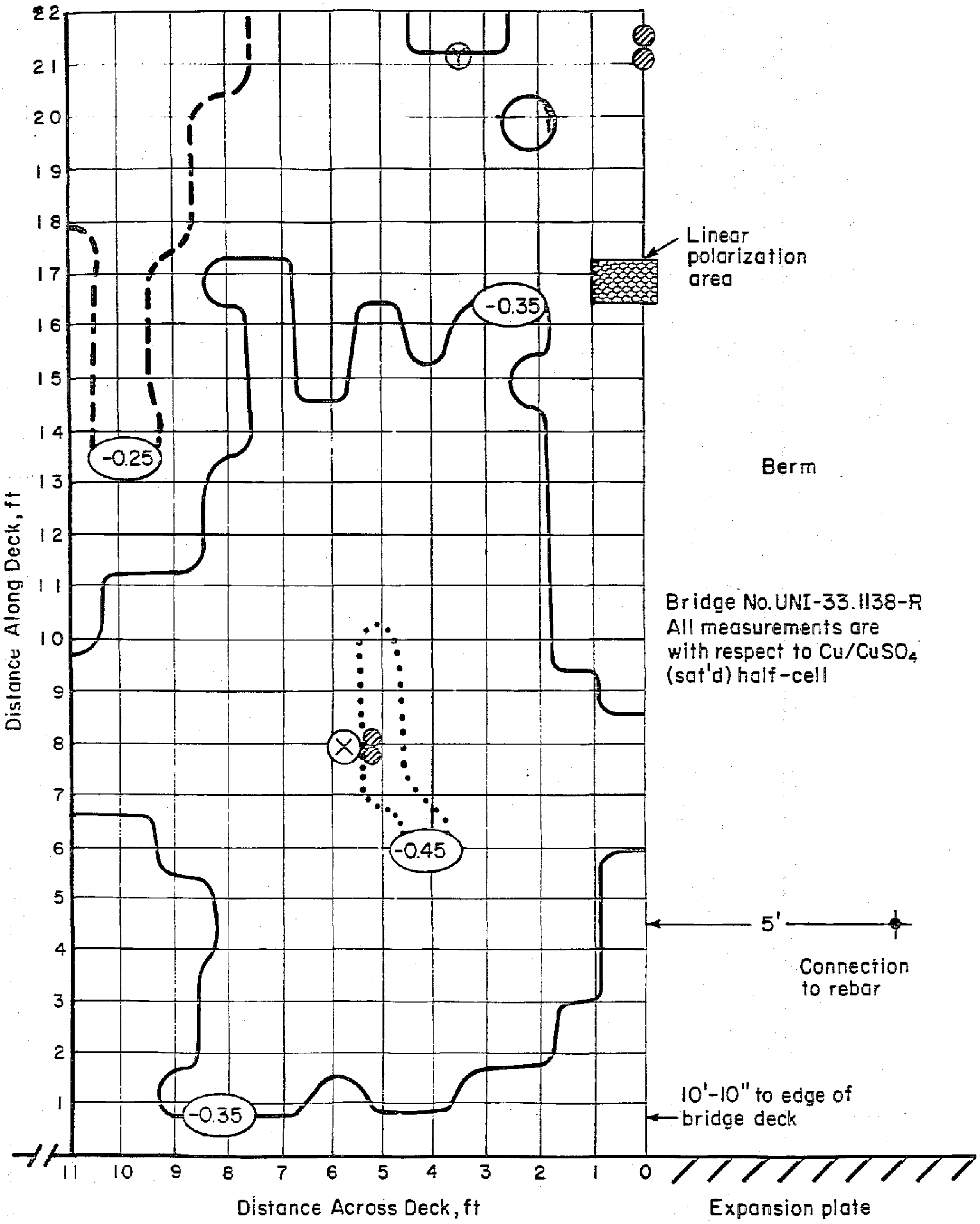


FIGURE 22. POTENTIAL PROFILE OF A 10 BY 20-FT SECTION OF BRIDGE NO. UNI-33.1138R (MARYSVILLE, OHIO) TAKEN DURING AUGUST, 1974

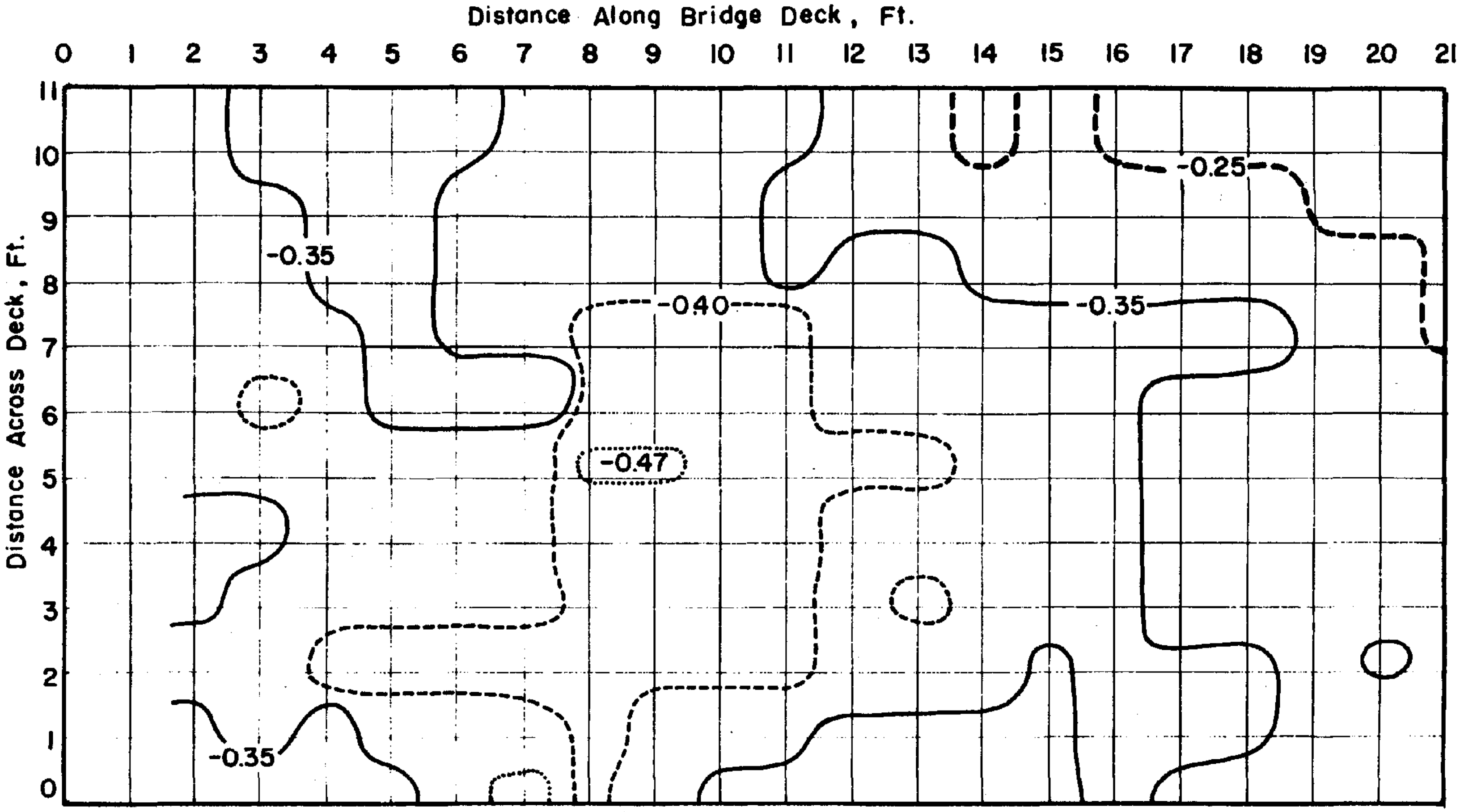


FIGURE 23. POTENTIAL PROFILE OF A 10 BY 20-FT SECTION OF BRIDGE NO. UNI-33.1138R (MARYSVILLE, OHIO) TAKEN DURING APRIL, 1975

It is worth emphasizing here that this area of the deck showed no overt signs of distress, even though the measured potentials were so active.

Linear Polarization Measurements

The philosophy and construction of linear polarization electrodes from steel in the top rebar mat is discussed in Appendix E. Measurements on these electrodes continued on a regular basis prior to electrochemical treatment for chloride removal. The results were as follows:

Date	Electrode Pair	Corrosion Rate, Mils per year
September, 1974	1 - 2	0.15
September, 1974	2 - 3	0.11
January, 1975	1 - 2	0.04
January, 1975	2 - 3	0.02
April, 1975	1 - 2	0.50
April, 1975	2 - 3	0.50

The fall in corrosion rate from September, 1974, to January, 1975, was probably due to the subfreezing temperatures on the latter date. The increased corrosion rate in April, 1975, reflects both the warm temperatures and an increased severity of corrosion.

Pretreatment Chloride Analyses of the Deck

A number of cores were removed from the 10 x 20 ft area of the deck over the 18-month period preceding the electrochemical treatment. The location of the cores on the deck are shown in Figure 24. Chloride content as a function of depth in the deck is shown in Tables 20, 21, and 22.

Table 20 shows the chloride ion content of concrete in an area of indicated "high" corrosion activity. Table 21 shows similar data on concrete in an area of indicated "low" corroison activity. Table 22 shows the averaged results of all cores taken over the indicated time period.

An increase in chloride content at all levels in the deck was noted over the 18-month observation period (approximately 4 lb/yd^3 at the 0-1 in. level; 2 lb/yd^3 at the 1-2 in. level; and 0.5 lb/yd^3 at the 2-3 in. level). Just prior to electrochemical treatment the chloride ion content of the top 1 in. of deck concrete exceeded 15 lb/yd^3 while the 1-2 in. level contained 4 to 10 lb/yd^3.

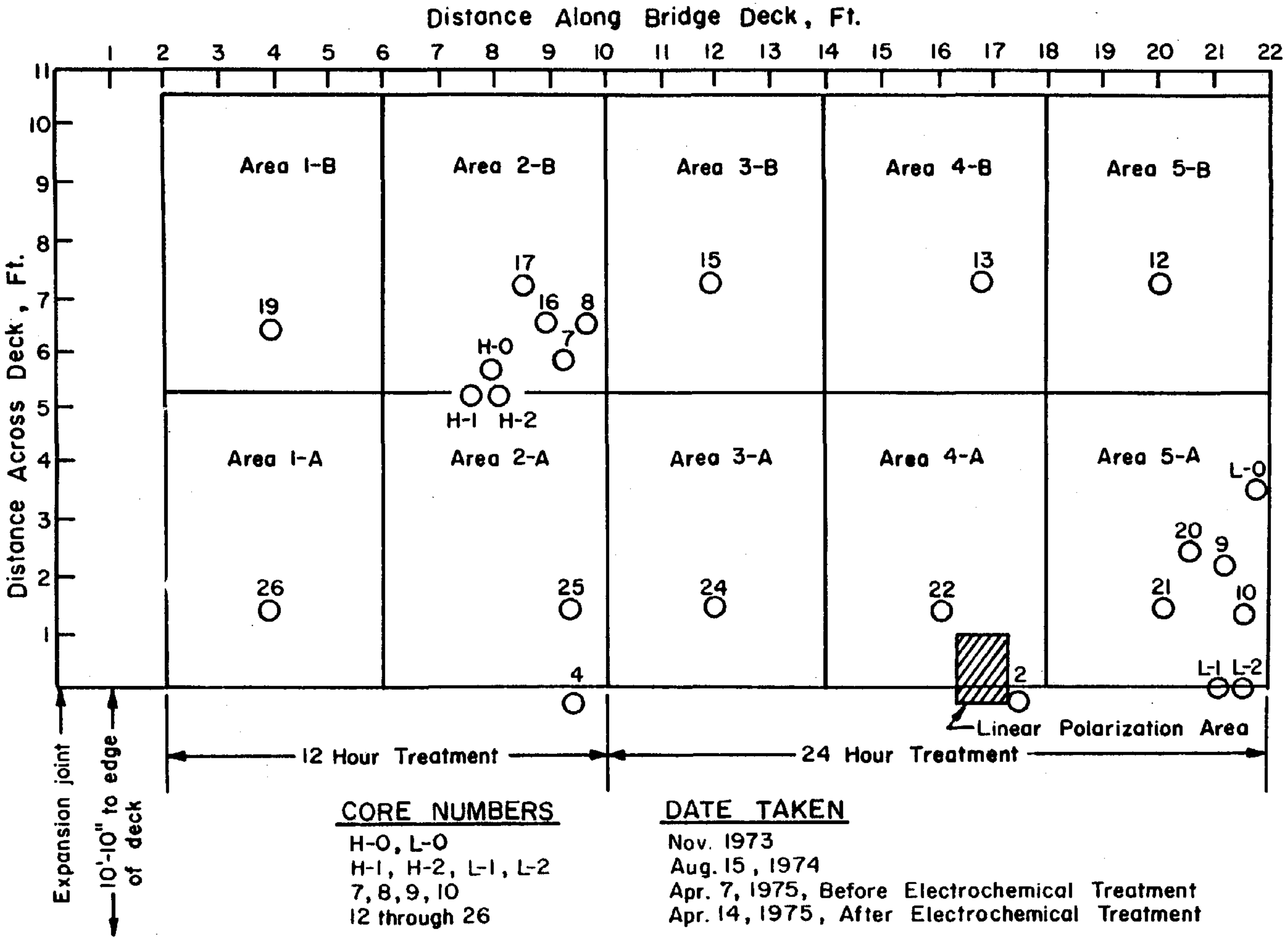


FIGURE 24. LOCATION OF CORES REMOVED FROM THE 10 BY 20-FT SECTION OF BRIDGE NO UNI-33.1138R

TABLE 20. PRE-TREATMENT CHLORIDE ANALYSES OF CORES TAKEN FROM PCC DECK (HIGH CORROSION ACTIVITY AREA NO. 2) OF BRIDGE NO. UNI-33.1138R

Depth of Core Sample From Wearing Surface, in.	Chloride Ion Content(a)									
	Core Taken in November, 1973 (No. H-0)		Core Taken in August, 1974 (No. H-1)		Cores Taken in April, 1975					
					No. 7		No. 8		Average	
	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3
0 - 1	0.34	12.9	0.42	15.9	0.42	15.9	0.40	15.1	0.41	15.5
1 - 2	0.20	7.6	0.21	7.9	0.26	9.8	0.21	7.9	0.24	9.1
2 - 3	0.06	2.3	0.08	3.0	---	---	0.05	1.9	---	---
3 - 4	0.01	0.4	0.02	0.8	---	---	0.01	0.4	---	---
4 - 5	0.01	0.4	0.01	0.4	---	---	---	---	---	---

(a) Based on dry concrete density of 140 lb per cu ft.

TABLE 21. PRE-TREATMENT CHLORIDE ANALYSIS OF CORES TAKEN FROM PCC DECK (LOW CORROSION ACTIVITY AREA NO. 5A) OF BRIDGE NO. UNI-33.1138R

Depth of Core Sample From Wearing Surface, in.	Chloride Ion Content[a]									
	Core Taken in November, 1973 (No. L-0)		Core Taken in August, 1974 (No. L-1)		Cores Taken in April, 1975					
					No. 9		No. 10		Average	
	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3
0 - 1	0.28	1[illegible].6	0.37	14.0	0.45	17.0	0.37	14.0	0.41	15.5
1 - 2	0.12	4.5	0.14	5.3	0.23	8.7	0.11	4.2	0.17	6.4
2 - 3	0.03	1.1	0.03	1.1	0.06	2.3	---	---	---	---
3 - 4	0.01	0.4	0.01	0.4	0.01	0.4	---	---	---	---
4 - 5	0.01	0.4	0.01	0.4	---	---	---	---	---	---

(a) Based on dry concrete density of 140 lb per cu ft.

TABLE 22. AVERAGE CHLORIDE CONTENT OF CORES TAKEN FROM PCC DECK OF BRIDGE NO. UNI-33.1138R DURING PERIOD OF NOVEMBER, 1973, TO APRIL, 1975, (BEFORE ELECTROCHEMICAL TREATMENT)

Depth of Sample From Wearing Surface, in.	Chloride Ion Content(a)					
	Cores(b) Taken in November, 1973		Cores(c) Taken in August, 1974		Cores(d) Taken on April 7, 1975	
	Percent	lb/ft^3	Percent	lb/ft^3	Percent	lb/ft^3
0 - 1	0.31	11.7	0.40	15.1	0.41	15.5
1 - 2	0.16	6.0	0.23	8.7	0.20	7.6
2 - 3	0.05	1.9	0.06	2.3	0.06	2.3
3 - 4	0.01	0.4	0.01	0.4	0.01	0.4
4 - 5	0.01	0.4	0.01	0.4	----	----

(a) Based on dry concrete weight of 140 lb per cu ft.

(b) Average value of data obtained on two cores, No. H-0 and L-0.

(c) Average value of data obtained on two cores, No. H-1 and L-1.

(d) Average value of data obtained on four cores, No. 7, 8, 9, and 10.

The rather large specimen-to-specimen variation in measured chloride observed when duplicate cores were taken precluded speculation on the differences in chloride content between the high- and low-corrosion-activity areas of the deck.

Pretreatment Delamination Detection

The selected area of the bridge deck (10 x 20 ft) was examined for delamination by maintenance personnel of the Ohio Department of Transportation in April, 1975, prior to electrochemical treatment. The method used was that of a sounding rod.

There was no evidence of any delamination in spite of the significant areas of high corrosion activity discussed previously.

Electrochemical Treatment of the Deck

Following the pretreatment characterization work, the electrochemical removal trials on the bridge deck were begun on April 7, 1975. The total area treated was 200 ft^2 (10 x 20 ft). The treatment area was broken down into five, 40-ft^2 (4 x 10-ft) sections (see Figure 24) which were treated individually. The treatment sequence of events included

(1) Placement of the electrolyte/resin ponding frame

(2) Placement of the electrolyte and ion exchange resin in the ponding frame

(3) Placement of anodes in the ponding frame

(4) Connection of all electrical contacts

(5) Initiating of d-c potential; monitor and record time, slab and electrolyte temperature, current, and voltage

(6) Turn off of generators

(7) Removal of electrolyte and ion exchange resin from ponding frame.

The 2-in.-deep wood ponding frames contained four 2.5 x 4-ft. compartments. The frames were sealed to the bridge deck surface (previously swept) with construction caulking compound.* Weights were placed on the frame to prevent movement and to aid in maintaining a leak-proof seal. The electrolyte solution of saturated $Ca(OH)_2$ was placed in the ponding frame to a depth of 0.5 to 1.0 in.

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* DAP Caulking Compound, DAP Inc., Dayton, Ohio.

Dowex 2-X8 ion exchange resin was slurried into the electrolyte to a depth of 1/4 to 3/8 inch. It was rather difficult to maintain a homogeneous dispersion of the resin in the electrolyte.

A 2-1/4 x 4-ft platinized titanium anode was then placed in each of the four compartments within the ponding frame. The anodes were supported about 1/2 in. above the bridge deck by small wood blocks. The anodes were kept covered with electrolyte solution at all times. Figure 25 shows the compartmentalized ponding frames and one of the d-c generators used in the experiment. The frame in the background contains the electrolyte, resin, and anodes.

Electrical contact was made with the top layer of the reinforcing steel in the treatment area through 0.25 x 1 x 8 inch mild steel studs which were arc welded to the rebars. The rebars were exposed by coring along the berm side of the treatment area as shown in Figure 26. Direct current power leads were attached to the rebar contact studs (negative electrode) and to vertical studs that were welded to the titanium anodes (positive electrodes) in each compartment.

Electrical power was supplied by two trailer-mounted, gasoline-driven, d-c generators, with each generator supplying power for two anodes (20- ft^2 treatment area). A schematic of the experimental technique is shown in Figure 27.

Treatment Conditions

The five 40-ft^2 treatment areas were identified in Figure 24 as areas 1, 2, 3, 4, and 5. Each 40-ft^2 area was serviced by two d-c generators; one generator supplying power to a 20 ft^2 area. In all cases, effort was made to maintain generator output at the maximum rated capacity of 120 V. In practice the voltage generally fluctuated between 100 and 120 V. Areas 1 and 2 were treated for 12 hr while areas 3, 4, and 5 were treated for 24 hr.

The ion exchange resin was omitted in the treatment of Area 4. This resulted in a noticeable odor of free chlorine above the electrolyte ponds during the treatment period.

The temperature of the electrolyte ponds was measured during treatment periods by use of a thermometer. In addition, temperature of the concrete deck was measured by use of thermocouples inserted into small holes drilled into the concrete. Effort was made to monitor pavement temperature just above a rebar and about 1-1/2 in. below the concrete surface, midway between rebars.

Two-man crews provided full-time monitoring of the experiments throughout the treatment period. Data were obtained on current, voltage, and slab and electrolyte temperature as a function of treatment time.

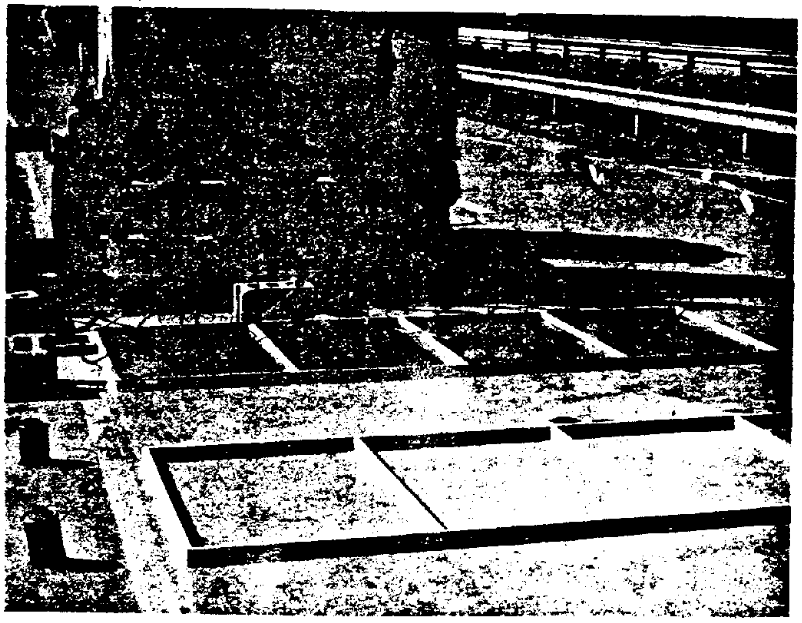


FIGURE 25. PONDING FRAMES AND RELATED HARDWARE USED IN THE ELECTROCHEMICAL EXPERIMENTS ON BRIDGE DECK NO. UNI-33.1138R

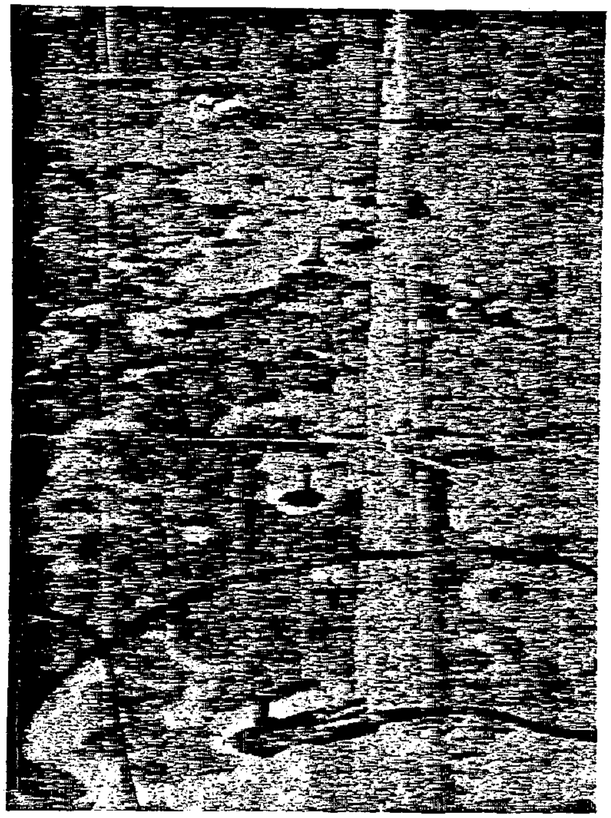


FIGURE 26. WELDED ELECTRICAL CONNECTIONS TO THE TOP REINFORCING STEEL (CATHODE)

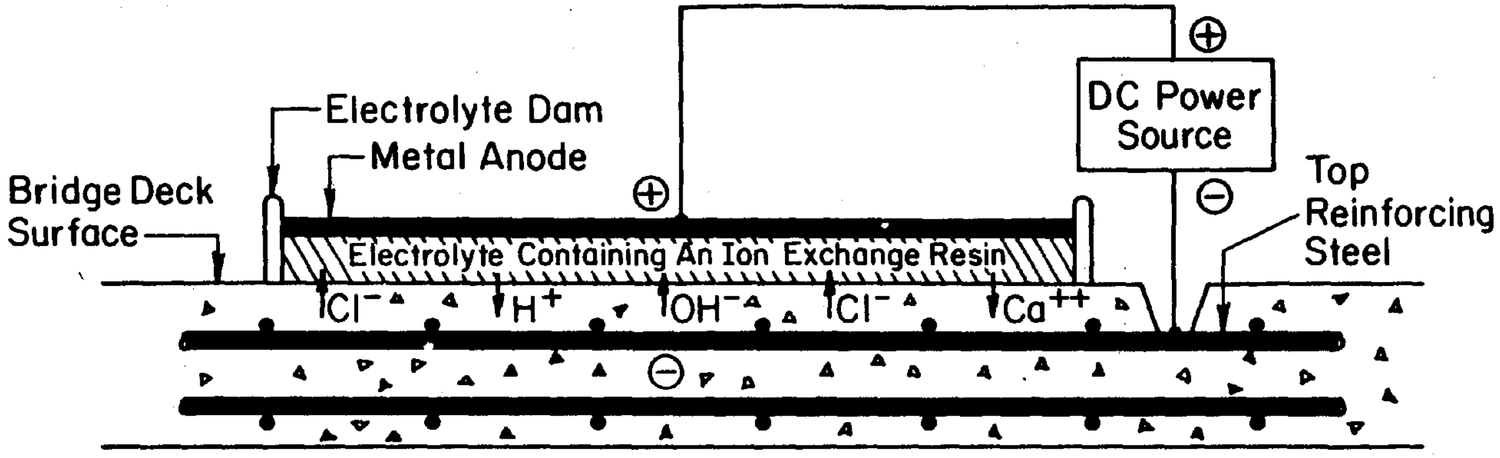


FIGURE 27. EXPERIMENTAL TECHNIQUE USED FOR THE ELECTROCHEMICAL REMOVAL OF CHLORIDE IONS FROM A PCC BRIDGE DECK

Following completion of the electrochemical treatment the electrolyte/resin solution was pumped off and 3 in. core samples obtained from the treated area. The resin was returned to the laboratory for regeneration.

No major problems were experienced during the experiment. No cracks in the concrete occurred as a result of the treatment as evidenced by a careful posttreatment visual examination.

Results

The results of the electrochemical treatment were monitored in terms of posttreatment measurements of chloride content, electrical potential measurements, and LP electrode measurements.

Chloride Analyses

Posttreatment cores (3 in. diam) were taken from the treated areas as identified in Figure 24. (Cores 12, 13, 15, 16, 17, 19, 20, 21, 22, 24, 25, and 26). Cores 16 and 20 were taken 5 in. deep. All other cores were taken only to the level of the top reinforcing steel (about 2 in.). Most of the cores were sectioned in 1 in. thick slices although Cores 15, 16, and 17 were sectioned in 1/2 in. slides to permit a better discrimination of the chloride concentration profile.

In several cases, the concrete immediately adjacent to the reinforcing rod (about 1/4 in. radius) was analyzed separately.

The results of the chloride analyses, reported by treatment area, are presented in Tables 23 through 27. Salient operational parameters are also reported in the tables.

Table 28 presents a summary of the pre- and posttreatment chloride analyses. A wide specimen to specimen variation in measured chloride is evident in the results. Despite this situation, it is possible to reasonably quantify the effect of the treatments on the amount of chloride removed.

0 to 1.0-In. Level

The average pretreatment chloride ion content in the top 1.0 in. of the treated area of the deck was 0.409 percent (15.5 lb/yd^3) as measured on Cores 7, 8, 9, and 10. Using 0.409 percent as the initial chloride content the reduction in chloride as affected by the treatments is shown in Table 29 for the various treatment areas.

TABLE 23. CHLORIDE-ION CONTENT OF CORES TAKEN FROM BRIDGE DECK AREAS 1A AND 1B AFTER 12-HOUR ELECTROCHEMICAL TREATMENT

Depth of Sample From Wearing Surface, in.	Chloride Ion Content					
	Core 26 (1A)		Core 19 (1B)		Average of Two Cores	
	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3
0 - 1	0.229	8.66	0.262	9.91	0.245	9.28
1 - 2	0.065	2.46	0.063	2.38	0.064	2.42

	Area 1A	Area 1B
Treatment Time, hours	12	12
Maximum Current, amps	47	45
Time to Reach Maximum Current, hours	10	11
Maximum Deck Temperature, F	ND	ND
Maximum Pond Temperature, F	ND	ND
Maximum Current Density, $amps/ft^2$	2.35	2.25

TABLE 24. CHLORIDE ANALYSES OF CORES TAKEN FROM BRIDGE DECK AREA 2 AFTER 12-HOUR ELECTROCHEMICAL TREATMENT

Depth of Sample From Wearing Surface, in.	Chloride Ion Content							
	Core No. 16 (2B) (Between Rebars)		Core No. 17 (2B) (Over Rebar)		Core No. 25 (2A) (Over Rebar)		Average of Three Cores	
	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3
0 - 1/2	--	--	0.389	14.7	--	--	--	--
1/2 - 1	--	--	0.280	10.6	--	--	--	--
0 - 1	0.357	13.5	0.334	12.6	0.291	11.0	0.303	12.4
1 - 1-1/2	--	--	0.134	5.1	--	--	--	--
1-1/2 - 2	--	--	0.093	3.5	--	--	--	--
1 - 2	0.158	5.9	0.113	4.2	0.069	2.6	0.115	4.2
2 - 3	0.029	1.1	--	--	--	--	--	--
3 - 4	0.012	0.5	--	--	--	--	--	--

	Area 2A	Area 2B
Treatment Time, hours	12	12
Maximum Current, amps	100	50
Time to Reach Maximum Current, hours	5	8
Maximum Deck Temperature, F	ND	ND
Maximum Pond Temperature, F	66	105
Maximum Current Density, $amps/ft^2$	5.0	2.5

TABLE 25. CHLORIDE ION CONTENT OF CORES TAKEN FROM BRIDGE DECK AREA 3 AFTER 24-HOUR ELECTROCHEMICAL TREATMENT

Depth of Sample From Wearing Surface, in.	Chloride Ion Content					
	Core 15 (3B) (Over Rebar)		Core 24 (3A) (Over Rebar)		Average of Two Cores	
	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3
0 - 1/2	0.039	1.5	--	--	--	--
1/2 - 1	0.035	1.3	--	--	--	--
0 - 1	0.037	1.4	0.045	1.7	0.041	1.5
1 - 1-1/2	0.025	0.9	--	--	--	--
1-1/2 - 2	0.016	0.6	--	--	--	--
1 - 2	0.020	0.8	--	--	--	--

	Area 3A	Area 3B
Treatment Time, hours	24	24
Maximum Current, amps	96	87
Time to Reach Maximum Current, hours	6	9
Maximum Deck Temperature, F	ND	ND
Maximum Pond Temperature, F	138	134
Maximum Current Density, amps/ft^2	4.8	4.35

TABLE 26. CHLORIDE ION CONTENT OF CORES TAKEN FROM BRIDGE DECK AREA 4 AFTER 24-HOUR ELECTROCHEMICAL TREATMENT

Depth of Sample From Wearing Surface, in.	Chloride Ion Content					
	Core 13 (4B) (Over Rebar)		Core 22 (4A) (Over Rebar)		Average of Two Cores	
	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3
0 - 1	0.311	11.8	0.332	12.5	0.321	12.1
1 - 2	0.099	3.7	0.099	3.7	0.099	3.7

	Area 4A	Area 4B
Treatment Time, hours	24	24
Maximum Current, amps	35	28
Time to Reach Maximum Current, hour	8	8
Maximum Deck Temperature, F	142	ND
Maximum Pond Temperature, F	104	88
Maximum Current Density, amps/ft^2	1.75	1.4

TABLE 27. CHLORIDE ION CONTENT OF CORES TAKEN FROM BRIDGE DECK AREA 5 AFTER 24-HOUR ELECTROCHEMICAL TREATMENT

Depth of Sample From Wearing Surface, in.	Chloride Ion Content							
	Core 12 (5B) (Over Rebar)		Core 20 (5A) (Between Rebar)		Core 21 (5A) (Over Rebar)		Average of Three Cores	
	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3
0 - 1	0.323	12.2	0.094	3.5	0.218	7.8	0.217	7.8
1 - 2	0.085	3.2	0.041	1.5	0.058	2.2	0.061	2.3
2 - 3	---	---	0.018	0.7	---	---	0.018	0.7
3 - 4	---	---	0.012	0.4	---	---	0.012	0.4

	Area 5A	Area 5B
Treatment Time, hours	24	24
Maximum Current, amps	53	30
Time to Reach Maximum Current, hour	12	15
Maximum Deck Temperature, F	236	ND
Maximum Pond Temperature, F	108	80
Maximum Current Density, $amps/ft^2$	2.7	1.5

TABLE 28. SUMMARY OF CHLORIDE CONTENT OF BRIDGE DECK BEFORE AND AFTER ELECTROCHEMICAL TREATMENT

Depth of Sample From Wearing Surface, in.	Average Cl^- Content Before Treatment (Cores Taken 4/7/74)(a)		Average Cl^- Content After Treatment (Cores Taken 4/14/75)(b)				Average Cl^- Removed, percent	
			12-hour		24-hour			
	Percent	lb/yd^3	Percent	lb/yd^3	Percent	lb/yd^3	12-hour Treatment	24-hour Treatment
0 - 1	0.409(a)	15.5	0.295(e)	11.2	0.194(h)	7.3	28	53
1 - 2	0.201(b)	7.6	0.093(f)	3.5	0.059(i)	2.2	54	71
2 - 3	0.054(c)	2.0	0.029(g)	1.1	0.019(j)	0.7	46	67
3 - 4	0.013(d)	0.5	0.012(g)	0.4	0.012(j)	0.4	Nil	Nil

(a) Data obtained on 4 cores (7, 8, 9, 10) Range 0.374 to 0.448.
(b) Data obtained on 4 cores (7, 8, 9, 10) Range 0.113 to 0.258
(c) Data obtained on 2 cores (7, 9) Range 0.049 to 0.059
(d) Data obtained on 2 cores (7, 9) Range 0.013 to 0.014
(e) Data obtained on 5 cores (26, 19, 16, 17, 25) Range 0.229 to 0.357
(f) Data obtained on 5 cores (26, 19, 16, 17, 25) Range 0.063 to 0.158
(g) Data obtained on 1 core (25)
(h) Data obtained on 7 cores (15, 24, 13, 22, 12, 24, 21) Range 0.037 to 0.332
(i) Data obtained on 7 cores (15, 24, 13, 22, 12, 24, 21) Range 0.015 to 0.099
(j) Data obtained on 1 core (20).

TABLE 29. AMOUNT OF CHLORIDE REMOVED FROM THE VARIOUS TREATMENT AREAS OF THE BRIDGE DECK (CONCRETE IN THE TOP 1.0 INCH)

Treatment Area	Duration of Treatment, hours	Maximum Current, amps	Charge Passed[a]	Percent Chloride Removed
1A	12	47	54	44
1B	12	45	56	36
2A	12	100	100	29
2B	12	50	54	15
3A	24	96	70	89
3B	24	87	70	91
4A	24	35	--	19
4B	24	28	26	24
5A	24	53	45	62
5B	24	30	13	21

Average chloride removed, 12-hour treatment = 31 percent
Average chloride removed, 24-hour treatment = 51 percent

(a) Calculated as the area under the current/time curve divided by treatment time. 2A arbirtarily assigned value of 100.

In general, a correlation existed between maximum current and charge passed and the amount of chloride removed. There were, however, several exceptions to this generalization (Treatment Area 2A and 2B).

The average chloride removed in the top 1.0 in. was 31 percent in 12 hr and 51 percent in 24 hr.

1.0 to 2.0-In. Level

The average chloride ion content in the 1.0 to 2.0-in. level of concrete in the treated area was 0.201 percent (7.6 lb/yd^3) as measured in Cores 7 and 9. Using this pretreatment value, the reduction in chloride in the 1 to 2-in. level of concrete as affected by the treatment is shown in Table 30.

Again, with several exceptions, there was a correlation between maximum current and charge passed and the amount of chloride removed. The average chloride removed at the 1-2-in. level was 59 percent in 12 hr and 70 percent in 24 hr.

A comparison of Table 29 and 30 shows that a greater percentage of chloride was removed at the 1-2-in. level than at the 0-1-in. level.

Concrete Adjacent to Reinforcing Steel

Chloride analyses were run on the concrete enclosing the reinforcing steel (about 1/4-in.-thick radius) both before and after treatment. The pretreatment data were obtained on Cores 2 and 4 taken from the berm section. The posttreatment data were obtained on the remnants of Cores 26 (Area 1A), 25 (Area 2A), 22 (Area 4A), and 21 (Area 5A). For the cores analyzed, the average reduction in chloride content in the concrete immediately adjacent to the reinforcing steel was 79 percent. Significantly, the posttreatment cores were from some areas which did not show exceptionally high chloride extraction at the 0-1 and 1-2-in. levels of concrete (see Tables 29 and 30).

Potential Scans

Potential scans were taken on the deck 24 hr after the final section was treated, and then 1 week, 1 month, and 3 months after treatment. The results are shown in Figures 28 through 31.

The scan after 24 hr (Figure 28) includes numerical values of the potential to show the effects of treatment on the potential. The first section treated (5 days prior to scan) exhibits passive potentials. This is in direct contrast to the active values shown by this section prior to treatment. The second section treated shows a range of potentials

TABLE 30. AMOUNT OF CHLORIDE REMOVED FROM THE VARIOUS TREATMENT AREAS OF THE BRIDGE DECK (CONCRETE AT THE 1-2 IN. LEVEL)

Treatment Area	Duration of Treatment, hours	Maximum Current, amps	Charge Passed[a]	Percent Chloride Removed
1A	12	47	54	68
1B	12	45	56	69
2A	12	100	100	66
2B	12	50	54	32
3A	24	96	70	93
3B	24	87	70	90
4A	24	35	--	51
4B	24	28	26	51
5A	24	53	45	75
5B	24	30	13	58

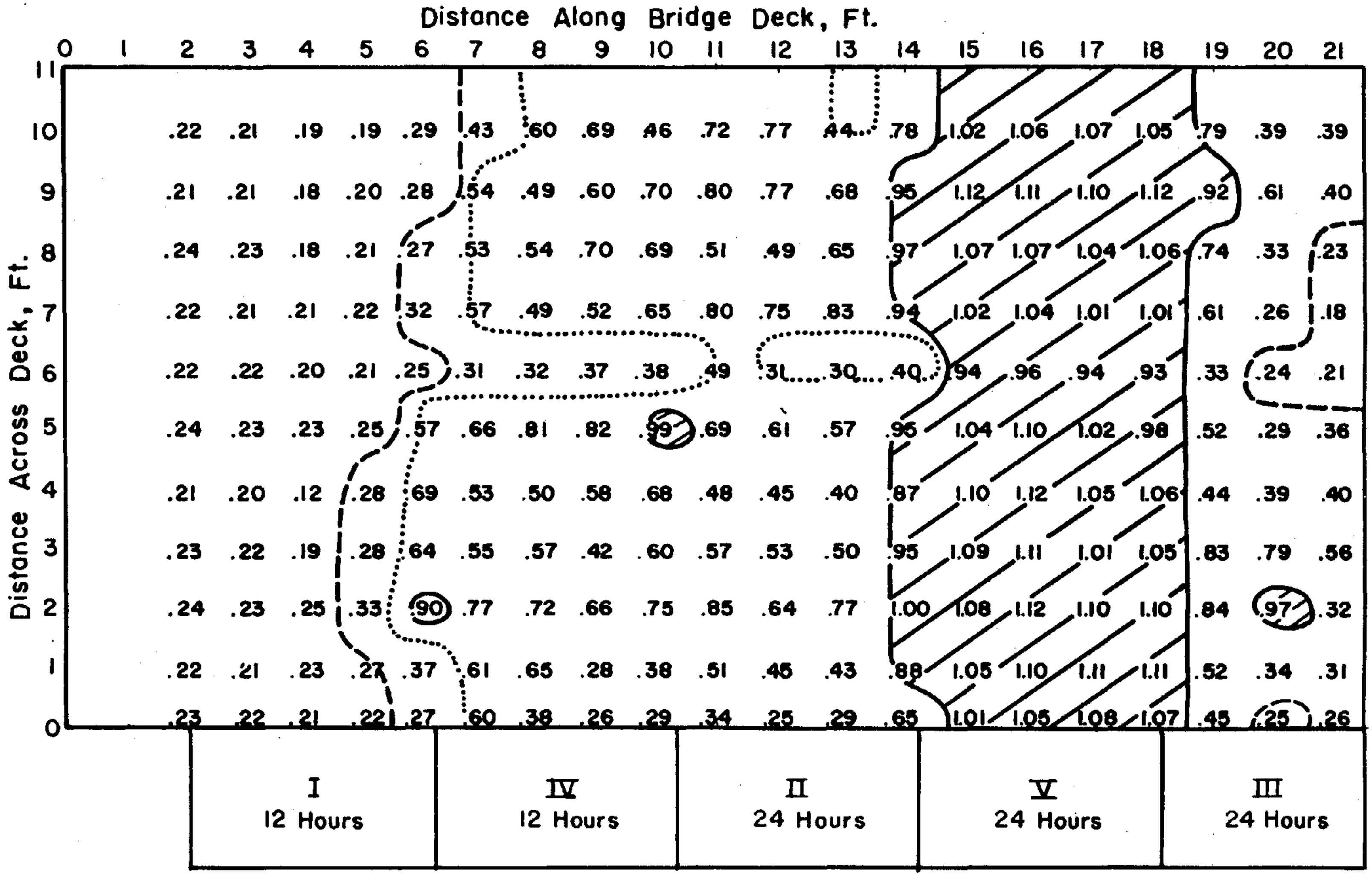
Average chloride removed, 12-hour treatment = 59 percent
Average chloride removed, 24-hour treatment = 70 percent

(a) Calculated as the area under the current/time curve divided by treatment time. 2A arbitrarily assigned a value of 100.

TABLE 31. CHLORIDE CONTENT OF BRIDGE DECK CONCRETE AT REBAR INTERFACE(a) BEFORE AND AFTER ELECTROCHEMICAL TREATMENT

Core Number (Treatment Area)	Chloride Ion Content					
	Before Treatment		12-Hour Treatment		24-Hour Treatment	
	Percent	lb/ft^3	Percent	lb/ft^3	Percent	lb/ft^3
2 (Berm)	0.091	3.4	--	--	--	--
4 (Berm)	0.058	2.2	--	--	--	--
26 (1A)	--	--	0.013	0.5	--	--
25 (2A)	--	--	0.012	0.4	--	--
22 (4A)	--	--	--	--	0.018	0.7
21 (5A)	--	--	--	--	0.021	0.8
Average	0.075	2.8	0.013	0.5	0.020	0.8

(a) Sample about 1/4-inch thick concrete surrounding upper half of rebar.



	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
10	.22	.21	.19	.19	.29	.43	.60	.69	.46	.72	.77	.44	.78	1.02	1.06	1.07	1.05	.79	.39	.39
9	.21	.21	.18	.20	.28	.54	.49	.60	.70	.80	.77	.68	.95	1.12	1.11	1.10	1.12	.92	.61	.40
8	.24	.23	.18	.21	.27	.53	.54	.70	.69	.51	.49	.65	.97	1.07	1.07	1.04	1.06	.74	.33	.23
7	.22	.21	.21	.22	.32	.57	.49	.52	.65	.80	.75	.83	.94	1.02	1.04	1.01	1.01	.61	.26	.18
6	.22	.22	.20	.21	.25	.31	.32	.37	.38	.49	.31	.30	.40	.94	.96	.94	.93	.33	.24	.21
5	.24	.23	.23	.25	.57	.66	.81	.82	.99	.69	.61	.57	.95	1.04	1.10	1.02	.98	.52	.29	.36
4	.21	.20	.12	.28	.69	.53	.50	.58	.68	.48	.45	.40	.87	1.10	1.12	1.05	1.06	.44	.39	.40
3	.23	.22	.19	.28	.64	.55	.57	.42	.60	.57	.53	.50	.95	1.09	1.11	1.01	1.05	.83	.79	.56
2	.24	.23	.25	.33	.90	.77	.72	.66	.75	.85	.64	.77	1.00	1.08	1.12	1.10	1.10	.84	.97	.32
1	.22	.21	.23	.27	.37	.61	.65	.28	.38	.51	.46	.43	.88	1.05	1.10	1.11	1.11	.52	.34	.31
0	.23	.22	.21	.22	.27	.60	.38	.26	.29	.34	.25	.29	.65	1.01	1.05	1.08	1.07	.45	.25	.26

FIGURE 28. POTENTIAL PROFILE OF A 10 BY 20-FT SECTION OF BRIDGE NO. UNI-33.1138R (MARYSVILLE, OHIO) TAKEN 24 HOURS AFTER ELECTROCHEMICAL TREATMENT

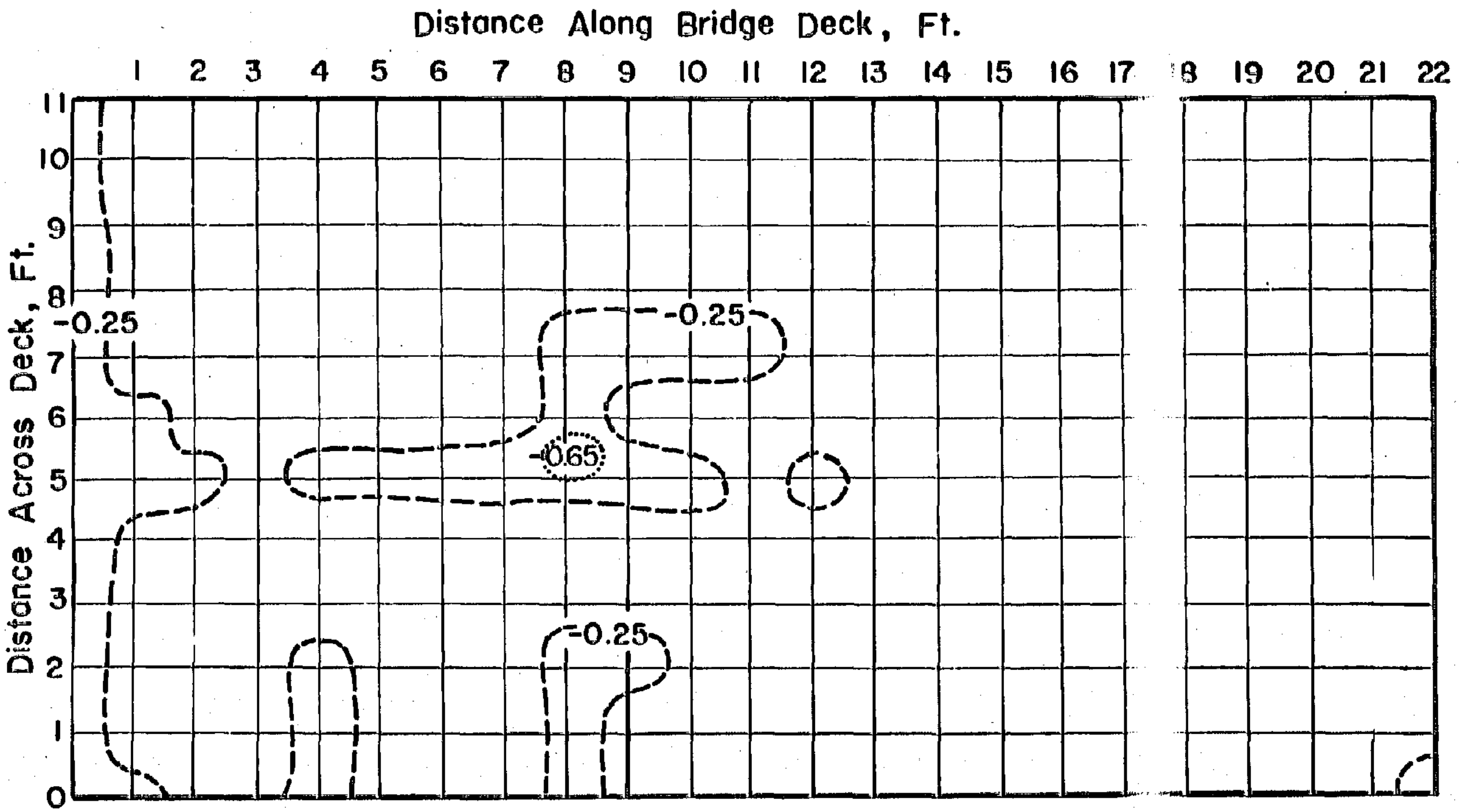


FIGURE 29. POTENTIAL PROFILE OF A 10 BY 20-FT SECTION OF BRIDGE NO. UNI-33.1138R (MARYSVILLE, OHIO) TAKEN 1 WEEK AFTER ELECTROCHEMICAL TREATMENT

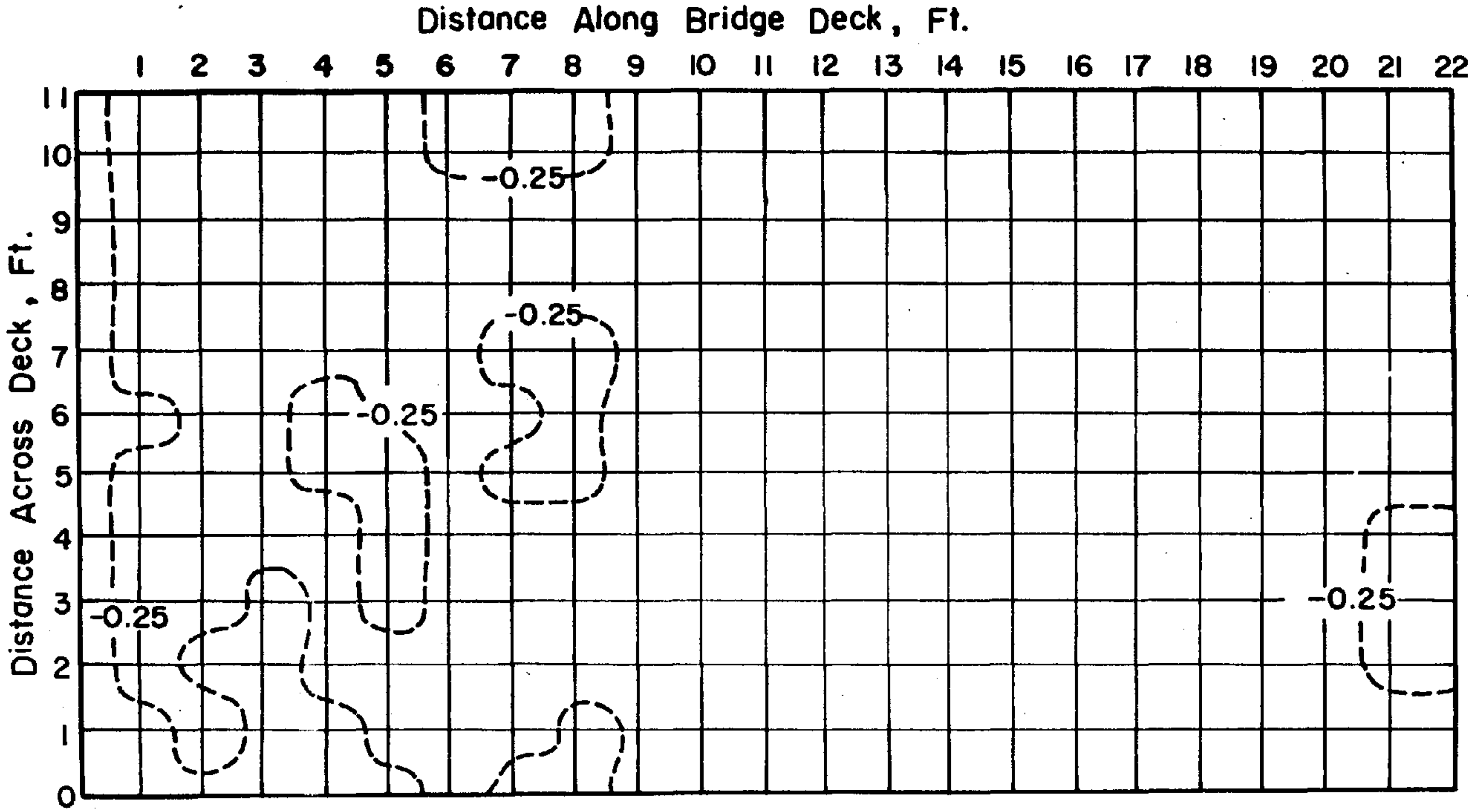


FIGURE 30. POTENTIAL PROFILE OF A 10 BY 20-FT SECTION OF BRIDGE NO UNI-33.1138R (MARYSVILLE, OHIO) TAKEN 1 MONTH AFTER ELECTROCHEMICAL TREATMENT

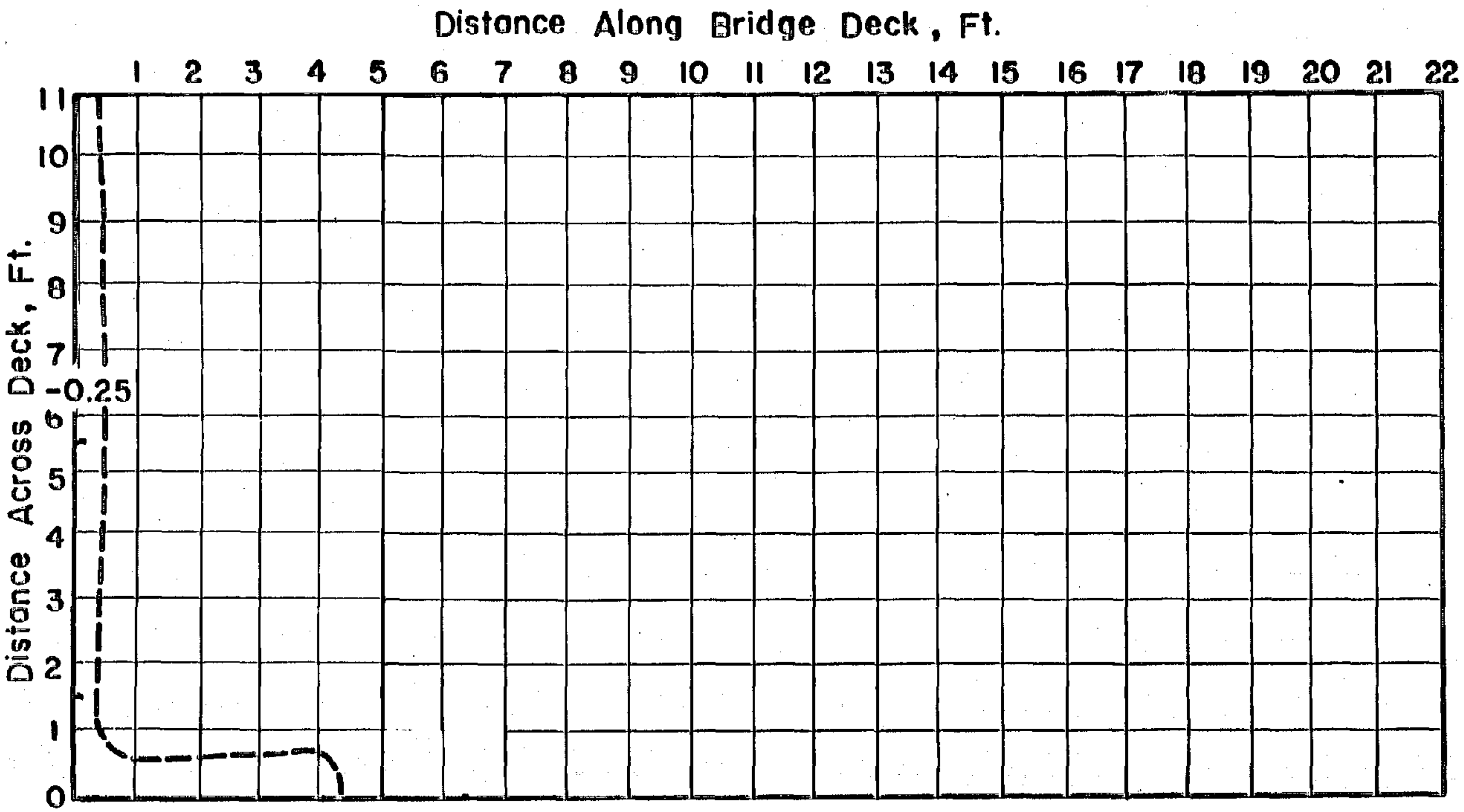


FIGURE 31. POTENTIAL PROFILE OF A 10 BY 20-FT SECTION OF BRIDGE NO. UNI-33.1138R (MARYSVILLE, OHIO) TAKEN 3 MONTHS AFTER ELECTROCHEMICAL TREATMENT

from extremely active to moderately passive. This indicates that the extreme cathodic polarization applied to the steel during treatments can take days to decay. Section III and IV show similar effects. The last section treated, Section V, shows potentials which are all well within the cathodic protection range (more active than -0.85 V) for steel.

The scan obtained 1 week after completion of treatment is shown in Figure 29. The obvious difference is the decay of the cathodic polarization in Sections II, IV, and V, and the maintenance of passive potentials in these areas. The exception to this is the band of polarization along the midsection of treatment Sections II and IV.

The results from the 1-month scan are shown in Figure 30. At this time, the vast majority of the deck exhibited a potential well within the passive range, with no readings on the treated surface being more active than -0.30 V. The most passive potentials are exhibited by steel in treatment Sections II and V. Similar results were observed after 3 months (Figure 31).

Linear Polarization Readings

Corrosion rates of the reinforcing steel comprising the linear polarization electrodes were measured 1 week, 1 month, and 3 months after treatment. The results were:

Date	Electrode Pair	Corrosion Rate, Mils per year
April 21, 1975	1-2	1.1
	2-3	0.8
May 23, 1975	1-2	0.6
	2-3	0.5
July 15, 1975	1-2	0.4
	2-3	0.3

Thus, 1 week after treatment, the linear polarization electrodes were showing a corrosion rate almost twice as high as before treatment. However, 1 month after treatment, the corrosion rate had dropped to that observed before treatment.

The reasons for this unexpected behavior may be due to the destruction of the passive oxide film on the rebar by the cathodic treatment, and its subsequent growth following treatment. This is discussed further in a later section.

DISCUSSION

The concept of electrochemically removing chloride ion from hardened concrete has been proven feasible in the laboratory and on a section of an actual bridge deck. Attempts to complement this technique with a preliminary flushing treatment were not successful.

This section of the report considers the technical and economic factors bearing on the implementation and effectiveness of the electrochemical removal technique. Although the procedures and equipment used in the present work could be used to treat an entire bridge deck, an intermediate research effort is needed to allow a successful transition between the current state of development and full implementation of the concept. Additional information and experience is required in a number of areas including procedural and technical considerations related to the cost/effectiveness of the technique.

Procedural Considerations

One of the obvious practical shortcomings of the current field experiment is the relatively small area treated in the 5 day working period (200 ft^2). If the technique is to be accepted for use on a full-size deck, it will be necessary to treat much larger areas within a reasonable time frame.

It is envisioned that on most bridges, traffic will be maintained in one lane while the other is undergoing treatment. On this basis, an estimate has been made in Table 32 of the time, power requirements, and anode costs for treating bridges up to 200 ft long. The anode costs are based on a scale-up of the platinized Ti anodes used in the experimental investigation.

Besides the anode cost and power requirements, there are further procedural questions to be raised, arising from scale-up of treatment. These involve the use and regeneration of the ion exchange resin, and the form which surface electrolyte containment (ponding) would have to take over larger areas. Posttreatment questions include the assessment of the treatment efficiency, and the use of methods to prevent further ingress of deicing salt into the deck. These topics are addressed in the following paragraphs.

Anodes

The costs of an electrocatalytically active, corrosion-resistant anode system are high, as evidenced by the figures given in Table 32. However, since such a system is essentially indestructible, then amortization of the cost over a number of deck treatments, say 100, brings the cost down per treatment to low levels.

TABLE 32. TIME AND COST ESTIMATES FOR ELECTROCHEMICAL TREATMENT OF BRIDGE DECKS FROM 50 TO 200 FEET IN LENGTH

Length of Treatment Area, ft	Deck Area Treated,(a) sq ft	Total Power Requirements,(b) KW	Time, days, to Treat Two Lane Deck of Indicated Length(c), ft				Cost of Platinized Ti Anode for Treating One Lane at Indicated Length, $
			50	100	150	200	
20	240	120	5	10	15	20	18,000
35	420	210	3	6	9	12	31,500
50	600	300	2	4	6	8	45,000

(a) Based on lane width of 12 ft.

(b) Based on a maximum requirement of 5 amps per sq ft, and an applied voltage of 100 V.

(c) 24-hr treatment for each.

The use of a consumable (corrodible) anode was considered but not pursued in any depth in the present investigation. Such an anode must be capable of passing the necessary current through faradaic reactions at its surface. Further, the corrosion product must not interfere with that process (a problem with titanium alloys, as discussed earlier). The corrosion product, either soluble or insoluble, must not interfere with the efficiency or ease of regeneration of the ion exchange resin, if it is used. The advantage of a consumable anode would be its low initial cost.

Some exploratory experiments were conducted to assess the suitability of steel and copper for use as a consumable anode, using 0.1N $Ca(OH)_2$-based electrolytes, with and without chloride additions. It was found that, in chloride free solutions, neither material would pass sufficient current (set at 10 A/ft^2, or 1 mA/cm2) to be of use as a treatment anode. However, neither did the anode corrode appreciably. Thus, it appeared that insoluble corrosion products were passivating the surface. When chlorides were added to the solution at the 0.01M and 1 M levels, however, the materials became active, passed the required current, but corroded appreciably. The corrosion of the copper appeared to be less objectionable than the iron.

This behavior indicates that, if iron or copper are to be used as consumable anode materials, the ponding electrolyte must be chosen so as to prevent passivation of the electrode. Thus, the currently used basic solution and ion exchange resin would have to be replaced with an initially neutral salt only. The use of the ion exchange resin would probably be precluded, because the ponding solution pH would rise as OH^- ions moved towards the anode, leading to corrosion product precipitation, and poor efficiency of the ion exchange resin in both use and regeneration. This situation is discussed later under ion exchange resins.

The use of a fairly inert but mechanically weak anode material, of which graphite is the best example, was investigated in the initial selection of anode materials for this study. Although the graphite was electrocatalytically active, the graphite was too weak to be of use as a field anode. However, in view of the recent advent of graphite cloth, a re-evaluation of that situation is in order. The cloth could be used in conjunction with the currently employed electrolyte/ ion exchange resin combination. Alternatively, it could be used with a radically different method of electrolyte application. This alternative is discussed more fully in the section on ponding techniques. A problem which remains with the use of graphite cloth, however, is the method of attachment of current leads to the material, since it is not possible to use welding techniques. Any adhesive would have to be conductive and one of the silver-filled conducting epoxy formulations may be useful. While the cost of the graphite electrode would be greater than the cost of steel or copper electrodes, its much lower rate of consumption would be extremely advantageous. The cost is not expected to reach the $\$75/ft^2$ of the platinized Ti electrode.

In summary, it appears that there are several different approaches to the ultimate selection of an anode material for larger-scale field use. Platinized titanium is proven but has a higher initial cost. Consumable anodes of steel or copper are not proven and would require modification of present electrolyte/ion exchange resin practices. The use of graphite cloth, possibly in conjunction with new electrolyte application techniques, shows promise and is worthy of further investigation.

Power Requirements

Approximately 500 W of d-c power at 100 V are needed for every square foot of deck surface which is treated. Obviously, with large treatment areas, the total power requirements increase dramatically, as is shown in Table 32.

It does not appear feasible that d-c generators such as were used in the bridge deck experiment could be found of sufficient power capacity. Thus, a-c generators would probably have to be used, together with one or several rectification system(s) to provide the necessary d-c supply. A survey of local suppliers revealed that portable diesel-powered a-c generators are available with power capacities to 500 KW, more than enough to treat a 50 ft length of one lane of a deck (Table 32). The cost of such a generator would appear to be in the neighborhood of $60,000. Such apparatus is available on a rental basis, but purchase would probably be the most cost-effective method of procurement for the treatment of many bridge decks.

Rectification assemblies are routinely available with a 1000-A capacity at 100 V at fairly nominal cost, and it is no doubt possible to purchase 5000-A rectifiers. Such rectifiers must be carefully cooled, however, and water cooling is usually employed in the large capacity units. Thus, although the power requirements initially seem extremely high and difficult to attain, it appears that such requirements fall well within the bounds of established technology, and should not present an insuperable difficulty to larger scale electrochemical treatment of salt-contaminated bridge decks. Amortization of costs over a number of treatments would bring the initially large capital expenditure down to realistic values.

Ion Exchange Resin

The basic concept in this research program was that the discharge of chlorine into the atmosphere, after oxidation of chloride ion to chlorine at the anode, was basically undesirable. This concept was fostered by the toxicity of gaseous chlorine, and by its generally deleterious effects on materials, particularly the material of construction of the anode. Thus, an ion exchange resin was used to prevent or at least minimize the chloride ion reaching the anode.

The concept was tested during the extraction procedures on the bridge deck. One section of the area was treated without any resin being present in the surface electrolyte. As expected, the extraction efficiency was not noticeably affected, but the odor of chlorine was significantly greater than during treatment of other areas.

It is instructive to calculate the amount of chlorine which would be evolved during treatment, if no chloride ion was absorbed by the resin. If it is assumed that 7 lb Cl^-/yd^2 of concrete is removed electrochemically, this corresponds to 19.6 g Cl^- removed per sq ft of concrete surface, for a 2-in. cover over the reinforcing steel. Thus, at STP, 6.2 liters of chlorine would be evolved per sq ft of concrete, a considerable amount. However, other factors to be considered are the time period of treatment (24 hr, corresponding to 0.26 l/hr) and the total area of treatment, particularly on the full-scale treatment of a bridge deck. At present, it is not known what EPA guidelines on accumulation limits of chloride might be. However, any method which might reduce chlorine evolution must be seriously considered.

The ion exchange resin used in the present study, Dowex 2-X8, was chosen as a result of its good balance of selectivity versus ease of regeneration. Although during bridge deck investigation, the resin was returned to the laboratory for regeneration, the procedures used (5 min agitation with 10 percent NaOH solution then three washes with tap-water) could easily be performed in the field. There are further factors associated with the use of an ion exchange resin:

(1) The hydroxide form is generally unstable at elevated (> 100 F) temperatures, with breakdown of the "backbone" of the resin occurring. This will lead to a decreased efficiency of chloride take-up with increased use.

(2) The use of consumable anodes, with the attendant presence of corrosion product in the resin, will lead to both exchange and regeneration problems. The regeneration problem could be alleviated by going to an intermediate acid treatment to dissolve corrosion product, but this would cause difficulties for field regeneration.

(3) It was difficult to maintain the desirable even coverage of resin over the concrete surface during treatment of the bridge deck. This was due to the slope from center to edge of the deck. Such problems would be compounded on decks which were even less flat and level.

Notwithstanding these difficulties, the ion exchange resin was fairly effective during the bridge deck experiments. Any alternative method would have to be at least as effective. Possible alternatives which might be considered include chlorine-absorbers, such as activated charcoal, above the anode, or even the presence of an auxiliary electrode, which might reduce the chlorine back to chloride. It is interesting to note that, in chloride solutions, the use of a consumable anode may obviate the need for an ion exchange resin. This would be possible if the corrosion reaction provided sufficient current at a potential below that required for chlorine evolution. Such a concept requires further consideration.

In summary, it is not possible at present to unequivocably state the need for an ion exchange resin during chloride extraction procedures. The possible alternatives must be examined before a firm decision can be made.

Surface Electrolyte Containment Procedures

The method of surface electrolyte containment developed for the laboratory studies on large slabs, a wooden dike sealed to the concrete surface with caulking compound, was also used in the treatment of the section of bridge deck. While the technique worked fairly well under those conditions, there are problems associated with its use for large-scale field extraction treatments. Such problems include the physical size of the dams necessary, and the presence of deck surface irregularities and gradients. The gradients from the middle to the edge of the bridge deck utilized in the present work necessitated dividing the ponding frame into four compartments, each with a separate anode.

A technique which appears to circumvent these problems would be a sponge containing the electrolyte. The sponge would be self-supporting, and the (metal) anode could possibly be permanently attached to its surface. Alternately, if a graphite cloth anode were used, the graphite cloth could be made an integral part of the sponge, possibly as a "filler" in a sponge "sandwich". The electrolyte could be replenished as necessary, by spraying the upper surface of the sponge/anode combination. Ion exchange resin could be spread on the deck surface before placement of the sponge and would be successfully held in position by the sponge, particularly if the bottom surface of the sponge had a ribbed or waffled texture.

The use of such a sponge system obviously requires more investigation, but the concept is attractive, because of its ease of placement, its portability, and its ease of reuse.

Postextraction Surface Treatment

The application of a d-c current between the rebar and a surface anode has been shown to cause a marked reduction in chloride content of the concrete overlying the reinforcing bar, and in the maintenance of a passive condition on previously active reinforcing steel--at least over a 3-month time period. Such beneficial effects, however, will be transitory unless the deck concrete surface is effectively made impermeable after extraction procedures have been completed. If such an impermeable surface is not procured, then further applications of deicing salts will lead to buildup of chloride at the rebar, and again induce corrosion and ultimate spalling. This process may be more facile than it was prior to electrochemical treatment, because it is conceivable that such a treatment may render the concrete more permeable.

The surface of the section of the bridge deck which was electrochemically treated in this program was subjected to a linseed oil impregnation immediately after completion of treatment. While it is realized that this would not give complete surface impermeability, it was considered that it would at least be partially effective in preventing future ingress of deicing salt. More effective procedures, such as polymer impregnation or membrane placement, were beyond the scope of this investigation. Further, as discussed in a later section, the linseed oil treatment did allow continued measurements of the electrochemical potential behavior of the rebar that more permanent impermeability treatments would have precluded.

Treatments available for insuring impermeability of the concrete to deicing salts after electrochemical chloride extraction include polymer impregnation of the surface, or placement of a waterproof membrane together with a wearing course on the surface. Other techniques which might be considered would involve placement of a further layer of concrete on the deck surface. Concretes which could be used include the latex-modified variety, the low slump concrete overlays (the so-called "Iowa Method", also used by the State of Kansas), or the recently developed wax-impregnated concrete. These concretes have been demonstrated to have very low permeability.

At this stage, it is not possible to come to any decision regarding the order of merit of cost-effectiveness for these possibilities. However, one technique which is probably worth pursuing is the application of a monomeric compound to the surface of the concrete, its electromigration into the concrete, and subsequent polymerization. This concept has been explained by workers in Kansas, using a polymeric system based on furfuryl alcohol. Evidently, a cation is attached to the furfuryl alcohol, which then migrates towards the rebar under the influence of the electric field. The attraction of this technique is that polymer impregnation could be accomplished immediately after chloride extraction, using the same hardware.

In summary, it is imperative that some form of deck surface treatment be used to insure impermeability after electrochemcial extraction, if the latter is to realize its full utility. The most cost/effective method for accomplishing this has yet to be identified.

Long-Term Monitoring of Treatment Effectiveness

The short-term effectiveness of the chloride extraction procedure in removing chloride and in passivating the reinforcing steel has been demonstrated. As was discussed in the previous section, it will be necessary to make the treated surface impermeable if such short-term efficiency is to be maintained in the long term. This brings up the important aspect of long-term monitoring of the state of corrosion of the rebar.

Three techniques have been used to monitor the efficiency of the technique in the short term. These were analysis of concrete for chloride content, measurements of electrochemical potential of the reinforcing steel, and investigation of corrosion rate by construction of linear polarization electrodes from the in-place rebar mat. Modification of these techniques need to be considered for long-term monitoring. Coring and wet analysis of concrete for chloride ion content is a lengthy and tedious operation. Further, it is largely undesirable on a deck which has been effectively waterproofed since the waterproofing will be destroyed at the coring site. The advantage of chloride analyses is that they give a direct measure of possible redistribution of residual chloride after treatment and information on any new chloride penetration as a result of incompletely effective waterproofing procedures. A possible method which could be used to monitor the latter effect makes use of the good Cl^--sensing ability of the Ag/AgCl electrode. The behavior of this electrode in alkaline chloride solutions was investigated in the present program, and the results are discussed in Appendix A. There appear to be three possible placements for the Ag/AgCl electrode:

- Directly beneath the waterproofing membrane, if one is used
- Embedded in the overlay, if a concrete overlay is used
- Embedded in the bridge deck concrete, to give a measure of magnitude and depth of chloride penetration into the existing deck.

Periodic measurement of the potential of the electrode, and the magnitude of potential changes, will allow chloride levels at the electrode level to be ascertained.

While this technique is attractive for penetration of "new" deicing salts, it cannot give estimates of chloride redistribution within the deck. Such estimates could be derived from the proposed measurements on slabs at BCL, or less directly, by monitoring the corrosion behavior of the reinforcing steel as a function of time.

The measurement of electrochemical potential of the reinforcing steel is a direct measurement of the corrosion behavior of the steel, and thus periodic scans of the deck surface would monitor the long-term efficiency of the removal process in preventing corrosion. Such measurements are easily made when no impermeability treatment has been applied to the deck surface. However, a truly waterproof membrane system, with an asphaltic concrete wearing course, could induce such a high resistance into the potential measurement circuit that the technique becomes unworkable. This is not likely to occur in the other methods of giving impermeability, discussed in the previous section. One possible way to circumvent this problem would be to electrically isolate small sections of rebar within the mat at strategic places, and then attach electrical leads to these sections and bring the leads to the edge of the deck. The potential of these sections could then be measured; at times other than when the measurements were being made, the sections would be connected with the rest of the rebar mat.

The final technique which can be used is the method of linear polarization. This method is described and discussed in detail in Appendix E of this report. It is applicable whatever the state of the deck surface, and would be useful under most circumstances.

Technical Considerations

The procedural considerations just discussed dealt mainly with the hardware aspect of the electrochemical treatment concept. The primary intent of the treatment is to prevent or stop corrosion of the reinforcing steel and to maintain this condition for an acceptable period of time.

It was learned in the present work that it is not necessary to remove all of the soluble chloride in order to initially passivate the steel. However, it is not yet known how long the passive condition can be maintained in decks from which soluble chlorides have not been completely removed. The amount of chloride removed, the distribution of residual chloride, and the possible redistribution after treatment are factors to be considered.

Chloride Extraction Efficiency

The factors identified in the laboratory and field work as influencing the quantity of chloride ion removed include

(1) Treatment time
(2) Magnitude of applied d-c potential
(3) Current density.

In general, an increase in any of these variables resulted in an increase in the total amount of chloride ion removed from the concrete. Significant increases in chloride removal were observed when the voltage was increased from 50 to 100 V and when treatment time was increased from 12 to 24 hr. In the laboratory, increases in treatment time beyond 24 hr in general did not provide significant further reductions in chloride content except in those instances where the initial chloride content of the concrete was very high (ca. 10 lb per cu yd). At the present state of development, it appears that a minimum treatment time of 24 hr at 100 V can be recommended. The required treatment time in any given situation may be related to the distribution of residual chloride in the concrete as will be discussed.

Since current flow in the process through the concrete is ionic in nature, it is to be expected that increased current densities should correlate with increased removal rates. In general, this was found to be the case. However, in the work on the bridge deck an anomaly became apparent in this area. Despite the fact that the voltage was held reasonably constant, the maximum current density in the five treated areas ranged from 1.4 to 5.0 A/ft^2. Additional work is needed to identify what variables other than applied voltage influence the current density.

Distribution of Residual Chloride

Residual chloride refers to the chloride remaining in the concrete following the extraction process. Several considerations are in order here.

(1) Some portion of the residual chloride is in an insoluble form. On the basis of the laboratory work, it is estimated that 0.015 to 0.020 percent* of the chloride ion in hardened concrete is in this state (0.6 to 0.75 lb/yd^3). This chloride is not expected to be significant in initiating corrosion.

(2) The distribution of the remaining soluble chlorides with respect to the top mat of the reinforcing steel in the concrete is of prime importance. The primary consideration must be to keep chlorides away from the reinforcing steel. Considerable information has been gained in the present program concerning this situation.

The expected current flow under the influence of an applied voltage is depicted in Figure 32. The external anode is essentially planar while the cathode (rebar) is linear in form. This results in the greatest current flow occurring directly over the rebar. Current flow in the concrete between the rebars is necessarily attenuated due to the position of the cathodes and the relatively low conductivity of the concrete. This situation results in an increased efficiency of chloride ion removal from concrete directly over the reinforcing steel, due to the greater current flow and a decreased ion diffusion path relative to the concrete between the reinforcement.

During the electrochemical treatment period, chloride ions migrate upwards in the concrete away from the reinforcing steel. The concrete immediately above the reinforcement experiences a continual depletion of chloride ion. However, at higher elevations in the concrete, an increase in chloride can actually occur at early times in the extraction process.

Thus, depending on the time the treatment is stopped, the concrete immediately adjacent to the reinforcing steel may be free of chloride while concrete 0.5 to 1.0 in. away will still be heavily contaminated. This raises the question as to how long it will take for this chloride to migrate back to the reinforcing steel under the action of the concentration gradient, and once again initiate the corrosion process.

The solution of this diffusion problem is not simple. Concentration gradients exist in three dimensions, from surface to rebar and from rebar to rebar. Further, it is not known how the electrochemical process itself influences the permeability of the concrete. If further moisture ingress into the concrete is effectively stopped by making the surface impermeable, then any chloride diffusion must occur in the absence of moisture movement down capillaries, etc. Temperature fluctuations will also have an effect on diffusion rates.

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* Based on dry concrete weight.

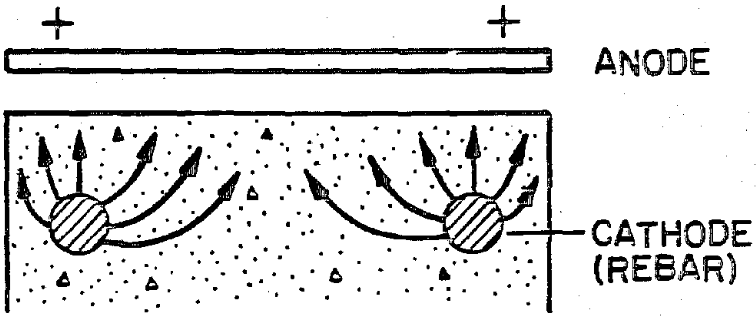

FIGURE 32. EXPECTED CURRENT FLOW DISTRIBUTION IN CONCRETE CLOSE TO REBAR DURING APPLIED VOLTAGE

It is considered that the solution of this problem is probably beyond computation and must rely on experimentation. The large slabs which were treated at Battelle in this experimental program would be ideal from this point of view. Since the slabs have been electrochemically treated, and are not subject to deicing salt application, then periodic coring at strategic locations on these blocks will allow the diffusion and redistribution behavior of chloride to be followed as a function of time. The results from such an investigation should be directly applicable to a full-size bridge deck.

Debonding

Questions have been raised concerning the effect of the rather high current densities which are present at the rebar surface during electrochemical treatment on the bond strength at the rebar/concrete interface. Such questions follow from previously published work (4), the consensus of which is that

(1) Reduction in bond strength can occur as a result of current flow

(2) Softening of the concrete close to the rebar is the cause of the loss of bond

(3) The loss of bond is proportional to the density of electric charge passed at the interface.

Any system which requires that a faradic reaction occur at the rebar/concrete interface must consider possible loss-of-bond problems. The present interest in cathodic protection of reinforced concrete bridge decks has therefore caused a reevaluation of possible debonding. While the current densities on the rebar being cathodically protected are much below those occurring during electrochemical chloride removal, the time period ensuing for cathodic protection (tens of years) is much larger than the tens of hours required for chloride removal. Since the magnitude of debonding is considered to be a function primarily of total charge density, then essentially the same experiment could be used to study debonding for both conditions.

The most recent investigation of debonding has been performed under NCHRP 12-13, "Cathodic Protection for Reinforced Concrete Bridge Decks". In this study, concrete prisms containing rebar were subjected to current densities at the rebar of 0.048, 0.48, and 0.96 A/ft^2 for times of 15, 30, 150, and 300 days. This corresponds to total change densities on the rebar of 346, 3460, and 6920 A hr/ft^2. Multiple regression analyses showed that bond strength values for the treated prisms had the highest simple correlation coefficient with charge density, and not with current density or time of current application. There was a 10 percent decrease in bond strength after 3460 A hr/ft^2 had been passed, with a further 10 percent decrease after 6920 A hr/ft^2.

It is important to compare these charge densities with those which were typical in the chloride removal procedures. In a bridge deck constructed of No. 6 rebar on an 8 x 16-in. grid approximately 0.55 ft^2 of rebar surface is beneath a square foot of deck surface. If we assume that the top half of the rebar surface sees the current, and that the average current is 3 A/ft^2 for 24 hr, then the charge density for the electrochemical removal procedure is roughly 260 A hr/ft^2. This is more than an order of magnitude below the level observed to cause a 10 percent reduction in bond strength in the work cited above. Thus, on the assumption that the above experiments are valid in this case, it appears that loss of bond as a result of electrochemical chloride extraction procedures would not be significant.

No experiments on change in bond strength as a result of current flow were carried out in the present investigation. However, care was taken to visually note any changes in concrete properties at or close to the rebar surface. Some darkening of the concrete around the rebar was evident in certain specimens and cores after electrochemical treatment. The reason for this is uncertain, but may result from the increase in pH at the rebar, as a result of the discharge of hydrogen as the cathodic reaction:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- .$$

This increase in pH may cause a precipitation of corrosion product close to the rebar.

It is instructive to speculate on the possible reasons for loss of bond and/or deterioration of concrete at the rebar during current flow. Because current is flowing through the concrete, from rebar (cathode) to surface anode, a faradaic reaction, involving electron transfer, must occur at the rebar surface. The probable reaction is hydrogen evolution by the above equation. At pH 12, approximately the pH of concrete, the equilibrium potential for this reaction is approximately $-0.71\ V_{SHE}$ or $-0.78\ V_{CSE}$. The equilibrium potential will, of course, become more negative as the hydroxide concentration builds up. This in turn will be a function of the solubility behavior of $Ca(OH)_2$, since $Ca(OH)_2$ will tend to precipitate as the hydroxyl ion concentration increases. Complicating this behavior is the ionic migration of the Ca^{2+} ions towards the reinforcing steel.

Besides the movement by electromigration of Ca^{2+} towards the cathode, other cations present in the concrete, such as Na^+ from the deicing salt, will also move in that direction. This will lead to a concentration of these elements at the rebar. However, they are not expected to enter into any electrochemical reaction, such as discharge at the cathode, since the equilibrium potentials are for Na^+/Na $- 2.71\ V_{SHE}$ and for Ca^{2+}/Ca, $- 2.87\ V_{SHE}$. Thus, there is almost a 2 V difference between the hydrogen evolution equilibrium potential and the metal deposition equilibrium potential. Metal deposition (Na or Ca) on the rebar is therefore quite out of the question.

The third possible cathodic reaction which could occur at the rebar is the reduction of corrosion product or scale present on the steel. Millscale, Fe_3O_4, and/or rust, $Fe_2O_3 \cdot \alpha H_2O$ are generally present on one steel surface during embedment, and if salt-induced corrosion has occurred, the thickness of the layer will have built up. Cathodic reduction involving these products would give, successively, $Fe(OH)_2$ and ultimately Fe at the rebar. Since it is known that the products of corrosion occupy more volume than the iron from which they came, then the reverse reaction will cause a diminution in volume. However, the kinetics of such a process will be very slow, and the electrical conductivity of Fe_3O_4 generally precludes its cathodic reduction. The magnitude of the role which these processes play in disbonding during cathodic polarization is, therefore, uncertain.

To summarize, the following are the possible results of cathodic current flow at the rebar:

(1) Evolution of hydrogen at the rebar

(2) Increase in pH close to the rebar

(3) Build-up of cations (Ca^{2+}, Na^{+}) at the rebar

(4) Reduction of corrosion product, with deposition of metallic Fe on the rebar.

It is conceivable that all of these processes could cause disbonding. Hydrogen evolution could cause a collection of hydrogen at the rebar/concrete interface. Strong alkali (NaOH) could give a degradation in concrete properties. Void formulation from volume changes could occur. It is not known at this time whether any or all of these processes actually lead to the disbonding which is evident after extreme current flow. However, it must be emphasized again that no evidence of disbonding was seen as a result of the electrochemical treatment, and none would be predicted at the charge densities used, on the basis of experimentation with this phenomenon.

CONCLUSIONS

The salient observations and conclusions of the research program are

(1) The removal of chloride ions from hardened concrete using the electrochemical technique developed in the program is technically feasible.

(2) The flushing of hardened concrete with deionized water as a means to selectively redistribute chloride ions and, thus, complement the electrochemical removal technique is not a technically feasible concept when practiced under the constraints of actual field conditions.

(3) The removal of chloride ion from an actual bridge deck produced the desired result of changing the potential of the reinforcing steel from an active to a passive value.

(4) The actual amount of chloride ion removed from hardened concrete using the technique was found to be influenced by the magnitude of the applied d-c voltage, the duration of treatment time, the starting chloride content of the concrete, and possibly the concrete and ambient temperature at the time of treatment. Additional work is needed to fully establish the relative contributions of these variables and perhaps other variables to the removal efficiency.

(5) Passivation of the reinforcing steel was achieved in the treated bridge deck even though the residual chlroide ion content was above the estimated threshold value in some portions of the treated area. This is probably due to the fact that chloride ion removal is greatest in the concrete immediately adjacent to the reinforcing steel. It remains to be established whether chloride ion remaining in the concrete away from the reinforcing steel will migrate to the reinforcing steel when the sole driving force for the migration is a chloride ion concentration gradient.

(6) Additional research is required before the electrochemical removal concept can be considered for full scale implementation by FHWA. In addition to the factors considered in (4) and (5) above, the required considerations include an optimization of procedures and hardware, determination of the optimum technique for waterproofing the deck following treatment, and a thorough evaluation of the economic factors bearing on bridge deck rehabilitation.

Additional laboratory and field work will be required to provide for the transition between the current state of development and full scale implementation.

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APPENDIX A

CHLORIDE MONITORING ELECTRODE INVESTIGATION

The convenience of a solid-state electrode which would give direct readings of the chloride content of a bridge deck when placed on the concrete surface is inestimable, when compared with standard wet analysis techniques. Such a device would not only give measurements of the chloride level for a given bridge deck, but would also be used to conveniently monitor the efficiency of any chloride-removal process.

Two solid-state devices exist for measurement of chloride in concentrations. The first of these is the well-known Ag/AgCl electrode, which takes up a potential corresponding to the chloride activity of the solution according to the equation

$$E_{Ag/AgCl} = E_{Ag/AgCl} - \frac{RT}{F} \ln a_{Cl^-} \quad ,$$

where $E_{Ag/AgCl}$ is the,"standard electrode potential" of the electrode and has the constant value of +0.22 V. This electrode is easily prepared by depositing a layer of AgCl on silver by making the silver the anode of an electrolytic cell in which the electrolyte is KCl. The second type of chloride-sensitive electrode has been developed more recently; in essence, this consists of a pellet of an $Ag_2S/AgCl$ mixture. When the surface of this pellet is placed in a chloride-containing solution, the pellet develops a potential difference across its faces, the magnitude of which is proportional to the logarithm of the chloride ion activity of the solution; that is, it obeys precisely the same form of relationship as the Ag/AgCl electrode. This electrode is marketed commercially in two forms: one has an integral reference electrode (the "combination" electrode) and one utilizes a separate external reference electrode. Both types of electrode have been used in this investigation. The electrodes were obtained from Orion Research, Inc.

The essential mechanism behind both the Ag/AgCl and the solid-state electrode (Orion) involves the dissolution of AgCl and the associated solubility product (K_s) of this dissolution,

$$AgCl \overset{K_s}{=} Ag^+ + Cl^- \, .$$

$$K_s = [Ag^+]\,[OH^-] = 1.5 \times 10^{-10} \text{ at } 25 \text{ C}$$

This small but finite solubility of AgCl puts a lower limit of $\sim 10^{-5}$ M/l on the detectability of the electrode, since in solutions containing less chloride than this, AgCl will dissolve until the chloride concentration reaches this level. While this situation holds true for neutral solutions, it worsens for alkaline solutions. Under these circumstances, the second solubility equilibrium

$$AgOH \overset{K_s}{\rightleftharpoons} Ag^+ + OH^- ,$$

$$K_s = [Ag^+][OH^-] = 1.5 \times 10^{-8} \text{ at } 20 \text{ C}$$

must be considered. At a solution pH of 12, $[OH^-] = 10^{-2}$; thus, from the AgOH equilibrium, $[Ag^+] = 1.5 \times 10^{-6}$. Substituting this value into the AgCl equilibrium $[Cl^-] \simeq 10^{-4}$ at pH 12. Therefore, the equilibrium concentration of Cl^- in an initially chloride-free solution of pH 12, resulting from solubility of AgCl, is 10^{-4} M: thus, the detectability limit of the electrode cannot be less than this value. This situation is of prime concern in the case of chlorides in concrete, where the pH can be of the order of 12.

A further complicating factor to be considered in the determination of chloride levels by solid-state electrodes involves the presence of possible interfering ions in solution. The anions SO_4^{2-}, CO_3^{2-}, and SiO_4^{4-}, and the cations Mg^{2+} and Ca^{2+} are present in concrete. These ions can influence solution pH, and hence the detectability limit of the electrode. They can also influence the activity coefficient, γ, of the chloride ion, according to the equation

$$\text{Activity of } Cl^- = \gamma \times (\text{concentration of } Cl^-).$$

Thus, since the electrodes respond to chloride ion activity, any changes in γ resulting from the presence of interfering ions will result in erroneous values of Cl^- concentration being measured. Any investigation of the suitability of either electrode for Cl^- determinations in concrete must, therefore, consider these factors.

Results

Because concrete has a pH of the order of 12, experiments were carried out to determine the behavior of the Ag/AgCl electrode and the Orion membrane electrode in chloride solutions of pH 12. The influence of other ions contained in the concrete on electrode response have also been studied.

Figure 33 shows the potential taken up by a Ag/AgCl electrode (Corning silver billet, chloridzed in KCl solution) as a function of Cl^--ion concentration in 10^{-2} N NaOH (pH 11.9). Potentials were measured against a saturated calomel electrode in an external container: connection between test solution and external container was made by a salt bridge of saturated KNO_3-Agar jelly, to avoid chloride contamination. The Ag/AgCl electrode shows an essentially linear response above 10^{-3} M; because of the pH effect discussed earlier, it is not linear below this value. The slope of the E versus log Cl^- plot is 57 mV/decade (theoretical value is 59 mV/decade).

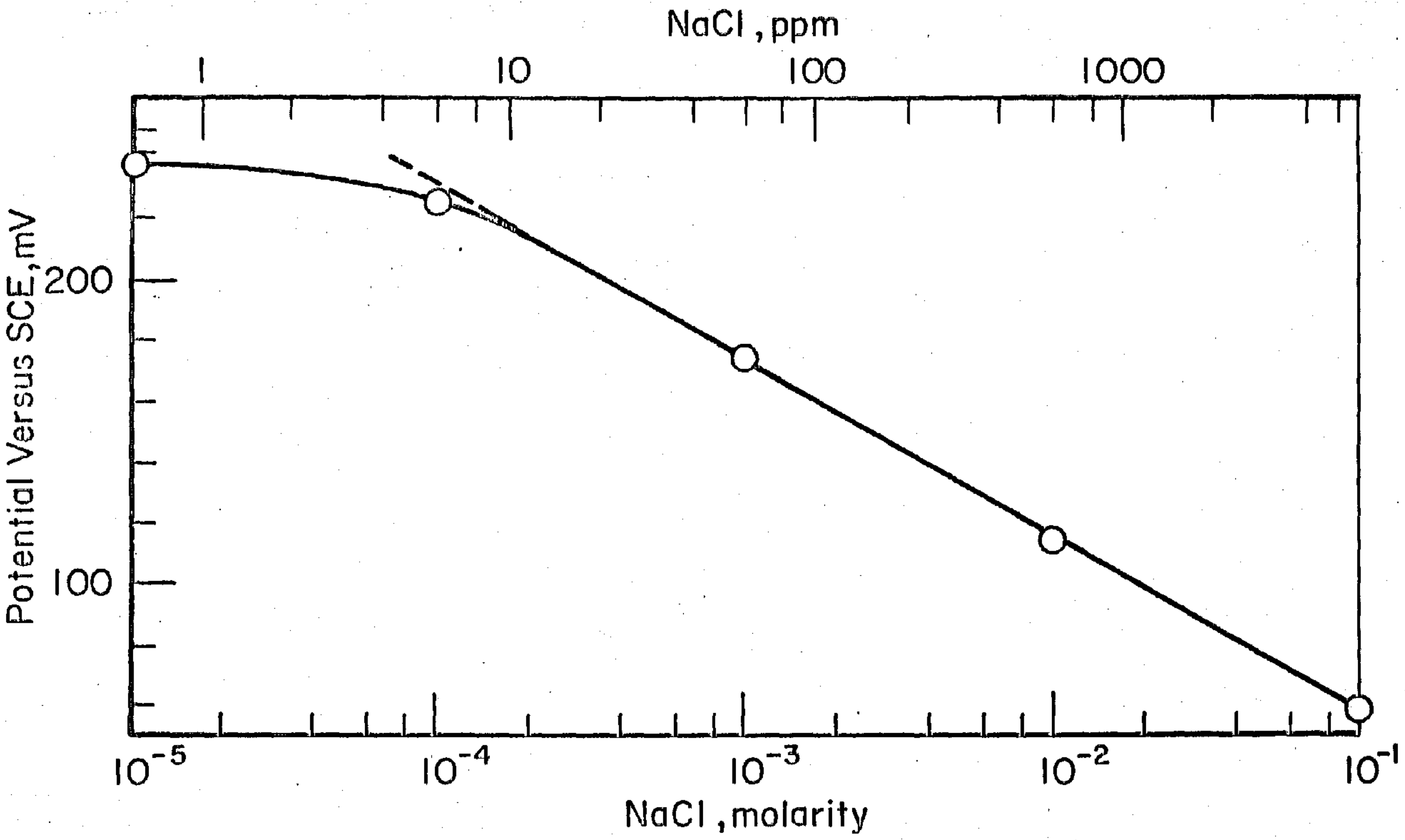

FIGURE 33. POTENTIAL OF Ag/AgCl ELECTRODE IN 10^{-2}N NaOH CONTAINING NaCl

Figure 34 gives data from a similar experiment conducted in 10^{-2} N $Ca(OH)_2$, pH 11.9. There is essentially no difference between the results of Figures 33 and 34 showing that the Ca^{2+} ion has no effect on measured potential; that is, it does not interfere with the electrode. This is important, because $Ca(OH)_2$ is the essential constituent of any concrete extraction by water.

Experiments on the determination of chloride ion concentration in 10^{-2} N NaOH and 10^{-2} N $Ca(OH)_2$ solutions containing chloride have been performed using Orion solid-state membrane electrodes. Two models have been used: the "combination" electrode (96-17-00) which has a built-in Ag/AgCl/KCl reference half cell, and a single electrode, used with a double-junction reference electrode in the same solution (Orion, Model 94-17A with an Orion Model 90-02 reference electrode). Results are given in Figures 35 and 36. In 10^{-2} N NaOH, the electrodes show linearity from 10^{-1} to 10^{-3} M NaCl, but depart from linearity at more dilute concentrations. The departure is less marked for the combination electrode. This electrode also showed some drift in readings at concentrations below 10^{-4} M. These results are probably attributable to slow leakage of chloride from the integral reference electrode into the solution. The double-junction reference electrode does not permit leakage since there is a KNO_3 bridge solution interposed.

The above behavior was also observed in $Ca(OH)_2$ solutions, but the difference between the readings for the two electrodes at a given Cl^- ion concentration was greater. This is possibly attributable to differences in junction potential between the two types of reference electrode.

These studies indicate that either the Ag/AgCl or the solid-state membrane electrode can be used to measure the chloride content of solutions containing Ca^{2+} at Cl^- concentrations down to $\sim 5 \times 10^{-4}$ M. Further work has been performed to study the effect of other anions on the response of these electrodes. Experiments were performed in solutions of 10^{-2} N NaOH, at two levels of Cl^-, 10^{-4} M and 10^{-2} M, containing 10^{-2} M Na_2CO_3, Na_2SO_4, or Na_4SiO_4. The results are given in Tables 33 and 34. The results show that both types of electrodes were affected similarly by the additions, and that SO_4^{2-} and CO_3^{2-} had essentially no effect on electrode response. SiO_4^{4-}, however, had a large effect, particularly at the low Cl^- concentrations. This is undoubtedly due partly to the effect which the SiO_4^{4-} had on the solution pH; the increase in pH decreases further the limit of detection of both electrodes. However, the effect, although smaller, persists at 10^{-2} M Cl^-, and care therefore must be exercised when making Cl^- determinations in solutions containing silicate ion, particularly if the concentration of the ion varies from one determination to the next.

Following these initially encouraging results on chloride-containing solutions, experiments were initiated to investigate the behavior of a chloride-sensing electrode in contact with salt-contaminated concrete. Concrete mortar specimens containing NaCl were made up for this investigation. The absence of aggregate was deliberate, to insure that the placing of the electrode would not be critically affected by an underlying large aggregate particle. Nominal chloride

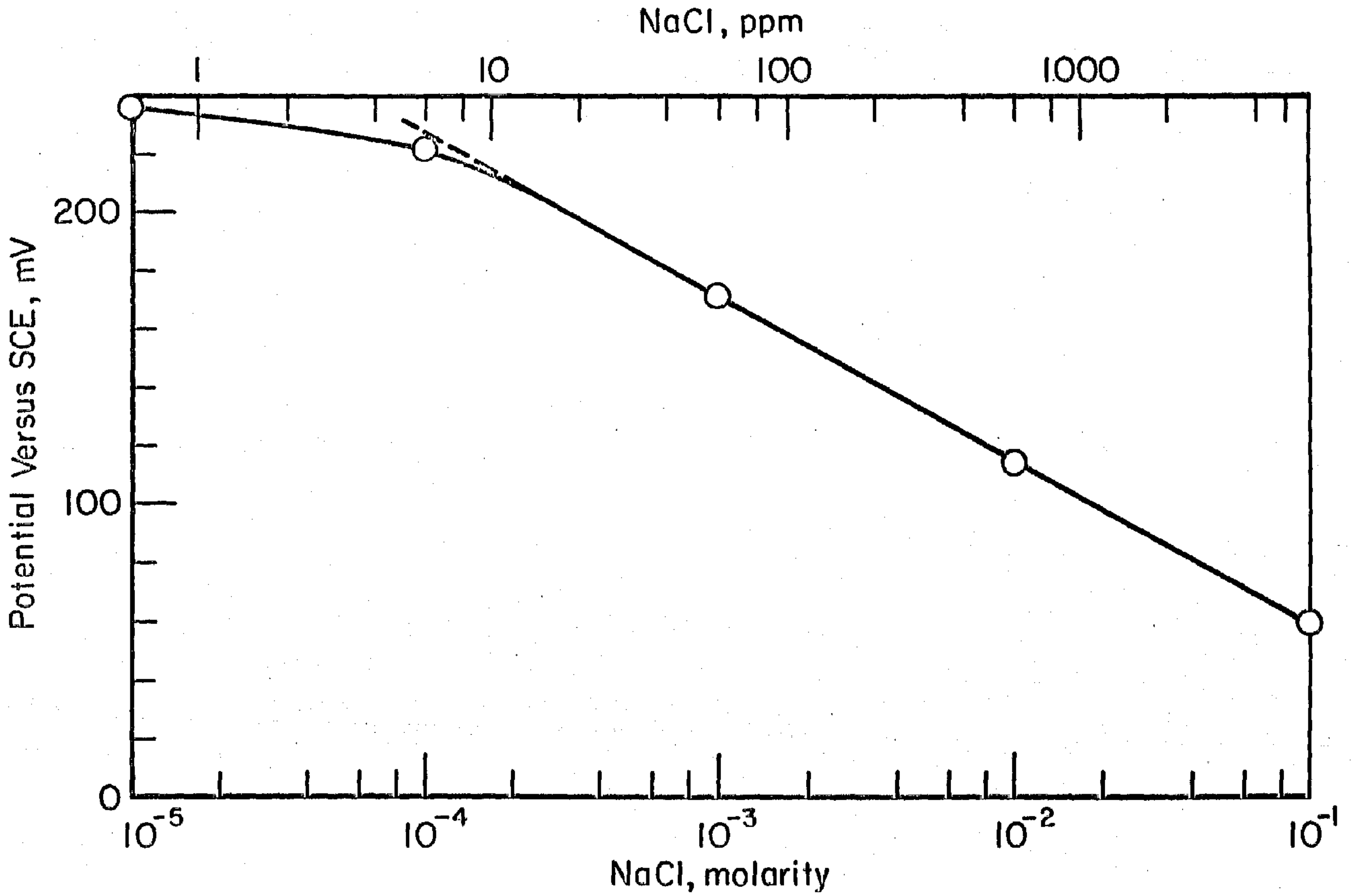

FIGURE 34. POTENTIAL OF Ag/AgCl ELECTRODE IN 10^{-2}N $Ca(OH)_2$, pH 12, CONTAINING NaCl

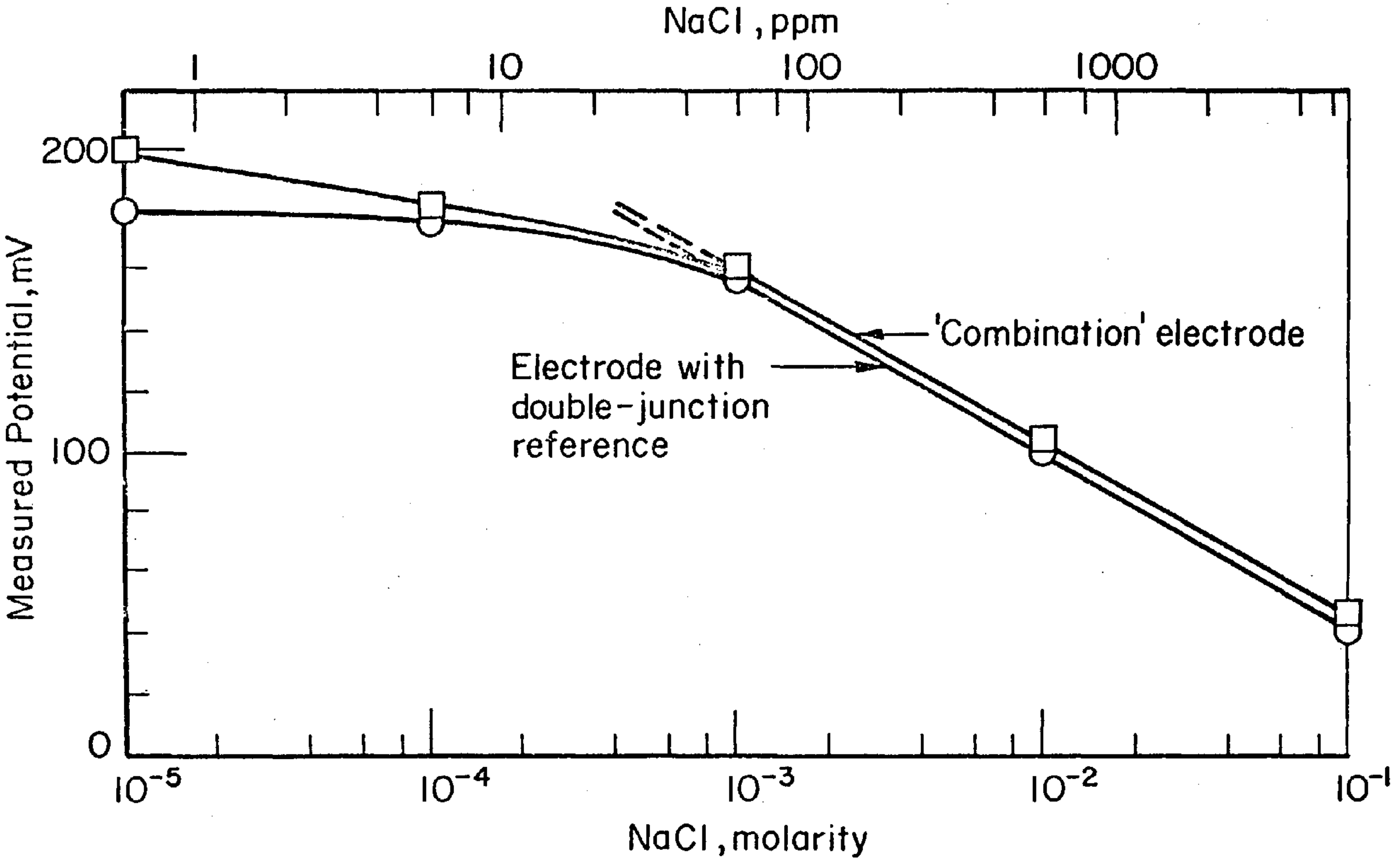

FIGURE 35. POTENTIAL OF ORION SOLID-STATE Cl^--ION ELECTRODES IN 10^{-2}N NaOH (pH 12) CONTAINING NaCl

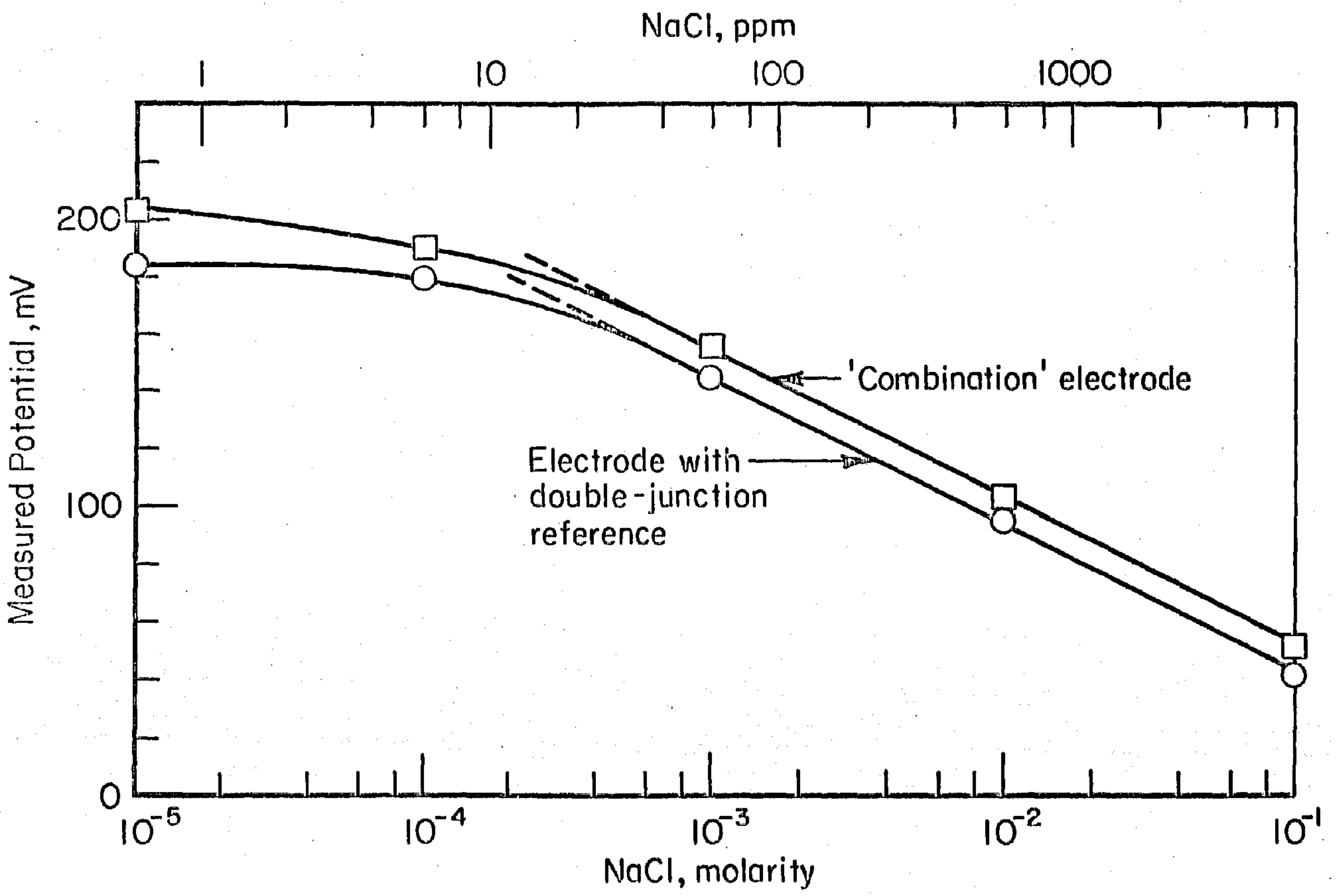

FIGURE 36. POTENTIAL OF ORION SOLID-STATE Cl^--ION ELECTRODES IN 10^{-2}N $Ca(OH)_2$ (pH 12) CONTAINING NaCl

TABLE 33. POTENTIAL OF Ag/AgCl ELECTRODE IN NaOH/NaCl SOLUTIONS CONTAINING OTHER ANIONS

	10^{-2} N NaOH/10^{-4} M NaCl		10^{-2} N NaOH/10^{-2} M NaCl	
	Potential, mV Versus SCE	pH	Potential, mV Versus SCE	pH
Base Solution	218	11.9	115	11.9
+ 10^{-2} M Na_2SO_4	213	11.9	115	11.9
+ 10^{-2} M Na_2CO_3	214	11.8	115	11.8
+ 10^{-2} M Na_4SiO_4	179	12.3	117	12.3

TABLE 34. POTENTIAL OF ORION SOLID-STATE CL^--ION ELECTRODE AGAINST DOUBLE-JUNCTION REFERENCE ELECTRODE IN NaOH/NaCl SOLUTIONS CONTAINING OTHER ANIONS

	10^{-2} N NaOH/10^{-4} M NaCl		10^{-2} N NaOH/10^{-2} M NaCl	
	Potential, mV	pH	Potential, mV	pH
Base Solution	186	11.9	91	11.9
+ 10^{-2} M Na_2SO_4	183	11.9	92	11.9
+ 10^{-2} M Na_2CO_3	184	11.8	91	11.8
+ 10^{-2} M Na_4SiO_4	155	12.3	91	12.3

levels of the specimens were from 0.01 to 1.0 percent as Cl^-, to cover the concentrations expected in the field. The specimens were cut into 1-in.-thick slices and the top and bottom of each slice could be used.

In preliminary experiments, 0.1 ml distilled water was placed in a wax pencil of 1 cm in diameter on the mortar surface, and a chloridized silver billet electrode (Ag/AgCl electrode) was applied to the water. About 2 cm away, a small piece of cellulose sponge wet with Na_2SO_4 solution was placed with a calomel electrode in contact with it. The potential developed between the Ag/AgCl and calomel electrodes was measured as a function of time.

In general, the potential of the Ag/AgCl electrode decreased with time, and with increasing chloride content of the mortar. However, a large scatter in the results was evident. To attempt to reduce the scatter, a more sophisticated experimental arrangement was used, as shown in Figure 37. A glass tube was affixed by means of wax to the surface of the mortar and was filled with distilled water. The (cylindrical) Ag/AgCl electrode was placed inside this tube, so that the electrode "saw" a constant volume of 3×10^{-4} ml of solution. The reference electrode for the measurement was a saturated calomel electrode, contacting the mortar through a wetted sponge, as before.

The potential developed by the Ag/AgCl electrode as a function of time, when in contact with mortars of differing Cl^--ion contents, is shown in Figure 38. It is apparent from these experiments that, in order for any meaningful results to be obtained by this technique, the solution must be in contact with the mortar surface for extended times. It is also evident that this period increases with increasing Cl^--ion content of the mortar. Further, the reproducibility and scatter with the improved solution holding arrangement does not appear to be significantly better than when the simpler arrangement was used.

It was noted earlier that the Ag/AgCl electrode has a lower limit of detectability for Cl^- of about 10^{-4} g/cm^3 in pH 12 solution. At Cl^- concentrations below this value, the electrode gives a nonlinear $\frac{dE}{d\log Cl^-}$ dependence. Thus, if the measurements of the Cl^- content of concrete by this water extraction technique are to be successful, then <u>at least</u> this concentration of Cl^- must be present in the solution resulting from extraction.

The following approximate calculation gives an estimate of the times necessary for this minimum concentration to be reached. We suppose the following data:

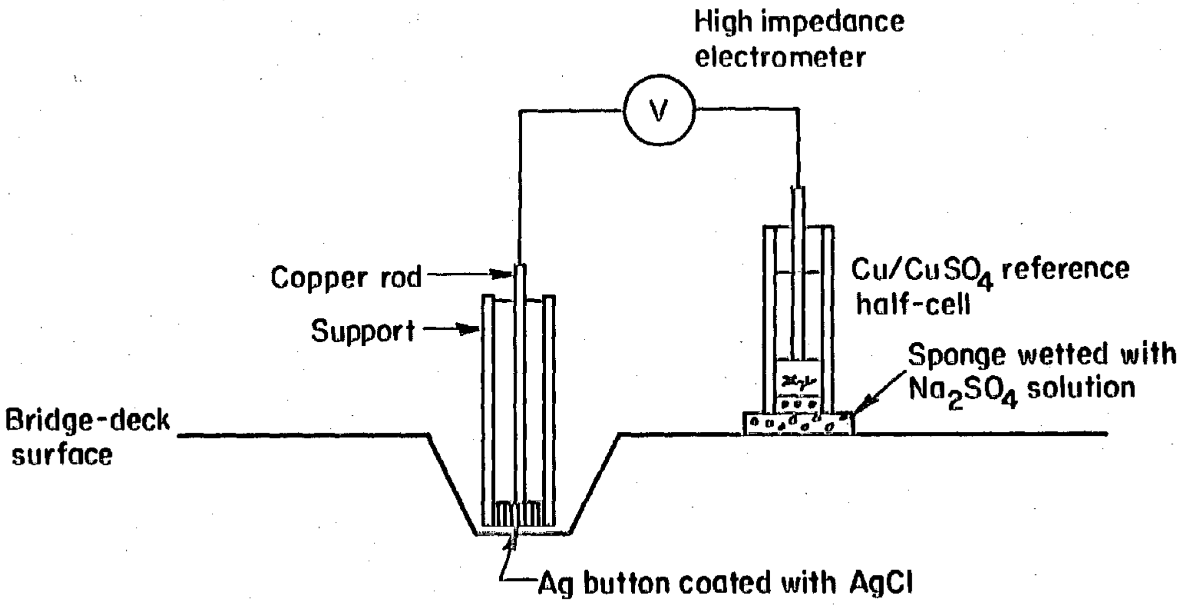

FIGURE 37. SCHEMATIC OF SETUP FOR CHLORIDE-ION DETERMINATION IN BRIDGE DECKS

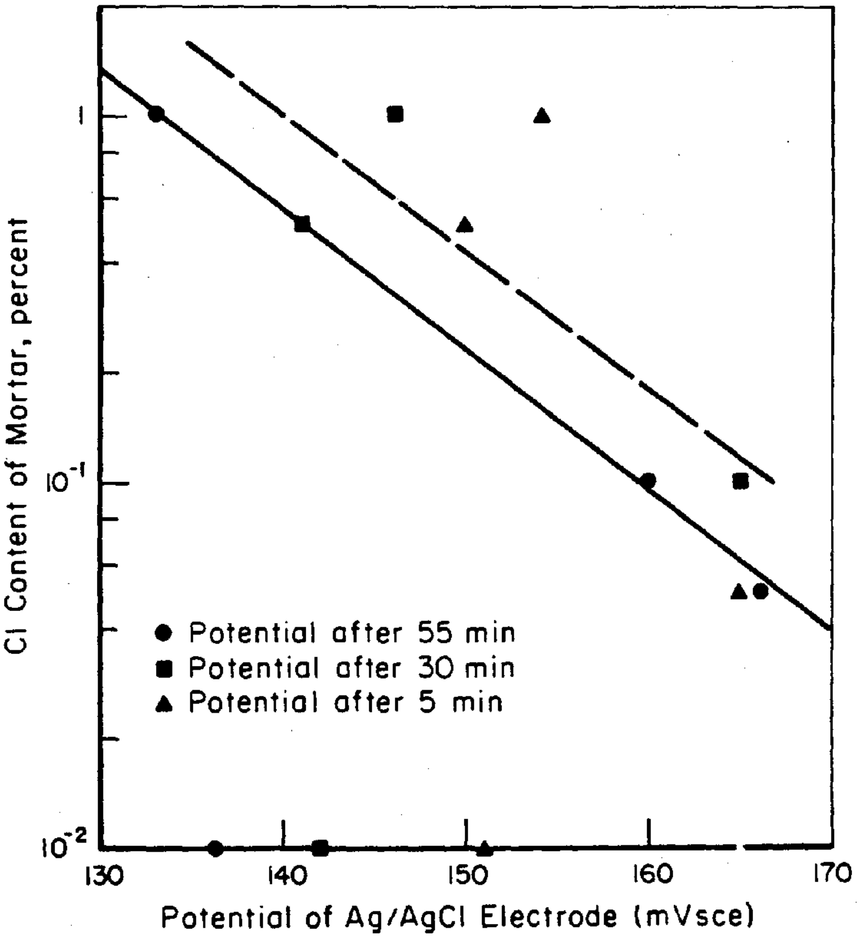

FIGURE 38. POTENTIAL OF Ag/AgCl ELECTRODE IN CONTACT WITH A Cl^- CONTAMINATED MORTAR AS A FUNCTION OF CONTAMINANT LEVEL AND TIME

Density, ρ, of mortar = $2.2\ g/cm^3$

Diffusion coefficient, D, of Cl^- in mortar = $10^{-7}/cm^2/sec$

Area of exposure, A = $0.46\ cm^2$

Volume of distilled water used, V = 3×10^{-4}

Minimum concentration of Cl^- required = 10^{-4}

Concentration of Cl^- in mortar = C g/g

Total quantity of Cl^- required = $10^{-4} \times V$

= 3×10^{-8} g ion

= 1.1×10^{-6} g.

Suppose δ is the depth from which Cl^- diffuses from the mortar into the solution.

Then total quantity of Cl^- migrating from mortar to water = $C \times A \times \delta \times P$.

Equating requirements and supply,
$1.1 \times 10^{-6} = 6 \times 0.46 \times \delta \times 2.2$.

δ can now be calculated for various C's.

C	δ
1 % (0.01 g/g)	10^{-4} cm
0.1 %	10^{-3} cm
0.01 %	10^{-2} cm

These values of δ are the minimum distances over which the Cl^- must diffuse to go into the water. However, this implies that all the Cl^- in the distance δ migrates and passes into the solution. This is obviously erroneous. Suppose we choose a more realistic diffusion distance, X, of 5 δ. Then, since $X^2 = Dt$, where t = time necessary for diffusion, t can be roughly calculated.

C, %	X, cm	t, sec
1	5×10^{-4}	2.5
0.1	5×10^{-3}	2.5×10^{2}
0.01	5×10^{-2}	2.5×10^{4}

Thus, a Cl^- concentration of 0.01 percent in the mortar requires approximately 7 hr for the minimum measurable concentration of Cl^- to accumulate in solution.

Notwithstanding that this calculation is simplistic and does not take into account such factors as sideways diffusion, it goes a long way towards rationalizing the experimental results with regard to the lower mortar Cl^- contents.

If this technique is to be used for estimating the Cl^- content of mortars and concretes, then a means must be found to accelerate the exchange between Cl^- in concrete and in the measuring medium. One possible means for this would be to apply an electric field and "electromigrate" the chloride ion, just as in the removal of Cl^- from contaminated concrete.

There are also problems associated with the use of a liquid extractant. The liquid will both evaporate, and diffuse into the concrete. If a gel (such as agar) were used instead of a solution, particularly in conjunction with electromigration, then this problem could possibly be circumvented.

In conclusion, the use of the Ag/AgCl electrode, or other chloride-sensitive electrodes, appears to warrant further study for measurement of the chloride content of contaminated concrete. However, considerable refinements to the simplistic techniques attempted here would be necessary before it became practicable.

At this stage of development, further work on the technique was stopped, at the discretion of FHWA officials.

APPENDIX B

PREPARATION OF CYLINDRICAL CONCRETE SPECIMENS FOR THE LABORATORY EXPERIMENTS

The concrete used was the Class C gravel concrete used by the Ohio Highway Department for bridge deck construction.* The proportioning is based on the development of a compressive strength at 28 days of 4000 psi. The concrete and aggregate properties are described in Table 35.

In order to simulate chloride distributions in actual bridge decks, specimens were prepared from concrete to which a known amount of chloride was added (as NaCl) to the fresh concrete. The specimens were being prepared in three lifts from concretes containing three levels of chloride.

In practice, three 108-lb batches of concrete were prepared within a 30-40 min period. The unit weight, slump, and air content of each batch was measured. Mixing of the concrete followed a 3-3-2 min sequence (mix-rest-mix). The 4 x 8-in. cylindrical steel molds were firmly clamped to a vibrating table. Initially, 1256 g of concrete (one-third the total specimen weight) containing no chloride was placed in the mold and vibrated at a known frequency and amplitude for 8 sec. A second lift of 1256 grams of concrete containing an intermediate level of chloride was then placed in the mold and vibrated for 8 sec. Finally, a third lift of 1256 g of concrete containing a high level of chloride is placed in the mold and vibrated for 8 sec.

The specimens were mold cured for 24 hr. then placed in polyethylene bags and subjected to fog curing (100 RH/74 F) for 28 days. Following the fog cure, the sides of the specimens were sealed with an epoxy moisture barrier.** A total of seventeen 4 x 8 in. specimens and (in some cases) eight 3 x 6 in. specimens*** were made for each set of variables investigated.

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* State of Ohio, Department of Transportation, "Construction and Material Specifications", Section 499.03, Air Content of Concrete to be 6 ± 2 percent. Slump to be 1-4 in., not to exceed 5 in. Water/cement ratio not to exceed 0.50.

** Aqua-Top, Sika Chemical Corporation, Lyndhurst, New Jersey.

*** The 3 x 6 in. cylinders were prepared for use in the laboratory work on electrochemical removal.

TABLE 35. OHIO HIGHWAY DEPARTMENT CLASS C GRAVEL CONCRETE SELECTED FOR USE IN CHLORIDE NEUTRALIZATION PROGRAM

Constituent	Lb/yd^3	ft^3/yd^3
Cement (Miami Type I)	607.1	3.09
Sand (SSD)(a)	1209.4	7.20
No. 57 Coarse Aggregate (SSD)(b)	1790.3	10.83
Water	266.0	4.26
Air (6 percent)(c)	--	1.62
	3872.8	27.00

Theoretical Unit Weight = 143.4 lb/ft^3

W/C = 0.438

(a) No. 400 Grade Crushed Silica Sand R. W. Sidley, Inc. Thompson, Ohio Sp.Gr. (SSD) = 2.69, Absorption (1.06 percent); Fineness Modulus = 2.45.

(b) Smokey White Quartz Gravel, Pyramid Aggregates, Detroit, Michigan. Blended from Three size fractions to yield No. 57 Grading. Sp. Gr. (SSD) = 2.65; Absorption = nil.

(c) MBVR used at rate of 3/4 to 1.0 oz per 100# cement to achieve desired air entrainment.

APPENDIX C

CHLORIDE ANALYSIS PROCEDURE

The technique for measuring the chloride content of the concretes in the present study was that reported recently by Berman.* Considerable effort was spent to develop a sampling technique for the concrete that would yield a truly representative sample. The procedure that was adopted was as follows:

(1) Each 4 x 8 in. concrete cylinder is sliced with a diamond saw to yield 1.0-in.-thick slices. Slice No. 1 is the concrete from the top surface to 1 in. below the surface; Slice No. 2 is the concrete from 1 in. below the surface to 2 in. below the surface and so on.

(2) The entire slice (4 in. in diameter x 1 in. thick) is passed through a large jaw crusher (set at 1/4-in. opening) then through a large roll crusher (set at about 1/16-in. opening). The pass through the roll crusher yields a crushed material that passes a No. 8 sieve.

(3) The crushed sample (about 450 grams) is passed through a riffle type splitter to yield four samples of about 10 to 12 g in size.

(4) The 10 to 12-gram samples are dried 24 hr at 212 F to eliminate free water and then are analyzed for chloride using the Berman titration method.

Preliminary work was done to indicate the precision of the method and to establish required population size.

Cement Paste Specimens

Initially work was done on mechanical mixtures of reagent grade NaCl and samples of a 5-yr-old hydrated Type I cement paste. Chloride was added to the crushed paste samples (minus 50 mesh) in amounts from 0 to 5.0 weight percent (based on the dried weight of the cement paste). Sample size was about 3.0 grams. Duplicate measurements were made at each add level. The results of these measurements are reported in Table 36. For the four measurements made at the 0.25 percent add level, the average value was 0.2495 percent, standard deviation was 0.0048 percent, coefficient of variation was 1.9, and the 95 percent level confidence internal (t distribution) was 0.2495 ± 0.0077 percent).

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* Berman, H. A., "Determination of Chloride in Hardened Portland Cement Paste, Mortar, and Concrete", Jour. of Materials, 7 (3), 330-335 (September, 1972)

TABLE 36. CHLORIDE ANALYSES[(a)] OF CEMENT PASTE–NaCl MECHANICAL MIXTURES

Mixture Number	Chloride Ion Addition. percent of dry paste weight	Measured Chloride Ion, percent of dry paste weight		
		Sample No. 1	Sample No. 2	Average
1	0	0.002	0.002	0.002
2A	0.25	0.245	0.246	0.246
2B	0.25	0.252	0.255	0.253
3	0.50	0.497	0.481	0.490
4	1.00	1.010	1.020	1.015
5	2.50	2.403	2.414	2.408
6	5.00	5.020	5.020	5.020

(a) Berman technique.

The measured chloride ion content of 0.002 percent for the plain cement paste samples was attributed either to chloride coming from the ion selective electrode or from the cement itself (which can contain up to 40 ppm Cl^-).

Concrete Specimens

Two 4 x 8 in. specimens of Series C2 (high chloride) were sliced after demolding and subjected to chloride analyses. Six 10 gram samples were analyzed from the 1.0-in. slice and four 10-gram samples from the 2.0, 3.0, 4.0, and 5.0-in. slice. The results of these measurements are presented in Table 37.

TABLE 37. CHLORIDE ANALYSES OF CONCRETE SERIES C2 AFTER 24-HR CURE

Specimen Number	Slice Number	Measured Chloride, percent of dry concrete weight						
		Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5	Sample No. 6	Average
C2-1	1.0	0.144	0.143	0.146	0.145	0.149	0.145	0.144
C2-1	2.0	0.120	0.121	0.123	0.199	--	--	0.121
C2-1	3.0	0.058	0.059	0.057	0.059	--	--	0.058
C2-1	4.0	0.026	0.024	0.025	0.024	--	--	0.025
C2-1	5.0	0.017	0.017	0.016	0.017	--	--	0.017
C2-10	1.0	0.133	0.132	0.137	0.133	0.140	0.138	0.135
C2-10	2.0	0.114	0.117	0.110	0.124	--	--	0.114
C2-10	3.0	0.061	0.061	0.060	0.059	--	--	0.060
C2-10	4.0	0.024	0.024	0.024	0.024	--	--	0.024
C2-10	5.0	0.019	0.018	0.020	0.020	--	--	0.019

APPENDIX D

PREPARATION OF SIMULATED BRIDGE DECK SLABS

Five concrete slabs (46 x 60 x 9 inches) were prepared for use in the laboratory studies on simulated bridge decks. Reinforcing steel was placed in the concrete to duplicate the rebar network in the bridge that was selected for field experiments. The rebar network consisted of two grids. The lower grid, placed 1 in. above the bottom of the slab, was formed with #6 rebars placed longitudinally on 8-1/2-in. centers, and #7 rebars placed transversely on 8-in. centers. The upper grid, placed 2 in. below the deck surface, was formed with #6 rebars placed longitudinally on 16-in. centers, and the same size bars placed transversely on 8-in. centers. All bars were tied at crossing points to provide electrical contact. Figure 39 is a photograph of the grid structure and form for one of the slabs prior to construction.

Each slab was formed by casting three 3-in.-thick layers of the freshly mixed concrete (Ohio, Class C), prepared in 6-ft^3 batches. The batch weights used were as follows:

Material	Lb
Cement (Type I	134.9
Sand (No. 400 quartz, dry)	265.9
No. 57 Quartz aggregate (composite)	397.8
Water	61.9
MBVR (to provide 6 vol/% air)	

To provide the desired chloride content for the middle and upper layers (3-in. depth, each layer), reagent grade NaCl was dissolved in the mix water, and added during batch mixing. The following amounts of NaCl were used:

Mix	Cl^- Concentration Desired, lb/yd^3	NaCl Added, lb/6 ft^3 batch
A	0	0
B	0.52	0.19
C	2.77	1.03
D	5.54	2.06

FIGURE 39. MOLD USED FOR THE CONSTRUCTION OF SIMULATED BRIDGE DECK SLABS (46 x 60 x 9 inches)

Each batch was prepared by mixing the components in a 6-ft^3 capacity rotary-type concrete mixer. Air content, unit weight, and slump were measured on samples taken from each batch, before casting was begun.

The slabs were cured 7 days before demolding. During this period, they were covered with wet burlap. After demolding, the sides of the slabs were coated with an epoxy resin* to prevent moisture loss from the sides.

The finished slabs were kept indoors for about 4 weeks. They were then placed outdoors on precast support columns 3 ft tall, where they were exposed to natural weather conditions during subsequent experimental procedures. Experiments on the slab were begun during April, 1974.

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* Aqua-Top, Sika Chemical Corporation, Lyndhurst, New Jersey.

APPENDIX E

LINEAR POLARIZATION TECHNIQUES

Introduction

The use of electrochemical measurements to monitor the corrosion behavior of steel in concrete was initiated by Stratfull using potential scan techniques. This approach, which relies on the fact that more actively corroding steel shows a more active or more negative potential than other steel, has been used with success to determine the location of severe corrosion in salt-contaminated concrete. It has also been used to monitor the efficiency of the chloride extraction procedure, as discussed earlier.

The drawback with the potential measurement technique is that it gives only a qualitative measure of the corrosion of the rebar. It is not possible to derive a quantitative corrosion rate from values of potential. A method which does allow such quantification is known as the "linear polarization" or more correctly the polarization resistance method.

Without going into a complete theoretical justification of the polarization resistance method (see Reference 5 for such a discussion), electrochemical kinetic considerations show that, for small perturbations around the free corrosion potential of a metal in a particular environment, the corrosion rate is directly proportional to the slope of the current-potential curve:

$$CR = k \cdot \frac{\Delta i}{\Delta E} \quad (\Delta i = \text{current density}, \ \ \Delta E = \text{polarizing potential}),$$

$$\text{where } k = 0.056 \times \frac{\beta a \ \beta c}{\beta a + \beta c} \times \frac{\text{equivalent}}{\text{density}}$$

Here, βa, βc are electrochemical constants: for steel in concrete,

$$\beta a \simeq 0.06 \text{ V/decade}$$

$$\beta c \rightarrow \infty$$

$$\therefore \ k \simeq 0.012$$

The small polarizing potential is generally applied to the system and the resulting current flow measured. The polarizing potential can be either a square wave or a ramp function, and can be applied either by means of an electronic potentiostat, using counter and reference electrodes as well as the specimen electrode—the so-called "three electrode method" or by applying the potential between two identical specimen electrodes.

In the latter case, a square-wave technique is used, with the potential being reversed when the current has reached a steady value.

Experimental Techniques and Results

Laboratory Investigation

These techniques have been applied to the study of corrosion rates for rebar in concrete with and without salt contamination. Initial studies were carried out in the slabs constructed at BCL for chloride extraction experiments. The specimens were in the form of #6 rebar, 4 in. long with a lead attached to each. The lead connection was insulated with epoxy and the cut ends of the rebar painted with epoxy paint. A part of the specimens was located in a chloride-free and in a chloride-containating slab, in the plane of the upper rebar mat; the specimens were placed approximately 6 in. apart.

Results for the electrodes in April, 1974, about 1 month after slab fabrication in the chloride-free slab and in the chloride-containing slab are as follows:

	k	Δi, $\mu A/cm^2$	ΔE, mV	CR, Mils per year
Slab + Cl^-	0.012	0.0268	2.5	0.13
Cl^--free slab	0.012	0.0394	10.0	0.05

Although there appears to be quite a difference here, some caution should be exercised; the linear polarization technique is generally taken to be accurate to about a factor of two. Thus, although the difference between the corrosion rates for rebar in the two slabs is noticeable, it is subject to some error. Nevertheless, the difference is in the expected direction.

Results in July, 1974, were as follows:

	k	Δi, $\mu A/cm^2$	ΔE, mV	Corrosion Rate, Mils per year
Slab + Cl^-	0.012	0.083	10	0.10
Cl^--free slab	0.012	0.054	10	0.06

Although the expected increase in corrosion rate in the chloride-containing slab was not observed at this point, this was felt to be due to the tendency for chloride added to the mix to be less corrosive than a similar quantity of chloride present as a result of application of salt to the concrete surface. Successful readings had been taken, however, and therefore the technique was extended for use in an existing rebar mat in a bridge deck.

Field Investigation

In order to explore the use of the concept further, in September, 1974, linear polarization electrodes were made from the rebar mat in the bridge deck on U. S. 33 selected for chloride extraction. A detailed plan of the system is shown in Figure 40. Rebars were located by pachometer and the potentials of the rebar measured against the Cu/CuSO$_4$ electrode. The values, which are presented in Figure 40, show that the steel is not corroding actively. After determination of rebar position and potential, diamond saw cuts were made at the locations shown to electrically isolate the rebar sections. Grooves were cut in the deck for lead wires with the left-hand groove going down to the edge of the deck.

In order to make connection to the rebar, holes were drilled (dashed circles) in the concrete down to the rebar. The rebars were drilled and tapered steel pins (with completely insulated lead wires attached) were forced into the holes. The lead wires were led to the edge of the bridge in the sawed grooves. The large hole (2-in. diam) was drilled to allow an insulating gasket to be placed and glued between the two pieces of rebar (#1 and #2). All holes and saw cuts were then filled with mortar.

The leads were brought to a terminal box on the side of the bridge. Except when measurements are being made, all of the electrodes are shorted together and connected to the rest of the rebar mat. A photograph of the set-up is shown in Figure 41.

It should be pointed out that the arrangement of electrodes for the linear polarization experiments is not considered optimum. The area over which current flow is occurring is not known accurately. Nevertheless, this arrangement was the best which was possible without placing new electrodes within the slab. The idea of installing new electrodes was dismissed because the concrete placed over such electrodes would be quite different from that over the rest of the rebar mat, and results from such electrodes would not allow reasonable conclusions to be drawn concerning corrosion elsewhere in the deck. However, on new deck construction, a pair of fairly closely spaced, planar linear polarization electrodes (not part of the rebar mat, but in the plane of the mat) would be the arrangement of choice, and would avoid the majority of the problems discussed above.

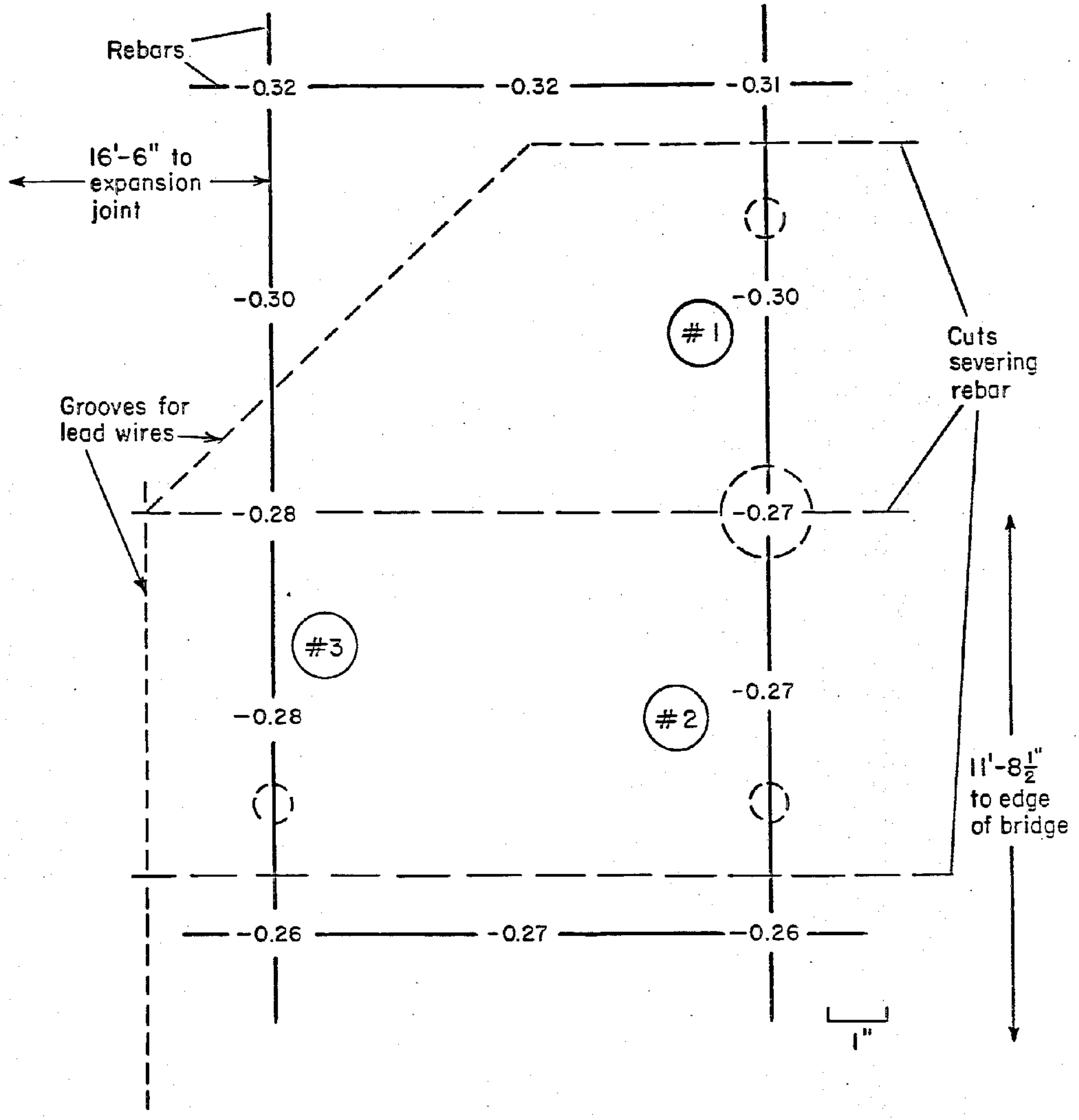

FIGURE 40. POSITION AND LAYOUT OF LINEAR POLARIZATION ELECTRODES FROM TOP REBAR MAT ON BRIDGE DECK (BRIDGE NO. 33.1138R)

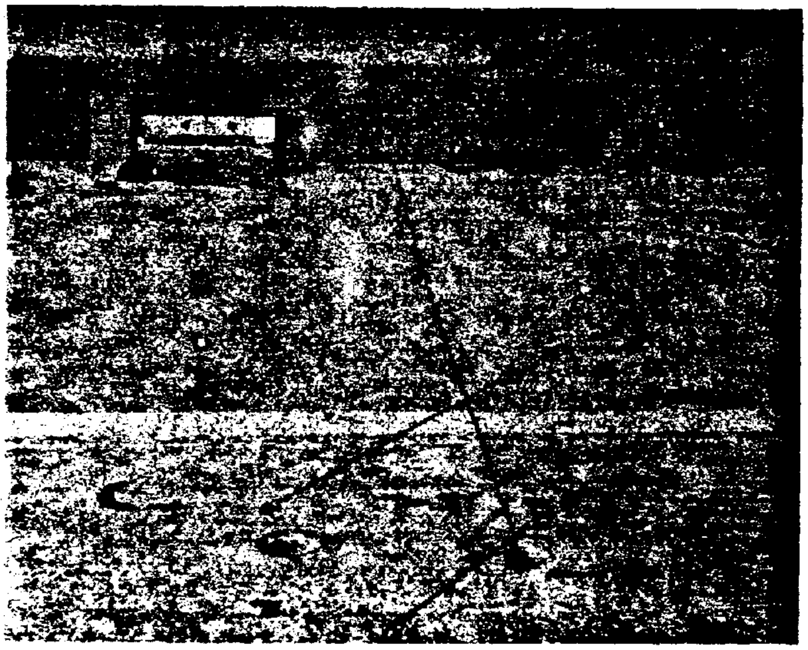

FIGURE 41. CORE HOLES AND SAW CUTS REQUIRED FOR THE CONSTRUCTION OF LINEAR POLARIZATION ELECTRODES IN BRIDGE UNI-33.1138R U.S. 33 NEAR MARYSVILLE, OHIO

Approximately 3 weeks were allowed for "aging" of the electrodes. Linear polarization measurements were carried out after this time between electrodes #1 and #2, and #2 and #3. Corrosion rates were calculated assuming that half of the total area of the electrode was contributing to current flow. The results obtained were as follows:

Electrode Pair	Corrosion Rate, Mils per year
1 - 2	0.18
1 - 2	0.12
2 - 3	0.12
2 - 3	0.10

The corrosion rates are fairly low, as would be expected for the potentials which were measured. Measurements were made in January, 1974, and again in April, 1975. The results in January were much lower than the above (0.04 and 0.02 mpy for electrode pairs #1 and #2 and #2 and #3, respectively) undoubtedly because of the extremely cold (< 30 F) weather, compared with the 70 F temperature when the first measurements were made.

Prior to starting electrochemical chloride extraction on the bridge in April, 1975, measurements of corrosion rate were made, as calculated from linear polarization data. The results were:

Electrode Pair	Corrosion Rate, Mils per year
1 - 2	0.5
2 - 3	0.5

This corrosion rate estimate is an order of magnitude greater than that calculated from measurements made in January, 1974, and more than twice as high as that measured in September, 1974. The January, 1974, reading was undoubtedly low because of the subfreezing temperature, but the comparison with the September, 1974, readings indicates that the increased salt content markedly increased the corrosion rate of the rebar. This also correlates with the more active potentials measured at this time.

Readings were taken 1 week, 1 month, and 3 months after electrochemical extraction treatment. The following results were obtained:

Date	Electrode Pair	Corrosion Rate, Mils per year
1 week after	1 - 2	1.1
	2 - 3	0.8
1 month after	1 - 2	0.6
	2 - 3	0.5
3 months after	1 - 2	0.4
	2 - 3	0.3

Thus, 1 week after treatment, the linear polarization electrodes were showing a corrosion rate almost twice as high as before treatment. One month after treatment, the corrosion rate had dropped to that observed after treatment and was still decreasing 3 months after treatment.

The reasons for this unexpected behavior may be due to the destruction of the passive oxide film on the rebar by cathodic treatment, and its subsequent growth following treatment.

Discussion

The results described above show that the linear polarization technique can be used to follow the progress of corrosion of reinforcing steel in concrete, and that the technique is fairly sensitive to changes in rates caused by changes in temperature, by removal of chloride from around the rebar, and by the application of cathodic polarization to achieve chloride removal. However, the corrosion rates which have been measured are generally much below 1 mpy, which is probably too low an estimate for the circumstances which the rebar sets. This reduction is undoubtedly due to the presence of a high resistance electrolyte (concrete) between the two electrodes making up the pair. This leads to a high IR drop between the electrodes and, thus, a reduction in actual applied potential. Methods are currently being investigated at BCL which will circumvent this problem. Even as it stands, however, the technique is a useful and sensitive tool for monitoring the corrosion rate of reinforcing steel in concrete, particularly if electrodes can be placed in a new structure and can be situated close together, thus minimizing the resistance and the IR drop.

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