

PREPRINT

**DEICING SALT CORROSION
WITH AND WITHOUT INHIBITORS**

by
Mark Callahan

**Final Report For
Iowa DOT Project MLR-87-8**

**For Presentation at the
Transportation Research Board
68th Annual Meeting
January 22-26, 1989
Washington, D.C.**

Highway Division



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DISCLAIMER

The opinions, findings, and conclusions expressed in this report are those of the author and not necessarily those of the Iowa Department of Transportation.

ABSTRACT

Chloride ion penetration through concrete to reinforcing steel is causing the premature deterioration of numerous bridge decks in Iowa. The purpose of this research was to determine if any of several additives/alternative deicing chemicals could inhibit corrosion of reinforcing steel. The deicers tested were calcium magnesium acetate (CMA), CMA+NaCl, Quicksalt+PCI and CG-90, a polyphosphate solution being developed by Cargill.

Two tests were established. First, steel coupons were placed in a 15% solution of a deicer and distilled water to determine which alternative deicer would cause the least amount of corrosion in a solution. The coupons were weighed periodically to determine each coupon's weight loss due to corrosion. The second test involved ponding a 15% solution of each material on reinforced concrete blocks. Weekly copper-copper sulfate electrical half cell (CSE) potential readings were taken on each block to determine if corrosive activity was occurring at the steel surface. When the ponding research was concluded, concrete samples were taken from one of the three blocks ponded with each deicer. The samples were used to determine the chloride ion content at the level of the steel.

Results show all the deicers were less corrosive than NaCl. However, only pure CMA significantly inhibited the corrosion of steel imbedded in concrete.

INTRODUCTION

Deicing chemicals have been used on Iowa's roads since the early 1950's. From 1953 to 1974, the mileage in Iowa's deicing program increased from 219 miles to 8,254 miles, and sodium chloride usage increased to over 90,000 tons per year.

Today, the DOT uses over 60,000 tons of sodium chloride in an average year to provide safe winter travel on the primary and interstate road systems.

Sodium chloride is relatively inexpensive and works well deicing roads in Iowa's climate. However, corrosion of auto bodies and bridge deck reinforcing steel by chloride ion penetration has made its use an ever increasing problem. The Iowa DOT repairs an average of 40 bridges each year due to reinforcing steel corrosion at an annual cost of nearly 4 million dollars.

Recently research has been conducted in several areas to solve the corrosion problem. One area of research involves the development of a salt additive corrosion inhibitor capable of preventing chloride ions from reacting with bridge deck steel reinforcement. A second area deals with developing an alternative deicer chemical capable of removing snow and ice without harming steel reinforcement or endangering the environment.

PROBLEM STATEMENT

Chloride ion penetration through bridge deck concrete to the underlying reinforcing steel is causing premature deterioration of a large number of Iowa's bridge decks. As chloride ions reach the steel, a reaction is initiated which causes the steel to corrode. Corroded steel would normally expand and occupy a volume up to three times that of the original uncorroded steel. However, the surrounding concrete confines the corroded material to the original steel volume. The expansive force creates a great amount of pressure within the concrete. As corrosion continues, the pressure becomes great enough to cause debonding of the steel and concrete and delamination of the overlying bridge deck concrete. This eventually leads to spalling of the surface and extensive maintenance.

OBJECTIVE

A number of alternative chemical deicers and salt additive corrosion inhibitors have been developed in recent years. In tests conducted recently by the Iowa DOT and other agencies, several of these products have displayed results favorable to their use as an additive to, or replacement for, NaCl. The objective of this research project was to determine the ability of four additives/alternative deicers to inhibit corrosion of reinforcing steel. The materials being tested include:

1. Quicksalt + PCI (PCI) - A deicer composed of 70 to 80 percent NaCl, 5 to 7 percent $MgCl_2 \cdot 6H_2O$, and 15 to 20 percent of a lignon sulfonate derivative known as PCI.
2. CG-90 - This product is a mixture of 90 to 95 percent NaCl and 5 to 10 percent of a polyphosphate corrosion inhibitor. The inhibitor is designed to form a protective barrier around steel such that chloride ions cannot initiate a reaction with the reinforcement. It is currently being produced by Cargill Inc. of Minneapolis, Minnesota.
3. Calcium Magnesium Acetate (CMA) - A metal-organic salt usually produced by reacting hydrated dolomitic lime with acetic acid.
4. CMA + NaCl - A combination of 1 part CMA to 2 parts NaCl by weight. This mixture was used to determine how effective CMA was as a corrosion inhibitor when used as an additive to NaCl.

TESTING

Two separate tests were run on each material. The first involved partially immersing a number 3 and a number 4 reinforcing steel coupon in a distilled water solution containing 15 percent by weight of a material being tested. The CMA-NaCl solution contained 5 percent CMA and 10 percent NaCl. For control specimens, a No. 3 bar was placed in a container of

tap water from the city of Ames water supply and a number 3 and a number 4 bar were placed in a 15 percent NaCl solution and a 15% CaCl₂ solution. The coupons were weighed at two month intervals to determine the amount of weight loss due to corrosion. A copper wire brush was used to remove the corroded material before weighing.

Results of the coupon immersion test are listed in Table 1. After more than 4 months of testing, it was determined the CG-90 was most effective in preventing weight loss due to corrosion of the coupons. Weight losses of only 0.35 percent and 0.46 percent were recorded for the number 3 and number 4 coupons respectively. Surprisingly, the coupons in the NaCl solution exhibited the second least amount of weight loss with 0.57 percent (No. 3) and 0.58 percent (No. 4). The coupons in the CMA and the CMA+NaCl solutions displayed the greatest amounts of weight loss. The coupons in CMA+NaCl lost 0.93 and 0.94 percent while the coupons in pure CMA lost 1.64 and 1.16 percent for the No. 3 and No. 4 bars respectively.

From these results, only the CG-90 was shown to be capable of inhibiting corrosion in a distilled water solution. It should be emphasized at this point the results of this immersion test do not necessarily indicate how a material will perform in the field. A material which prevents corrosion in a solution may not be capable of penetrating through concrete to protect re-

inforcing steel from corrosion due to the presence of chloride ions.

The second test was patterned after a FHWA study titled, "Time to Corrosion of Reinforcing Steel in Concrete Slabs". Nineteen 12"x12"x4" concrete blocks with reinforcing steel were constructed and used in a ponding test of each material. The reinforcing steel configuration for each block is shown in Figure 1. Compared to the immersion test, a ponding test to determine a chemical deicer's effectiveness in preventing steel corrosion in concrete gives a better indication of how the product will perform in the field. Again, a 15 percent by weight material solution in distilled water was prepared. Each solution was ponded on a set of three blocks. Also, three blocks were ponded with a 15 percent NaCl solution only, three blocks ponded with a CaCl₂ solution and one block ponded with city of Ames tap water. These blocks were designed to act as control blocks at opposite ends of the corrosion scale. Again, the CMA + NaCl solution contained 5 percent CMA and 10 percent NaCl.

The concrete mix proportions used for block construction are listed in Table 2. The concrete had a water/cement ratio of 0.58 and contained 6.1 percent entrained air. The high water/cement ratio and low cement factor (4.6 sacks per cubic yard) were designed to make the concrete more permeable to chloride ion penetration. The average 28-day compressive strength for the mix was 3250 psi.

Number 3 and 4 bars conforming to ASTM specification A615 for Grade 60 steel were used. Plastic chairs were used to support the steel in the proper position. The steel was positioned to allow one-half inch of cover over the top reinforcing steel.

Three evaluation techniques were employed to determine the effectiveness of each material. First, weekly copper-copper sulfate electrical half cell (CSE) potential measurements were taken to determine if corrosive activity was occurring. Also, concrete samples were taken from each set of blocks at the end of the 21 week research period to determine the chloride ion contents at various depths in the concrete. Finally, one of the three blocks from each set was broken to reveal the embedded steel. A visual observation was made to determine the degree to which corrosion had occurred. The chloride ion content measurements and the visual observations were made to verify the CSE readings.

Each Monday morning the solutions were ponded on the blocks. Ponding was continuous until Friday morning (approximately 100 hours), at which time the solutions were removed. The blocks were then washed clean of any surface chemicals and placed in an oven at 100°F. After drying over the weekend (approximately 68 hours), copper-copper sulfate electrical half cell (CSE) potential readings were taken each Monday before reponding. Five readings were taken on each block. The position of each reading is shown in Figure 2.

The readings were obtained in accordance with ASTM Standard Designation C876, "Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete".

The potential measurements are useful in determining whether or not corrosive activity is occurring on the steel surface. The ASTM standard places CSE potential readings into three categories:

1. If potentials over an area are more positive than -0.20 V CSE, there is a greater than 90 percent probability that no reinforcing steel corrosion is occurring in that area at the time of measurement.
2. If potentials over an area are in the range of -0.20 V to -0.35 V CSE, corrosion activity of the reinforcing steel in that area is uncertain.
3. If potentials over an area are more negative than -0.35 V CSE, there is a greater than 90 percent probability that reinforcing steel corrosion is occurring in that area at the time of measurement.

The standard further states that:

In laboratory tests where potentials were more negative than -0.50 V CSE, approximately half of the specimens cracked due to corrosion activity.

Based on this criteria, the only ponding agent found to be noncorrosive throughout the length of the project was the tap water solution. Of the four alternative deicers being tested, the CMA solution provided the most promising results. When the weekly reading of the three CMA ponded blocks were averaged, no average set of readings had a CSE potential measurement more negative than -0.30 V. Table 3 gives a partial list of these average readings. All but two of Block 10's weekly measurements, and a majority of Block 12's measurements, were more positive than -0.2 V. This indicates that a majority of the time no corrosion was likely taking place. An interesting occurrence took place in the PCI block numbers 8 and 9. CSE readings the first eleven weeks averaged above -0.45 V (block 8) and -0.40 V (block 9). Then, beginning in week 14, their CSE readings became less negative to a significant degree. Readings in the last 8 weeks averaged between -0.37 V and -0.44 V for block 8 and between -0.29 V and -0.34 V for block 9.

Cracking of both blocks was observed in the second week of ponding. The high initial readings were likely due to

chloride ion penetration through these cracks to the reinforcement. The PCI apparently could not penetrate to the reinforcement until after week 11. Once it did reach the steel, however, its results were better than all other materials except CMA. Because of the possibility the cracking may have influenced the testing, a second set of three PCI blocks was made. However, these blocks also cracked soon after ponding was initiated. CSE potential readings on these blocks gave similar results to those tested previously. Readings more negative than -0.35V were common in two of the three blocks.

A majority of readings of the CaCl_2 solution blocks averaged between -0.40 and -0.50 V while the majority of readings of the CMA + NaCl blocks were between -0.45 and -0.50 V. Of the four ponding solutions tested, the CG-90 material produced the largest negative CSE readings. Average CSE readings more negative than -0.55 V were common. These values were very close to what was obtained from the NaCl blocks.

Tests run on the material supplied by Cargill revealed the material contained only 0.16% phosphates. At the request of Cargill, a second set of blocks was ponded with the material now containing 1.6% phosphates. The increased phosphate content had little effect on the CSE results, however. Average readings more negative than -0.50V were obtained on two of the three blocks.

At the end of the 21 week ponding period, samples of concrete were taken in order to determine the amount of chloride ions present at two depths in the concrete. Measured from the ponded surface of the concrete block, the two depths evaluated were from 1/16 inch to 1/2 inch (concrete cover) and from 1/2 inch to 1 inch (level of reinforcing steel). The samples were obtained from block numbers 3 (NaCl), 6 (CaCl₂), 9 (PCI), 12 (CMA), 13 (H₂O), 16 (CG-90) and 19 (CMA+NaCl). Results of the chloride penetration work is provided in Table 4.

The penetration results verify chloride ions were available at the level of the steel for a corrosive reaction to occur.

The CMA and tap water chloride ion penetration results are, as expected, very low. Since no material containing chloride ions was added to the solutions, any chloride ions present were in the concrete materials prior to ponding.

Visual inspection of portions of the reinforcing steel revealed corrosion was occurring in all but the pure CMA ponded blocks. By comparing the upper level steel to the bottom level steel, it was observed that substantial corrosion had occurred in the upper level steel. This was true in all but the pure CMA block. (The one H₂O block was not broken, but all indications show corrosion has not taken place.)

The chloride ion penetration results substantiate the CSE potential reading findings. Having very little chloride ions present to react with the reinforcing steel, the CMA and tap water CSE potential readings indicated corrosion was not occurring. The high chloride ion contents of the other solutions corresponded to potential readings which indicated corrosion was likely taking place.

It should be noted the chloride ion concentrations recorded in Table 4 are exceedingly high. This is due to the highly permeable concrete which was used to shorten the time required for chloride ions to reach the reinforcing steel.

ANALYSIS

Results show that of the materials tested, only pure CMA was capable of effectively inhibiting corrosion of reinforcing steel due to chloride ion penetration. Although it did not perform well in the coupon immersion test, results of the ponding test revealed CMA dramatically inhibited corrosion of the steel in concrete. Without chloride ions available to initiate a half cell reaction, the alkalie environment of the concrete is sufficient to prevent corrosion.

Only two other deicers, PCI and CMA+NaCl, performed sufficiently better than the NaCl solution in the ponding test to warrant further consideration. Ponding test results of each showed corrosive activity was occurring. However, visual ob-

ervation showed the extent of corrosion was less than that of the NaCl. The early cracking of the PCI blocks has led to questions concerning its use. The cause of the cracking has not been determined. The coupon percent weight loss and the chloride ion contents for the PCI material were not excessive.

Although the CG-90 solution performed well in the immersion test, its performance in the ponding test was not encouraging. As stated previously, the ponding test is more representative of actual field conditions. CSE potential readings more negative than -0.5V were common.

CONCLUSIONS

Based on the test results, it can be concluded that:

1. Pure CMA is the only alternative deicer tested which significantly inhibited corrosion of reinforcing steel in concrete.
2. CMA as an additive to NaCl (in a 1 part CMA, 2 parts NaCl ratio) did not inhibit the corrosion of reinforcing steel in concrete.
3. The Cargill CG-90 formulation was effective in protecting steel in a solution. However, it did not protect reinforcing steel imbedded in concrete from corrosion due to chloride ion penetration.

The search for an economical solution to the problem of chloride ion corrosion of reinforcing steel must continue. Replacing bridge decks which are deteriorating prematurely is costing states money which could otherwise be used improving the overall highway system. Of the deicers tested in this project, straight CMA has the most promising potential of being able to fulfill a "bare roads" policy without causing bridge deck deterioration.

ACKNOWLEDGEMENTS

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TABLE TITLES

1. Coupon Immersion Test Results
2. Concrete Mix Design
3. Average Copper-Copper Sulfate Electrical Half Cell Potential Readings
4. Chloride Ion Penetration Results

TABLE 1
Coupon Immersion Test Results

Container No.	Solution Material	Bar Number	03-07-88		05-17-88		07-11-88	
			Initial Coupon Weight, grams		Coupon Weight, grams	Percent Weight Loss	Coupon Weight, grams	Percent Weight Loss
1	CaCl ₂	3	50.00		49.91	0.18	49.53	0.94
		4	95.26		95.10	0.17	94.58	0.71
2	NaCl	3	51.32		51.21	0.21	51.03	0.57
		4	98.54		98.34	0.20	97.97	0.58
3	PCI	3	51.57		51.25	0.62	51.09	0.93
		4	87.69		87.24	0.51	87.06	0.72
4	CMA	3	53.56		53.04	0.97	52.68	1.64
		4	86.85		86.25	0.69	85.84	1.16
5	CG-90	3	51.14		51.07	0.14	50.96	0.35
		4	89.21		89.11	0.11	88.80	0.46
6	CMA+NaCl	3	52.62		52.51	0.21	52.13	0.93
		4	89.22		89.00	0.25	88.38	0.94
7	Tap Water	3	52.41		52.22	0.36	52.00	0.78

TABLE 2
Concrete Mix Design

Material	Amount	Absolute Volume
Cement	430 lb.	0.0813
Water	250 lb.	0.1484
Coarse Aggregate	1586 lb.	0.3551
Fine Aggregate	1597 lb.	0.3552
Air Content	6±1 %	0.0600
Slump	5±1 in.	

TABLE 3

Copper-Copper Sulfate Electrical Half Cell
Potential Readings*

Block No.	Deicing Material	Week No.							
		1	3	6	9	12	15	18	21
1	NaCl	475	516	539	510	555	545	553	540
2	NaCl	505	528	531	518	548	552	552	542
3	NaCl	508	530	539	555	570	570	574	NR
Ave		496	525	537	528	558	556	560	541
4	CaCl ₂	353	424	430	472	465	487	512	512-
5	CaCl ₂	434	496	488	497	455	423	415	441-
6	CaCl ₂	406	488	491	478	NR	352	454	437-
Ave		398	469	470	482	460	421	460	463
7	PCI	345	369	351	367	NR	257	321	329
8	PCI	419	462	477	493	NR	360	416	394
9	PCI	395	453	454	478	NR	305	309	319
Ave		387	428	427	446	---	308	349	347
10	CMA	114	94	224	148	NR	73	104	75
11	CMA	241	276	347	291	205	176	153	158-
12	CMA	128	241	234	183	268	178	137	139-
Ave		161	204	268	207	237	142	131	124
13	Tap Water	116	72	28	8	---	184	179	125-
14	CG-90	559	593	NR	555	595	583	589	568
15	CG-90	391	542	NR	487	548	542	539	546
16	CG-90	395	543	NR	500	555	545	534	534
Ave		448	559	---	514	566	556	554	550
17	CMA+NaCl	505	453	NR	418	482	472	458	447
18	CMA+NaCl	528	452	NR	450	483	477	461	477
19	CMA+NaCl	422	489	NR	438	501	496	472	480
Ave		485	465	---	435	489	482	464	468

*Readings in negative millivolts

NR No Reading Taken

-- No Value Calculated

- Twenty week reading

TABLE 4
Chloride Ion Penetration Results

Block No.	Deicer Material	Depth of Penetration (Inches)	Percent Chloride (by Weight)	Pounds Chloride ^A Per Cubic Yard
3	NaCl	1/16 - 1/2	1.094	41.4
		1/2 - 1	0.617	23.3
6	CaCl ₂	1/16 - 1/2	1.727	65.3
		1/2 - 1	0.981	37.1
9	PCI	1/16 - 1/2	0.825	31.2
		1/2 - 1	0.709	26.8
12	CMA	1/16 - 1/2	0.012	0.5
		1/2 - 1	0.015	0.6
13	H 0	1/16 - 1/2	0.027	1.0
		1/2 - 1	0.011	0.4
16	CG-90	1/16 - 1/2	0.638	24.1
		1/2 - 1	0.431	16.3
19	CMA+NaCl	1/16 - 1/2	0.778	29.4
		1/2 - 1	0.454	17.2

A. Assumed concrete weight of 140 pounds per cubic yard

FIGURE CAPTIONS

1. Steel Reinforcement Placement
2. Copper-Copper Sulfate Electrical Potential Reading Locations

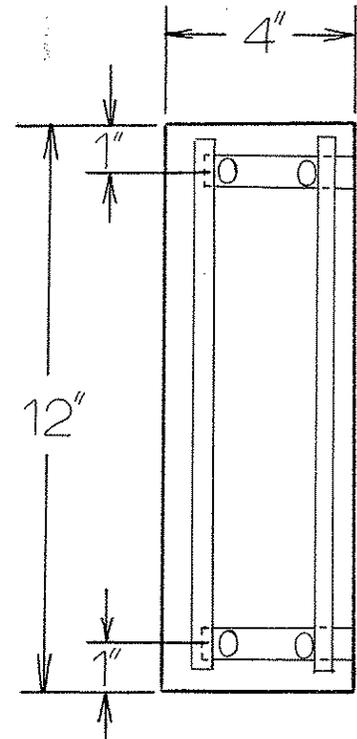
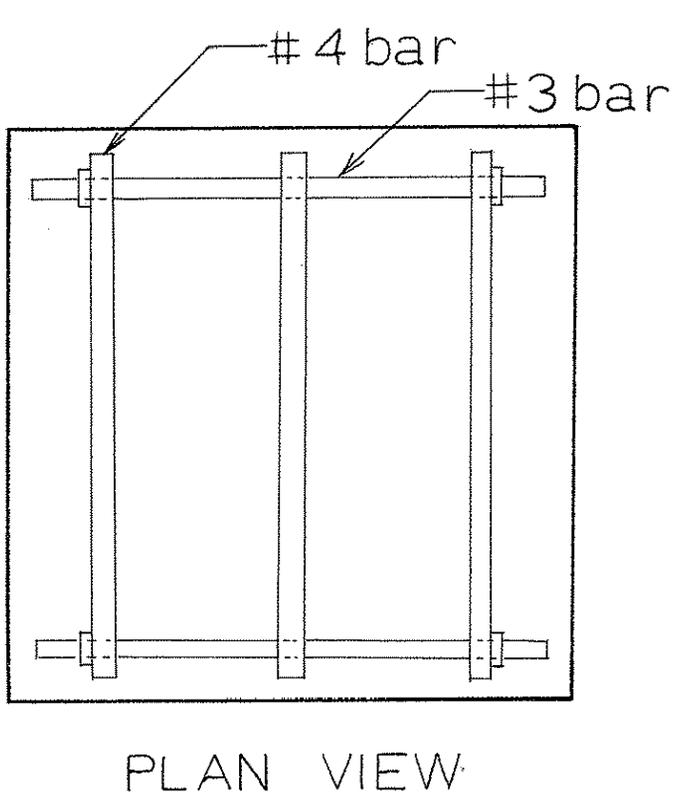
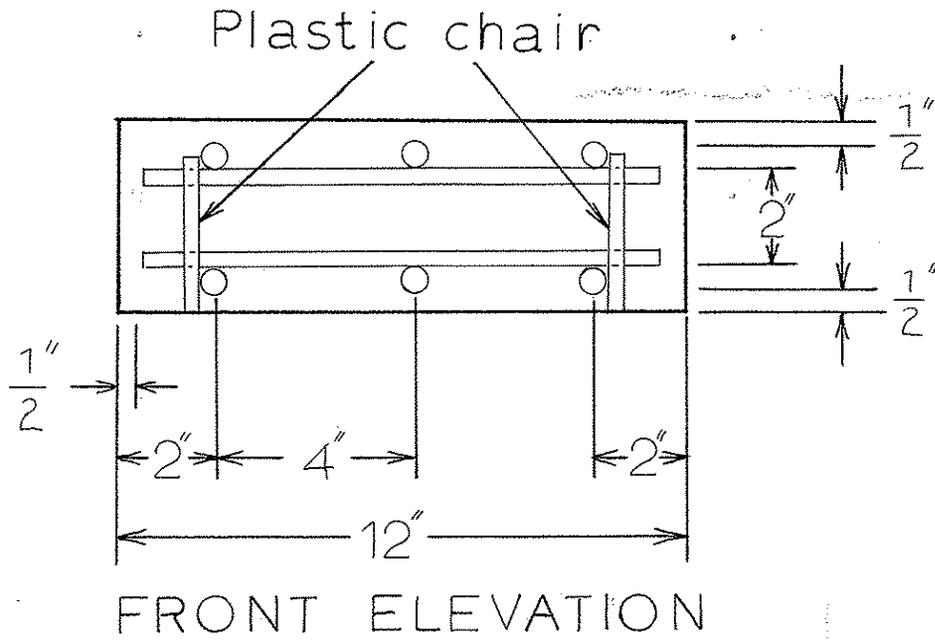


Figure 1 Steel Reinforcement Placement

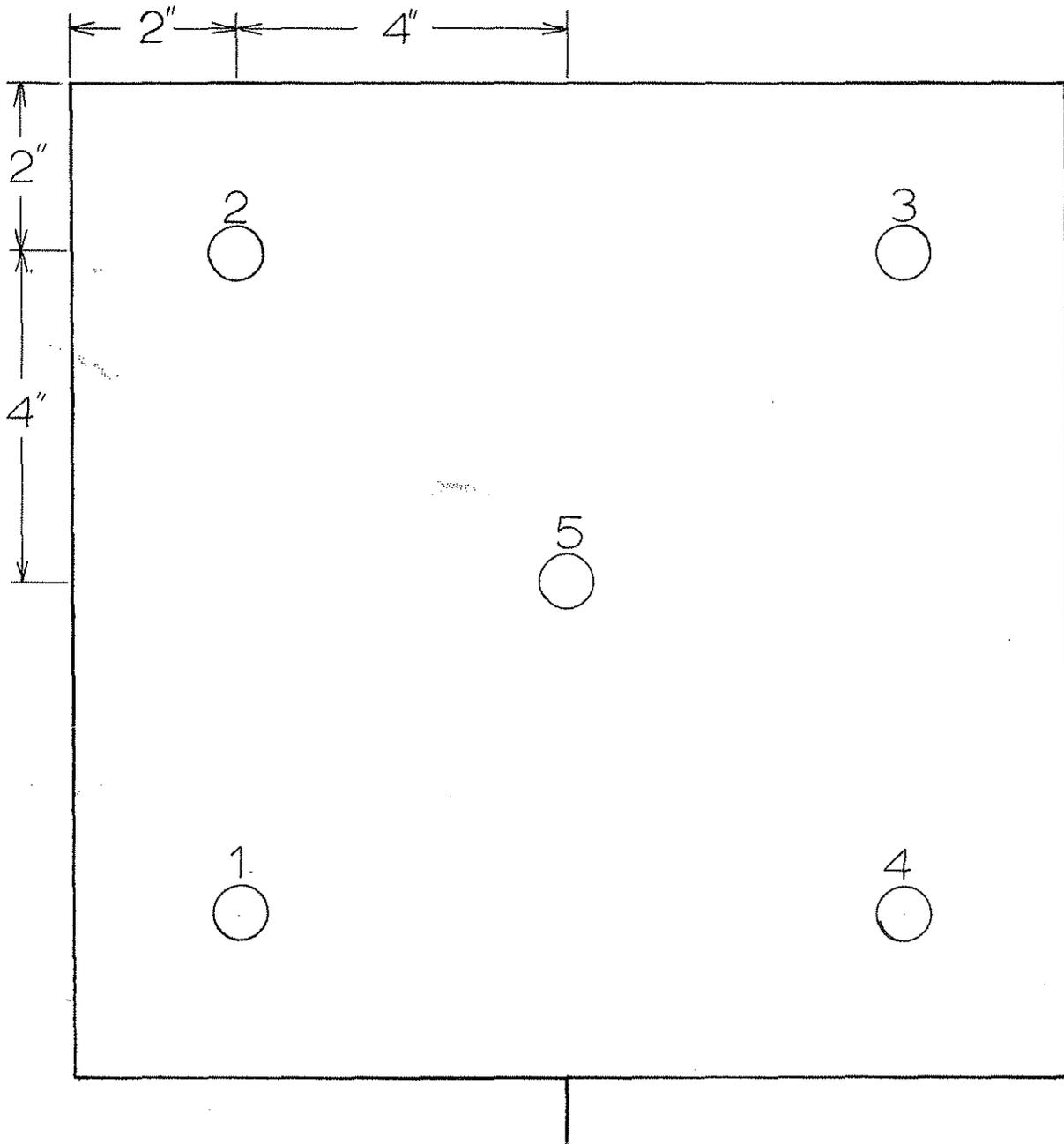


Figure 2 Copper-Copper Sulfate Electrical
Potential Reading Locations