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THE EFFECT OF ADDED CHLORIDE
ON THE RESISTIVITY AND ABSORPTION OF
MATURE CONCRETE

By

R. F. Stratfull

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THE EFFECT OF ADDED CHLORIDE ON THE RESISTIVITY AND ABSORPTION OF MATURE CONCRETE

I. Introduction

In a previous report, it was shown that the amount of concrete cracking in the San Mateo-Hayward Bridge varied with the specific electrical resistance of the concrete.¹ The data which are plotted on Figure 1, indicate that the concrete cracking in this 25-year old structure (in 1957) was negligible when the resistivity of the concrete exceeded approximately 65,000 ohm cm.

The data obtained in this previous report¹ also indicated that the amount of cracking of the concrete was not directly related to the chloride content. This fact is demonstrated on Figure 2. However, the data did indicate that steel is highly susceptible to corrosion when embedded in a chloride contaminated concrete, but the rate of corrosion or the visible evidence of deterioration is primarily controlled by the electrical resistivity of the concrete.

A search of the published literature indicated that the following observations could be considered as representing the state of the general knowledge concerning the electrical resistivity of concrete:

1. Chlorides lower the resistivity of concrete.^{2,3}
2. The resistivity of concrete when dry, may vary from in excess of 100,000 ohm cm to as low as 100 ohm cm.³
3. Calcium chloride in concrete acts as an electrolyte.⁴
4. Moist concrete is an electrolyte.⁵
5. The resistivity of "straight" cement mortar ranges between 14,600 and 23,500 ohm cm.⁶

6. The resistivity varies from an estimated 6500 to 11,000 ohm cm for cement mortar coatings with an absorption between an estimated 6.5 and 11.5% by weight respectively.⁷

Because of this evident importance of the electrical resistivity of concrete to the rate of corrosion of reinforcing steel, a series of controlled tests were performed to determine the relative influence of moisture content, absorption, and added chloride on the electrical resistivity of concrete. The results are here reported.

II. Summary and Conclusions

Highly absorptive concrete dries more rapidly than a low absorption concrete, and the former sustains a lower electrical resistivity for a longer period than would be suspected by a comparative weight loss of water. Thus, a highly absorptive concrete could result in the accelerated corrosion of the embedded steel. With other variables being constant, the absorption of a concrete can be increased by:

1. Increasing the amount of mixing water
2. Reducing the cement content
3. Adding calcium chloride

An empirical formula has been developed from data obtained by tests that relate the mixing water and cement content of a mature concrete to its evaporable water content. The use of this empirical formula may assist the engineer in estimating concrete quality as related to absorption.

Chlorides, when added to a concrete mix, change the absorption of the concrete. The trend in the data indicate that absorption may be first reduced, then increased with increasing amounts of added calcium chloride.

An empirical mathematical relationship was developed to describe the observed influence of added chloride per sack of cement and the resultant change of absorption in the concrete.

These data indicate that the slump of a fresh concrete mix per se, is not a relative indicator of the absorptive characteristics for concretes of various cement contents.

(Note: It should not be construed that this is any adverse reflection upon the importance and the known great value of the slump test when it is used as a measure of quality control for a particular concrete mix.)

When chloride-containing concrete is oven dried, the chlorides cause a reduction in the resistivity of the concrete if resoaked.

The effect of calcium chloride on the resistivity of concrete seems to be related to its influence on the internal

structure of the concrete as measured by absorption.

The data indicate that significant additions of calcium chloride increase the absorption of the concrete.

Except for the condition of oven drying and re-soaking, there was no measurable change in concrete resistivity as a result of adding calcium chloride per se, to the mix.

III. Test Specimens and Method

Three each for a total of sixty concrete blocks were cast, with each of variables shown in Table 1.

The grading of the noncrushed aggregates conformed to the 1954 Standard Specifications of the California Division of Highways. For all concrete batches, the volume of coarse aggregates was held constant while the volume of sand was varied as the cement factor was changed. As the cement content was increased, the sand was decreased.

After the concrete blocks were cast, they were cured in a fog room at 73.4°F and 100% relative humidity. At the conclusion of a 20-month curing period, the weight of the blocks and their specific electrical resistivity was determined. Thereafter, the blocks were removed from the fog room and stored in laboratory air for the ensuing periodic testing. While stored in the laboratory, the entire set of blocks was covered with a canvas cloth to reduce the influence of variable velocities of the drying air currents.

At the conclusion of 111 weeks of laboratory weighing and resistance testing of the concrete, the blocks were oven dried at 230°F for 24 hours; then submerged in water for 48 hours, reweighed, and again tested for electrical resistivity.

To facilitate the electrical resistivity measurements, each concrete block specimen had a copper mesh (ordinary screen wire) cast into each end. The copper screens were used as electrical contacts when the direct electrical current was forced through the length of the specimen. Voltage drops were used for determining resistance.

When making the voltage drop measurements on the concrete surface while current was flowing, two copper sulfate half-cells were placed at specific but repeated locations across the width of the concrete block, at right angles to the current flow. The copper sulfate half-cells were constructed by using a chemically pure copper wire that was encased in a cloth sheath. The cloth was wetted with a solution of copper sulfate just prior to each measurement of voltage. The overall diameter of the copper sulfate half-cell was approximately 0.06-inch and was only in physical contact with the central 5-inch width of the concrete during measuring of the electrical resistivity.

Each tabulated resistivity measurement was an average of the two resistance values which were sometimes obtained after the direction of current flow was reversed. This average was required in some cases as the potential difference between the two copper sulfate half-cells was not always zero.

A direct current power supply was constructed which consisted of batteries, variable resistors, and a current (polarity) reversing switch. The power supply had controlled output voltages that could be varied from 1 through 675 volts.

Figure 3 is a photograph of the laboratory equipment currently used for measuring the electrical resistivity of concrete blocks.

This equipment eliminates problems concerning the casting of copper screens into the ends of the concrete blocks and the necessity for handling of potential electrodes.

The end plates of the laboratory resistivity equipment are made of copper plate and covered with a cloth which is wetted with tap water just prior to the insertion of a concrete block.

The potential electrodes are in the central third of the equipment and are made as previously described herein.

Figure 4 is a schematic of the equation⁸ used for calculating the resistivity of concrete blocks.

Figure 5 shows the type of field equipment for measuring the resistivity of concrete which has been in use since 1956.¹

Figure 6 is a close-up of the hand-held resistivity equipment. The outer electrodes are the ones through which the electrical current is forced to flow through the concrete. Each of these electrodes are connected through a plastic enclosed cloth bridge to the inner part of the base of the container which has two compartments. Each compartment to one electrode and contains a saturated solution of cupric sulfate and a copper screen. The copper screen is electrically connected to the external DC power supply. The cloth bridge also comes in direct contact with the concrete surface through the hollow glass tube which is held by the plastic and clamped by means of the nuts and bolts shown in Figure 6. The two outer electrodes are rigidly attached to the frame.

The inner two electrodes are potential electrodes that contain a copper electrode, a cloth bridge, and a

saturated cupric sulfate solution. These potential electrodes can move vertically when pressed against the concrete because they are mounted at the end of a cantilevered strip of plastic.

The electrodes are otherwise fixed at 10 cm spacing.

Figure 7 is a schematic of the equation⁸ used for measuring the resistivity of concrete from the surface.

IV. Test Results

A. Chlorides and the Resistivity of Concrete

As shown in Table 1, there appears to be no significant difference in the resistivity of any of the moisture saturated concrete at the conclusion of 20 months of moist curing in the fog room.

During the drying cycle of equally absorptive concrete, there was also no great observed difference in concrete resistivity which could be attributed to the presence of chlorides per se. However, after the concrete was oven dried for 24 hours at 230°F and then soaked in water for 48 hours, the data indicated that added chlorides caused a significant reduction in concrete resistivity. The influence of chlorides on the resistivity of concrete is shown on Figure 8, and indicates that the reduction in the concrete resistivity after oven drying increases with the chloride content.

There is a possibility that the minimum resistivity of the concrete after 48 hours of resoaking may be less than that shown in Figure 8. At the end of the 48-hour resoaking, it was found that the concrete contained about 8% to 15% less water than it did at saturation prior to oven drying. Also, the high chloride-contaminated concrete generally absorbed less water during the 48-hour resoaking period.

As a check on the laboratory investigation, field resistivity measurements were made on a structure in which calcium chloride was added to the mix. For the 5-sack concrete mix for this structure, the design called for non and also 1, 1.5 and 2.0 percent calcium chloride by weight of the cement. Table 2 shows the results of the resistivity measurements and contained chloride-ion. The variations in the concentration of the chloride-ion in the concrete are probably the result of an incomplete dispersion of the admixture. The chloride content was determined on approximately 2-inch thick concrete fragments that were chemically analyzed in the laboratory.

These field data also indicate that there is no direct relationship between chloride content per se, and the resistivity of the concrete.

B. Chlorides and Concrete Absorption

As shown in Table 1, the evaporable water content (absorption) was calculated by means of the weight and also the volume of the tested concrete. In a previous report, the data indicated that the volumetric ratio of the evaporable water content of concrete may be more significant than a weight ratio because the former is not influenced by the specific gravity of the concrete.

As shown in Table 1, chlorides seem to influence the evaporable water content of the concrete.

With all other factors being equal, an analysis of these data indicate the following relationship between the chloride content and the related change in the concrete absorption:

$$\Delta E_v = 0.42 K_s - 0.16 \dots \dots \dots (1)$$

Wherein:

ΔE_v = difference in concrete absorption between a chloride-free and a chloride-containing concrete, in percent of concrete volume

K_s = pounds of chloride-ion (as calcium chloride) per sack of cement

The statistical significance¹⁰ of this relationship was:

$$n = 15$$

- Coefficient correlation = 0.651
- Level of significance = <0.01
- Standard error of estimate = +0.33%

For convenience, this equation can be mathematically related to indicate the change in concrete absorption due to the addition of calcium chloride in terms of pounds of evaporable water per cubic yard, as follows:

$$\Delta E_w = 7.08 K_s - 2.7 \dots \dots \dots (2)$$

Wherein:

ΔE_w = difference in concrete absorption between a chloride-free and a chloride-containing concrete in pounds of water per cubic yard of concrete

K_s = pounds of chloride-ion (as calcium chloride) per sack of cement

C. Evaporable Water in Concrete

In a previous report⁹, the results of numerous tests indicated that the quantity of water that would be absorbed and evaporated by mature concrete between the environmental exposures of (a) fog room, and (b) 50% relative humidity at 73.4°F, could be represented by the following formula:

$$V_w = \frac{0.85(W_m)^{1.17}}{C^{0.717}} \dots \dots \dots (3)$$

Wherein:

V_w = water voids, water absorbed and evaporated between saturation and exposure to 50% relative humidity, in percent of concrete volume

W_m = Concrete mix water, including that contained in aggregate, in percent of concrete volume

C = Sacks of cement per cubic yard of concrete

The salt-free concrete mix variables in this test were substituted into Equation 3 for a possible correlation by the method of least squares.

The following equation for correlation of the test variables was found:

$$E = \frac{0.85(W_m)^{1.17}}{C^{0.717}} + 4.3 \dots \dots \dots (4)$$

Wherein:

E = Evaporable water content, in percent of concrete volume, for saturated concrete that is air dried for 111 weeks and then oven dried at 230°F for 24 hours

W_m = Concrete mix water, including that contained in the aggregates in percent of concrete volume

C = Sacks of cement per cubic yard of concrete

By the method of least squares, the use of Equation 4 when compared to the actual evaporable water content of the concrete, has an indicated correlation coefficient of 0.900, a standard error of estimate of 0.619%, and a level of significance of greater than .001. It is suspected that the constant 4.3 in Equation 4 would be increased if the oven drying time exceeded 24 hours, or if the minimum dimension of the concrete was less than 5 inches.

Equation 4 has not been compared for accuracy when the concrete mix variables and test conditions exceed those described for this test. The empirical relationships shown in Equation 4 may be useful as a preliminary means for estimating and comparing concrete quality with regard to absorption.

These data indicate that, with other factors being constant, the absorption, or evaporable water content of the concrete, increases with (1) increasing quantities of mixing water, and (2) decreasing amounts of cement.

Field tests have shown that with other factors constant, corrosion of the steel is more severe in a concrete made with the greater amount of mix water¹⁴. Therefore, it would seem to follow that corrosion severity would increase in proportion to concrete absorption. The 5.36-sack per cubic yard mixes with approximately 40 gallons of water per cubic yard concrete used in the deck unit of the San Mateo-Hayward Bridge¹ was found to absorb approximately 10% more water than the 4-sack concrete made with 32 gallons of water per cubic yard in the laboratory tests. Therefore, there is an implication that the advanced deterioration of the San Mateo-Hayward Bridge may be related to its highly absorptive concrete. From the water-cement relationship described in Equation 4, it appears that the attempt to reduce concrete absorption by using a high cement factor can be nullified by an excessive amount of mix water.

D. Concrete Resistivity

As previously mentioned, no relationship was determined between the chloride content per se, and the electrical resistivity of the concrete during the one drying cycle of 111 weeks. The relationship that was determined between the concrete variables and resistivity is shown on Figure 9. The data indicated that the electrical resistivity of concrete depends upon two variables, which are:

1. The evaporable water content of the concrete
2. The relative amount of water contained in the same concrete

Also, for the same degree of saturation or contained water, the more highly absorptive concrete has a lower specific electrical resistance.

From the standpoint of the flow of electrical current in a corrosion cell, it appears that under equal conditions of relative moisture saturation of concrete, the metal loss of the steel will be more rapid in the concrete having the greater absorption because of its lower electrical resistance.

It is not known if the curves of resistivity versus the concrete variables shown on Figure 9 can be extrapolated beyond the limitations of these test data. The reason is that with other variables being constant, the evaporable water content of a concrete can be changed by altering the amount of mix water. In this test, the amount of water was held constant at 32 gallons per cubic yard of concrete, and the cement content and volumetric proportion of the aggregate was changed for the concrete mixes.

E. Concrete Drying

The amount and rate of moisture loss that was found to vary for each concrete mix is shown on Figure 10. As indicated by these test results, the greater the absorption of the concrete, the more rapid the loss of water. For example, it took the 10% absorption concrete approximately 97 weeks to lose 50% of its evaporable water. This is a loss of approximately 3.1 pounds of water per cubic foot of concrete. Conversely, the concrete of 14% absorption took about 17 weeks to lose 50% of its evaporable water, or approximately 4.4 pounds of water per cubic foot.

In terms of the time to reach 65,000 ohm cm which was the resistivity of concrete in which reinforcing steel had no visible evidence of corrosion after 24 years¹, the 10% absorption concrete took approximately 100 weeks while the 14% absorption concrete took about 70 weeks to dry to an electrical resistivity of 65,000 ohm cm.

The foregoing does not necessarily imply that an aggressive corrosion attack will occur in a low absorption concrete because its electrical resistance is less for a longer period of time. The difference in performance can occur as a result of the difference in concentration of chlorides. For example, if the same number of pounds of chloride are contained in the same volume of concrete, the retained concentration of chloride in the concrete at 65,000 ohm cm will approximately double for the 10% absorption and more than triple for the 14% absorption concrete. Therefore, an aggressive level of chloride within the concrete can occur more readily in the concrete of high absorption.

It should also be considered that if the concrete does not initially contain a significant amount of chloride but the environment does, chloride will not only accumulate faster in the higher absorption concrete because of its greater absorption, but also because of its ability to lose water more rapidly. It is assumed that when water evaporates, the salt it contains remains resulting in a more highly concentrated chloride solution each time a wetting-drying cycle takes place.

V. Discussion

Although this test did not establish why the chlorides per se affected the concrete resistivity only after oven drying, test results reported by Roberts¹¹ may offer a possible explanation for the observed behavior. Although Roberts steam cured his specimens for 17 to 18 hours at approximately 212°F, he made the following observations concerning the greater corrosion of steam cured, chloride-containing concrete that was stored out-of-doors.

"This effect of steam curing appears to be connected mainly with an increased amount of free chloride in solution in steam-cured concrete, but it is also possible that steam curing has other effects on the properties of the concrete. There may be, for example, an increase in porosity which may have a bearing on the subsequent corrosion of embedded steel."

These foregoing observations indicate that additional work is required to investigate the effect of curing temperature and also cyclic drying on the influence of chlorides on the conductivity of concrete and also the corrosion of steel in concrete.

Duplicating resistivity measurements of concrete in the field has at times been difficult in the late afternoon hours in California. The reason for this difficulty seems to be that the surface of the concrete dries to such an extent that the contact resistance of the resistivity equipment becomes abnormally high and the measurements begin to include "surface effects" with regard to the paths of current flow.

This apparent cycling of the moisture content as indicated by resistivity measurements in the thin surface of the concrete, has been observed on numerous occasions on California structures. Sometimes the length of time which resistivity measurements can be made can be extended by wetting the concrete surface. However, even wetting of the concrete surface to reduce contact resistance eventually proves to be of no further avail.

Empirical relationships that were developed in previous work⁹ has indicated that concrete 1/16-inch thick and containing five sacks of cement per cubic yard, could be calculated

to dry from near saturation to equilibrium at 50% relative humidity at 73.4°F in approximately five hours. Therefore, it appears that during the daytime drying conditions, it is possible that the "skin" of the concrete could dry to a depth of somewhat more than 1/16-inch, but probably less than 1/8-inch. Current but unreported tests in our laboratory have shown that concrete which has dried to the calculated conditions has had a measured resistivity in the range of 100,000 to 200,000 ohm cm.

From the preceding, it seems that measuring the resistivity of concrete in the field could be difficult. However, depending upon the circumstances, the dimension of the contacting surface of the electrodes and/or the time at which resistivity measurements are taken, could have a great bearing on the accuracy of resistivity measurements.

One other factor that should be pointed out is that the trend shown by some of our unpublished data has indicated that the resistivity of relatively saturated concrete increases with time up to about five years. The increase in resistivity is most rapid during the first six to nine months of concrete aging.

Data have been related regarding the absorption characteristics of these concrete mixes. Serious consideration was given to the reporting of the derived relationships because of the 20-month curing time, the 111-week air and 24-hour oven drying of the concrete. This technique for measuring the absorption of concrete is not considered to be a normal, or even convenient procedure. However, it was included because it does reflect concrete mix variables and their influence on the absorption values determined during this investigation.

Because of the probable importance of concrete absorption to the incidence of the corrosion of steel in concrete, we have been diligently investigating test methods for measuring and duplicating concrete absorption measurements over the last few years.

As a result of these previous observations, it appears that the influence of chlorides per se on the resistivity and absorption of concrete cannot be considered as firmly established until additional tests are made with chloride-containing concrete that has been exposed to cyclic levels of moisture as well as various curing temperatures, methods, and type of salt that is added.

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DETERIORATION VERSUS RESISTIVITY

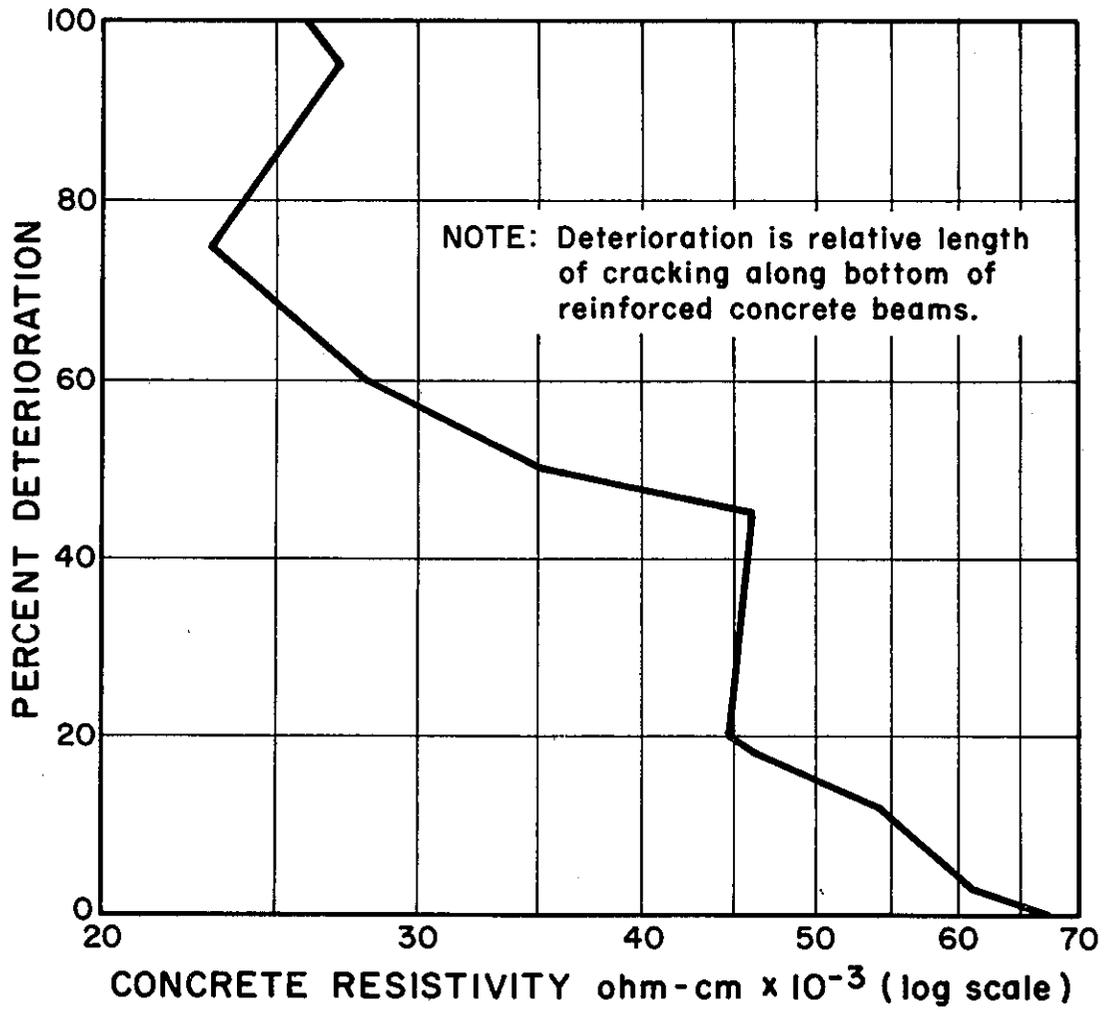
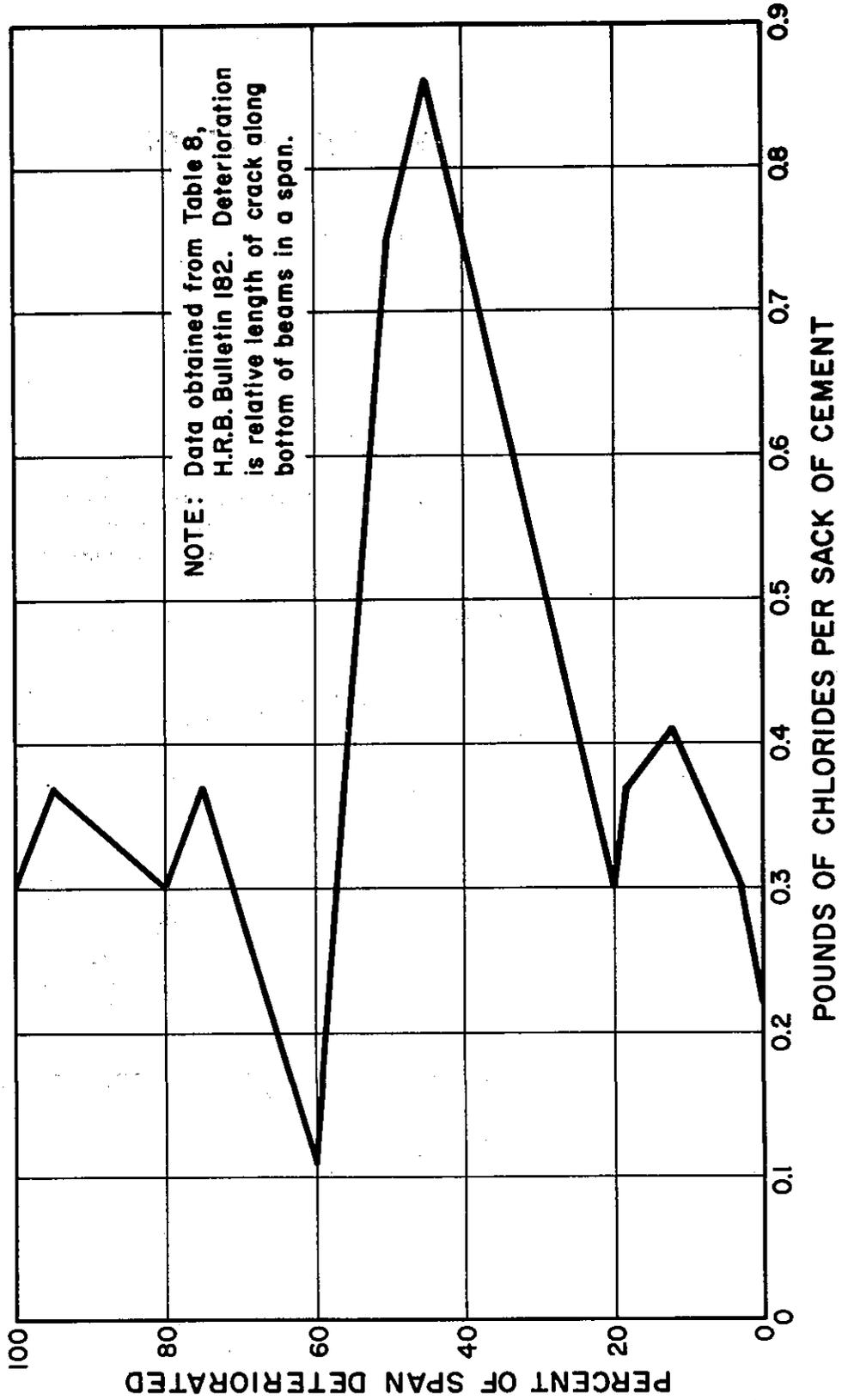
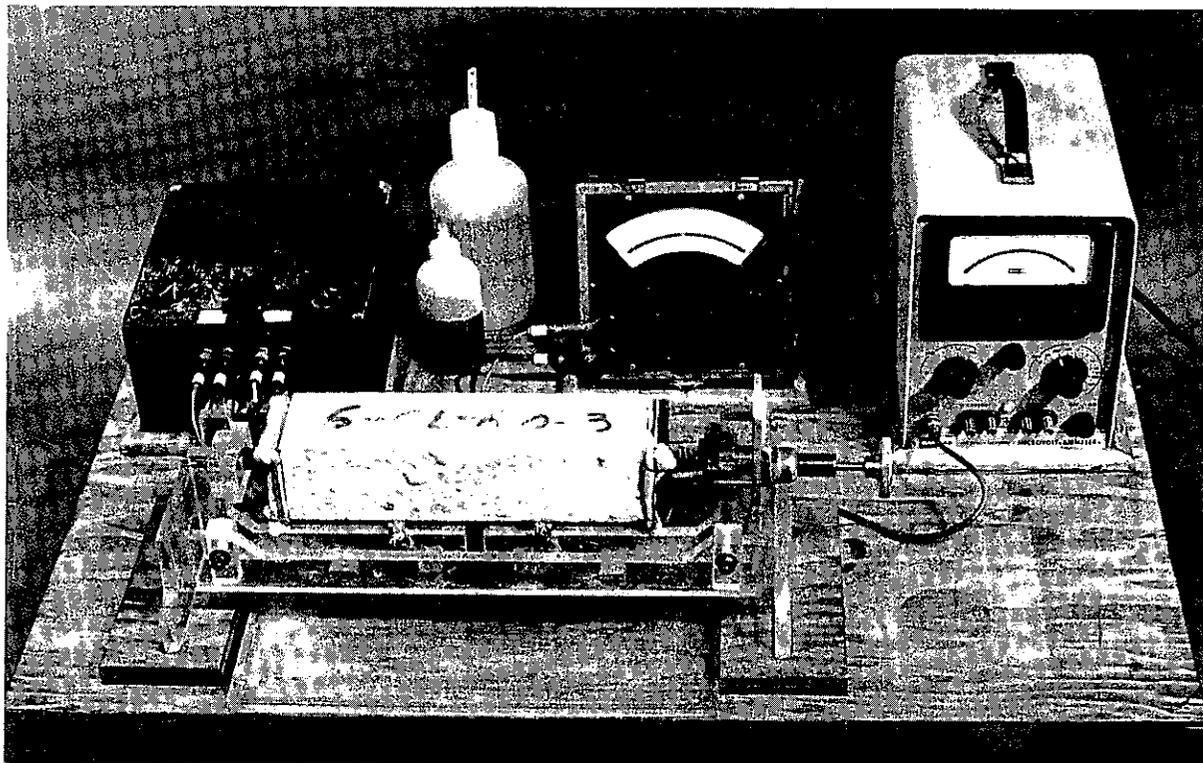


Figure 2

DETERIORATION OF A STRUCTURE
VERSUS
CHLORIDE CONTENT

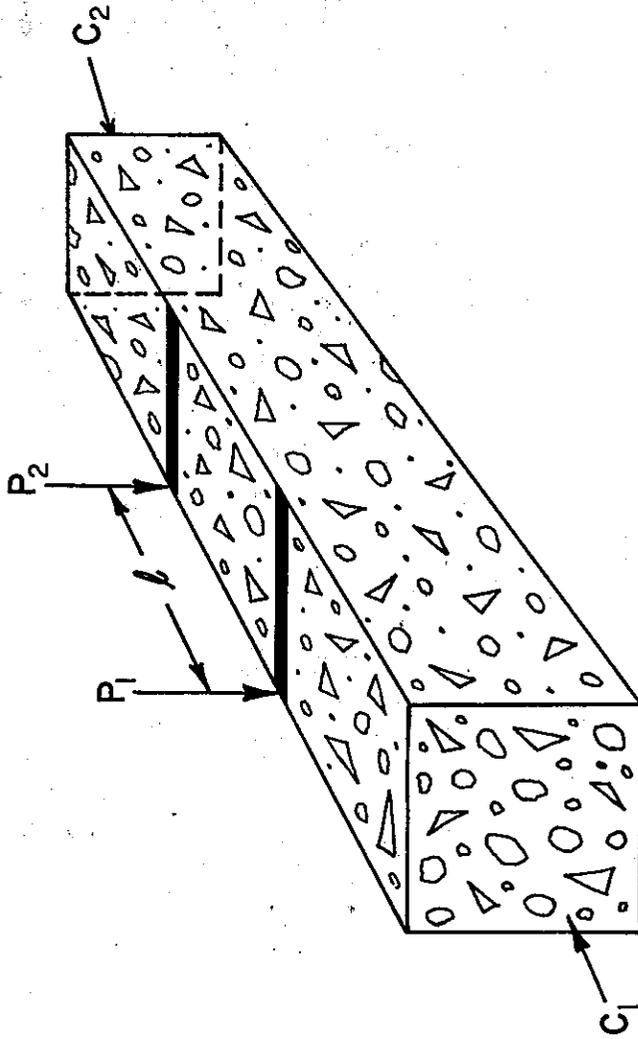




Equipment for measuring resistivity of concrete blocks

Figure 4

MEASURING RESISTIVITY OF CONCRETE BLOCK



$$\rho = \frac{RA}{l}$$

ρ = RESISTIVITY, OHM-CENTIMETER.

R = RESISTANCE IN OHMS.

A = CROSS SECTION AREA-CENTIMETERS.

l = LENGTH IN CENTIMETERS.

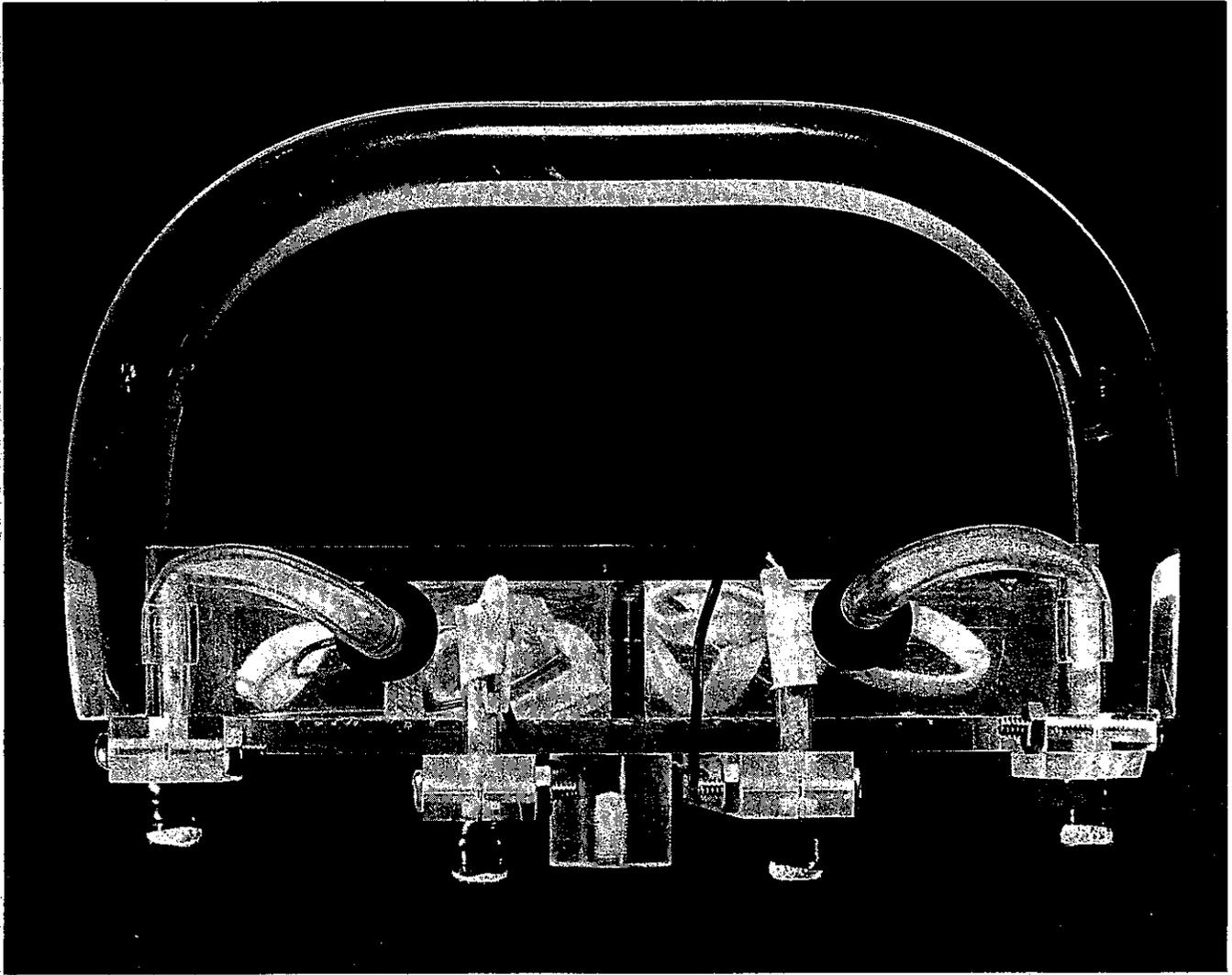
C₁ AND C₂ = CURRENT ELECTRODES.

P₁ AND P₂ = POTENTIAL ELECTRODES.



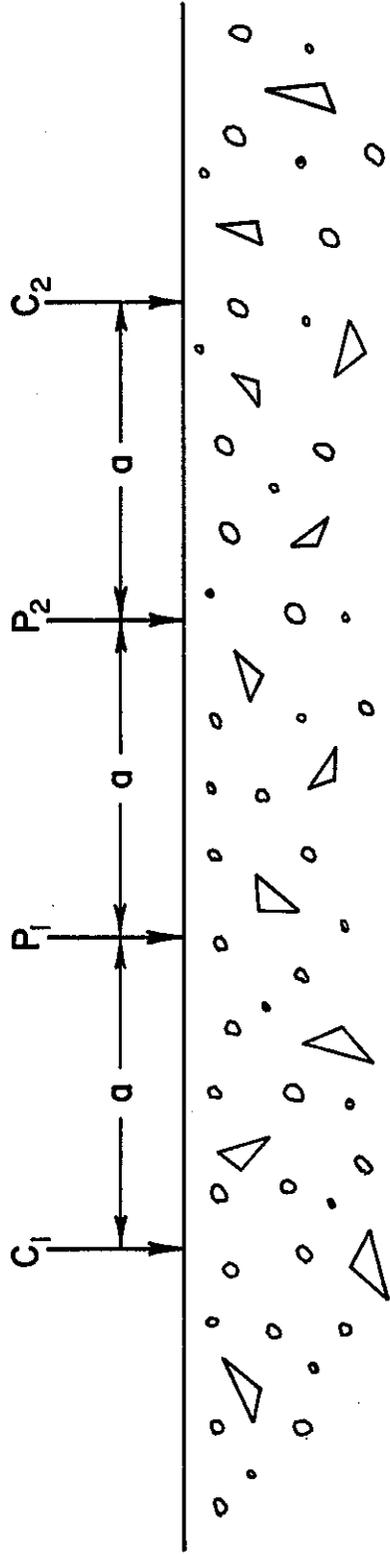
Hand-held equipment for
measuring resistivity on
concrete surface

Figure 6



Detail of hand-held equipment for measuring resistivity
on concrete surface

MEASURING RESISTIVITY OF CONCRETE FROM SURFACE



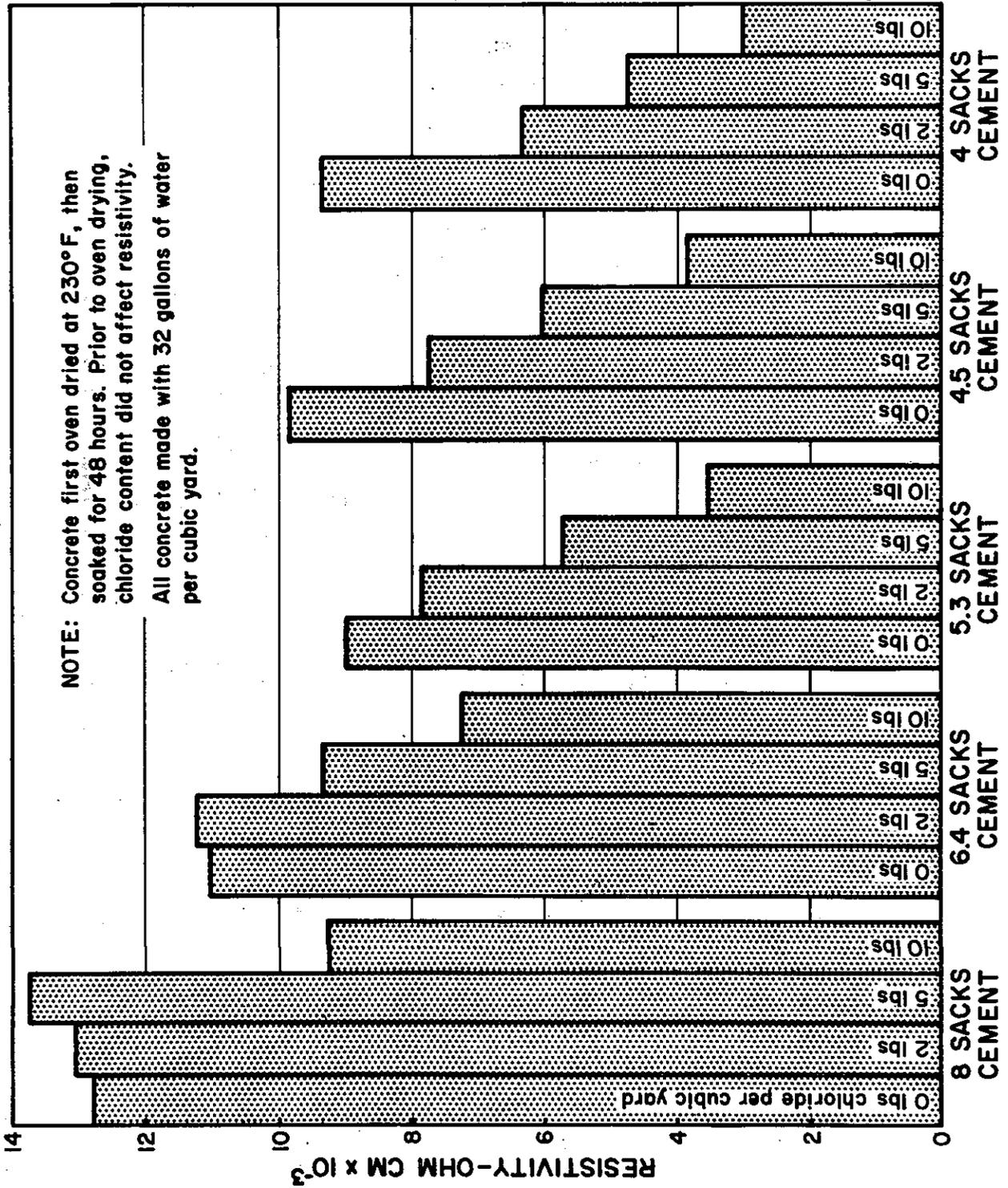
$$\rho = 2\pi aR$$

- ρ = RESISTIVITY, OHM-CENTIMETER
- a = SPACING IN CENTIMETERS
- R = RESISTANCE IN OHMS
- C_1 AND C_2 = CURRENT ELECTRODES
- P_1 AND P_2 = POTENTIAL ELECTRODES

Figure 7

Figure 8

THE INFLUENCE OF MIX VARIABLES ON RESISTIVITY OF SATURATED CONCRETE



RESISTIVITY OF CONCRETE VERSUS SATURATION

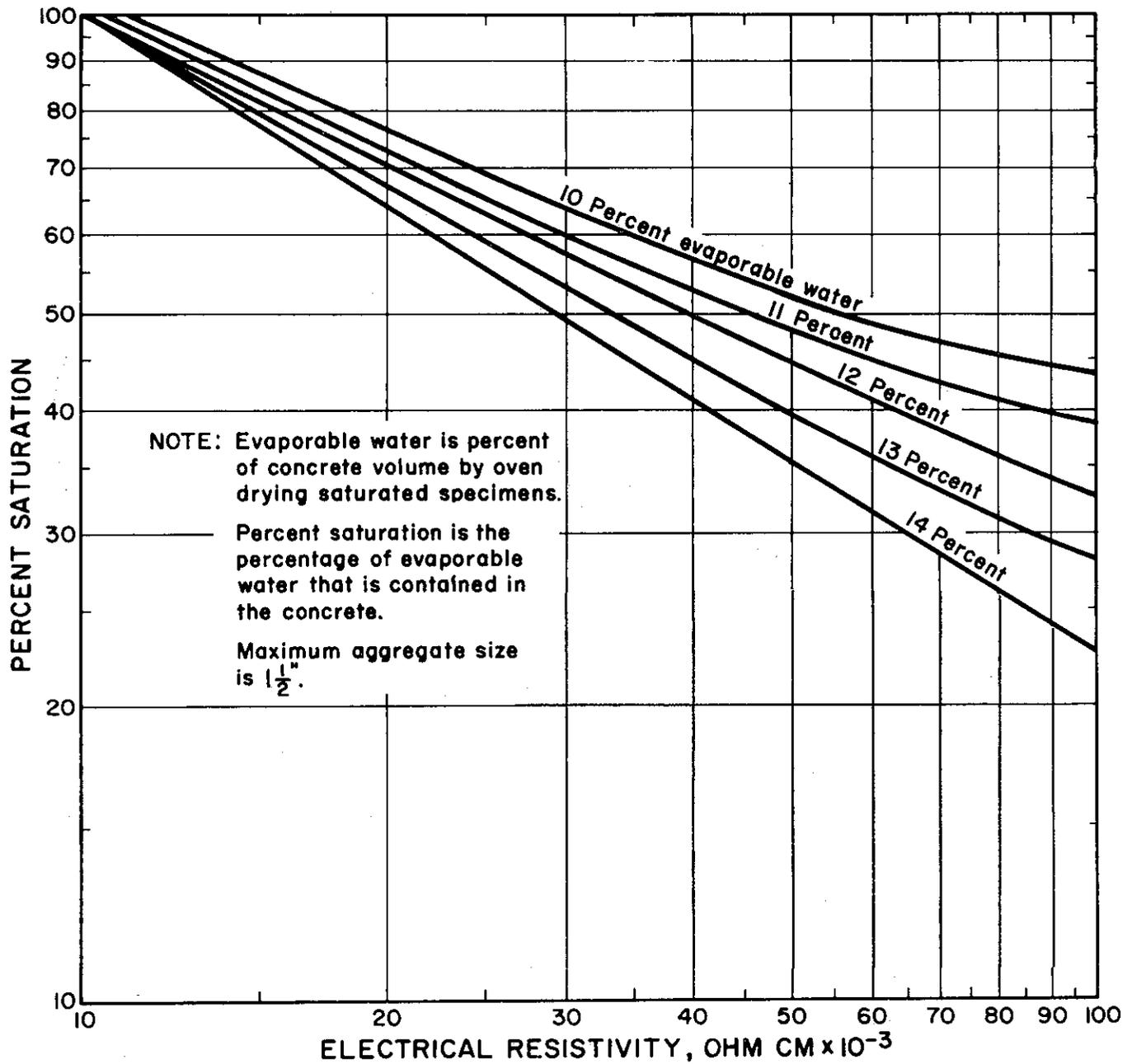


Figure 10

DRYING TIME VERSUS
% MOISTURE SATURATION OF CONCRETE

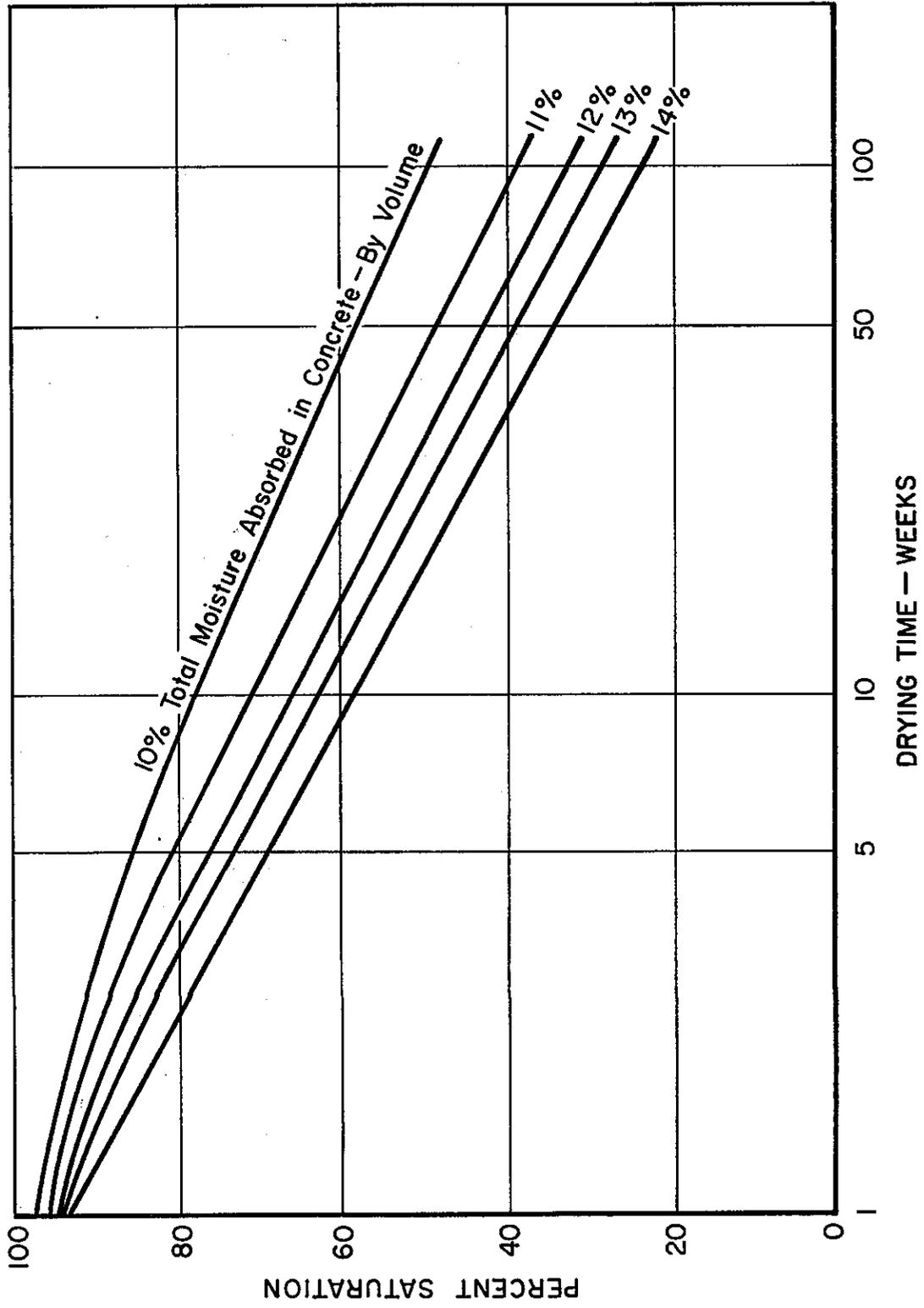


TABLE 1
VARIATIONS OF 6" X 5" X 12" CONCRETE BLOCKS

GALLONS WATER PER SACK	SACK CEMENT PER CU. YD.	SLUMP	POUNDS CHLORIDE PER CU. YD.	% WATER ABSORPTION (Evaporable Water)		MINIMUM ELECTRICAL RESISTIVITY ohm-cm
				DRY WT. CONC.	VOLUME	
4	8	1 1/2"	0	4.03	10.4	10,300
4	3	1 1/2"	2	4.09	10.2	10,300
4	8	3 4"	5	4.14	10.3	12,500
4	8	1 1/2"	10	4.21	10.8	11,600
5	6.4	1"	0	4.29	10.6	10,300
5	6.4	3 4"	2	4.36	11.0	10,200
5	6.4	1"	5	4.55	11.1	11,600
5	6.4	1"	10	4.21	11.2	12,000
6	5.3	1 1/4"	0	5.40	11.9	10,600
6	5.3	1 1/2"	2	5.32	12.6	11,100
6	5.3	1 1/4"	5	5.82	12.9	11,700
6	5.3	1 1/4"	10	5.58	13.6	10,400
7	4.5	1 1/2"	0	5.40	13.0	10,700
7	4.5	1 1/2"	2	5.38	13.1	11,400
7	4.5	1 1/2"	5	5.37	13.3	12,700
7	4.5	1 1/4"	10	5.92	14.2	9,500
8	4	1 1/2"	0	5.78	13.7	9,900
8	4	1 1/2"	2	5.78	14.2	11,800
8	4	1 3/4"	5	5.48	13.2	13,200
8	4	1 3/4"	10	6.07	14.4	10,600

NOTE: Each figure is an average of three specimens. Water absorption (Evaporable water) is the contained water after 20 months of fog room exposure, then atmospheric drying for 111 weeks and then oven drying at 230°F for 24 hours. Minimum Resistivity obtained at conclusion of 20 months exposure to fog room. Concrete specimens were 6" x 5" x 12" with 1 1/2" maximum size aggregate. Sand portion of mix was varied.

Table 2

***Resistivity Measurements of a Structure
Containing Calcium Chloride**

Chloride-ion Lbs. per Cu. Yd.	Resistivity Ohm cm
0.9	15,500
1.2	20,000
1.9	18,000
2.3	11,700
4.7	14,500
5.0	21,000
5.6	27,000
5.7	14,000
5.7	15,000
6.1	10,000
6.4	30,000
7.1	20,000
7.5	10,000
7.8	11,000
7.9	14,100
8.0	12,400
8.4	11,300
9.4	20,000
10.0	9,000

*Resistivity is for a depth below the surface of 2 inches.

Concrete contains 5 sacks of cement per cubic yard.

