MICHIGAN
STATE HIGHWAY DEPARTMENT
Charles M. Ziegler
State Highway Commissioner

THE APPLICATION OF CHLORIDE SALTS TO
CONCRETE PAVEMENTS FOR ICE CONTROL

By

C. C. Rhodes

Research Project No. 39 B-11 (5)

Research Laboratory
Testing and Research Division
Report No. 74
August 17, 1945

TABLE OF CONTENTS

i

LIST OF FIGURES

LIST OF TABLES

THE APPLICATION OF
CHLORIDE SALTS TO CONCRETE PAVEMENTS
FOR ICE CONTROL

At the present time it is the policy of the Michigan State Highway
Department to permit the application of rock salt without abrasives to
bituminous road surfaces for ice control. The question has arisen as to
whether or not such a practice may be safely extended to include concrete
pavements of a definite minimum age which have been constructed without the
use of air-entraining cements. The advantages to be gained by such a pro-
cedure are quite obvious and can be readily appreciated by the highway
engineer. It would not only effect a considerable economy of materials,
men, and equipment, but would also eliminate troublesome abrasive residues
which may clog drains and contribute materially to the deterioration of the
pavement by their grinding action under traffic and infiltration into
joints and cracks.

With these considerations in mind, the Testing and Research Division
was requested by the Maintenance Division and authorized by H. C. Coons,
Deputy Commissioner and Chief Engineer of the Department, to make a study
of the problem during the past winter in order that conclusive data might
be obtained upon which to base future policy in the matter.

In the literature on the subject of scaling caused by the application
of chloride salts to concrete pavements, the statement has frequently been
made that concrete pavements more than about four years of age are less
vulnerable to attack by these salts than those of lesser age (1) (2). Al-
though this statement appears to have been founded upon reliable general

---

* See bibliography appended to this report.

observation and experience, no definite statistical data have been found
which could be used to determine the minimum age at which chlorides could
be safely applied to concrete pavements in Michigan in sufficient concen-
tration for ice control without the use of abrasives.

The first problem to be solved, then, was: What is the minimum age
of the concrete after which rock salt may be used for ice control? Other
questions naturally arose. What characteristics of the concrete itself,
other than age, will influence its resistance to this type of attack?
Will rock salt (sodium chloride) be more or less harmful than 77-80 percent
calcium chloride? What will be the effect of concentration of salts on the
severity of attack? How will excessive amounts of impurities in the rock
salt (i.e., sulfates) affect the concrete surface? Will rock salt be as
effective in melting ice and packed snow on concrete pavements as it is on
bituminous surfaces? What effect will temperature at the time of applica-
tion have on the comparative efficiency of the two methods in eliminating
traffic hazards?

Some of these questions have been answered for all practical purposes
by the results of field studies. Others have been answered in the labora-
tory. Of the pavements selected for the accelerated test, ranging in age
from four to nine years and all in good initial condition, none showed any
appreciable scaling at the end of the test except the youngest. Observa-
tion of some other pavements whose history is known definitely establishes
the fact that age is of no benefit to intrinsically poor concrete; rather
the reverse. Rock salt and flake calcium chloride appeared to be about
equal in their scaling effect on the younger concretes, while evaporated
fine salt of a relatively pure grade had a noticeably less effect than
either. Since the use of salt without abrasives necessarily implies bare

- 2 -

pavement maintenance and the melting power of the chlorides diminishes with decreasing temperatures, some difficulty may arise when applications are made at temperatures below approximately 10 degrees Fahrenheit.

The several phases of the study mentioned above will be discussed in this report under two general headings, field studies and laboratory studies. The first part will deal with the results of the work designed to evaluate the age factor, relative severity of the three types of chloride salts and the effect of the quality of the concrete on resistance to scaling. The second will deal with properties of salt solutions and phase relations as they affect the problem under consideration, the comparative effect of sodium chloride and calcium chloride on thin concrete plates, and finally, some theoretical considerations concerning the mechanism of salt action and age effect.

US 10 ranging in age from 6 to 9 years in yearly intervals lay within a few miles of the test road. The following paragraphs describe briefly the materials used, location and construction of test panels, test procedure and data obtained.

Materials: Rock salt and flake calcium chloride conforming to standard specifications of the Department, and a commercial evaporated fine salt were used in the tests.

The calcium chloride was a well-known brand meeting the following requirements as to chemical composition:

Calcium Chloride, $CaCl_2$ (anhydrous)	77% Min.
Magnesium Chloride, $MgCl_2$	0.5% Max.
Total alkali chlorides	2.0% Max.
Other impurities	1.0% Max.

Chemical analyses of the rock salt and evaporated fine salt (Table I) show that the evaporated salt was of a high degree of purity, but that the rock salt contained an appreciable amount of calcium sulphate.

TABLE I

CHEMICAL ANALYSES OF ROCK SALT AND EVAPORATED SALT

	Rock Salt	Evaporated Salt
Moisture, as received, percent	0.62	0.65
Calculated composition (dry basis) percent		
$CaSO_4$	1.65	0.06
$MgCl_2$	0.42	0.11
$CaCl_2$	0.06	0.24
Fe_2O_3, Al_2O_3, SiO_2	0.69	0.04
NaCl (by difference)	97.18	99.55

- 5 -

Location and Construction of Test Panels: Six test areas were laid out at the locations given in the following table:

TABLE II

LOCATION OF TEST AREAS

Test Area Number	Route	Project	General Location	Station	Built	Age Years
1	M-115	18-20,C3	Series 4E Cement No. 1	464+00	10-1940	4
2	M-115	18-20,C3	Series 4I Cement No. 2	499+55	10-1940	4
3*	US-10	18-16,C9	M-115 to Lake Station	860+00	5-1938	6
4*	US-10	18-16,C9	M-115 to Lake Station	893+00	11-1937	7
5	US-10	18-10,C6	Clare to Farwell	71+00	7-1936	8
6	US-10	18-16,C1	Farwell to M-115	300+00	6-1935	9

* Project 18-16,C9, Stations 830+00 to 862+00 constructed in 1938. Balance constructed in 1937.

Each test area consisted of three sections, one each for tests with rock salt, fine salt, and calcium chloride. These sections were each 2 feet wide, 18 feet long, and dyked at the boundaries by means of 3/4 inch wooden strips cemented and sealed to the pavement surface with tar. Additional dykes were added to each section across the short dimension to facilitate the daily work and create a more uniform layer of water or ice over the surface of the pavement. Figure 1 shows a view of a typical test area after the installation of panels.

Figure 1. Typical installation of test panels.

Test Procedure: The test procedure adopted was essentially the same as that used in the accelerated scaling studies conducted on the Durability Project of the Test Road during the winters of 1940-1941 and 1941-1942. Water was added to each section of the test area to a depth of 1/4 inch and allowed to freeze over night. The following morning commercial rock salt, evaporated fine salt and calcium chloride were applied to their respective panels at the rate of 5 pounds per 36 square feet. After decomposition of the ice, the surface of the pavement was cleared, flushed and again covered with water to a depth of 1/4 inch. This constituted a daily cycle of freezing and thawing. When scaling occurred the amount was determined at each successive cycle by superimposing a grid with cross pieces 12 inches apart on the test panel and estimating the extent of the affected area.

Test Results: Freezing and thawing with the two types of sodium chloride was begun January 23, 1945 and thirty cycles had been completed when the tests were discontinued on March 10, 1945. The calcium chloride tests did not get under way until January 30th, and ran for 26 cycles. At test area No. 1, located on the durability project of the Michigan Test Road (standard construction, brand No. 1 cement), the calcium chloride was applied to concrete of an adjoining series containing Orvus. Complete data of the study are given in Table III.

Discussion of Results

The data obtained from this study throw some light on the subject of age effect and the comparative effect of different types of chloride used, which topics will be discussed in order. There is, however, a third important factor which must be considered in connection with the age effect. This factor is the quality of the original concrete. Although no data of

- 8 -

this kind were obtained in the present field study, all of the test areas

being located on unscaled and apparently sound concrete, the subject of

the effect of quality on the subsequent scaling of concrete will be

touched on here because of its association with the age effect.

TABLE III

SUMMARY OF DATA FROM CONTROLLED FIELD STUDIES

Test Area Number	Age Years	Percent Scale		26 cycles
		30 cycles		
		Fine Salt	Rock Salt	Calcium Chloride
1	4	19	38	0*
2	4	8	13	11
3	6	0	0	0
4	7	0	0	0
5	8	0	0	0
6	9	0	0	0

* This panel placed on concrete containing Orvus.

Effect of Age of the Concrete: From the data in Table III it can be

seen at once that no significant scaling occurred on any of the concretes

6 to 9 years of age. This is shown by Figures 2A, B, C and D which illus-

trate the condition of the rock salt panels at test areas 3, 4, 5 and 6

at the end of 30 cycles of freezing and thawing. Figures 3A and 3B show

that concrete containing Orvus is still as resistant to the action of

calcium chloride as it was three years ago. Both of the four year old

concretes scaled to some degree in this test, the extent of the scale in

test area No. 1 being more than double that of No. 2. Both, however,

have improved definitely in scale resistance since similar tests were

made when they were a little more than a year old. The following data are

taken from the results of durability tests on the Michigan Test Road

during the winter of 1941-1942:
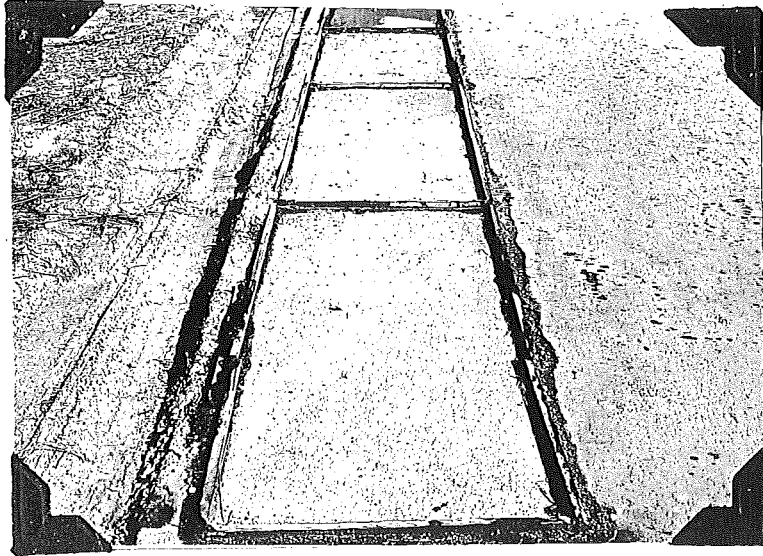
Figure 2A. Rock Salt panel of test area No. 3 after
            30 cycles. Concrete 6 years old. No
            scale.
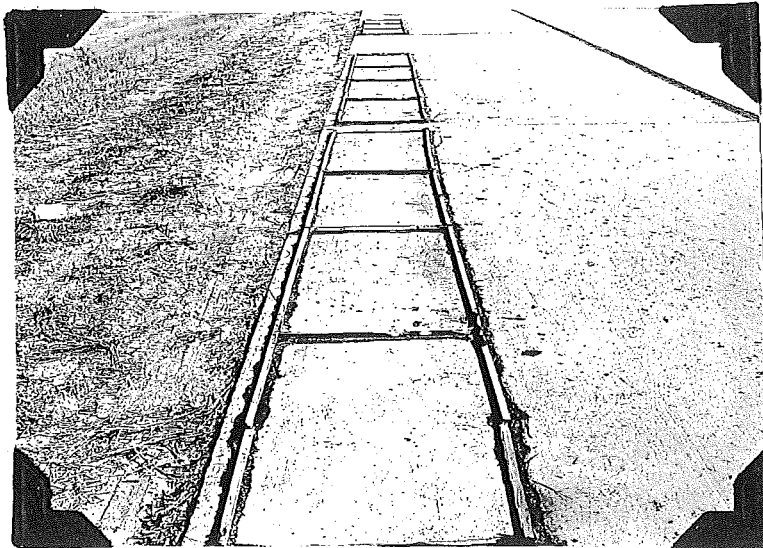
Figure 2B. Rock Salt panel of test area No. 4 in
            foreground after 30 cycles. Concrete
            7 years old. No scale.
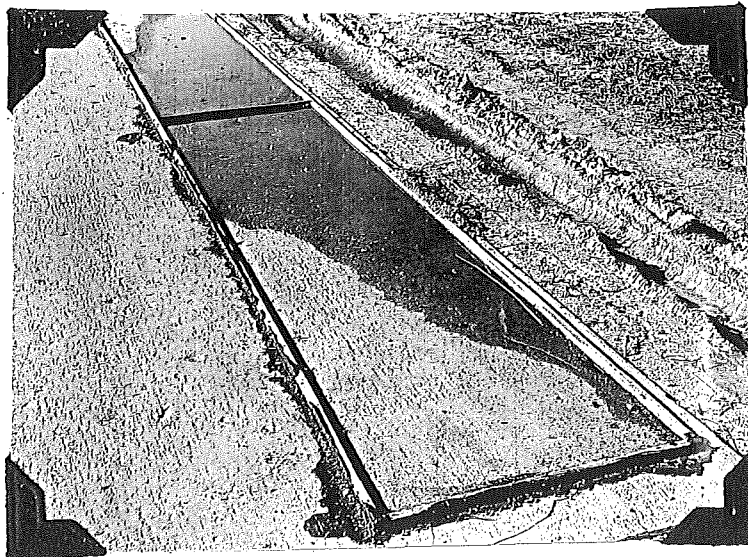
Figure 2C. Rock Salt panel of test area No. 5 after 30 cycles. Concrete 8 years old. No scale.
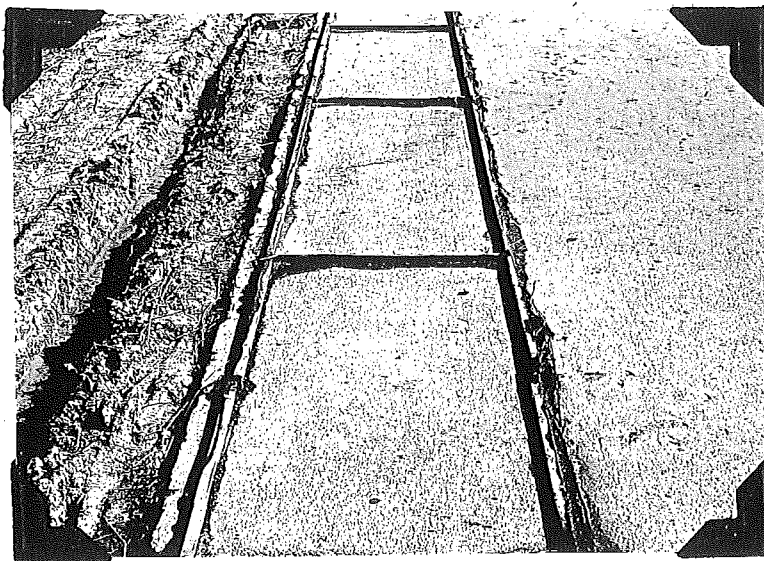
Figure 2D. Rock Salt panel of test area No. 6 after 30 cycles. Concrete 9 years old. No scale.
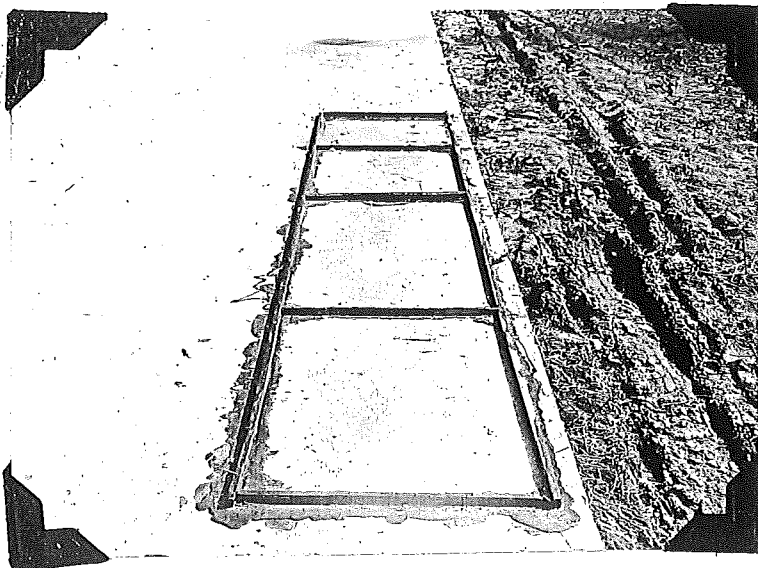
Figure 3A.   Calcium Chloride panel of test area No. 1
             after 26 cycles.   Pavement 4 years old
             containing Orvus.   Project 18-20,C3.
             Station 463+50.   No scale.
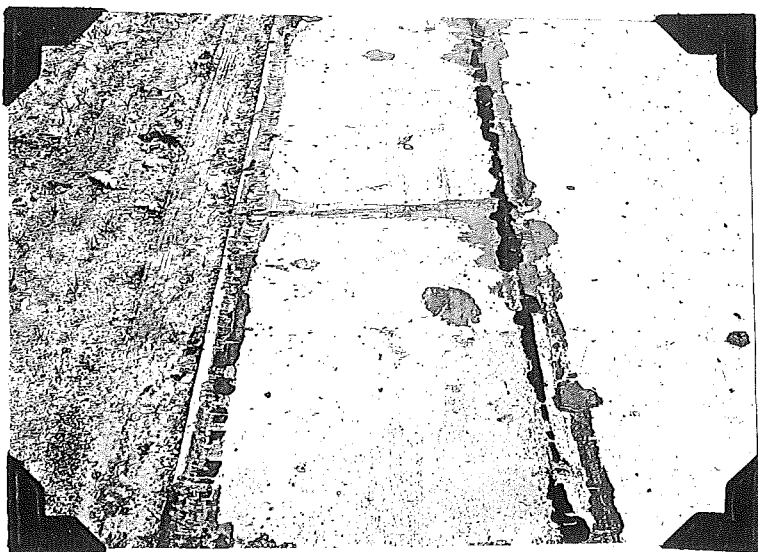
Figure 3B.   Calcium Chloride panel No. 12 after 93
             cycles.   Pavement 1 year old containing
             Orvus.   Project 18-20,C3.   Station 464+54.
             No scale.

Scaling Studies 1941-1942

Factor Studied	Panel No.	Cycles	Percent Scale
Standard Construction			
Cement Brand No. 1	11	41	100
Cement Brand No. 2	21	32	100
Cement Brand No. 1	27	9	100
Cement Brand No. 2	16	9	100
Cement Brand No. 2	34	7	100
Cement Brand No. 2	33	9	100

Calcium chloride was used in the tests recorded in the above table.
Note that all concretes of standard construction scaled 100 percent in
7 to 41 cycles, with the majority failing completely at less than 10
cycles. At four years of age, concretes of the same materials and con-
struction show a maximum of 38 percent scale at 30 cycles of freezing and
thawing. Photographs illustrating the condition of standard concrete in
Series 4I of the durability project containing cement brand 2 after tests
at ages of 1 and 4 years are shown in Figures 4A and 4B. The conclusions
to be drawn from the foregoing data confirm prevailing opinion that there
is a progressive beneficial effect of age on the resistance of good con-
crete to scaling from the action of chloride salts. For these pavements,
and under the conditions of this test, the minimum age for practical
immunity seems to lie somewhere between 4 and 6 years.

Effect of Type of Chloride Used for Ice Control: Again referring to
Table III, it may be seen that, on the two areas where scaling occurred,
the action of rock salt was considerably more vigorous than that of the
evaporated fine salt. Although it is dangerous to draw final conclusions
from the limited data available, the wide difference between the severity
of action of the two sodium chloride salts is certainly significant, and
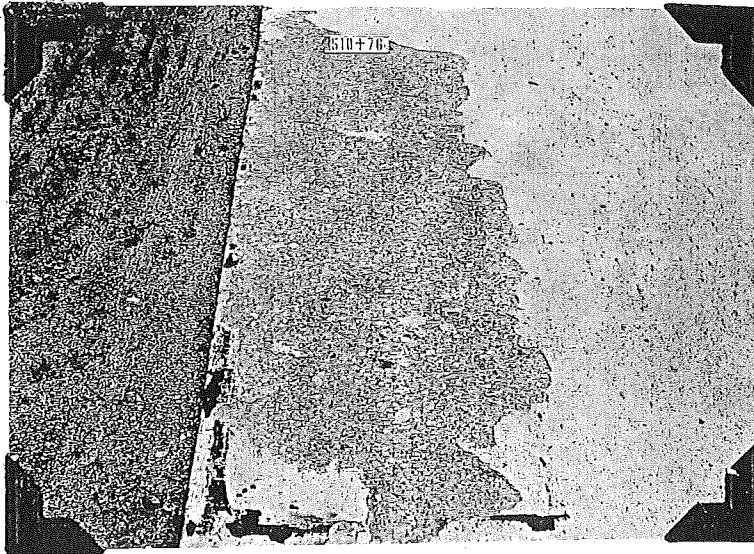
- 13 -

Figure 4A.   Calcium chloride panel No. 16 after 9
cycles. Pavement 1 year old containing
cement brand No. 2. Project 18-20,C3.
Station 510+76. 100 percent scaled.

Figure 4B.   Calcium chloride panel of test area No. 2
after 26 cycles. Pavement 4 years old
containing cement brand No. 2. Project
18-20,C3. Station 500+50. 11 percent
scaled.

- 14 -

additional field tests should be performed to verify the results of this phase of the study. Photographs in Figures 5A, B, C, and D show the relative effect of the two types of sodium chloride at 30 cycles.

Because of the fact that scaling occurred on only two of the areas, one of which did not receive calcium chloride on a section of standard concrete, we have the data from only one set of panels from which to make a comparison of the effect of calcium chloride and sodium chloride salts. At test area No. 2, where these panels were located, 11 percent of the surface was scaled by calcium chloride compared to 8 and 13 percent by fine salt and rock salt respectively. Since the section treated with calcium chloride was subjected to only 26 cycles of freezing and thawing as against 30 cycles for the sodium chloride panels, it appears that rock salt and calcium chloride were about equal in scaling power, with the fine salt producing noticeably less effect than either. The photograph of the calcium chloride section of test area No. 2 shown in Figure 4B may be referred to for comparison with those of the rock salt and fine salt sections of the same test area given in Figures 5C and 5D.

Effect of Quality of the Concrete: The purpose of this paragraph is to emphasize the fact that initially poor concretes cannot be expected to derive benefit in salt resistance from the aging process. Characteristics of the cement, quality and grading of the aggregates, proportioning and placing of the mix, finishing, and curing all have an influence on permeability to salt solutions and subsequent durability. Figure 6 illustrates the effect of chlorides on a concrete pavement 12 years old carrying inferior aggregates. Even air-entraining agents cannot be expected to protect such aggregates (5) (6). The most essential requirement of a potentially resistant portland cement concrete is a dense, more or less

impermeable surface which prohibits the entrance of water and salt solutions. In such a concrete, impermeability or "tightness" will increase with age. Some or all of these considerations may have influenced some authors to modify the statement referred to in the introduction of this report to read "unscaled pavements more than four years old - - - " (3) (4). There may be pavements, however, which are fundamently sound, and still show a light surface scale due to laitance formed by excessive manipulation at the time of placing the concrete. Unless the scaling has been progressive, it may be taken for granted that the concrete is sound and its condition can be considered to come within the meaning of the term "unscaled".

Figure 5A. Fine salt panel of test area No. 1 after
30 cycles. 19 percent scaled.

Figure 5B. Rock salt panel of test area No. 1 after
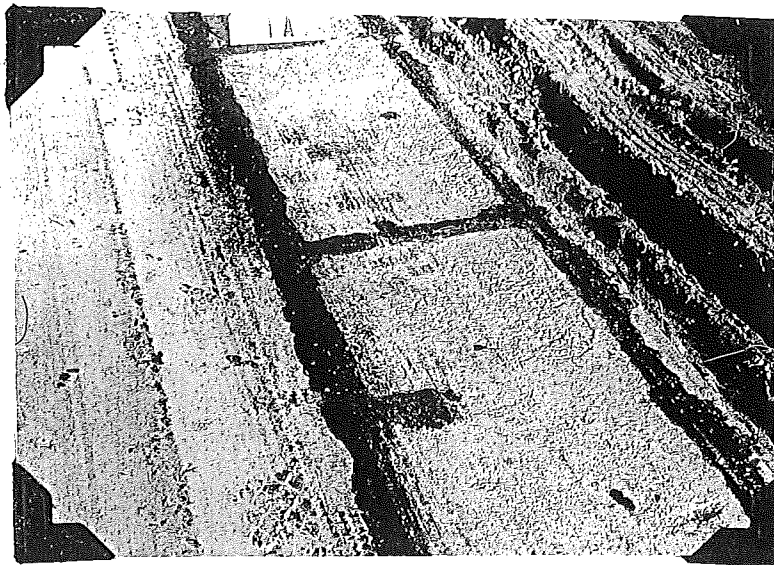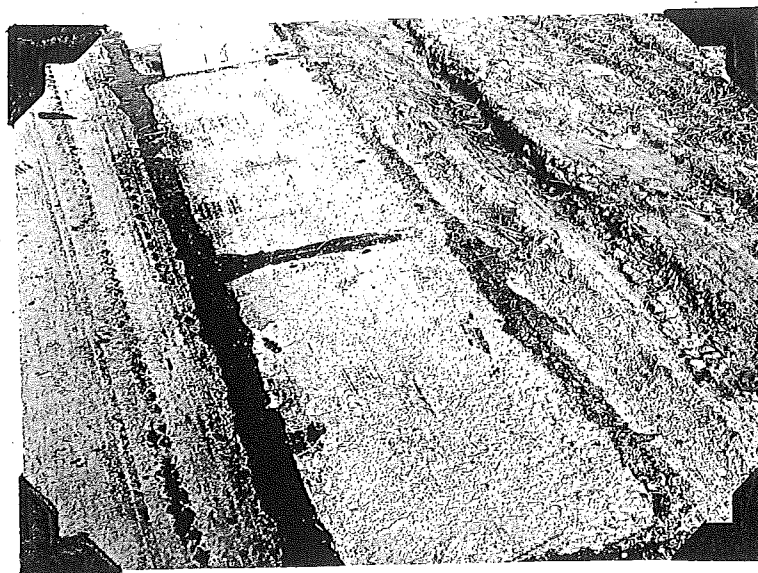30 cycles. 38 percent scaled.

Figure 5C. Fine salt panel of test area No. 2 after
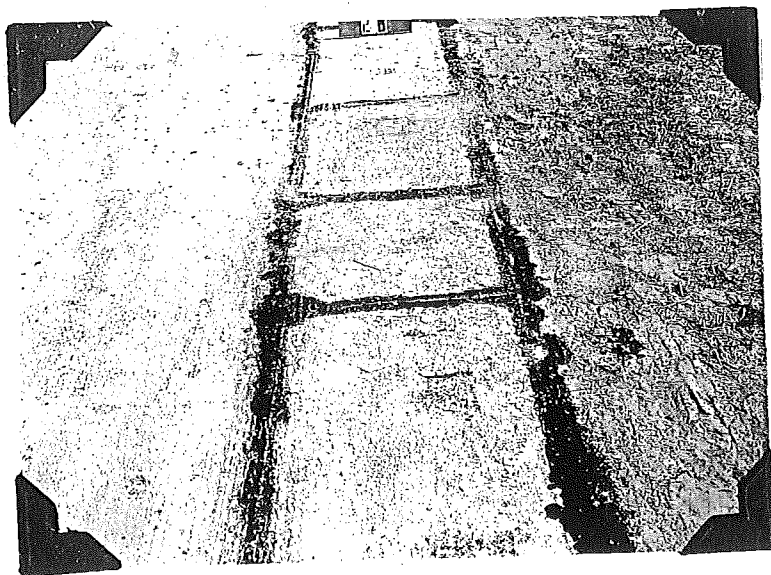30 cycles. 8 percent scaled.

Figure 5D. Rock salt panel of test area No. 2 after
30 cycles. 13 percent scaled.

Figure 6.   Photograph showing the effect of chloride
            salts on concrete containing inferior
            aggregates.

LABORATORY STUDY

In addition to the field tests described in the preceding para-
graphs supplementary studies were undertaken in the laboratory to obtain
further information of value bearing on the subject, and to aid in the
interpretation of the field data. The laboratory work may be most con-
veniently and simply presented under the three general topics mentioned
in the introduction of this report. Under the first will be found a brief
review of some of the properties of calcium and sodium chloride solutions
and phase relations of the system salt-water-ice. Under the next a des-
cription will be given of the action of calcium and sodium chloride solu-
tions on thin concrete plates; and finally an attempt will be made to
point out some of the factors having a bearing on the mechanism of salt
action and the age effect.

Properties of Salt Solutions and Phase Relations

In order to fix in mind some of the fundamental principles involved
in the action of salts on ice and snow, attention is called to the equili-
brium diagrams presented in Figure 7. These diagrams give all of the
conditions of equilibrium, exclusive of the vapor phase, which exist in
the two systems $CaCl_2$-water-ice and NaCl-water-ice at normal atmospheric
pressure, and are of considerable practical value in the study of salt
action on ice or snow. Both of the diagrams were prepared from solubility
and freezing point data of the pure salts (7), but may be applied without
appreciable error to the materials used in this investigation. For the
purpose of the present discussion, attention will be confined to the por-
tions of the two diagrams which lie below the normal freezing point of
pure water (32°F.).
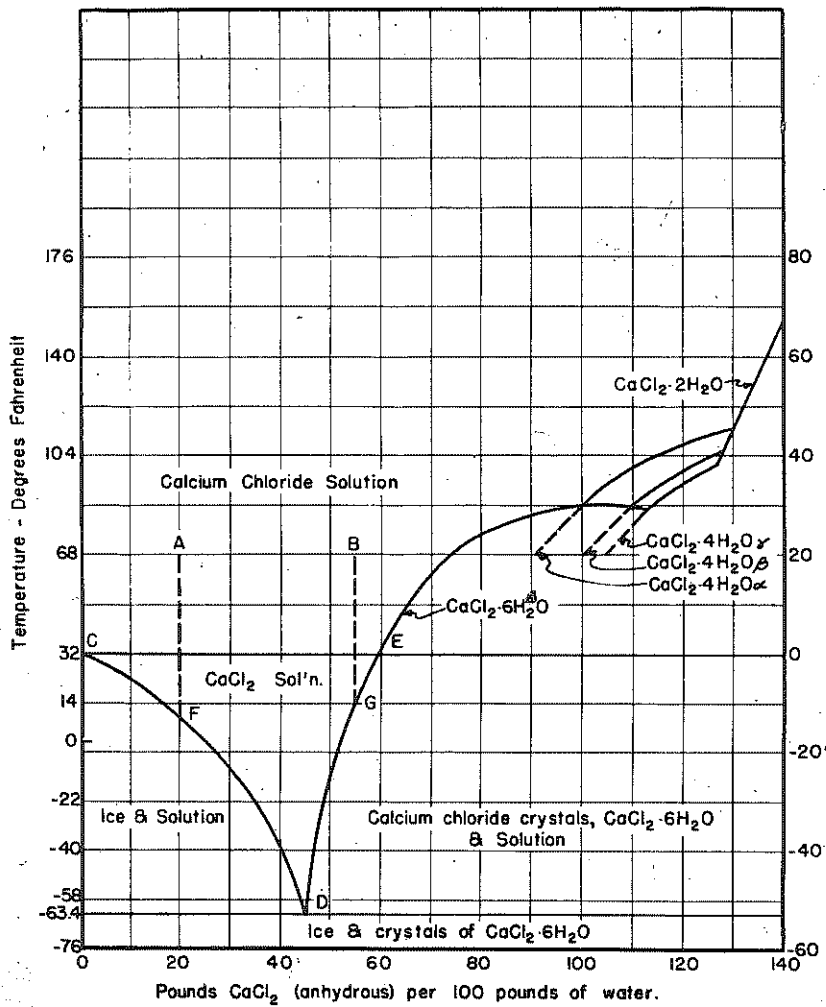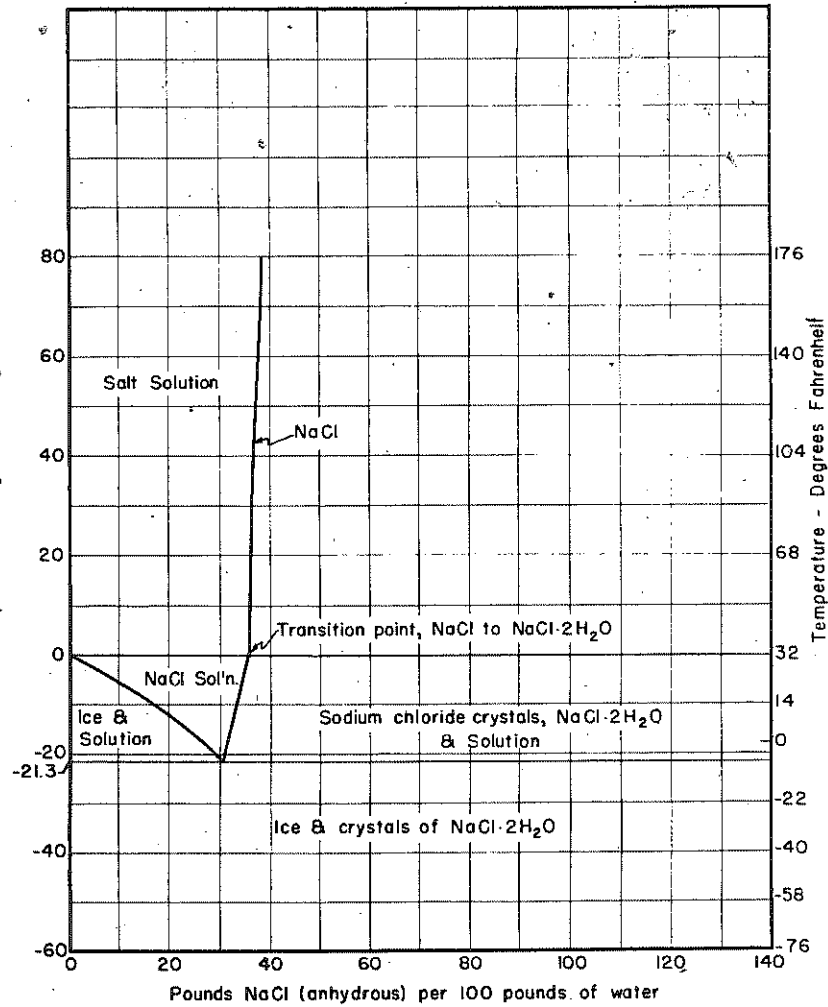
EQUILIBRIUM DIAGRAMS FOR SALT SOLUTIONS AT ATMOSPHERIC PRESSURE

Figure 7

M-1027

Referring to the first diagram in Figure 7, CD represents the freezing point curve of aqueous solutions of calcium chloride and DE the solubility curve of calcium chloride in water at temperatures below 32°F. Interpreting the curves, this means that at concentrations of calcium chloride of less than 45 pounds of the salt to 100 pounds of water, only ice can exist in contact with the solution at temperatures from 32°F down to the eutectic point D at - 63.4°F, and that at greater concentrations than this, calcium chloride hexahydrate is the only possible solid phase in the same temperature range. Two examples will illustrate. First, suppose we start with a solution of 20 pounds of calcium chloride in 100 pounds of water at 68°F. (point A on the diagram) and then cool it gradually. No solid phase will form from the solution until the freezing point curve CD is reached at point F, corresponding to a temperature of about 6°F. At this point solid ice begins to form which automatically increases the con- centration of salt by removal of some of the solvent from the liquid phase, and, on further cooling, ice continues to form at temperatures and concen- trations of salt solution represented by the curve CD until the eutectic point D is reached where the whole solidifies into a mass of ice and cal- cium chloride crystals. Below the point D no liquid phase can exist.

Now suppose we take a solution containing 55 pounds of calcium chloride, instead of 20 pounds, per 100 pounds of water and cool in the same manner. Here no solid phase will leave the solution until point G (14°F.) on the solubility curve DE is reached. At this point solid crys- tals of the hexahydrate of calcium chloride, $CaCl_2.6H_2O$, begin to form and, on further cooling, more of the salt continues to crystallize from the solution due to its decreased solubility at lower temperatures. Calcium chloride crystals constitute the only solid phase in contact with the

- 21 -

solution, and, on still further cooling, continue to form at temperatures
and concentrations of the salt solution given by the curve DE until the
eutectic point D is again reached. Below this point the whole solidifies
into a mixture of ice and salt crystals as before. From these examples,
it may be seen that only at the single point D, corresponding to a con-
centration of about 45 pounds of chloride (anhydrous) to 100 pounds of
water at a temperature of - 63.4°F. is it possible for both solid phases
to exist simultaneously in contact with the solution.

The two preceding examples serve to present a general picture of
equilibrium conditions encountered in the use of calcium chloride for
ice control. Of more particular significance from our standpoint, how-
ever, is the reverse process, which takes place when salt is used to melt
ice. In other words, what happens if, instead of starting with a given
calcium chloride solution and cooling to below 32°F., we now take a de-
finite amount of calcium chloride, say 10 pounds, and add it to an excess
of ice at a given temperature, say 0°F? If the temperature is kept con-
stant, it may be seen at once from the freezing point curve CD of the
diagram that this quantity of calcium chloride will melt sufficient ice
to produce a solution in equilibrium with ice at the given temperature.
The amount of ice melted by the 10 pounds of chloride is perfectly definite
at this temperature and may be computed directly from the curve. At 0°F.
a solution of calcium chloride in equilibrium with an excess of ice con-
tains about 25 pounds of the salt per 100 pounds of water. By a simple
calculation we find that the 10 pounds of chloride will melt approximately
40 pounds of ice, or 1 pound to 4. The diagram for sodium chloride may be
interpreted in a similar way, and it will be found that 1 pound of salt
will melt about 3.7 pounds of ice under the same conditions. These

figures agree with the experimental results published by the Committee on Highway Maintenance of the Highway Research Board (8). The element of time is also a factor in the melting process since the addition of salt to ice produces a "freezing mixture" which spontaneously lowers the temperature of the system below that of its surroundings, resulting in a temporary decrease in melting power.

Comparing the two diagrams of Figure 7, it is immediately evident that sodium chloride has no melting power below its eutectic point (about – 6.5°F.) while calcium chloride continues to melt ice at much lower temperatures. On the other hand, sodium chloride has greater melting power in the region just below the freezing point of water, the margin of superiority decreasing at lower temperatures, and becomes approximately equal to calcium chloride in its ability to melt ice at about 10°F. Below this point calcium chloride has the greater melting power. Published data referred to in the preceding paragraph on the melting efficiencies of the two salts are reproduced here as Table IV for convenience.

TABLE IV

COMPARISON OF MELTING CAPACITIES OF CALCIUM AND SODIUM CHLORIDE

Temperature Deg. F	Pounds of Ice Melted Per Pound of Chemical	
	77-80 Percent Flake Calcium Chloride	Pure Sodium Chloride
− 30°F.	2.9	--
− 20	3.2	--
− 10	3.5	--
− 6.5	3.7	3.
0	4.0	3.7
5	4.4	4.1
10	4.8	4.9
15	5.5	6.3
20	6.8	8.6
25	10.4	14.4
30	31.1	46.3

Action of Chloride Salts on Thin Concrete Plates

This phase of the investigation was planned to supplement the field

work in securing information on the age effect and the relative action of

different salt solutions on concrete by subjecting specimens of different

ages to several types of exposure and different concentrations of salt

solution. The work in the laboratory centered chiefly around the study

of the action of solutions of rock salt, commercial fine salt and chemi-

cally pure sodium chloride on thin concrete and mortar plates. A few

tests using calcium chloride were added later. Thin specimens were chosen

because of the fact that breakdown is much more rapid in this type than in

heavier sections, and it was thought that variations in severity of attack

would thus be more easily detectable.

Materials: Rock salt, evaporated fine salt and calcium chloride

sampled from materials used in the field study and a c.p. grade of sodium

chloride were used in the laboratory tests. The chemical composition of

the first three of these salts has been given previously and the c. p.

sodium chloride was, of course, of practically 100 percent purity. Two

concentrations of sodium chloride solution were used, 12 percent and satu-

rated. Saturated solutions contained approximately 26 grams of salt per

100 grams of solution and the 12 percent solutions were made up with 12

grams of the salt to 100 ml. of solution.

In order to accentuate the differences in salt resistance due to age,

specimens were taken from a 1:3 mortar, mixed in the laboratory and cured

7 days in water, and from a concrete core four years old drilled from a

section of standard construction in the Michigan Test Road. Specimens were

prepared by cutting vertical slices about 1/4 inch thick from the mortar

and from the top section of the core. These slices were then ground on the

faces to a thickness of about 1/8 inch using medium carborundum powder.

Procedure: Three methods of exposure were tried in an attempt to gain a clue as to nature of the mechanism causing breakdown: (1) continuous immersion in salt solution at room temperatures; (2) daily cycles of alternate wetting in the solution and drying in air at room temperature; and (3) alternate freezing in the solution at - 20°F. and thawing at room temperatures. Specimens were examined periodically under the microscrope to determine the time at which first cracks occurred.

Results and Discussion: Data obtained in the tests are recorded in Table V. The results shown can be regarded only as qualitative, since small variations in the thickness of different plates probably have some influence on the time required to cause initial cracks and final disintegration. They do indicate several interesting trends, however, some of which are well defined. In the first place, under all conditions of the tests, the 7 day old mortar plates were attacked and finally disintegrated long before the corresponding 4 year old concrete core slices. Second, rock salt was definitely more destructive than either the commerical evaporated fine salt or the c.p. grade. Third, with a single exception, all sodium chlorides were more destructive in 12 percent concentration than in saturated solution. Finally, in all sodium chloride tests, salt action combined with freezing and thawing was the most rigorous of the three methods tried, most specimens failing in less than 10 cycles of this treatment, with wetting and drying next in severity, and continuous immersion producing the least destructive effect.

The preceding observations concerning methods of exposure do not apply when calcium chloride solutions are used. It should be mentioned here that, both in these tests and in previous tests of a like nature,

TABLE V

SUMMARY OF DATA FROM LABORATORY DURABILITY TESTS

Continuous Immersion

		Rock Salt		Fine Salt		c.p. Salt		CaCl$_2$	
		12%	26%	12%	26%	12%	26%	12%	30%
Fresh	First Cracks*	21 days	28 days	35 days	42 days	25 days	45 days	–	–
Mortar	Disintegration	28 days	35 days	70 days	84 days	35 days	98 days	5 days	–
Concrete	First Cracks	35 days	42 days	42 days	70 days	38 days	77 days	–	30 days
Core	Disintegration	100 days+	100 days+	100 days+	100 days+	72 days	100 days+	–	40 days

Wetting and Drying

		12%	26%	12%	26%	12%	26%	12%	30%
Fresh	First Cracks	14 days	21 days	28 days	28 days	31 days	–	–	–
Mortar	Disintegration	21 days	24 days	56 days	70 days	42 days	–	–	–
Concrete	First Cracks	42 days	35 days	49 days	70 days	35 days	–	–	–
Core	Disintegration	100 days+	100 days+	100 days+	100 days+	100 days+	–	–	–

Freezing and Thawing

		12%	26%	12%	26%	12%	26%	12%	30%
Fresh	First Cracks	3 cycles	3 cycles	3 cycles	–	3 cycles	–	–	–
Mortar	Disintegration	5 cycles	4 cycles	5 cycles	–	5 cycles	–	–	–
Concrete	First Cracks	6 cycles	4 cycles	7 cycles	–	8 cycles	–	–	–
Core	Disintegration	10 cycles	10 cycles	12 cycles	–	12 cycles	–	–	–

* For sodium chloride specimens this term refers to first
noticeable loss of bond strength.

there is a remarkable difference in the visible effects produced by immersion in calcium chloride and sodium chloride solutions. Thin plates of concrete continuously immersed in calcium chloride solutions at ordinary room temperatures spontaneously disintegrated and crumbled to a heap in a comparatively short time; the more concentrated the solution, the more rapid was the attack. This phenomenon never took place in sodium chloride solutions. In the latter case there was usually a gradual and progressive loss of strength, although disintegration was not apparent and no crumbling occurred.

In the calcium chloride tests the end point, or time at which complete disintegration took place was quite sharp; end points for specimens in sodium chloride solutions could be determined only approximately by estimating the force required to break off pieces of the plate with the fingers. Similarly, the term "initial cracks", when applied to specimens in sodium chloride solutions at room temperature refers to the point at which first weakening of the bond was noticed. This difference in behavior, along with other significant indications brought out by the investigation will be discussed further in connection with the mechanism of salt action and the age effect.

Mechanism of Salt Action

From the information gained in the field and laboratory studies some general conclusions can be drawn regarding the nature of the processes which take place in the action of chloride salts on concrete. Because of essential differences in chemical composition the salt-cement reactions involved in the use of rock salt, fine salt and calcium chloride are, in some respects, different for each material and will be considered separately.

Calcium Chloride: When solutions of calcium chloride act on set cement, disintegration is probably brought about through three general processes: (1) the formation of addition products from certain lime compounds of the cement and calcium chloride, which is accompanied by an increase in volume; (2) migration and recrystallization of calcium hydroxide in local masses through the intermediate formation of the more soluble calcium oxychloride, and (3) removal of calcium hydroxide from the gel structure due to its greater solubility in calcium chloride solutions than in water.

The formation of calcium chlor-aluminate, one of the addition products mentioned above, not only causes an increase in volume of about 63 percent over that of the original compound, but also retards the formation of hydrated tricalcium aluminate. In the second process, interstitial pressures are built up through crystal growth, and in the third, calcium hydroxide is removed from the hydration products, thus weakening the gel structure and accelerating all reactions which are dependent upon hydration and hydrolysis of the calcium silicates. These concepts are well supported by research reported in the literature (9) (10) (11) and work conducted in our own laboratory (12). It is possible too that transitions of crystalline calcium chloride from the tetrahydrates to the hexahydrate (Figure 7) may have some effect during wetting and drying at room temperatures. The photomicrographs of Figures 8A and B showing the effect of immersion of a concrete plate in a 30 percent solution of calcium chloride at 30 and 40 days respectively illustrate this sort of breakdown. The first picture shows the formation of initial cracks and the second was taken after the specimen had broken spontaneously into four pieces.
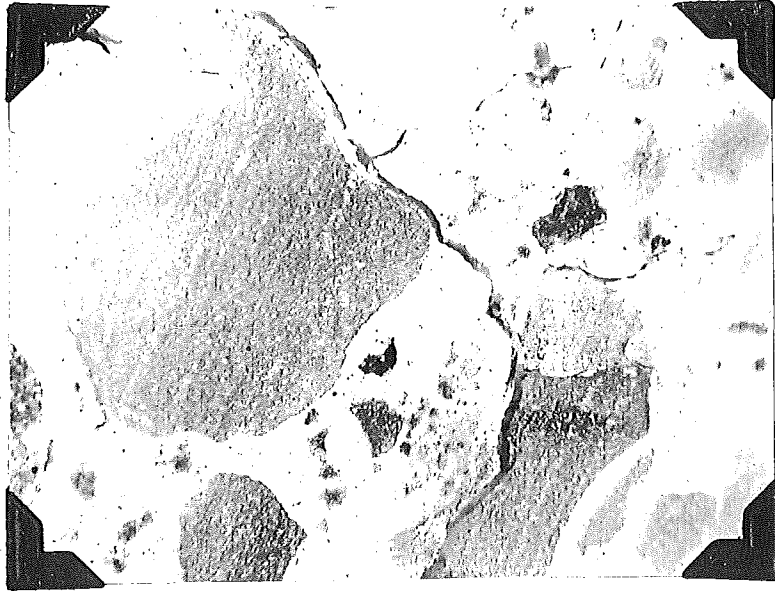
Figure 8A.   Formation of initial cracks in concrete
plate immersed 30 days in 30 percent
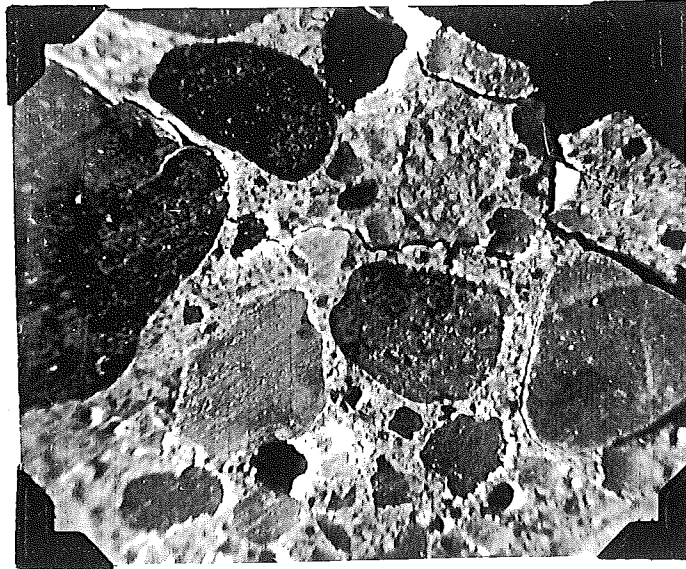calcium chloride solution.
Magnification, 40X.

Figure 8B.   Advanced disintegration of the same specimen
shown in Figure 8A.after 40 days immersion
in 30 percent calcium chloride solution.
Magnification, 40X.

Sodium Chloride: In regard to the action of pure sodium chloride on hydrated cement, some investigators (13) (14) are of the opinion that solutions of this salt depend for ultimate action on their interaction with the lime of the cement to form calcium chloride which in turn reacts with hydration products as described in the preceding paragraph. To some extent this is probably true, but the amounts of calcium chloride formed in this manner are limited by the comparatively low solubility of calcium hydroxide in sodium chloride solutions. Bogue (9) found that immersion of mortar cubes in 3 percent sodium chloride solution had little effect on their strength. Lea and Desch (15) state that alkali chlorides have no effect on matured concrete. It has already been noted in this report that the action of pure sodium chloride solutions on concrete plates at room temperature is very slow.

The photomicrograph in Figure 9 shows the condition of a fresh mortar plate after 30 days' immersion in 12 percent c.p. sodium chloride solution. Some attack is shown by the relief of aggregate particles against the surrounding matrix, but the condition of the specimen is in sharp contrast to that of a similar plate immersed in 12 percent calcium chloride solution which disintegrated completely in five days. Comparing this photomicrograph with the one given in Figure 10, which shows the condition of a matured concrete plate after 20 days' immersion in 12 percent sodium chloride solution, it is apparent that the attack was less severe in the latter case. Here the matrix seems to have swollen above the surface of the larger aggregate particles which are surrounded by a margin of differently colored gel. Attack at the aggregate boundaries with the resulting loss of bond strength seems to be characteristic of salt action on concrete.
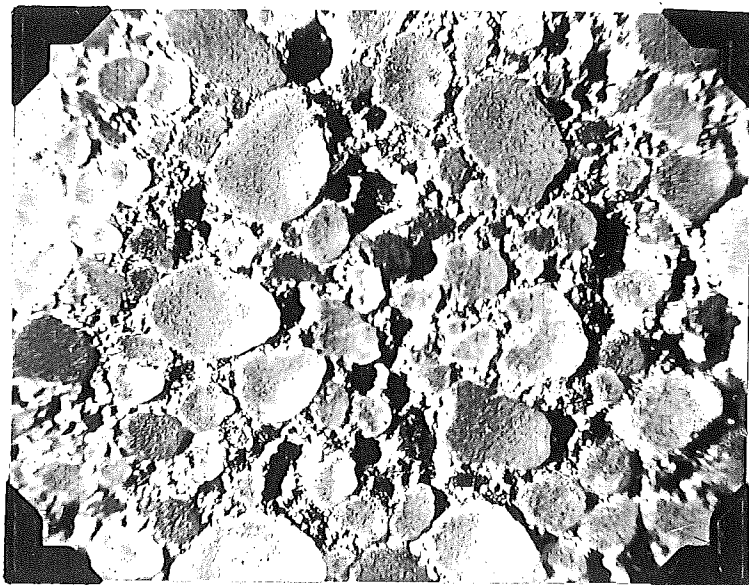
Figure 9.   Condition of Mortar plate after 30 days'
            immersion in 12 per cent c.p. sodium
            chloride solution. Magnification, 40X.
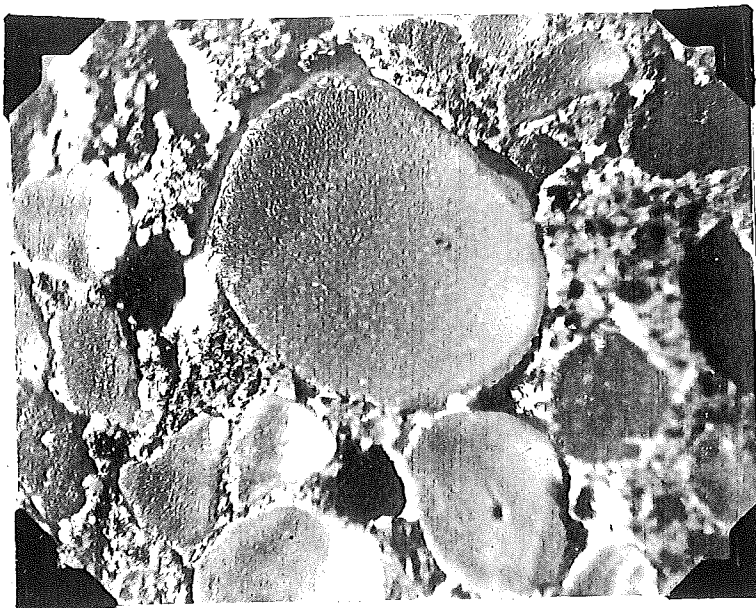

Figure 10.   Condition of Concrete Plate after 20 days'
             immersion in 12 percent sodium chloride
             solution. Magnification, 40X.

The fact that sodium chloride reacts with lime to form calcium chloride would indicate that the observed breakdown is due in part to the removal of lime from the structure of the set cement. From Figure 11 which gives the solubility of calcium hydroxide in sodium chloride solutions (7), it is apparent that maximum amounts of lime are dissolved when the concentration of salt is slightly under 10 percent. This probably explains the phenomenon observed in our tests that deterioration of specimens was in general more rapid in 12 percent than in saturated salt solutions.
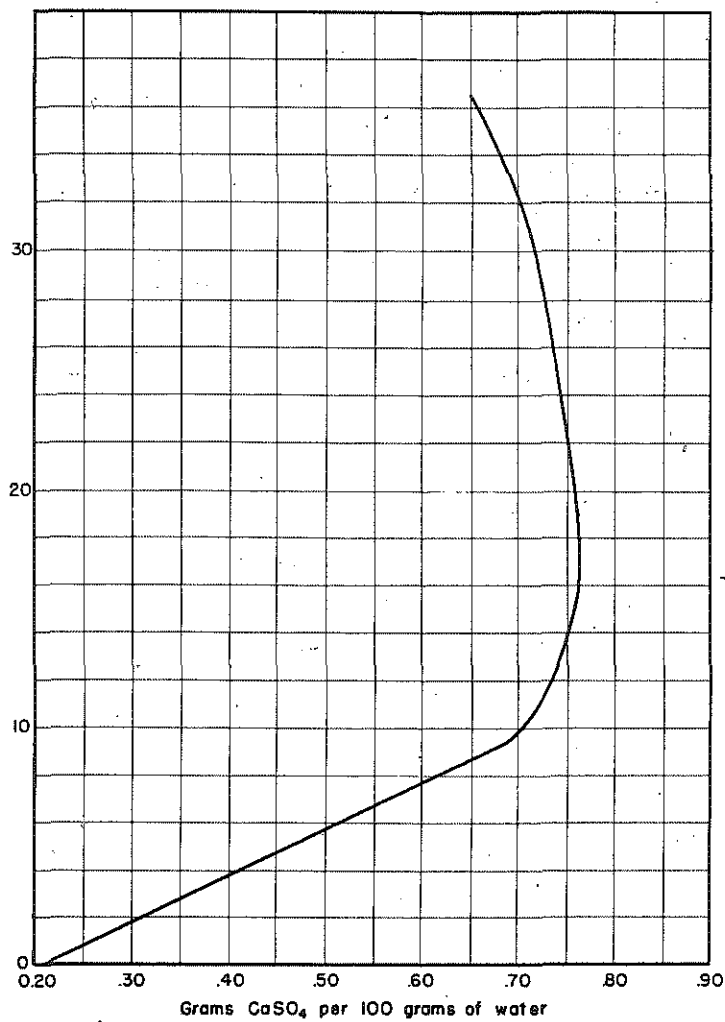
The attack of concrete specimens by sodium chloride solutions is greatly accelerated, however, by freezing and thawing. Referring once more to the equilibrium diagram for sodium chloride solutions in Figure 7 it may be seen that there is a transition point at - 0.15°C. at which anhydrous solid NaCl changes to the dihydrate $NaCl.2H_2O$ in contact with the solution. It is possible that alternate volume changes accompanying this transition contribute to the disrupting effect of freezing and thawing.

Rock Salt: There can be no doubt that the observed difference in the action of solutions of rock salt and the pure sodium chloride, both in the field and laboratory tests, is directly attributable to the calcium sulphate content of the former. Chemical analyses of the two sodium chloride salts given in Table I show that the rock salt contained 1.65 percent of this impurity while the fine salt contained little more than a trace. Although calcium sulphate is ordinarily soluble only to the extent of less than 1/4 percent in plain water, more than three times this amount can be carried in sodium chloride solutions of 10 to 25 percent concentration. The solubility curve of calcium sulphate in sodium chloride solutions is also given in Figure 11. Here, as in the case of calcium hydroxide, we see that maximum solubility occurs at concentrations of sodium chloride considerably less than the saturation values - another fact tending to explain the

Figure 11

Grams NaCl per 100 grams of water

Grams Ca(OH)₂ per 100 grams of water
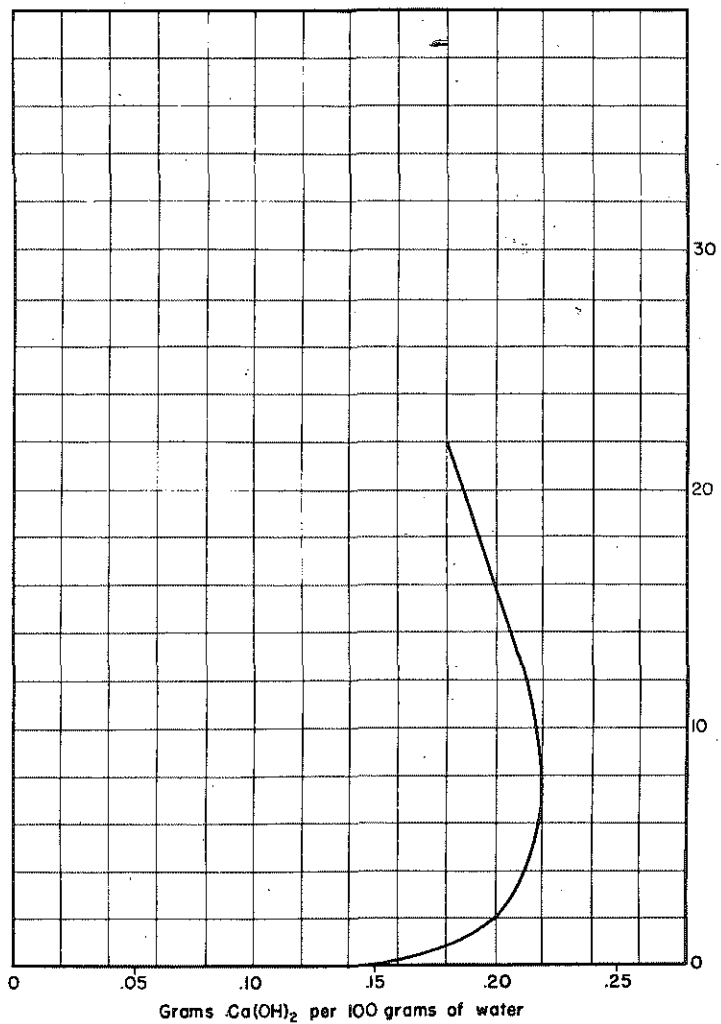
SOLUBILITY OF CALCIUM HYDROXIDE IN SOLUTIONS
OF SODIUM CHLORIDE AT 77°F.

Grams CaSO₄ per 100 grams of water

SOLUBILITY OF CALCIUM SULFATE IN SOLUTIONS
OF SODIUM CHLORIDE AT 78.8°F.

greater activity of 12 percent salt solutions in our laboratory tests.

When set cement is exposed to sulphate solutions, even in concentrations of a few tenths of a percent, calcium sulphoaluminate is formed and a marked expansion occurs which is sufficient to disrupt the mortar or concrete (15) (9). This effect is more pronounced in cements of high calcium aluminate content, and which contain smaller initial amounts of gypsum added as a retarder when the clinker is ground at the mill.

The Age Effect

The statement was made earlier in this report that the most essential requirement of a durable portland cement concrete is a dense, more or less impermeable surface which prohibits the entrance of water and salt solutions. A natural corollary, then, would state that any factor which tends to produce this kind of surface would improve durability. Herein lies the key to the explanation of the effect of age on the salt resistance of concrete pavements. The two most important processes which tend to increase the impermeability and which progress with age are the gradual closure of capillaries and small voids through the continued hydration of cement compounds, and the formation of an impermeable calcium carbonate skin by atmospheric carbonation of calcium hydroxide on the surface.

Effect of Hydration of Cement Compounds: Normal concretes of good quality consistently decrease in permeability with age. It is known that hydration of cement particles continues for years after the concrete is placed, which process is accompanied by an increase in strength and slight lengthening of dimensions. The additional hydrated material produced increases the impermeability of the mass, for it occupies a greater volume than the unhydrated material from which it was formed. Porous aggregates, deficient grading of aggregates, poor curing and all the other defects which produce an intrinsically poor concrete will, of course, vitiate the beneficial effect of this process.
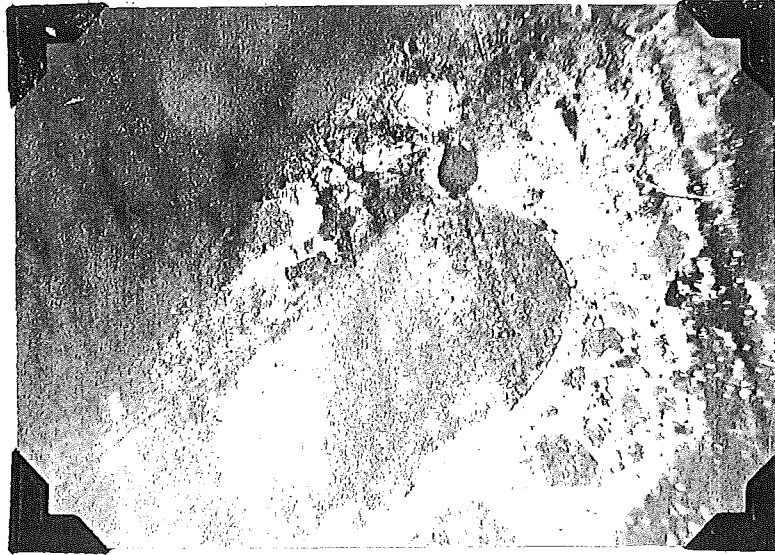
Figure 12. Photomicrograph of the same specimen in
Figure 8B, showing effect of carbonated
surface layer. Note absence of cracks
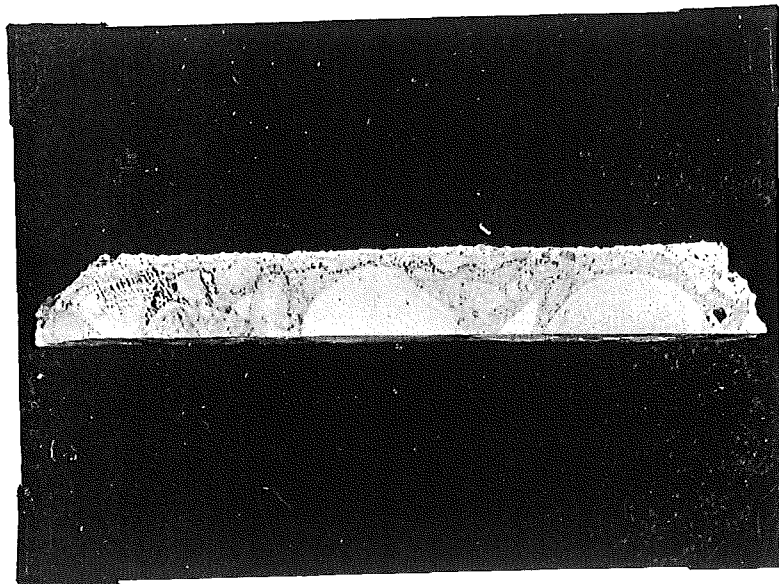at the edge of the specimen. Magnification
40X.

Figure 13. Carbonated layer on the top surface of
concrete pavement core 4 years old. This
layer is visible as a lighter colored band
across the top of the specimen. Photograph
about natural size.

Previous experiments in our laboratory, in which carbonation was accomplished by exposure to an atmosphere of carbon dioxide gas indicated definitely beneficial results from the treatment.

It was thought at first that there might be some relation between the depth of carbonation and the age of the concrete. Samples of concrete were taken from several pavements of different ages and specimens prepared for examination by cutting vertical sections about 1/4 inch thick through the top surface, which were then ground on the faces and stained with phenolphthalein. The carbonated surface was immediately visible as a colorless band in contrast to the brightly colored red of the concrete below, which still contained considerable amounts of basic calcium compounds. This carbonated layer may be seen in the specimen illustrated in Figure 13. Recent determinations of the distribution of calcium hydroxide near the surfaces of concrete cores indicate that partial conversion extends below the colorless margin but the reaction has not progressed sufficiently to neutralize all of the calcium hydroxide present.

The depth to which the carbonation extends in any particular concrete pavement probably depends upon a number of characteristics which are related to its permeability. From the examination of pavements in this manner no correlation was found between age and depth of visible carbonated layer. It should be kept in mind, however, that the permeability of this carbonate skin is not necessarily related to its thickness. The depth of apparent carbonation in samples studied ranged on an average between 1/64 and 1/16 of an inch.

Several other factors usually incident with age, but not involved in chemical or physical changes in the concrete itself, may contribute to increasing immunity of pavements with time. Among these may be mentioned the protective effect of crank case oil drippings, silting of external pores in the concrete, and possibly a sealing action due to traffic.

SUMMARY

The combined results of the field and laboratory studies may be summarized as follows:

1. Aging of normal concrete of good quality is benefical in increasing its resistance to the action of chloride salts used for ice control.

2. For the pavements tested in this investigation, the minimum time necessary to accomplish immunity to salt action was somewhere between four and six years.

3. Concrete of poor quality does not improve in salt resistance with age.

4. The age effect is considered to be due primarily to the gradual continuation of the hydration process in the cement, and to the formation of a strong, impermeable carbonate skin through the reaction of lime compounds in the set cement with atmospheric carbon dioxide. Other external factors, such as the deposition of oil films from crankcase drippings incident with age and associated with traffic conditions, may contribute somewhat to the improved salt resistance of pavements with time.

5. Where scaling occurred, rock salt and calcium chloride were about equal in severity of action, with evaporated fine salt producing a noticeably less effect than either.

6. The observed difference in scaling action of the rock salt and evaporated fine salt is considered to be due to the calcium sulphate content of the former.

7. Calcium chloride has greater ice melting capacity than sodium chloride below 10°F.; above this point the reverse is true.

8. Sodium chloride appears to be more harmful in 12 percent than in saturated solutions; with calcium chloride the destructive effect increases with the concentration

9. The use of raw chloride salts will probably not be as effective on concrete pavements as on the darker bituminous surfaces due to the higher temperatures attained at the surface of the latter from the absorption of radiant heat.

CONCLUSION

Translation of the above facts and conclusions into a definite policy to be followed in using chloride salts for ice control must of necessity be modified by practical and economic considerations. In concluding this report, the effects of some of these factors are considered and recommendations made concerning the revision of present ice control methods.

Practical and Economic Considerations

Because of the fact that sulfates are nearly always present in rock salt in deleterious amounts, it does not seem practicable to limit the sulfate content by specification for obvious economic reasons. Some maintenance men like fine salt better than rock salt. It does not roll on the ice during spreading as rock salt does, and, because of its greater surface area and intimate contact with the ice, acts more quickly. On the other hand, fine salt has not the advantage of the boring action of larger grains, which helps to dislodge ice without complete melting, and larger

amounts of the fine salt would probably have to be used for this reason.
The difference in cost of the two salts is not excessive, the price of
rock salt being around four dollars a ton against six dollars a ton for
fine salt, the latter price f.o.b. St. Louis, Michigan. Both of these
salts are priced considerably below flake calcium chloride which costs
around eighteen dollars a ton.

Weather conditions also play an important part in the determination
of a specific treatment for ice control. Under most circumstances any of
the three salts, rock salt, fine salt, or calcium chloride, could be used
without abrasives for bare pavement maintenance, provided they are used in
sufficient amounts during the period of moderate temperatures which usually
prevail during and immediately after a snow storm. If, however, application
is delayed until the temperature falls again to a point below about 10°F.
it may be difficult or even impossible to melt the ice sufficiently to
eliminate traffic hazards by this method. In such cases the use of abra-
sives with salt would probably have to be resorted to in order to prevent
skidding.

There seems to be no reason why fine salt (sodium chloride) cannot be
substituted for calcium chloride when it is necessary to use sand-chloride
mixtures, except under the most extreme temperature conditions. In the
low temperature range (below 10°F.) there is not a great deal of difference
in the embedding power of the two salts down to the eutectic point of sodium
chloride solutions at - 6.5°F. Differences in cost, not only of the raw
materials but also of the damaging effect on the concrete surface favor the
use of evaporated fine salt instead of calcium chloride with abrasives, at
least in those sections of the state where temperatures no lower than about
0°F are apt to be encountered during ice control operations.

Recommendations

On the basis of the foregoing considerations the following recommendations seem justified:

1. Raw chlorides of all three types, rock salt, fine salt and calcium chloride, may safely be applied to sound and/or unscaled concrete pavements five or more years of age.

2. Use of raw chlorides should be restricted to applications at temperatures above 10°F., and when the temperature is rising.

3. When the temperature is less than 10°F., or when the temperature is falling, sand chloride mixtures should be used.

4. Where temperatures are not expected to fall below 0°F. during and immediately following operations, the use of fine salt (sodium chloride) instead of calcium chloride is recommended.

ACKNOWLEDGEMENT

Acknowledgement is made to E. A. Finney, Assistant Testing and Research Engineer in charge of Research, for many valuable criticisms and suggestions during the progress of the work; to Richard Thurm, Chemical Research Engineer, who performed most of the laboratory tests and aided materially in developing some of the ideas presented herein; and to H. Bentley and A. Smith who carried on the controlled field tests at the test road and vicinity.

Although the field studies utilizing routine ice control methods have not progressed far enough to yield noticeable results at present, the author wishes to express his thanks also to the Maintenance Division and all of the District and County Engineers taking part in this phase of the work for their full and unfailing cooperation at all times.

BIBLIOGRAPHY

1. Anderson, A. A.
      (1942)
   Treated Cement Resists Scaling.
   Explosives Engineer, Jan. 1942, p. 3.

2. Gonnerman, H. P.
   Timms, A. G.
   Taylor, T. G. (1937)
   Effect of Calcium and Sodium Chloride on
   Concrete. American Concrete Institute
   Journal, Nov.-Dec. 1936, Proc. V. 33 p.107

3. Committee on Maintenance,
   Highway Research Board
      (1944)
   Recommended Practice for Treatment of Icy
   Pavements. Wartime Road Problems, No. 9
   Oct. 1944.

4. Engineering News-Record
      (1944)
   Skid Prevention on Highways. Engineering
   News-Record, Nov. 16, 1944, p. 90.

5. Reagel, F. V.
      (1944)
   Air-Entraining Agents not a Cure-all.
   American Concrete Institute Journal.
   June, 1944. V. 15, p. 563.

6. Axon, E. O.
   Willis, T. F.
   Reagel, F. V.
      (1943)
   Effect of Air-Entrapping Portland Cement
   on the Resistance to Freezing and Thawing
   of Concrete Containing Inferior Aggregates.
   American Society Testing Materials. Proc. V
   43, p. 981 (1943).

7, Seidell, Atherton
      (1940)
   Solubilities of Inorganic and Metal
   Organic Compounds. D. Van Nostrand, 1940.

8. Committee on Maintenance
   Highway Research Board
      (1934)
   Report of Committee on Maintenance,
   Highway Research Board. Proc. V. 13 Part I,
   p. 330.

9. Bogue, R. H.
   Lerch, Wm.
   Taylor. W. C.
      (1934)
   Influence of Composition on Volume Constancy
   and Salt Resistance of Portland Cement
   Pastes. Industrial & Engineering Chemistry.
   V. 26, p. 1049 (1934).

10. Platzmann
      (1926)
   Rock Products
   February 6, 1926, p. 78.

11. Lefol
      (1934)
   Compt. Rend. V. 199, p. 1412 (1934).

12. Finney, E. A.
      (1944)
   Microscopic Investigation of Scaled and Un-
   scaled Concrete. Bulletin 101, Michigan
   State College Engineering Experiment Sta-
   tion, East Lansing, Michigan (1944).

13. Moskvin
      (1938)
   Kalii, V. 7, p. 23 (1939).

14. Hundeshagen   Zement. V. 26, p. 103 (1937).
   (1937)

15. Lea, F. M.   The Chemistry of Cement and Concrete.
  Desch, C. H.   Edward Arnold Co., London, 1940.
   (1940)

16. Bessey, G. E.   Effect of Carbon Dioxide on the Strength
   (1933)   of Some Building Materials. Journal
             Society Chemical Industries. Transactions
             V. 52, p. 287 (1933).