AD-A147 812 SALT ACTION ON CONCRETE(U) COLD REGIONS RESEARCH AND ENGINEERING LAB HANOVER NH J M SAYWARD AUG 84 CRREL-SR-84-25 1/1

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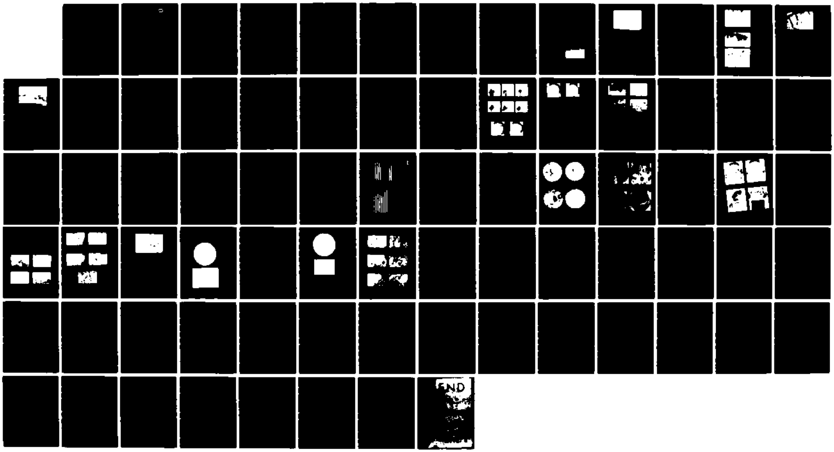

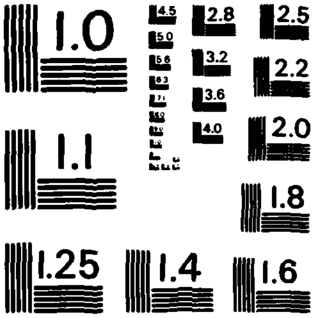

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Special Report 84-25

August 1984

US Army Corps of Engineers
Cold Regions Research &
Engineering Laboratory

Salt action on concrete

John M. Sayward

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REPORT DOCUMENTATION PAGE		**READ INSTRUCTIONS BEFORE COMPLETING FORM**
1. REPORT NUMBER Special Report 84-25	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SALT ACTION ON CONCRETE		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) John M. Sayward		8. CONTRACT OR GRANT NUMBER(s) ILIR 6XX71210, TXX71230, 77XX71243; DACA 89-80-M2117
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Cold Regions Research and Engineering Laboratory Hanover, New Hampshire 03755		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE August 1984
		13. NUMBER OF PAGES 76
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Concrete
Corrosion
Salts

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Serious deterioration of concrete bridges by deicing salts is generally ascribed to depassivation and corrosion of reinforcing steel, as growth of its corrosion products causes spalling. Here, simple evaporative tests simulated the salt weathering that slowly crumbles rocks in nature, where crystals growing from pore water fed from below stress the matrix just as do ice crystals in frost heaving soil. Like needle ice (surface frost action in soil) the salt columns exuded from concrete also lifted tiny particles, signifying crumbling. Microcracks developed in 1-3 years of after-test dry storage. In a four-month

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20. Abstract (cont'd)

simpler repeat test with salt, such cracks developed in all six concretes tested (five dolomitic, one siliceous). The siliceous one developed eye-visible cracks in three-year storage and a visible stone chip in the short repeat test, both with ~~NaCl~~. The siliceous concrete also cracked badly within one week with strong $CaCl_2$ and deteriorated completely in three-year storage. It also cracked badly with dilute ~~$CaCl_2$~~ or ~~$Ca(NO_3)_2$~~ in a few weeks or a year of after-test dry storage. The small or nil exudation in tests with seawater may signify internal reaction plugging pores with insoluble ~~$Mg(OH)_2$~~. This suggests a hypothetical means of control by addition of Mg^{++} to deicers or concrete. Present results suggest that neither corrosion of steel nor the Cl^- ion are requisite in salt action on concrete but that salt-caused microcracks may facilitate access of salt for cracking and also of ~~CO_2~~, oxygen, water and salt for ultimate corrosion effects.

calcium nitrate

calcium chloride

sodium chloride

carbon dioxide

magnesium hydroxide

PREFACE

This report was prepared by John M. Sayward, former Research Chemist, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. The work was done under ILIR 6XX 71 210 and extensions TXX 71 230 and 77 XX 71 243 begun in 1976. This report is a major revision of a 1977 draft and includes later observations and work; it was prepared by Mr. Sayward after his 1980 retirement, under contract DACA 89-80 M2 117. Further details appear in Internal Report 813.

The technical reviewers of this report were David Minsk and Dr. Iskandar Iskandar. The author is grateful to Dr. Jerry Brown for the opportunity to carry out the later efforts and to formalize this publication.

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CONVERSION FACTORS: U.S. CUSTOMARY TO METRIC (SI) UNITS OF MEASUREMENT

These conversion factors include all the significant digits given in the conversion tables in the ASTM Metric Practice Guide (E 380), which has been approved for use by the Department of Defense. Converted values should be rounded to have the same precision as the original (see E 380).

Multiply	By	To get
gallons	3.785412	liters
inches	0.0254*	meters
$\mathrm{lbf/in}^2$(psi)	6894.757	pascals

*Exact

SALT ACTION ON CONCRETE

John M. Sayward

INTRODUCTION

Concrete is a coherent material of good compressive but low tensile strength; embedded reinforcing steel (rebars) increases its usefulness for buildings and bridges. Alkaline components -- $Ca(OH)_2$ and traces of alkali (NaOH) - give concrete a pH of 12.5 to 13. This passivates and protects the steel rebars against corrosion.

As highway construction has expanded, much concrete has gone into pavements and bridges. Increased dependence on the auto has aggravated winter traction problems. In recent decades it had seemed logical and expedient, as a control measure, to apply salts (NaCl and/or $CaCl_2$) to melt snow and ice on roads. Though messy at times (and occasionally hazardous), this has given bare pavements most of the winter, notwithstanding some undesirable effects on vehicle corrosion,* water and air quality and roadside vegetation.

An unanticipated result of using deicing salts is that they can seriously deteriorate public highway property (Fig. 1). The extensive need for bridge work in 1977 (Hillansbrand 1977) has further increased (NCHRP 1982); 40% of the 600,000 bridges in the U.S. were in need of extensive repair or replacement, at an estimated cost of $47 billion. Deterioration of highways likely exceeds the value of new construction (Jones 1977). While increasing traffic density and vehicle loads are

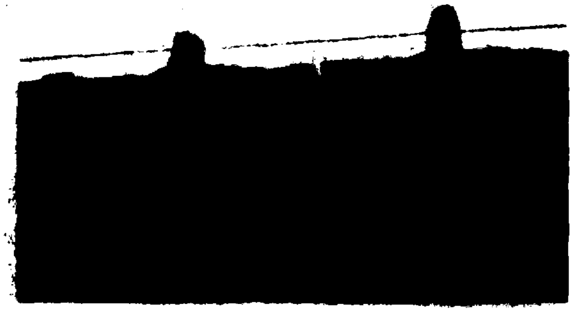

Figure 1. Salt damage on the Ompompanoosuc River bridge, U.S. Route 5, north of Norwich, Vermont, 1980.

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*In 1976 the cost of vehicle corrosion nationally was estimated to be $2 billion annually (Ahlborn and Poehlman 1976).

Figure 2. Salt damage on the Central Vermont Railway station, Randolph, Vermont, 1976. Salting of the platform had ended with train service in 1966.

also factors, deicing salts, and in some cases marine salts, are much involved in this deterioration.

Corrosive effects were blamed when rusty discoloration of affected concrete and corrosion of rebars accompanied salt-induced deterioration of concrete. Corrosion results from galvanic action as salt, water, CO_2 and oxygen diffuse to the steel. The CO_2 lowers the pH enough (to 11.5) to depassivate the steel (Neville 1973), and the iron corrodes. This results in oxygenated products such as goethite [FeO(OH)], magnetite (Fe_3O_4) and hematite (Fe_2O_3). As these develop, the mass of the solid may increase some two-fold, and its volume some four-fold (even up to 13-fold for some more complex, hydrous products). As these grow, internal pressures exceed concrete's low tensile strength. Cracking and spalling result, exposing the rebars and accelerating the process. Eventually corrosion weakens the steel itself, but the trafficability of bridge decks suffers much sooner.

These effects are conspicuous, troublesome, dangerous and expensive. They have slowed traffic, necessitated early repair or replacement, and overburdened public budgets. They have also overshadowed other mechanisms, though highway experts are beginning to recognize attack unrelated to rebar corrosion (Stevens 1977). Concrete and masonry may become "punky" from salt and freeze-thaw cycles even with no steel involved (Fig. 2). Freeze-thaw cycles with salt are far worse on concrete than either alone, as Williams and Robinson (1981) pointed out for sandstone. Salt also aggravates winter cracking of bituminous concrete.* Fookes and French (1977) have reported on salt damage to bituminous roads in the Middle East.

Much effort and money have gone for repairs and research on salt damage. Cordon (1966) and Idorn (1969) did some of numerous studies. As for freeze-thaw alone, air entrainment appears to help (Bergstrom 1959, Franklin 1967, Neville 1973); the myriads of tiny air bubbles help take up the expansion of growing ice crystals and corrosion products (Steiger and Hurd 1980). However, this benefits only newer and more carefully built structures, and some consider it less favorably (Axon et al. 1969). Cathodic protection (Vrāble 1977, Ellis and Colson 1980, Whiting and Stark 1981, and others) shows some promise but also only for new or extensively retrofitted units, and it is costly. In some areas, bridges are hosed with water in spring to mitigate salt effects, but its value is limited if not dubious. Linseed oil may be applied every two or three years. Other coatings or penetrants are being considered (Pfeifer and Scali 1982). Except for air entrainment, which is not the full answer (Powers 1956, Axon et al. 1969), all entail extra effort and expense.

In seeking another mechanism for salt action on concrete, let's look at a phenomenon familiar to CRREL. Roads are heaved and building foundations disrupted (Figs. 3 and 4) by crystals growing in a porous material, i.e. by frost action in soils (Beskow 1935). Its mechanism and control concern many technologists at CRREL and elsewhere. While the familiar 9% volume expansion of water upon freezing can burst closed vessels and pipes, this is not the cause of frost heaving in soil, nor of frost damage to concrete (Litvan 1976).

As cold penetrates soil, ice crystals form in larger pores, while capillary forces keep soil moisture unfrozen in adjoining finer pores. These crystals grow, drawing water from surrounding pores and from warmer soil below. They grow to form finite "lenses" of ice, of microscopic size to many centimeters thick, heaving the soil accordingly. At the surface this process forms columns called needle ice (Fig. 5), which may lift particles or layers of soil and surface debris. This growth of crystalline ice develops pressure

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*Personal communication, Frederick M. Boyce, Materials and Research Engineer, Maine Department of Transportation, Bangor (1976).

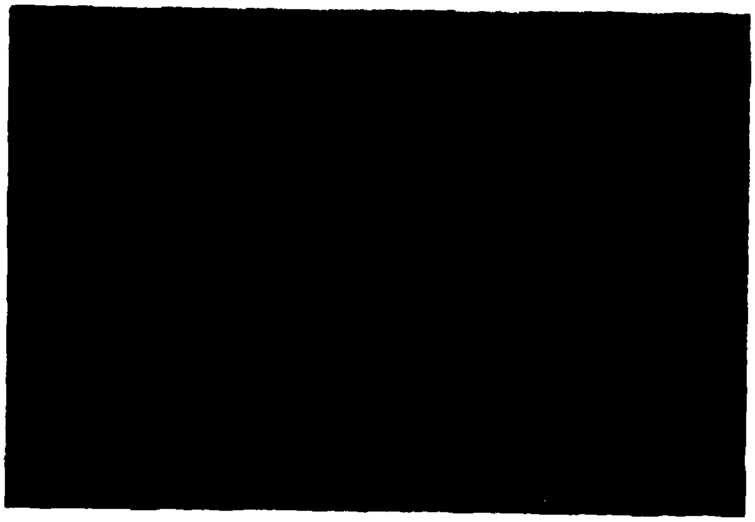


Figure 3. Frost-heaved schoolhouse steps, Nome, Alaska.

Figure 4. Frost-heaved piles of bridge approach, Nome, Alaska.

Figure 5. Needle ice from a leaf-covered, moist forest floor, Braintree, Vermont, 1980. Note the ground debris lifted by the growing ice.

Figure 6. Seashore rocks pitted by salt and waterborne sand erosion, Sachuest Point, Middletown, Rhode Island, 1980. Note the dime for scale.

-- theoretical calculations give hundreds of atmospheres (Hoekstra 1969), and up to 100 atm has been measured (Radd and Oertle 1966, 1968).

Wellman and Wilson's (1965) paper on salt weathering, which they considered a neglected erosive agent of desert and seashore rocks (Fig. 6), drew our attention to a mechanism clearly analogous to frost action. Logically it must also occur in salt action on concrete, where it has also been neglected. The concepts involved in salt weathering, frost action and crystallization pressure in porous matrices and their applicability to salt effects on concrete are further discussed in Appendix A.

This report considers related literature and the results of a preliminary laboratory investigation at CRREL, begun in 1976, aimed at demonstrating salt effects on concrete. Concrete specimens were partially immersed in salt solution. Impinging air flow enhanced evaporation and transpiration and the movement of solute toward the surface. The original tests were only for four months and at room temperature. Nevertheless, observations then, and also one to three years later, when specimens had dried up in storage, showed significantly:

1) Exudation of tiny crystalline salt columns very reminiscent of needle ice (Fig. 7).
2) Physical attack (erosion) by salt on concrete even in the absence of steel.

Figure 7. Lab-grown needle ice, 1964. Note the soil particles lifted by the growing ice columns.

3) Two special effects:

a) one highly destructive for a certain concrete-salt combination.

b) another for a certain salt composition that may lead to means of mitigating detrimental salt effects.

4) Salt action on concrete resembling that known as salt weathering in rocks and reminiscent of frost action and needle ice in soil, i.e. also involving the crystallization pressure of growing crystals.

These relationships are logical and warrant further investigation.

EXPERIMENTAL

Materials

Concrete. Concrete samples were obtained from the Concrete Division, U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, through Bryant Mather, Chief. All were experimental; their properties appear in Table 1. They came as 3-in.-diameter cores: four each cut from 4-in.-thick rectangular pieces of A, B, C, D and E, and two 18-in.-long pieces cut from larger cores of F.

Solutions. Six solution compositions were chosen (Table 2). The solids of the first four are used in deicing. The others represent marine salt-

Table 1. Concrete properties.

No.								Durability Factor	Cycles to Dilation
CRREL	WES	W/C	C/A	Air (vol. %)	Density (lb/ft^3)	Slump (in.)	Strength (psi)	(DF)	
Mortars									
A	7M3	0.4	0.46	2.5	133	3.8	9320	9	7
B	1M3	0.4	0.39	9.5	147	3.8	6120	85	10
C	10M3	0.6	0.22	8.6	130	3.2	3440	82	10
D	2M3	0.8	0.16	8.6	132	3.5	1920	67	10
Concretes									
E	1C3	0.5	0.33	5.7	143	2.5	4120	76	10
F	(5D)	0.38	0.30	3.0	143	3.0	4980	-	-

W/C = water/cement ratio
C/A = cement/aggregate ratio
Air = entrained air
DF = durability factor from rapid freeze-thaw cycling
Cycles to dilation = cycles of slow freeze-thaw before dilation
(10 is maximum)
Slump = slump test on fresh concrete
Strength = compressive, at 28 days

A,B,C,D,E are all considered frost resistant (even for low DF).

Mix details on file at WES.

A,B,C,D (4-in.-thick lab samples for freeze-thaw tests)
Cement: Type II, low-alkali, Portland cement, Lonestar Co.
Fines: Crushed dolomitic limestone, CRD-MS-17(9)
Air entraining agent: Neutralized Vinsol resin

E (4-in.-thick lab sample for freeze-thaw tests)
Cement: Type II, low alkali, Portland cement, Lonestar Co.
Fines: Limestone
Coarse: Dolomite, 3/4 in. (1.9 cm)
Air entraining agent: Neutralized Vinsol resin

F (18-in. experimental airfield pavement at WES, 1973 --
Soil Stabilization Test Program -- Rigid Pavement Section, Item 5D)

Cement: Type I (?)
Fines: Presumably common sand (siliceous)
Coarse: "Chert gravel" -- siliceous but considered "non-reactive," from and commonly used in Vicksburg, Mississippi area, rounded stones.
Air entraining agent: Vinsol resin (usage too low for desired 5% air)

Table 2. Solution properties.

Solution			Satn.	g per 100 g H_2O	% solute	Density (g/mL)	g/L soln.	M	FP (°C)	Mol solute / Mol H_2O
No.	Solute	Concn.								
1	NaCl	low	0.1	3.6	3.5	1.025	36	0.6	-2.36	0.011
2	NaCl	high	0.6	21.6	17.8	1.132	202	3.4	-13.6	0.067
3	$CaCl_2$	low	0.1	7.5	6.9	1.058	65	0.6	-3.15	0.012
4	$CaCl_2$	high	0.6	44.7	30.9	~1.30	~292	2.6	-14.5*	0.073
5	Urea	low	0.1	10.4	9.4	1.026	89	1.5	-2.8*	0.031
6	Urea	high	0.6	62.4	38.4	~1.1	~349	~5.8	-10.8*	0.186
7	3 NaCl/ 1 $CaCl_2$ Mix	low	0.1	4.2	4.0	~1.03	~39	~0.6	-2.2*	0.011
8	Seawater	low	-	3.56	3.44	1.026	33.5	~0.52	-1.85	0.0094
9	Na_2SO_4	low	0.1	1.94	1.90	1.017	19	0.1	-0.44	0.0025
10	$Ca(NO_3)_2$	low	0.1	12.9	11.4	1.088	105	1.0	-5.6*	0.014

Satn. = fraction of saturation (i.e. of solubility at 20°C)
~ = approximate

Density g/L solution M = molarity (g mols/L) FP = freezing point	All interpolated from handbook tables, except *FP estimated from molecular (ionic) FP depression of 1.86°C

Molecular weights (ions per molecule)

NaCl	58.5(2)	Mix	~ 71.5 avg (~2.15)
$CaCl_2$	111.0(3)	Seawater	~ 75 avg (~2.12)
Urea	60.0(-)	Na_2SO_4	142 (3)
		$Ca(NO_3)_2$	104.1 (3)

water, a salt found in natural ground water, and a highly soluble salt containing no chloride. The composition of the seawater appears in Table A2; it was prepared as shown in Table A3.

Concentrations of 0.1 (low) and 0.6 (high) saturation were chosen because field concentrations would vary from very low to saturation in the wet-dry alternation of conditions. Of the solutions used, NaCl low, 3 NaCl/1 $NaCl_2$ and seawater are within the 2-4% range. Verbeck and Klieger (1957) had found this the most detrimental to concrete in freeze-thaw, as later workers have also noted in salt-freezing-weathering experiments on stone (McGreevy 982). The $CaCl_2$ low is not far above and the Na_2SO_4 just below this range; the high solubility of urea and $Ca(NO_3)_2$ made them 4-5 times higher.

Apparatus

Figure 8 shows the simple apparatus for permeation-evaporation, i.e. salt-effect test. Figure 9 depicts the means for preliminary vacuum saturation.

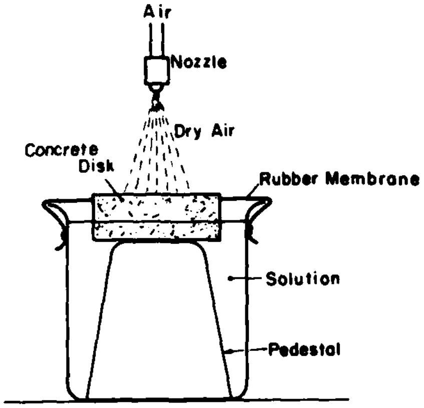


Figure 8. Apparatus for salt action tests on concrete.

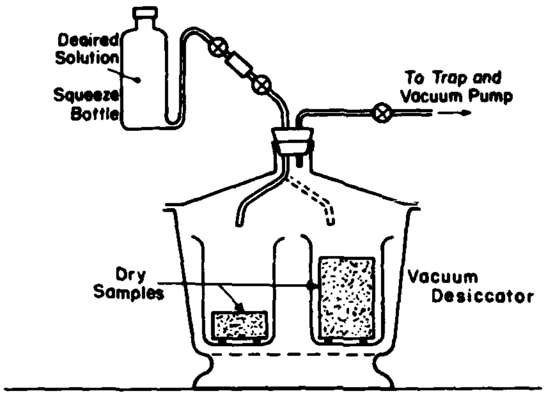
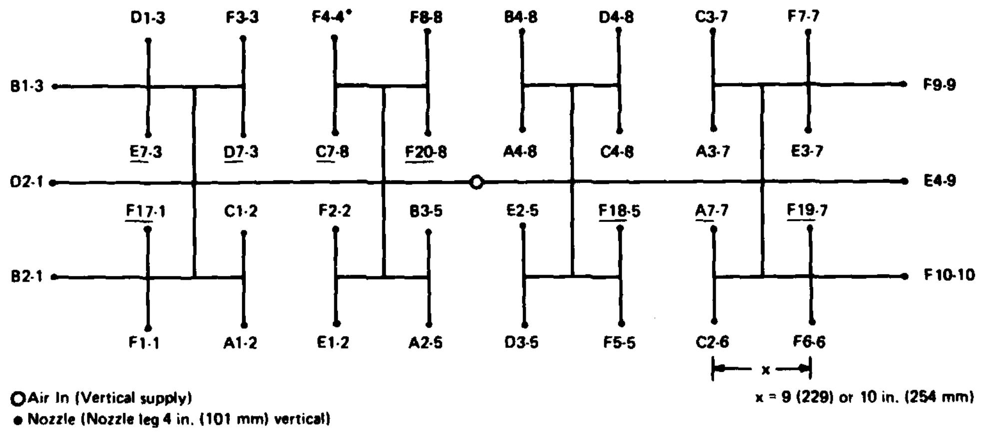


Figure 9. Apparatus for vacuum saturation of concrete disks.

There were 38 stations like Figure 8, each fed evaporative air through an array of pipes (Fig. 10). For the flows, pipe size and balanced configuration used, calculated pressure drops were small and differences negligible, so each nozzle had the same pressure and flow rate within perhaps 10%.

The array was fed by house compressed air (95 psi) through a filter and reducing regulator. The house air was dried over activated alumina to a dew point of -70°C (-94°F), and it carried very little oil.

The nozzles were Hago 60° ES solid cone, rated for 1.0 gal/hr for #2 heating oil at 100 psi. Nozzles were located about 7 cm (2.8 in.) above



○ Air In (Vertical supply)

● Nozzle (Nozzle leg 4 in. (101 mm) vertical)

x = 9 (229) or 10 in. (254 mm)

Key:
A-F = Concrete sample no.
A1-F20 = Individual specimen no.
D1 etc = 1 in. (25.4 mm), E7 etc = 3 in. (76.2 mm) thick
-1 to -10 = Solution no.:

1 = NaCl low
2 = NaCl high
3 = $CaCl_2$ low
4 = $CaCl_2$ high
5 = Urea low
6 = Urea high
7 = 3 NaCl/1 $CaCl_2$ low
8 = Seawater low
9 = Na_2SO_4 low
10 = $Ca(NO_3)_2$ low

*E5-4 after F4-4 cracked.

Figure 10. Test array.

the concrete disks. The pump for vacuum saturation was an old Cenco Hyvac Pressovac, now able to develop only about 2.5 mm.

The equipment was in a basement room where the temperature is normally about 20-22°C (68-72°F). While air conditioning may have controlled temperature and removed some humidity, the latter was not controlled and was evidently higher on rainy days and in summer (the main operation ran from late May to late September).

Procedure

The concrete cores were cut into disks. For A, B, C, D and E, six were 1 in. thick and two were 3 in. thick; for F, 16 were 1 in. thick and five were 3 in. thick. The disks were smoothed somewhat by wet rubbing on a coarse carborundum filter stone. This worked fairly well on the mortars (A, B, C, D), less so on the dolomitic aggregate (E), and ineffectively on the cherty aggregate (F).

Silicone RTV rubber was applied around the upper 1 in. of each specimen to prevent side evaporation and creep of solution. Peripheral tick marks at the specimen number and opposite enabled orienting a transparent protractor with 1-cm-spaced concentric circles for locating features by circular coordinates. Tests were designated A1-2, C2-6, E3-7, F18-5, etc., indicating concrete, disk and solution numbers, with underlining indicating the 3-in.-thick disks. The combinations shown in Table 3 were chosen for the 38 stations available.

Table 3. Concrete-solution pairings.

Solution			Concrete Samples	
No.	Solute	Concentration	1 in.	3 in.
1	NaCl	low	B D E	F
2		high	A C E F	
3	$CaCl_2$	low	B D F	D E
4		high	F (E F)*	
5	Urea	low	A B D E F	F
6		high	C F	
7	3 NaCl/1 $CaCl_2$	low	A C E F	A F
8	Seawater	-	A B C D F	C F
9	Na_2SO_4	low	E F	
10	$Ca(NO_3)_2$	low	F	

*Started later after first F disk cracked.

All specimens were dried at 100-105°C for a week or more. For vacuum saturation, two to four disks at a time were removed from the oven during the next week. The warm disks were placed in 600-mL beakers in the dessicator to cool, and the vacuum was started. After the first set, cooling was aided by placing the dessicator in a deep tray of ice and water.

Meanwhile, the appropriate solution was heated to just above 100°C (to expel dissolved air) and poured brimful into a 250-mL plastic squeeze bottle, which was then quickly closed free of air. Two or three bottles were thus filled with a given solution. When cool, these were attached one at a time to the dessicator, avoiding occlusion of air.

After 1-1.5 hours of cooling the dessicator was isolated from the pump. With the rotatable inlet tube over a specimen beaker, when clamps were opened, the vacuum drew in the air-free solution, collapsing the squeeze bottle. The specimens bubbled considerably as adsorbed air was displaced. Rotation of addition among the several specimens allowed more gradual immersion of each. Pressure went up appreciably, owing to displaced air and solution vapor pressure.

Bubble release had nearly stopped after 1-1.5 hours. The immersed disks were then mounted as shown in Figure 8, avoiding trapping of air beneath. With the solution level adjusted to 2-3 mm below the beaker spout, the annular space around the disk was closed with rubber film (dental "rubber dam"). Having a hole about 3 cm in diameter, this stretched tightly around the silicone-coated disk and over the beaker top and was held tight by a rubber band to prevent direct evaporation from the solution surface.

Test Operation

A chronology of the test and storage periods appears in Table A4 of the Appendix, to clarify the time-frame.

Period I. By repetition of the above saturation procedure, all tests were in place within one week. Air was not started, however, until all had had at least five days without air flow.

In the initial 5 to 11 days without air, crystal filaments or whiskers grew or exuded from a number of the disks. After being photographed, the 15 having significant exudation were scraped into vials; weights were 170-5200 mg.

During Period I, solution levels needed adjustment two or three times even without air flow. The measured increments permitted rough calculation of the permeation rate in mL/day.

Period II. After Period I scraping, air flow was started at about 360 mL/min to each station. Solids again appeared on many specimens. Photographs were taken midway and at the end of this period. Solution usage was replaced as before.

After 66.3 days, air was stopped, photos taken, and Period II solids scraped from 27 of the 38 disks; the weights were 8-7100 mg. In eight cases (having 700-7100 mg), the scraping was in two portions: easily scraped and remainder.

This time all 38 disk surfaces were swabbed, using 0.17-g squares of absorbent cotten wetted with about 1.5 g of deionized water, and were wiped with a dry one. This was to remove traces of exuded salts left from scraping and also traces of solution and possible erosion product particles for later examination. To show whether permeation rates decreased as time and solids deposits increased, solution usages were segregated into subperiods A and B of 37.8 and 28.5 days for separate calculation of average rates.

Period III. Air flow for Period III was about 630 mL/min per nozzle. Again solids appeared, though generally less than before. Period III was terminated after 52.7 days. After photos, solids were scraped from 19 of the 38 disks; the weights were 10-3000 mg. The surfaces were again swabbed with cotton, this time twice moist, then one dry. Solution increments were again segregated into subperiods A and B, of 27.7 and 20.8 days (period total was 48.5 days for permeation but extended to 52.7 days for exudation). The A/B ratio of 1.33 closely matches the 1.36 of Period II.

Period IV (Storage). The specimens were stored in petri dishes containing the same solutions (except F4-4 and F11-4', which were stored in the test set-up). They were sheltered under inverted beakers, and the petri dishes were kept full of solution for the first five weeks for possible resumption of testing. Some were than rephotographed to show further crystal growth. They were then unattended for about 10 months. The solutions evaporated dry (except that hygroscopicity kept some $CaCl_2$ liquid). Further evidence of salt effects developed in about a year, and more in three years after termination.

Analysis

Analyses were planned -- composition of scraped solids and their insolubles, solution compositions and changes, and possibly the concretes -- but were not done for limitations of help and funds. While Period III was still in progress, eight of the tests from Period II were selected and processed for intended analysis. These paired high exudation and permeation with low, and good concrete with poor, for the same solutions. These permitted some appraisal of solids dislodged from specimens by exudate.

Special later test

After more evidence of cracking and chipping had appeared on test pieces drying up in storage for three years, some even simpler tests were devised. These omitted air flow and evacuation and used petri dishes to hold salt solutions -- three of the same stock solutions prepared originally.

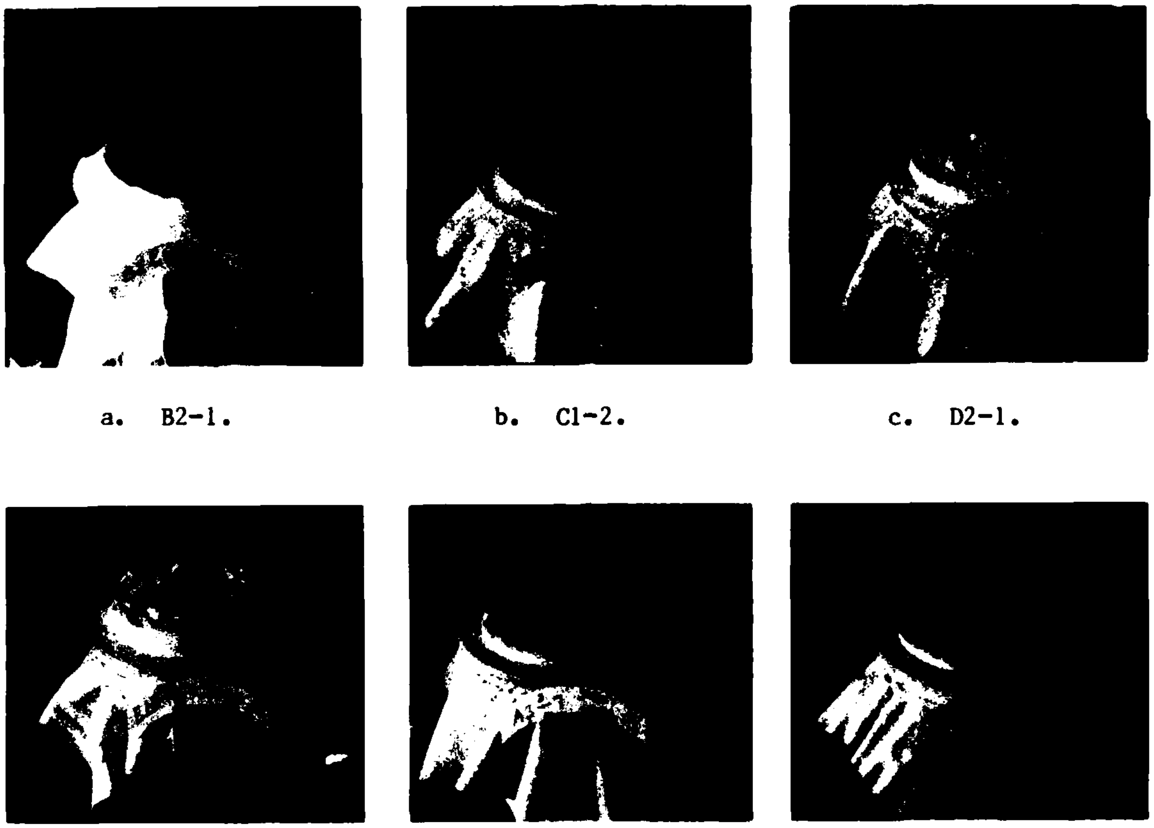
The 13 remaining 1-in. disks had been stored at 105°C for some weeks after the start of the main tests and were then stored in a dessicator for nearly three years. Examination by microscope at X15 revealed that not all were necessarily free of cracks initially; results of the pretest scan for cracks are included in Table 14 along with the solution pairings: six with NaCl low, five with NaCl high, one with 3 NaCl/1 $CaCl_2$, and one with water. The solution level was set at 10 mm; it was adjusted occasionally, but not in the final five weeks. The annular space was sealed with saran wrap. This operation lasted about four months, from late November 1979 to late March 1980, i.e. at low winter humidities.

RESULTS AND DISCUSSION

Visual and photographic observations of exudations and concrete surfaces and evaluation of permeation and exudation and of insolubles in exudates provided the experimental base for this report. Information from the literature is tied in with the results and with the salt-freeze-thaw-concrete interaction in general. A drastic destructive interaction in certain circumstances and a hypothetical countermeasure for salt action, deduced from other results, are discussed. Background and supplemental material appear in Appendix A.

Visual observations

Permeation, exudation, cracking, chipping and particle lifting are described in the following sections. Solid crystalline exudations had many forms: almost imperceptible hair-like fuzz, silky thread-like filaments or whiskers, uniform "grassy" white cover, thinly scattered or localized, straight, curved or curly, widely varying filament diameter and height, single or multiple filaments, plant-like clusters of columns, chunky or platy, fused crust and filaments patterned around stones. The photographs of Figures 11 and 12 are typical. Presumably the filaments may represent



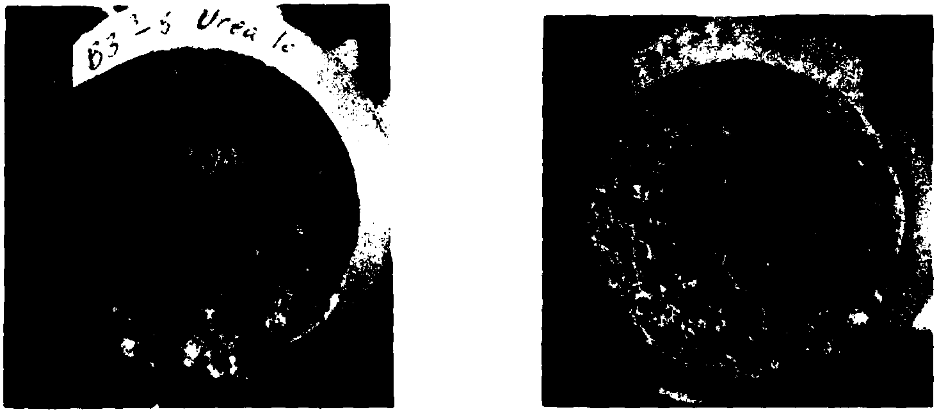
a. B2-1. b. C1-2. c. D2-1.

d. F18-5. e. A3-7. f. E3-7.

Figure 11. Typical crystal exudations, Period II (38 days).

a. E1-2. b. F2-2.

Figure 12. Typical crystal exudations, Period II (66 days).



c. B3-5.   d. D4-8.

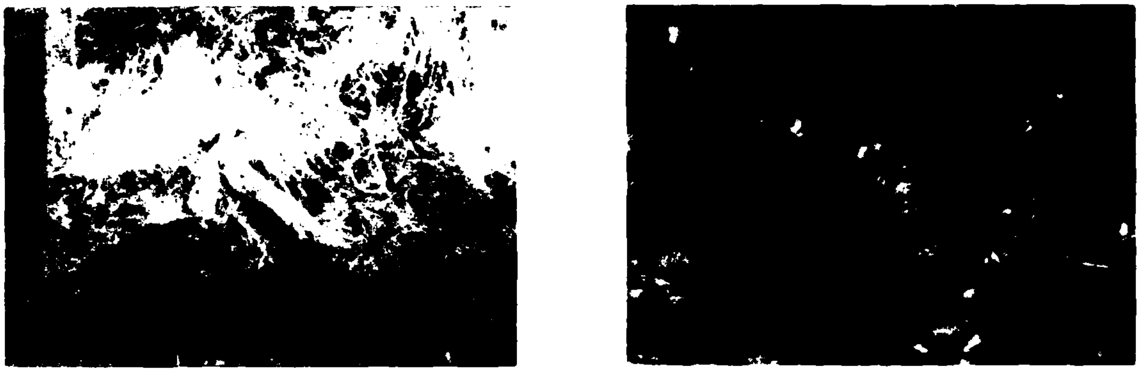
Figure 12 (cont'd). Typical crystal exudations, Period II (66 days).

the size of the pores from which they grow. However, in the special later tests on these same concretes, with salt and no air flow, the filamentous exudations were finer and more thinly scattered. [Crumpton and Jayaprakash recently found salt fibers that were much larger than the concrete pores from which they grew (Civil Engineering - ASCE 1982).] Perhaps diameter depends on rate of growth.

Some exudates were more chunky and scattered, and some formed an incomplete crust. These may represent more profuse permeation of solution through certain larger or interconnecting pores. Another possibility is that, upon increased ambient humidity and decreased evaporation rate, undersaturated solution may have reached the surface, partially redissolving and "fusing" the previous growth.

The filamentous and cluster growths were best examined by hand lens or low-power stereomicroscope; Figure 13 shows some examples. These are very reminiscent of the larger-scale forms seen in frost action "needle ice," particularly in laboratory studies at CRREL (Sayward 1966, 1979). Figures 5 and 7 show field and lab-grown needle ice. Similar salt crystal whiskers were observed when moisture was evaporated from concrete made with seawater for the Navy in World War II (Griffin and Henry 1961, Henry and Kurtz 1963), as well as recently by Crumpton and Jayaprakash (Civil Engineering - ASCE 1982).

The mechanism of salt filament growth must be similar to that of frost action needle ice. In either case a liquid capable of forming crystals (by evaporation or by cooling) diffuses via liquid-like layers in a porous medium in which capillarity inhibits crystallization in the finer pores. This feeds



a. C1-2 (x6). b. A2-5 (x6).

c. F5-5 (x6). d. D1-3 (x6).

Figure 13. Typical crystal exudations after the disks had dried for one year (September 1977).

crystals that have been able to nucleate at the surface or in larger pores or cavities near the surface, producing the observed growths.

Often the exudate was somewhat patterned, suggesting varying permeability or the effect of grains of aggregate. On stones, crystals were often absent, sparse or only around the periphery. In a few instances, notably concrete with NaCl or 3 NaCl/1 $CaCl_2$, white solid exudate showed only as a narrow band around stones, indicating the stone/mortar interface to be a preferred passage, as has been suggested by others. The myriads of filaments seem to rule out the existence of only a limited number of through passages, as some authorities have postulated.

Solid exudates were absent where the solution was $CaCl_2$ or $Ca(NO_3)_2$. These were evidently too hygroscopic-deliquescent to dry out and crystallize, at least at the somewhat humid conditions during this work (May-September).*

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* See December test under <u>Drastic cracking</u> below.

Their concrete surface looked damp to wet, and sometimes even seemed to have discrete globules of liquid resting on the surface, as though the latter were hydrophobic; such was also noted on occasion with urea high.

Most of the seven disks exposed to seawater and the two exposed to Na_2SO_4 had little or no solid exudate; they also appeared dry. Of those showing exudate (the lower quality concretes), solids were generally minimal. Perhaps some components may react to clog pores, as discussed later.

Physical changes like erosion were not generally observable in the four-month active test period. Only where there was extensive macrocracking of concrete F with $CaCl_2$ high -- and with $CaCl_2$ low and $Ca(NO_3)_2$ in Period IV (storage) -- did examination show cracking, as discussed later.

After 10 months of drying in Period IV (storage), microscope examination and photography did reveal distinct microcracks in several disks. Also, a few small chips seemed dislodged, and tiny mineral grains were seen lifted by the growing columns, as occurs in needle ice. These and also the insolubles noted upon dissolving exuded solids are indicative of erosion due to salt action.

Permeation

Evaporation at or within the surface induces permeation, the migration of solution into and through the specimens. Tables 4 and 5 show permeation

Table 4. Permeation: Comparing solutions for each concrete.

Concrete	Test	Permeation by periods (mL/day) I	II	III	Solution
A (1")	A2-5	1.45	0.36	0.40	low urea
	A3-7	2.00	0.30	0.24	mix*
	A4-8	2.66	0.18	0.23	seawater
	A1-2	0.94	0.10	0.16	high NaCl
(3")	A7-7	4.60	0.29	0.26	low mix
B (1")	B2-1	3.04	0.28	0.25	low NaCl
	B1-3	2.49	0.37	0.24	$CaCl_2$
	B3-5	2.73	0.39	0.29	urea
	B4-8	2.56	0.27	0.31	seawater
C (1")	C3-7	3.40	0.46	0.33	low mix
	C4-8	2.94	0.51	0.34	seawater
	C1-2	2.18	0.18	0.18	high NaCl
	C2-6	3.26	0.41	-	urea

Table 4. (cont'd). Permeation: Comparing solutions for each concrete.

Concrete	Test	Permeation by periods (mL/day)			Solution
		I	II	III	
(3")	C7-8	8.49	0.48	0.43	low seawater
D (1")	D2-1	5.50	1.04	0.70	low NaCl
	D1-3	3.30	0.54	0.51	$CaCl_2$
	D3-5	3.40	0.63	0.28	urea
	D4-8	4.06	0.75	0.28	seawater
(3")	D7-3	6.32	0.71	0.41	low $CaCl_2$
E (1")	E2-5	2.02	0.52	0.34	low urea
	E3-7	1.97	0.36	0.29	mix
	E4-9	3.29	0.31	0.31	Na_2SO_4
	E1-2	1.11	0.14	0.13	high NaCl
	E5-4'	0.32	-	0.07	$CaCl_2$
(3")	E7-3	2.70	0.36	0.20	low $CaCl_2$
F (1")	F1-1	1.91	0.37	0.35	low NaCl
	F3-3	1.23	0.40	0.31	$CaCl_2$
	F5-5	2.36	0.48	0.40	urea
	F7-7	1.97	0.43	0.40	mix
	F8-8	2.16	0.27	0.17	seawater
	F9-9	1.40	0.43	0.36	$NaSO_4$
	F10-10	1.40	0.29	0.14	$Ca(NO_3)_2$
	F2-2	1.19	0.29	0.08	high NaCl
	F4-4	1.50	-	-	$CaCl_2$
	F6-6	2.80	0.42	-	urea
	F11-4'	2.22	-	-	$CaCl_2$
F (3")	F17-1	6.20	0.33	0.25	low NaCl
	F18-5	3.69	0.40	0.31	urea
	F19-7	3.30	0.48	0.33	mix
	F20-8	4.24	0.34	0.26	seawater

*"Mix" = 3 NaCl/1 $CaCl_2$

NOTE: C2-6 and E6-6 omitted for Period III due to excessive creep of urea high.

F4-4 and F11-4' omitted for Periods II and III because of drastic cracking in Period I, in $CaCl_2$ high.

E5-4' omitted from Period II because started late with F11-4' after F4-4 cracked.

Table 5. Permeation: Comparing concretes for each solution.

Solution		Concrete and test	Permeation by periods (mL/day)		
			I	II	III
NaCl	low	B2-1 (1")	3.04	0.28	0.25
		D2-1	5.50	1.04	0.70
		F1-1	1.91	0.37	0.35
		F17-1 (3")	6.20	0.33	0.25
	high	A1-2 (1")	0.94	0.10	0.16
		C1-2	2.18	0.18	0.19
		E1-2	1.11	0.14	0.13
		F2-2	1.19	0.29	0.08
$CaCl_2$	low	B1-3 (1")	2.49	0.37	0.24
		D1-3	3.30	0.54	0.52
		F3-3	1.23	0.40	0.31
		D7-3 (3")	6.32	0.71	0.41
		E7-3	2.70	0.36	0.20
	high	E5-4' (1")	0.32	-	0.07
		F4-4	1.50	-	-
		F11-4'	2.22	-	-
Urea	low	A2-5 (1")	1.45	0.36	0.40
		B3-5	2.73	0.39	0.29
		D3-5	3.40	0.63	0.28
		E2-5	2.02	0.52	0.34
		F5-5	2.36	0.48	0.40
		F18-5 (3")	3.69	0.40	0.31
	high	C2-6 (1")	3.26	0.41	-
		F6-6	2.80	0.42	-
3 NaCl/	low				
1 $CaCl_2$		A3-7 (1")	2.00	0.30	0.24
		C3-7	3.40	0.46	0.33
		E3-7	1.97	0.36	0.29
		F7-7	1.97	0.43	0.40
		A7-7 (3")	4.60	0.29	0.26
		F19-7	3.30	0.48	0.33
Seawater	low	A4-8 (1")	2.66	0.18	0.23
		B4-8	2.56	0.27	0.35
		C4-8	2.94	0.51	0.34
		D4-8	4.06	0.75	0.28
		F8-8	21.6	0.27	0.17
Seawater	low	C7-8 (3")	8.49	0.48	0.43
		F20-8	4.24	0.34	0.26

Table 5. (cont'd). Permeation: Comparing concretes for each solution.

Solution		Concrete and test	Permeation by periods (mL/day) I	II	III
Na_2SO_4	low	E4-9 (1")	3.29	0.31	0.31
		F9-9	1.40	0.43	0.46
$Ca(NO_3)_2$	low	F10-10 (1")	1.40	0.29	0.14

NOTE: C2-6 and E6-6 omitted for Period III due to excessive creep of urea high.

F4-4 and F11-4' omitted for Periods II and III because of drastic cracking in Period I, in $CaCl_2$ high.

E5-4' omitted from Period II because started late with F11-4' after F4-4 cracked.

rates arranged by concrete and by solution. Average data for each concrete appear in Table 6, combining the different solutions but showing high and low concentrations and 1 and 3 in. disks separately. All are combined in Table 7, where the subperiods are separated.

Permeation rate generally decreased with time, both between and within periods (Table 7). This suggests gradual plugging of pores by deposited crystals. Leakage and excessive creep past the rubber film may explain exceptions. That some permeation rates are higher for Period III vs II or for IIIA vs IIB may also be due to dissolution of plugging crystals at or near the surface by the moist swabbing between these periods, as well as due to the higher air flow rate of Period III.

Permeation data for each concrete appear as bar graphs for each period in Figure 14. Superimposed points and lines show the individual results for each test; the broad bars are averages for 1-in. disks and low concentrations only. Comparing these bar graphs with those in Figure 15 shows how permeation relates to concrete properties. Permeation is inversely related to strength and to C/A (cement/aggregate ratio) but directly related to W/C (water/cement ratio) and to air content (except for B). Permeation is generally inversely related to durability factor and density (except for A).

The apparent direct relation of permeation to air content may bear further study. Air properly entrained is commonly considered to improve resistance to freeze-thaw and salt damage, because air voids absorb expansion forces. However, if entrained air should mean greater permeation, no air may be preferable, using increased density or other means to reduce penetration

Table 6. Permeation: Average rates for each concrete by periods.

	Average permeation rate by periods (mL/day)			
Concrete	I	II	III	Avg.*
1" Disk, low				
A	2.04	0.28	0.29	3,3,3
B	2.70	0.33	0.28	4,4,4
C	3.17	0.48	0.33	2,2,2
D	4.06	0.74	0.44	4,4,4
E	2.43	0.40	0.31	3,3,3
F	1.78	0.38	0.30	7,7,7
1" Disk, high				
A	0.94	0.10	0.16	1,1,1
B				
C	2.72	0.30	0.19	2,2,1
D				
E	0.72	0.14	0.10	2,1,2
F	1.93	0.36	0.08	4,2,1
3" Disk, low				
A	4.60	0.29	0.26	1,1,1
B				
C	8.49	0.48	0.43	1,1,1
D	6.32	0.71	0.41	1,1,1
E	2.70	0.36	0.20	1,1,1
F	4.36	0.39	0.29	4,4,4

*No. in average for each period.

Table 7. Permeation: Average rates for each concrete by subperiods (combining low, high, 1 in. and 3 in.).

Concrete	Average permeation rate by subperiods (mL/day)							No. in
(all tests)	I	IIA	IIB	IIΣ	IIIA	IIIB	IIIΣ	Avg.*
A	2.33	0.28	0.21	0.25	0.26	0.25	0.26	5,5,5
B	2.70	0.39	0.25	0.33	0.28	0.27	0.28	4,4,4
C	4.05	0.46	0.33	0.40	0.32	0.32	0.32	5,4,4
D	4.52	0.87	0.56	0.73	0.43	0.44	0.44	5,5,5
E	1.90	0.36	0.30	0.34	0.24	0.19	0.22	6,5,6
F	2.50	0.42	0.32	0.37	0.29	0.27	0.28	15,13,12

*No. in average for each period.

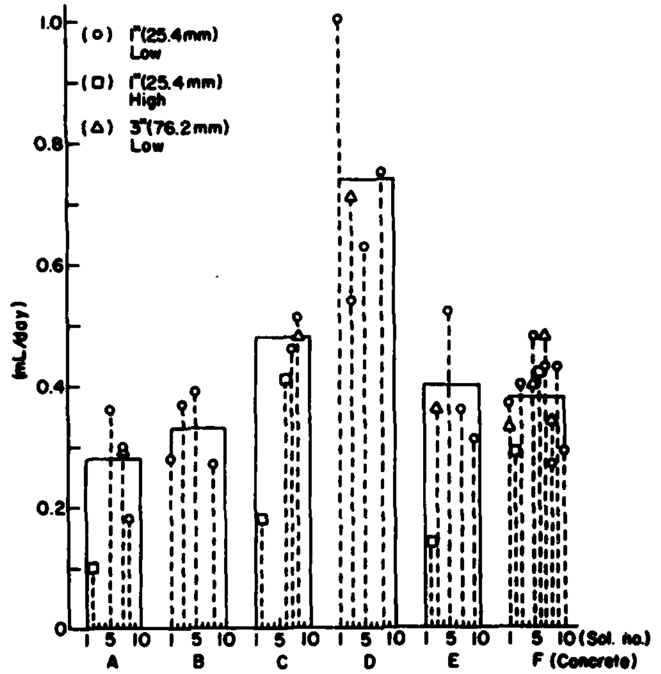


Figure 14. Permeation for Period II. The bars represent averages for the 1-in. disks at low concentration.

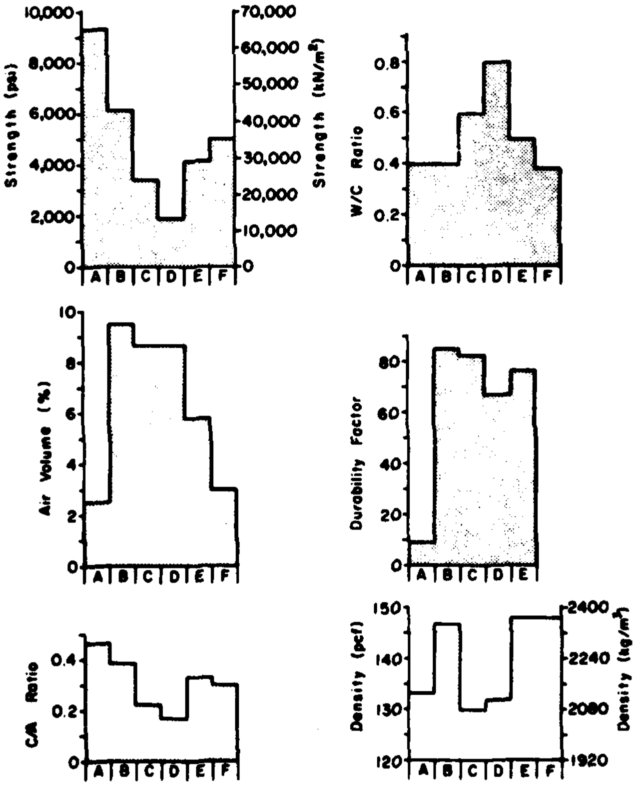


Figure 15. Properties of the concretes.

of salt, as discussed by Schaffer (1932), Snyder (1965), Timms (1968), Stewart and Schaffer (1974), Stratful (1974), Clear and Ormsby (1975), Jenkins and Butler (1975) and Hay (1976).

Exudation

Exudation is the growth of visible crystalline solids, often filamentous, on the concrete surface. Examples of its appearance are shown in Figures 11 and 12. Exudation obviously decreased with time; accumulations did not seem to increase as much in the later weeks of each period, owing no doubt to surface blockage. It is therefore best compared by period totals. Tables 8 and 9 show exudation arranged by concrete and by solution.

Comparing the exudation data with Figure 15 shows that exudation is related to concrete properties much as permeation is. While exudation tends to increase with permeation, the data and plots showed no systematic relation. As is evident in Figure 16, exudation was not general; it apparently depended on concrete, time, conditions and notably solution. With $CaCl_2$ and $Ca(NO_3)_2$, which were hygroscopic-deliquescent at existing conditions, the surfaces merely appeared damp or wet. Of the 31 remaining, 15, 27 and 19 produced scrapable solids in the three periods, or 48, 87 and 61%, respectively.

Most of the remaining non-scrapable tests involved seawater or Na_2SO_4. Of seven seawater tests, scrapables for the three periods occurred on 0, 3 and 2 (0, 43 and 20%), only on the poorer concretes C and D, and also in smaller amounts than NaCl on the same concretes. Likewise, for the two tests on Na_2SO_4, scrapables occurred on 0, 2 (traces) and 0 for the three periods.

The urea solutions generally exhibited much greater exudation and some tendency to creep. This may relate to its physical-chemical properties, as well as to its higher concentration. Thus, lower surface tension would help it wet and penetrate through fine structure more readily, and by its nonionic nature it would be more inert and less attracted to the mineral matrix.

Insolubles in exudates

For intended analysis, the scraped exudate solids for eight Period II cases were dissolved in water, left overnight, and filtered to separate insolubles, small amounts of which were noted in each case (Table 10).

The corresponding damp swabs were stirred and shaken with water to dislodge insolubles from the cotton and to dissolve solubles. After several such rinsings the liquid was filtered twice to separate the trace of insolubles noted in all cases and the turbidity (Table 11).

Table 8. Exudation: Comparing solutions for each concrete.

Concrete	Test	Exudate by periods (mg) I	Δ†	II	Δ†	III	Σ	Solution
A (1")	A2-5	670	+	728	-	340	1,738	low urea
	A3-7	-	+	171	-	-	171	low mix*
	A4-8	-	0	-	0	-	-	low seawater
	A1-2	710	-	47	+	109	866	high NaCl
(3")	A7-7	-	+	278	-	-	278	low mix
B (1")	B2-1	-	+	21	-	-	21	low NaCl
	B3-5	520	-	215	-	-	735	low urea
	B4-8	-	0	-	0	-	-	low seawater
C (1")	C3-7	-	+	316	-	102	418	low mix
	C4-8	-	+	90	+	116	206	low seawater
	C1-2	840	-	522	-	444	1,806	high NaCl
	C2-6	1,980	+	5,916	-	2,571	10,477	high urea
(3")	C7-8	-	+	10	-	-	10	low seawater
D (1")	D2-1	330	+	1,118	-	260	1,708	low NaCl
	D3-5	960	+	1,595	-	86	2,641	low urea
	D4-8	-	+	446	-	24	470	low seawater
E (1")	E2-5	670	+	1,347	-	96	2,455	low urea
	E3-7	-	+	242	-	10	252	low mix
	E4-9	-	+	8	-	-	8	low Na_2SO_4
	E1-2	760	-	335	+	438	1,191	high NaCl
F (1")	F1-1	-	+	89	-	13	102	low NaCl
	F5-5	1,060	-	825	-	215	2,100	low urea
	F7-7	170	-	161	+	181	512	low mix
	F8-8	-	0	-	0	-	-	low seawater
	F9-9	-	+	8	-	-	8	low Na_2SO_4
	F2-2	1,320	-	694	-	195	2,209	high NaCl
	F6-6	5,200	+	7,080	-	2,965	15,245	high urea
(3")	F17-1	-	+	25	-	-	25	low NaCl
	F18-5	770	+	1,294	-	253	2,357	low urea
	F19-7	430	-	174	-	10	614	low mix
	F20-8	-	0	-	0	-	-	low seawater

*"Mix" = 3 NaCl/1 $CaCl_2$

Not tabulated because no exudate due to hygroscopicity:
3 $CaCl_2$ low
4 $CaCl_2$ high
10 $Ca(NO_3)_2$ low

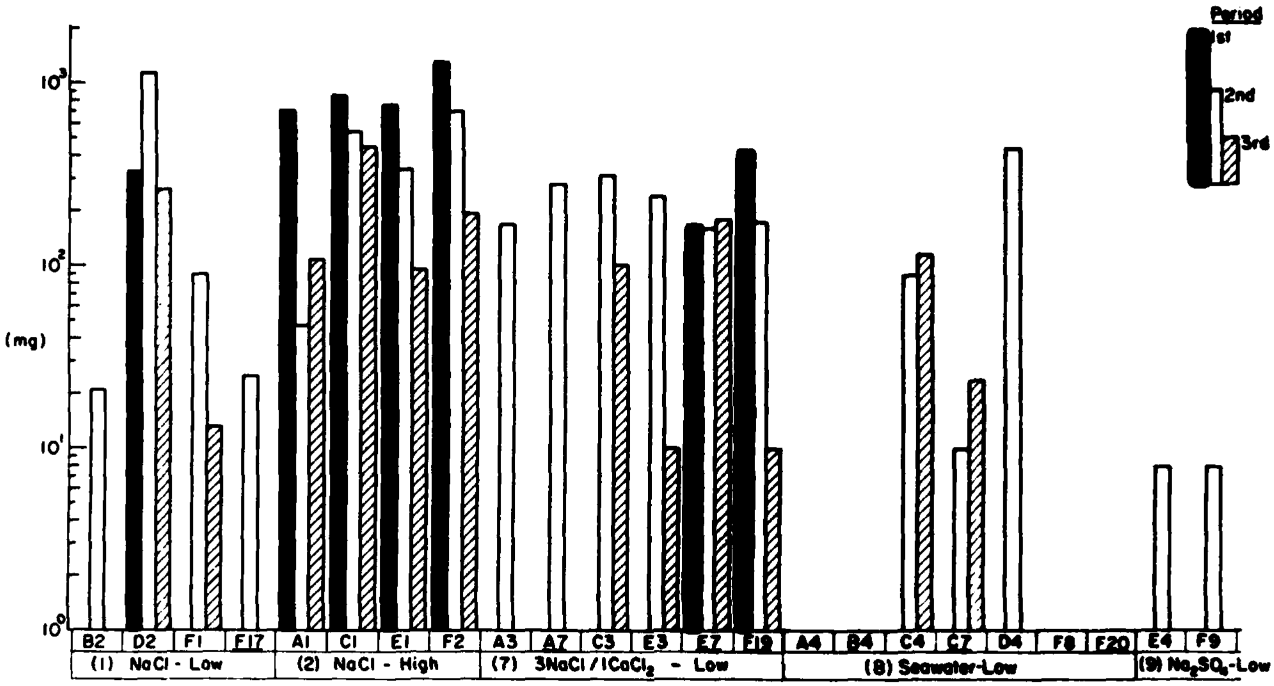
†Sign of change, Period I to II and II to III.

Table 9. Exudation: Comparing concretes for each solution.

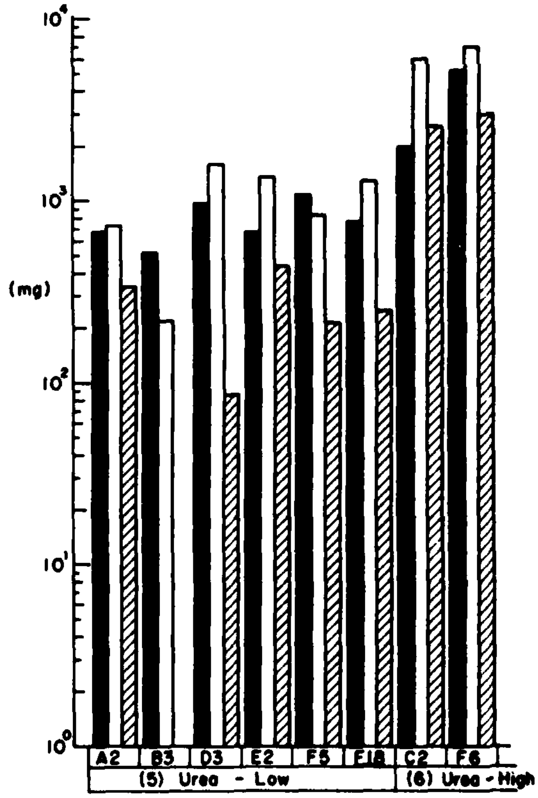
Solution*		Concrete and test	Exudate by periods (mg)			
			I	II	III	Σ
NaCl	low	B2-1 (1")	-	21	-	21
		D2-1	330	1118	260	1,708
		F1-1	-	89	13	102
		F17-1 (3")	-	25	-	25
	high	A1-2 (1")	710	47	109	866
		C1-2	840	522	444	1,806
		E1-2	760	335	96	1,191
		F2-2	1,320	694	195	2,209
Urea	low	A2-5 (1")	670	728	340	1,738
		B3-5	520	215	-	735
		D3-5	960	1595	86	2,641
		E2-5	670	335	438	2,455
		F5-5	1,060	825	215	2,100
		F18-5 (3")	770	1294	293	2,357
	high	C2-6 (1")	1,990	5916	2,571	10,477
		F6-6	5,200	7089	2,965	15,245
3 NaCl/	low					
1 CaCl$_2$		A3-7 (1")	-	171	-	171
		C3-7	-	316	102	418
		E3-7	-	242	10	252
		F7-7	170	161	181	512
		A7-7 (3")	-	278	-	278
		F19-7	430	174	10	614
Seawater	low	A4-8 (1")	-	-	-	-
		B4-8	-	-	-	-
		C4-8	-	90	116	206
		D4-8	-	440	24	470
		F8-8	-	-	-	-
		C7-8 (3")	-	10	-	10
		F20-8	-	-	-	-
Na$_2$SO$_4$		E4-9 (1")	-	8	-	8
		F9-9	-	8	-	8

*Not tabulated because no exudate due to hygroscopicity:

3 CaCl$_2$ (concretes A,D,E,F)
4 CaCl$_2$ (concretes E,F)
10 Ca(NO$_3$)$_2$ (concrete F)



a. Salts.



b. Urea.

Figure 16. Exudation for each solution, concrete and period.

Table 10. Insolubles in exudates.
(Tests selected for possible analysis, Period II).

Solution		Concrete specimen	Exudate, mg		Insolubles on filter appearance (Per. II)
			Period I*	Period II	
NaCl	low	D2-1	330	1118	buff, sandy
		B2-1	0	21	brownish†
Urea	low	D3-5	960	1595	gray-brown, sandy
		B3-5	520	215	gray-brown, sandy†
3 NaCl/	low	C3-7	0	316	gray-brown, sandy
1 $NaCl_2$		F7-7	170	161	lt. brown-gray, sandy
Seawater	low	D4-8	0	446	brown-gray, sandy
		A4-8	0	0	brown-gray, sandy

*Amounts shown for comparison; only Period II processed.
†Amount of insolubles on filter noted as "very slight."

Table 11. Insolubles in exudate swabs (Period II).

Solution		Concrete specimen	Milkiness swirled in water	Particles after filter dry overnight	Turbidity of stirred filtrate
NaCl	low	D2-1	more moderate	slight	slight
		B2-1	moderate	moderate	very slight
Urea	low	D3-5	almost clear	trace	clear
		B3-5	less moderate	very slight	very slight
3 NaCl/	low	C3-7	more moderate	moderate	trace
1 $CaCl_2$		F7-7	slightly more moderate	slight	slight
Seawater	low	D4-8	more moderate	slight-moderate	trace
		A4-8	almost clear	slight	clear

Although the amounts were smaller from the higher-quality concrete B, some insolubles were apparent in all the exudates and swabbings processed. The swabbings were usually slightly off-white; the insolubles were gray-brown or sandy. These are additional evidence of some chipping or fine crumbling of the surface and some lifting of resulting particles by the growing crystal filaments, even in a test period of only ten weeks and at constant temperature.

Cracking

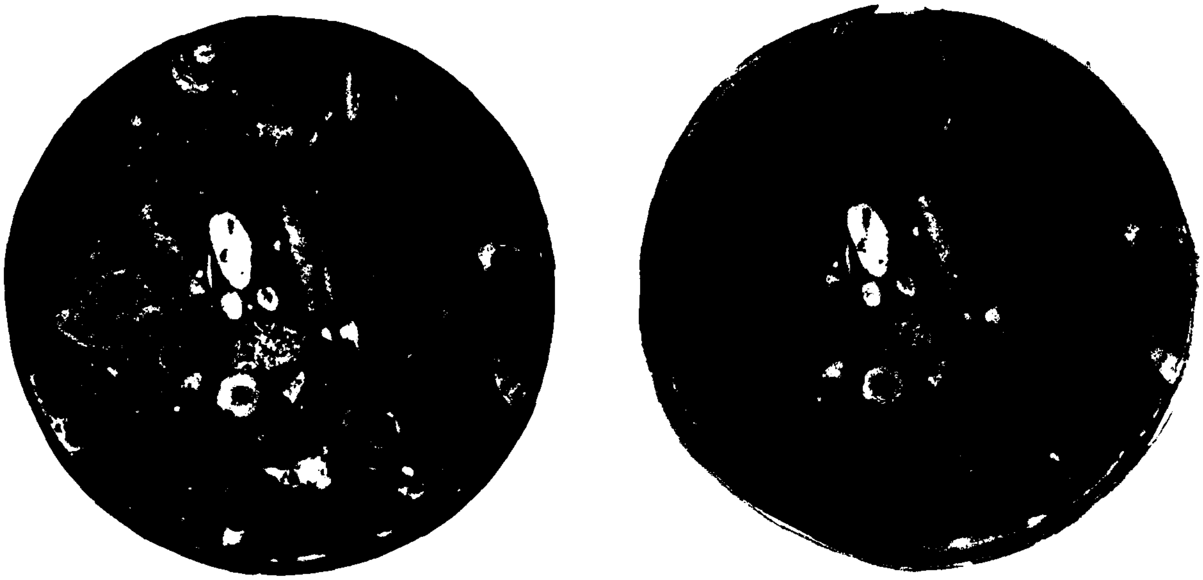
Since salt weathering is a slow, microprocess occurring at pores, visible cracking was hardly expected. Microcracks were observed after the specimens had dried out some months in Period IV (storage). However, very early in the work some major cracking occurred.

Drastic cracking. Within a week of starting the tests, drastic cracking began in one case. By chance, concrete F and $CaCl_2$ high had been paired in the only use of the latter initially, test F4-4. A crack through mortar and stone was noted only eight days after preparation, just as air flow was started for Period II. It showed up on a photo taken the previous day and developed more drastically by the next day. Figure 17 shows it before the test and at 9 days.

When no visible cracking had appeared with other concretes after five weeks, the above test was repeated, using a completely fresh preparation of $CaCl_2$ high (designated 4'). Besides this recheck on F, concrete E was now also exposed to this solution. Disks F11 and E5 had been in the 105° oven about eight weeks before make-up. To duplicate the original treatment the newly prepared tests were held a few days without air flow. Within five days F11-4' had developed cracks around two stones. Further cracking within the next few days shows in Figure 17. E4-4', however, showed no cracking. It was then put in place of F4-4 under air flow for Period III.

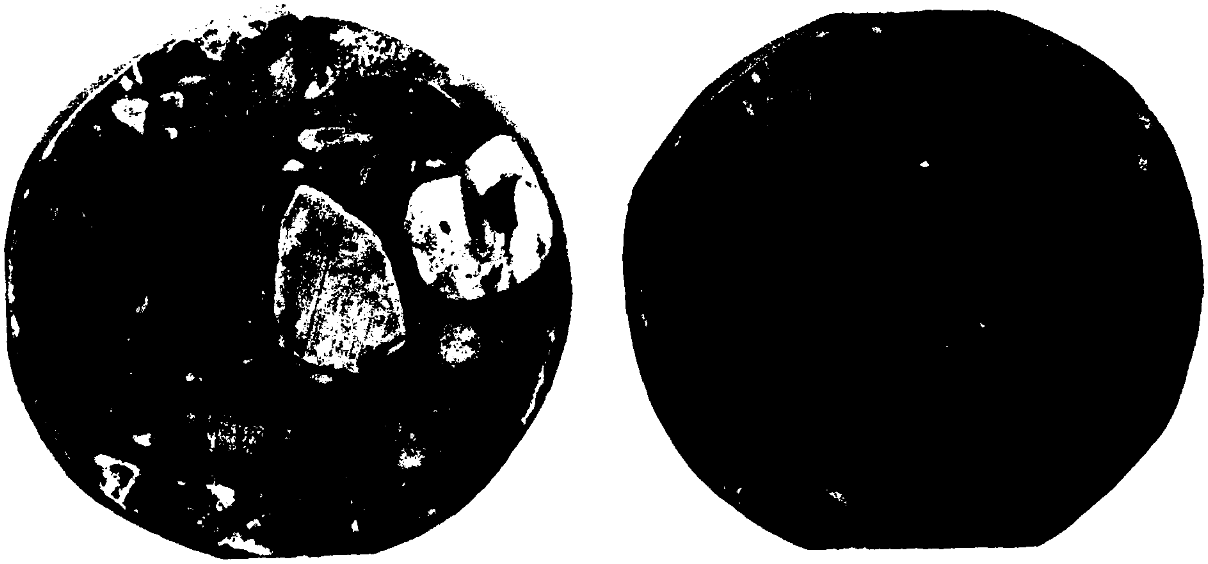
Although intact at first (Fig. 18a), within seven weeks of cessation, in storage Period IV, similar cracking developed in F3-3, $CaCl_2$ low (Fig. 18b). The solution had dried out since the last adjustment (petri dish 2/3 full) three weeks earlier. No others had dried out or cracked at this time. A year later, the dried-out F3-3 disk had not changed further (Fig. 18c).

That the hygroscopic-deliquescent $CaCl_2$ would dry out in one case and not others was surprising. A test made a month later, in December, did show that at the low indoor humidity of cold weather, both $CaCl_2$ and $CaCl_2 \cdot 2H_2O$



a. F4-4 before the test.

b. F4-4 after 9 days



c. F11-4' after 6 days.

d. F11-4' after 11 days.

Figure 17. Drastic and early cracking of concrete F with $CaCl_2$ high.

[illegible]

b. [illegible] after 49 days.

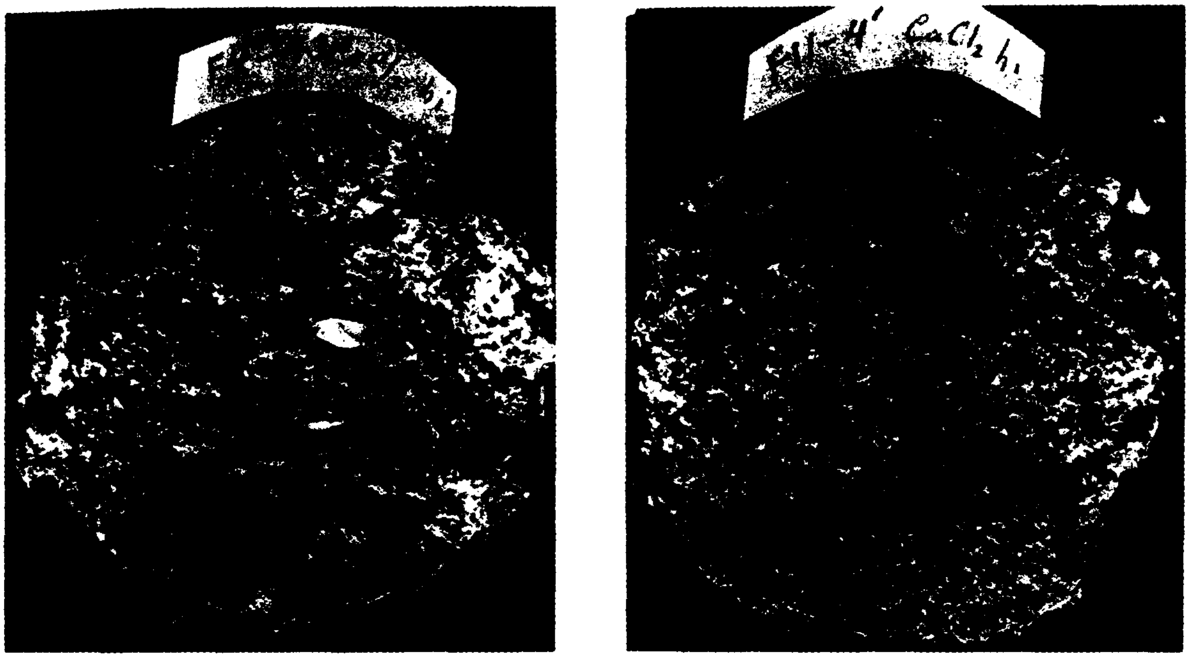
were not deliquescent as in summer; there was only slight crusting on the fine solid in two weeks. Other tests in water solution went in and out of solution, probably as $CaCl_2 \cdot 6H_2O$, as humidity changed with the weather. (An air conditioning failure in October may have allowed higher temperature and lower room humidity and affected F3-3.)

Although apparently intact at 1 and 7 weeks, drastic cracking had also developed in F10-10, $Ca(NO_3)_2$ (Fig. 18d) within a year after suspension of the tests, when the disks had dried out unattended in the petri dishes. Thus, the cracking of F must not depend on the chloride ion. It may be due to the Ca^{++} ion, to the acidity of the salt reacting with the $Ca(OH)_2$ of the cement paste, or to its hygroscopic property and ability to form hydrates [both $CaCl_2$ and $Ca(NO_3)_2$ do so].

In the three-year storage Period IV, disks F4-4 and F11-4' had been left assembled on their beakers (as shown in Fig. 8) rather than in petri dishes. For some time the $CaCl_2$ high solution must have maintained contact and was still at or only slightly below the disks. These solutions were now brown and had buff granular solids at the bottom (probably disintegrated concrete). The disks by September 1979 were considerably more expanded and disintegrated (Fig. 19a and b). When examined two years earlier (fall 1977), they were not much changed from the first two weeks (Fig. 17).

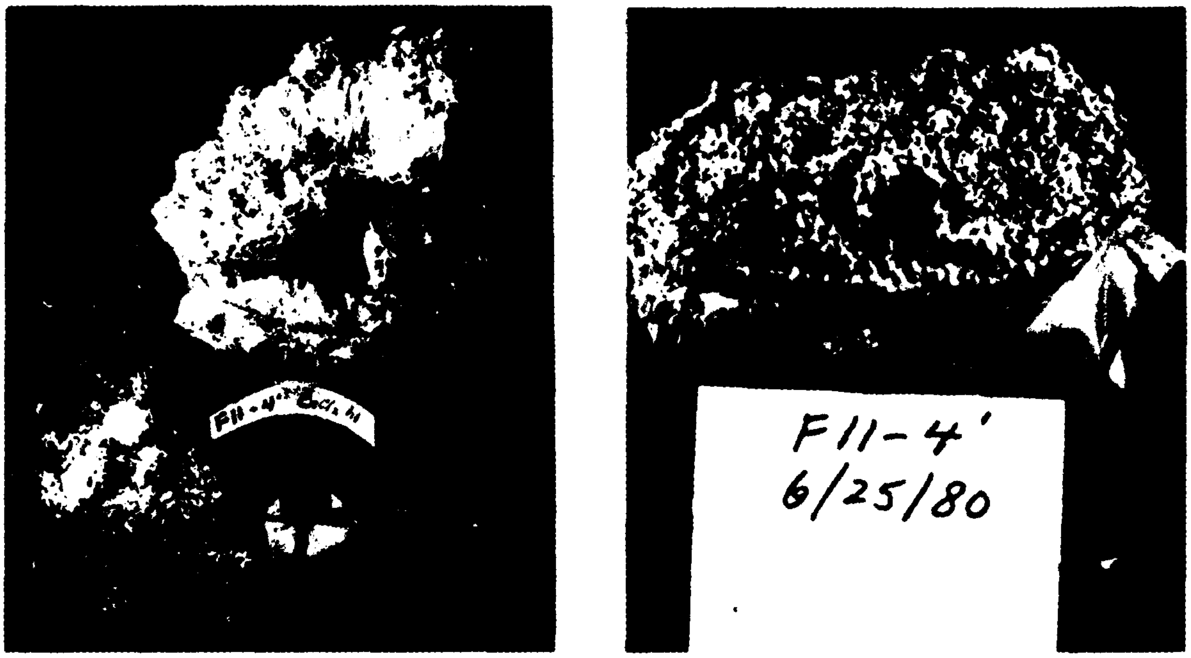
After another four months (February 1980), expansion-disintegration had progressed even more dramatically (Fig. 19c). At the September 1979 viewing (under summer humidity), the mass must have contained considerable solution. Now this must have crystallized (at lower winter humidity), for the granular mass had expanded greatly and was full of fibrous crystals, presumably $CaCl_2 \cdot 6H_2O$. The original concrete had lost its integrity. Upon return of higher humidities in summer (late June 1980), the erupted crystals subsided considerably, revealing some dislodged stones (Fig. 19d).

The cracking of F4-4 and F11-4' and not E5-4' with $CaCl_2$ high, and of F3-3 with $CaCl_2$ low and F10-10 with $Ca(NO_3)_2$ low upon drying in storage, while no cracking occurred in B3-3 or D1-3 in similar treatment, suggests that F has some particular sensitivity. The properties in Table 1 offer no clues. However, F contained a "chert gravel" of the Vicksburg, Mississippi, area. Though siliceous, it is considered "nonreactive" and suitable for concrete, being used in commercial construction there. This specimen had come from an experimental airfield pavement laid down by WES three years earlier; the pavement had been subjected to testing but no air traffic.



a. F4-4 after 3.3 years.

b. F11-4' after 3.2 years.



c. F11-4' after 3.7 years.

d. F11-4' after 4.0 years.

Figure 19. Disintegration of concrete F with CaCl$_2$ high in storage.

One hypothetical explanation of this cracking is that cherty silica has some water in its structure, held to varying degrees of tightness. Some, not removed by a few weeks at 105°C, may be attracted by the hygroscopicity of strong $CaCl_2$, creating stress in the rock and mortar, causing cracking. Also, the acidity of $CaCl_2$ may influence water inbibition (swelling) of the chert. Another factor may be the reported reactivity of $CaCl_2$ (but not NaCl) to concrete (Berman and Chaiken 1972, Browne et al. 1970), although opinions differ on this. Whatever is behind the unique interaction of $CaCl_2$ and $Ca(NO_3)_2$ with concrete F, the ability to form hydrates at test conditions must play a part.

Other factors must also be involved, since E, D and B did not crack as did F in similar exposures to $CaCl_2$, even though D is a poorer-quality mix, and E was of lower strength and greater W/C ratio. Perhaps the alkalinity of the limestone sand and dolomitic aggregate of E conveys resistance. Possibly in the presence of $CaCl_2$ and the $Ca(OH)_2$ of the concrete, solubility, solubility product and common ion effects may allow the $MgCO_3$ of the dolomite to ionize enough to precipitate $CaCO_3$ and $Mg(OH)_2$, both of which are insoluble, and plug pores. Since the sand of B and D (mortars) was dolomitic limestone, this explanation might extend to them, although there still may be something that makes F peculiarly sensitive.

While the exposure here was not exactly what may occur in the field, it leaves one wondering just how good salt, especially $CaCl_2$ with its ability to form several hydrates, may be for concrete. And is the result unique with this particular concrete or aggregate, or is it to be more widely expected? Further investigation is needed.

Cracks, chips and particle lifting. At 10 months after termination, unusual, white, dome-like growths drew attention to F9-9 [Na_2SO_4, now dried up]. The microscope at X20 also revealed a crack extending inward some 1.5 cm.

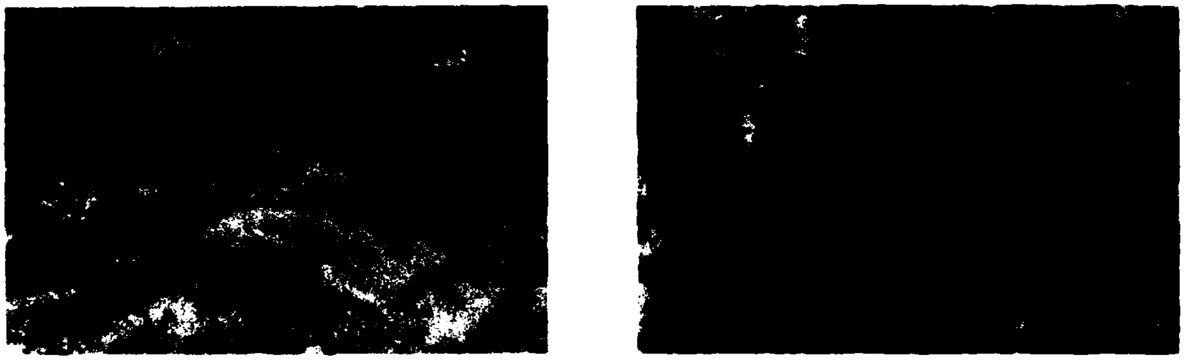
Examination by microscope at termination had been deferred, since crystals and wetness impaired observation and comparison with the initial photos. In the fall of 1977 all disks were re-examined, some at up to X80. There were microcracks in several cases. There were also chips dislodged at the surface on several. Further, tiny, dark grains of mineral had been lifted by salt filaments (much as needle ice columns lift soil grains, Figs. 5

and 7). Table 12 lists these occurrences and their locations. Some representative cracks, chips and particle lifting are shown in Figures 20-22, respectively.

Table 12. Cracks, chips and particle lifting after one year in storage (Fall 1977).

Cracks (microscope)	B2-1, F1-1, C1-2, B1-3, D7-3, B3-5, E3-7, F7-7, C4-8, E4-9, F9-9, F10-10
Chips (microscope)	B2-1, D2-1, F1-1, C1-2, B1-2, E7-3, F9-9
Particles lifted (microscope)	E2-1, C1-2
Drastic cracking* (by eye)	F4-4, F11-4, F3-3, F10-10

*F4-4 and F11-4' had been retained in original assembly over breakers (Fig. 8); solution level had fallen below contact.



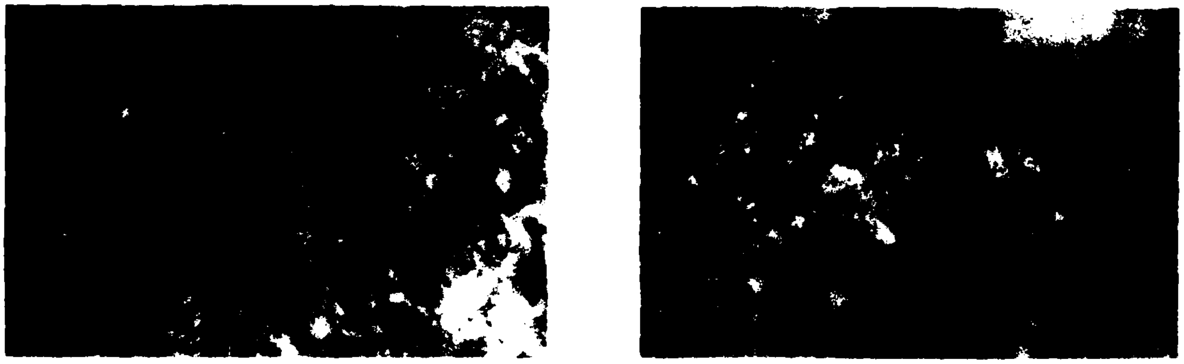
a. B2-1 (NaCl low, x38). b. D3-5 (urea low, x8).

c. E4-9 (Na_2SO_4 low, x19). d. F1-1 (NaCl low, x12, angle view).

Figure 20. Examples of microcracks after 1 year in storage.

e. F7-7 (3 NaCl/1 $CaCl_2$, x12, angle view). f. F9-9 (Na_2SO_4 low, x12).

Figure 20 (cont'd). Examples of microcracks after 1 year in storage.



a. Cl-2 (NaCl high, x8). b. Fl-1 (NaCl low, x12, angle view).

c. F9-9 (Na_2SO_4 low, x19).

Figure 21. Examples of chips dislodged after 1 year in storage.

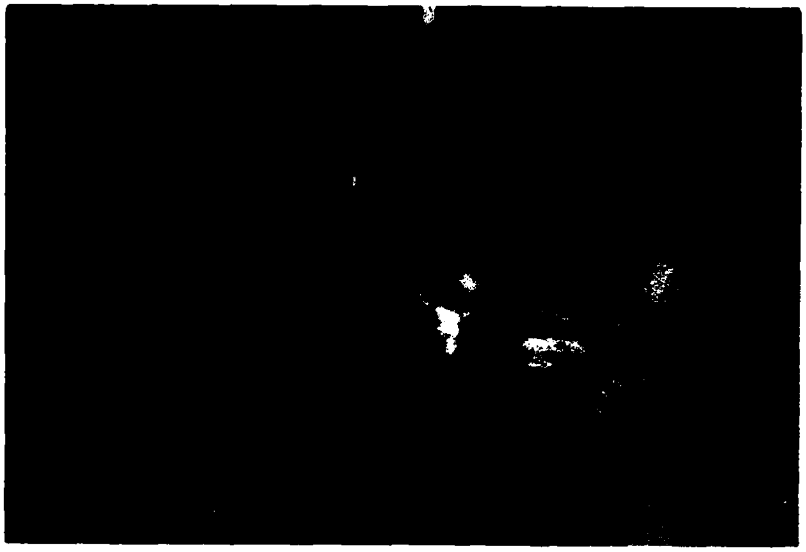


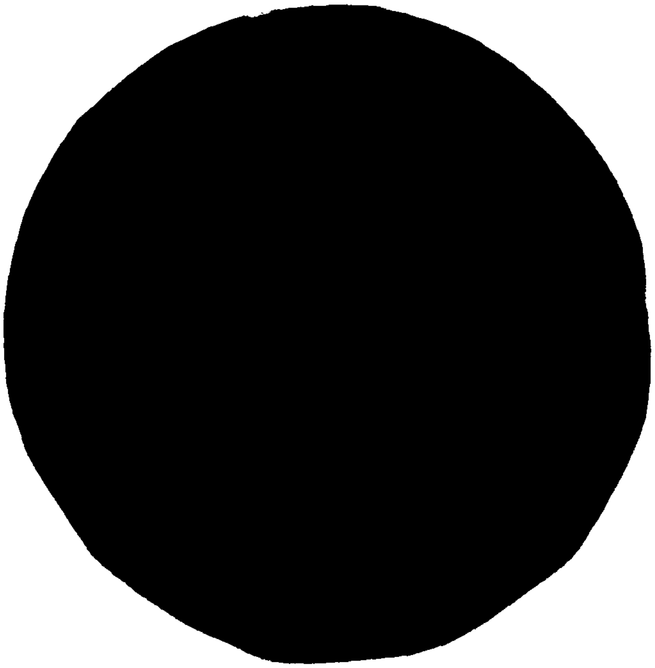
Figure 22. Example of particles lifted by growing salt crystal columns after 1 year in storage (Cl-2, NaCl high, x17, angle view).

Most cracks were clearly evident under the stereomicroscope. That some may have existed or been heat-induced before the tests cannot be ruled out rigorously, for pretest examination had been before the oven drying. (However, compare F14-X trial, not heated, in the next section.) Existence of significant microcracks before the tests seems nevertheless not generally likely, for such cracks would likely have imposed a "signature" in the exudations. Knowing that salt crystallization contributes to the weathering of rocks, one concludes that most of these cracks had probably developed in the 10-month drying-up period.

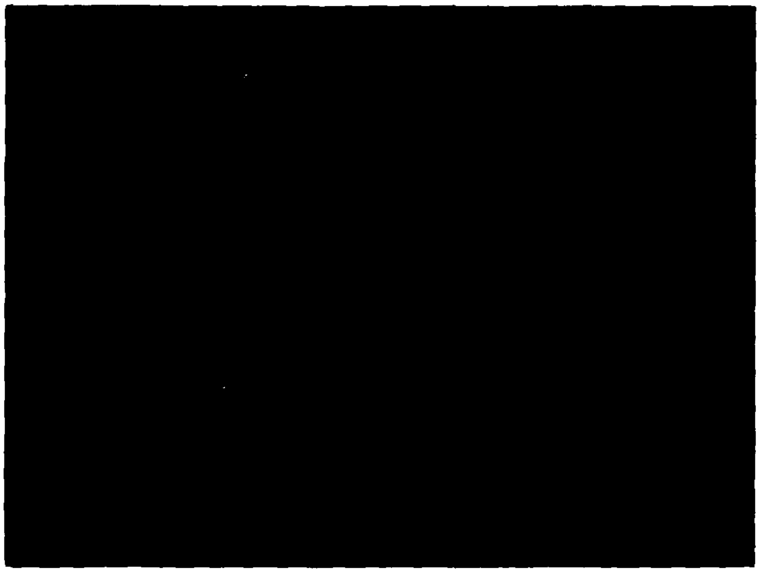
<u>More cracks in three-year storage</u>. Small but eye-visible cracks did develop in disk F14-X exposed to NaCl for over 3 years. F14-X had been set up on 9 April 1976 in a beaker as shown in Figure 8 with an unknown concentration of rock salt (commercial, impure NaCl) merely to try out the arrangement and rubber film closure before the main tests. As F14-X was not exposed to oven drying, vacuum saturation or air flow, its cracking could not be blamed on them. In September 1979 it showed exudate, some of which could be seen by hand lens to have lifted mineral particles, and the disk had swelled slightly at two points, accompanied by visible cracking near the edge (Fig. 23).

That cracks were indeed developed by salts (and even urea) was then confirmed in further re-examination of all the test disks in September 1979, after three years of storage and drying out. (All except F4-4 and F11-4' had been removed to petri dishes with protecting covers.) Most had at least a fine fuzz of exudation, some more obvious, notably on A1-2 and C1-2 (NaCl high) and C2-6 and F6-6 (urea high); this obscured these surfaces from examination.

By microscope, and on a few by eye, cracks, dislodged chips and particle



a. Before the test.



b. After 4 years in storage.

Figure 23. Effect of NaCl on concrete F (F14-X).

Table 13. Cracks, chips and particle lifting after three years in storage (September 1979).

Crack (by eye)	A2-5, E2-5, F18-5
(microscope)	B2-1, D2-1, F1-1, E5-4', A2-5, D3-5 E2-5, F18-5, A4-8, D4-8, F9-9, (?C1-2), (?E1-2)
Chips (by eye)	D3-5
(microscope)	D3-5, F5-5, A7-7
Particles lifted (microscope)	C1-2, D1-3, A2-5, E2-5, E5-5, (?F1-2)
Slightly moist (by eye)	D1-3, E7-3, (?D2-1), (?C1-3)
Droplets (by eye)	D1-3, (?F2-7)
(microscope)	D1-3
Disintegrated*	F4-4, F11-4'
Drastic cracking (by eye)	F3-3, F10-10

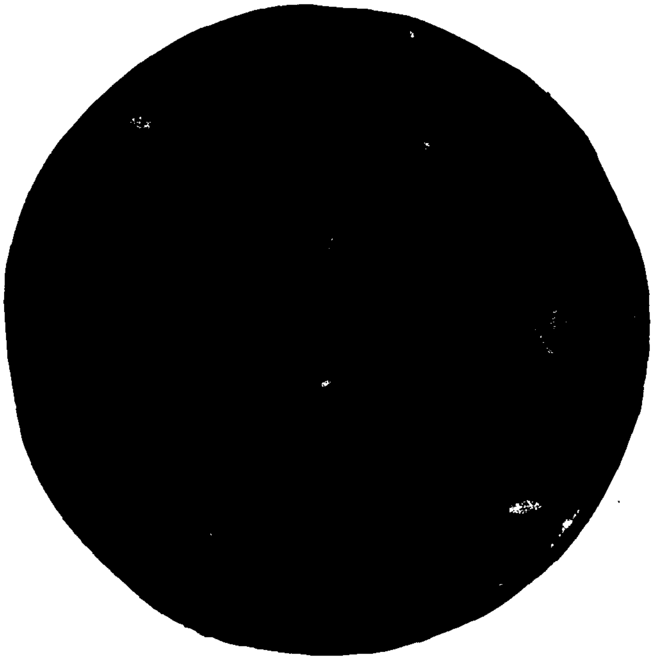
*F4-4 and F11-4' had been retained in original assembly over beakers (Fig. 8); solution level had fallen below contact.

lifting by exudate were noted (Table 13). These encompassed all solutions (except urea high, which was obscured) and all concretes tested. The specimens were retained. These observations led to the simple tests described below.

Special later tests

At the end of the four-month simpler, no-evacuation, no-air-flow test in 1979-80, re-examination by microscope at X7 to X25 revealed cracks in all disks exposed to salts (11 with NaCl, one with 3 NaCl/1 $CaCl_2$); i.e. there were generally more cracks than seen in the pretest survey (Table 14). Of the 12 disks in salts, only three showed no apparent increase in the number of cracks. Chips were evident in several. Notably, one such chip was eye-visible on a buff stone near the center of F13-2 (Fig. 24).

All these new salt tests developed exudation, although, without evaporation due to air flow, these were generally very sparse, scattered filaments. These also were very fine -- finer than in the main experiment. Chips or mortar dislodged at the surface were seen on six disks (Table 14). A few particles lifted by these fine filaments were seen on D6-1 and rarely on some others (fine filaments may be less able to hold particles).



a. Before the test (x1.15).

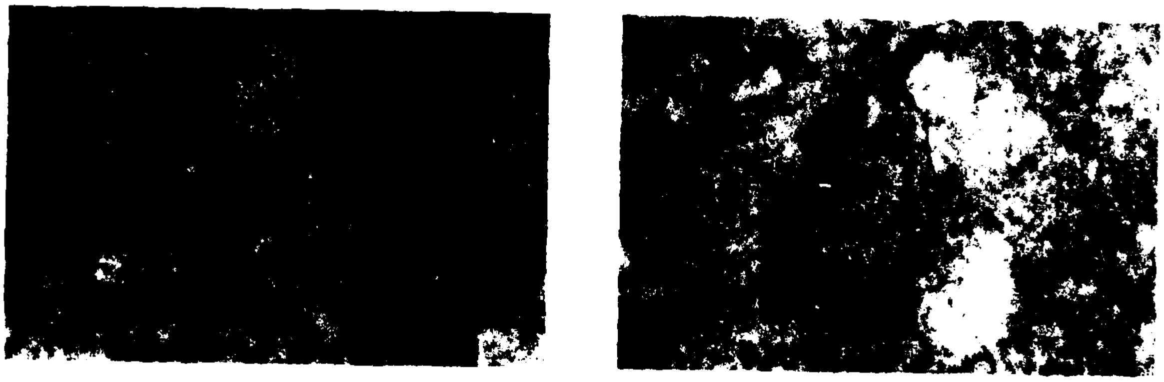
b. After 46 days (x3.6).

Figure 24. Chips in special later test (F13-2, NaCl high).

Some examples of cracks, and possibly particle lifting, as seen under the microscope, appear in Figure 25. They encompass all six concretes tested. Thus, they lend more support to the idea that salt per se in an evaporative, crystallizing situation can damage concrete.

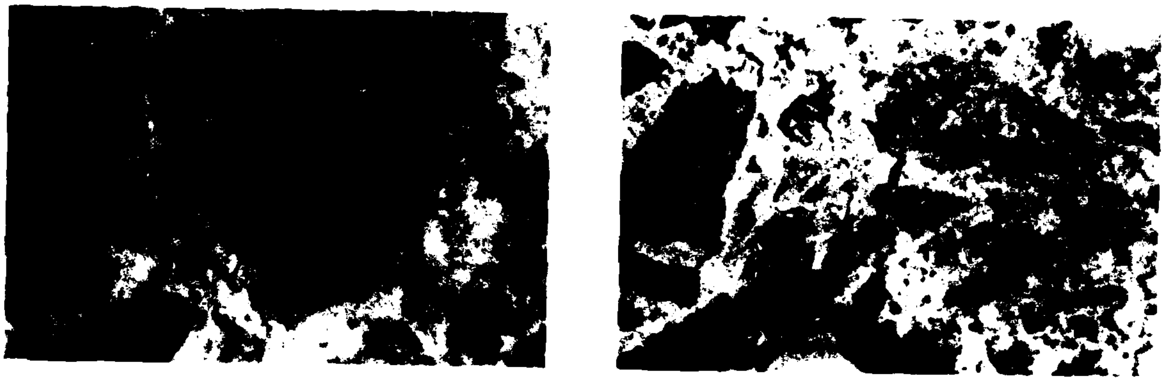
<u>Clogging reactions</u>

Permeation (solution take-up) was about an order of magnitude greater in Period I with no air flow than in II and III with increasing air flow.



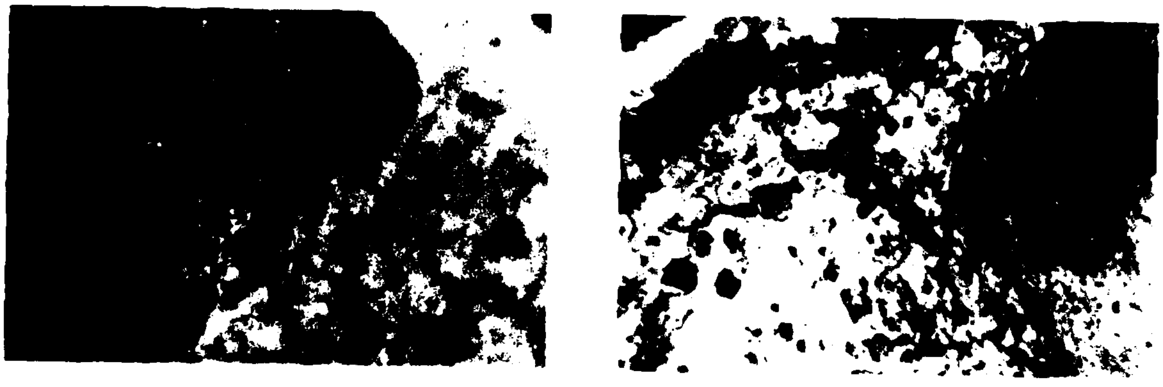
a. A6-1 (NaCl low, x19).

b. B6-1 (NaCl low, x19).



c. C5-2 (NaCl high, x16).

d. (NaCl high, x12).



e. E6-1 (NaCl low, x12).

f. F15-7 (3 NaCl/1 $CaCl_2$ low, x6).

Figure 25. Cracks in special later test at 4 months.

Table 14. Cracks and chips in special later test (by microscope).

Solution	Specimen	Initial cracks	(3/31/80) Cracks	Chips
NaCl low	A6-1	1	1	
	B6-1	0	6	1
	C6-1	?	4	3
	D6-1	0	5	6
	E6-1	3	2	1
	F12-1	2±	4	
NaCl high	A5-2	0	2	
	B5-2	3±	3	
	C5-2	0	1	1
	D5-2	0	3	
	F13-2	0	3	3
3 NaCl/ low 1 $CaCl_2$	F15-7	1	4	

Also, while seawater usually showed low permeation for Periods II and III but was not necessarily the lowest, seawater and Na_2SO_4 were notable in having developed little or no exudation (Fig. 16). Several factors could be contributing:

1) As indicated in the Appendix, initial incomplete saturation probably accounted for higher take-up of solution in Period I.

2) Continued evaporation of water from diffusing solution could reduce flow (permeation) through the concrete by depositing crystals or producing more concentrated (lower vapor pressure, higher viscosity) solution in pores, gradually reducing permeation.

3) Chemical interactions may tend to clog the pores with insoluble precipitates. These could involve certain components present in some concretes or aggregates or in some solutions. Some possibilities (precipitates underlined) are

$$CaCl_2 + MgCO_3 \rightarrow \underline{CaCO_3} + MgCl_2 \qquad (1)$$

$$MgCl_2 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + CaCl_2 \qquad (2)$$

$$CO_2 \text{ (from air)} + Ca(OH)_2 \rightarrow \underline{CaCO_3} + H_2O \qquad (3)$$

$$Na_2SO_4 + Ca(OH)_2 \rightarrow \underline{CaSO_4} + 2NaOH \qquad (4)$$

$$Na_2SO_4 + CaCl_2 \rightarrow \underline{CaSO_4} + 2NaCl \qquad (5)$$

$$MgCO_3 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + \underline{CaCO_3} \qquad (6)$$

Precipitation of an insoluble is governed by its solubility product (SP). This is the product of the activities of its component ions in saturated solution, each raised to the power of its subscript in the chemical formula; in dilute solutions, mol/L concentrations are virtually equivalent to activities. The significance of the SP is the common-ion effect. If the concentration of one of the precipitating ions is high, the concentration of the other will be lower. Thus, the degree to which Ca^{++} is removed from solution in eq 1 will be greater if there is a greater supply of $CO^{=}_3$ ions (which may be increased by dissolution of CO_2 from the atmosphere). Conversely $CO_3^{=}$ may be more completely removed when more Ca^{++} ions are present. Of course, actual relationships in a real system will be complex, with a number of components all having effects on the equilibria among them.

Table 15 lists some pertinent solubility data. Note that SPs calculated from them show much wider variation than do the solubilities, because SP is affected differently for uni-bi-valent salts than for uni-uni or bi-bi. The SP goes relatively lower than solubility for uni-bi compounds than where the positive and negative ions have the same valence. Thus, $Mg(OH)_2$ not only has the lowest solubility but decidely the lowest SP of those shown in eq 1-6.

Reaction 1 might involve magnesite ($MgCO_3$) or dolomite ($CaCO_3 \cdot MgCO_3$) in aggregate or sand in the concrete, since $MgCO_3$ is more soluble than $CaCO_3$ (Table 15).

Reaction 2 may occur with the $MgCl_2$ present in seawater (solution 8), since the solubility and SP of $Mg(OH)_2$ are so much lower than those of $Ca(OH)_2$ (Table 15). Where $MgCl_2$ is not initially present, $Mg(OH)_2$ might also result, but more slowly, by prior exchange of other salts present with

Table 15. Solubility data.

		Solubility		Solubility	Normalized	
Compound	MW	%	mol/L	Product	Solubility*	S.P.
$CaSO_4$	136.1	0.209	0.0154	2.36×10^{-4}	1.00	1.0
$Ca(OH)_2$	74.1	0.18	0.025	6.25×10^{-5}	1.61	2.6×10^{-1}
$MgCO_3$	84.3	0.0106	0.00126	1.59×10^{-6}	0.08	7.0×10^{-3}
$CaCO_3$	100.1	0.0014	0.00014	1.96×10^{-8}	0.009	8.3×10^{-5}
$ZnCO_3$	125.4	0.001	0.00008	6.40×10^{-9}	0.005	2.7×10^{-5}
$Mg(OH)_2$	58.3	0.0009	0.00015	1.35×10^{-11}	0.01	5.7×10^{-8}
$Zn(OH)_2$	99.4	2.6×10^{-7}	2.6×10^{-8}	3.5×10^{-22}	1.7×10^{-6}	1.5×10^{-18}

*mol/L basis

$MgCO_3$ in the concrete, to form $MgCl_2$ as in eq 1, followed by 2, as well as directly by 6.

Reaction 3, being dependent on gaseous diffusion and solution, may not occur as much internally, but it is known to occur on concrete surfaces, where $Ca(OH)_2$ may exude. It may occur internally if the water or aggregate contains $CO^{=}{}_3$ or $HCO^{-}{}_3$ ion or if CO_2 gains better access through microcracks.

Reaction 4 may occur with test solution 9 or Na_2SO_4 present in small amounts in seawater, or possibly in the field as a trace component of groundwater or crude NaCl deicer, or arising from environmental pollution with sulfur oxides.

Reaction 5 may occur likewise where $SO^{=}{}_4$ ions are present and Ca^{++} ions are available or released as in equation 2.

Reaction 6, a double precipitation, may occur where magnesitic or dolomitic aggregate or sand is present in the concrete. It depends on $MgCO_3$ being more soluble than either $CaCO_3$ or $Mg(OH)_2$.

Concretes A-D (mortars, no coarse aggregate) all had crushed dolomitic limestone as fine aggregate ("sand"), while E had limestone fines and dolomite ($MgCO_3 \cdot CaCO_3$) stone as coarse aggregate. In contrast, F had a siliceous ("chert gravel") coarse aggregate and presumably a siliceous (common sand) fine aggregate. Reactions 1 and 6 might, then, have influenced the present results for A - E vs F; i.e. they might have mitigated against drastic cracking, or affected permeation and exudation. Tests with siliceous (nondolomitic) concretes of similar properties would be of interest.

Reactions 7 and 8, very similar to 2 and 6, should be even more effective in forming precipitate, for the solubility and SP of $Zn(OH)_2$ are far lower than any of the others (Table 15).

$$ZnCl_2 + Ca(OH)_2 \rightarrow \underline{Zn(OH)_2} + CaCl_2 \qquad (7)$$

$$ZnCO_3 + Ca(OH)_2 \rightarrow \underline{Zn(OH)_2} + \underline{CaCO_3}. \qquad (8)$$

By reducing the concentration of Ca^{++}, eq 4 permits a higher concentration of OH^- to be tolerated without exceeding the SP of $Ca(OH)_2$. At the same time the depletion of Ca^{++} in solution causes more $Ca(OH)_2$ to dissolve and reprecipitate as $CaSO_4$ by eq 4, also increasing the alkalinity (NaOH concentration) of the system. Possibly this has implications in the alkali-silica reaction. This damages concrete by the reaction of free alkali with certain siliceous components present in some aggregates, forming an alkali-silicate gel of the unlimited water-swelling (expansive) type. Reaction 4, by producing alkali, might conceivably have a beneficial effect, too, in keeping the pH up for continuing passivation of rebar steel.

When small amounts of Na_2SO_4 are present (as in seawater or groundwater, air pollution or some minerals, or as an impurity in deicers), reaction 5 would tend to precipitate sulfate. Hypothetically this has deteriorative implications in the ability of $CaSO_4$ to form hydrates or in the "sulfate reaction," which could damage concrete by expansion as hydrate crystals grow or as sulfate attacks tricalciumaluminate to form calcium sulfoaluminate, developing pressure.

Where $MgCl_2$ may be present, as in seawater, reaction 2 is logical. If within concrete pores, this should be especially effective in plugging them. Since $Mg(OH)_2$ is very insoluble, the precipitate should be quite inert. It should not, then, be subject to further reaction and formation of larger-volume products. In contrast, MgO expands as it hydrolyzes to $Mg(OH)_2$ and is therefore to be avoided in cement.

Hypothetical countermeasures

The precipitation reactions above, especially 2 and 6 (also 7 and 8), may have valuable applications in mitigating concrete deterioration by salt action. Whether the attack entails salt crystallization action as such, enhancement of freeze-thaw effects, or corrosion of rebars, there must first be penetration of salt solution into the concrete. Very fine-grain, highly insoluble and inert precipitate produced in situ may block pores without the stress accompanying the growth of salt crystals in them. Deicer, water, oxygen and CO_2 penetration might then be much reduced.

Plugging with fine-grain precipitate should also decrease effective capillary size. This would lessen the likelihood of pore water freezing and thus would also reduce freeze-thaw effects.

This suggests a means of control of salt (and freeze-thaw) action in concrete: addition of Mg^{++} (or Zn^{++}) might meet this need. Hardened concrete might be treated with $MgCl_2$ before exposure to deicers, or $MgCl_2$ might be purposely added to deicers (also increasing their "bite"). Possibly Mg^{++} might be added to the concrete mix as $MgCl_2$ or other soluble salt or perhaps as $MgCO_3$; i.e. magnesite or dolomite might be added as fines when not generally present in an aggregate. Since $MgCO_3$ is more soluble than $CaCO_3$ and especially $Mg(OH)_2$, reactions 1, 2 and 6 might all occur to produce pore-blocking precipitates. The double precipitation of eq 6 may be particularly effective. The same may be true for similar reactions involving Zn^{++}.

$MgCl_2$ is incorporated in NaCl deicers for higher elevations in Utah.* It is used in Italy and other parts of Europe (Scotto 1975), at proportions not presently known. In their six years of use (1970-1976), Utah DOT restricted $MgCl_2$ to 0.5% of the NaCl for fear of increasing corrosion of rebars or salt application equipment. This was considered enough to improve the "bite" of the salt in colder areas and to antifreeze stockpiles. It is much like $CaCl_2$: it is hygroscopic-deliquescent, it never dries out, and it forms hydrates.

Utah officials have not noticed any difference in corrosion of trucks (as of 1976). In the higher, colder areas, where $MgCl_2$ is added, they have some bridges that have never had plain salt. They have not been aware of any benefit in reduced salt attack on these bridges or rebars, but they had not anticipated such an effect. It may take more than six years to see this effect, or a mere 0.5% of the salt (0.015% $MgCl_2$ in a resulting 3% NaCl solution) may be too little; in seawater $MgCl_2$ is 0.52%, or 35 times higher.

A simple demonstration of eq 2 supported the above idea. Saturated $Ca(OH)_2$ with excess solid was placed in two porous-bottom filter crucibles. These were partially immersed in beakers of seawater and of $MgCl_2$ solution. Turbidity appeared overnight in both cases, and levels in the crucible tended to equalize with the beakers. Within 24-40 hours a precipitate was settling, leaving the lower solutions clearer.

Other factors

Some other mechanisms logically may also be involved in salt action on concrete. Though perhaps touched on elsewhere in this report, several are discussed briefly here.

Thermal expansion. Some linear expansion coefficients appear in Table 16. Differences in these may play an important part in concrete or other porous body deterioration where some pores are full of salt, ice or other solid when temperature changes. The comparability of expansion for rocks, steel and concrete is fortunate. However, the much larger coefficients for salt and ice (and also sulfur, plastics and asphalt) may produce stress when pores are filled with these and temperature increases.

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*Personal communication with Robert Weedon, Utah Department of Transportation, October 1976.

Table 16. Thermal coefficients of expansion.

Cement and concrete	$10\text{-}14 \times 10^{-6}$/°C
Masonry	4-7
Granite	8
Sandstone	7-12
Quartz	8-13
Limestone	9
Marble	11-15
Slate	6-10
Glass	6-10
Porcelain	2-6
Steel	10-13
Rock salt (NaCl)	40
Ice	51
Sulfur	64
Plastics	50-100-200
Asphalt and tar	200

Salt hydrates. The formation of salt hydrates at certain specific temperatures may produce sudden and marked disruptive stress when pores filled with such salts cool through the transition temperature and when water is available from adjacent pores, as occurs when ice crystals grow and cause heaving upon cooling and freezing of moist soil. This is particularly evident and recognized for salts that form several hydrates at common temperatures, e.g. Na_2SO_4, $MgSO_4$, $CaSO_4$, $CaCl_2$. Use is made of this effect in a test for aggregates (ASTM 1977) and in separating fossils from more porous rock (Glaessner 1948).

At temperatures below 0°C, excess salt exists in equilibrium with saturated solutions as $NaCl \cdot 2H_2O$. Its formation from NaCl in a pore and water drawn from other pores entails volume change and pressure development, as does ice growth in soil. This transition must occur often in pavement as 1) salt keeps the freezing point below 0°C, 2) its hygroscopicity keeps the concrete more damp, and 3) temperatures, wetness and salt concentrations cycle in and between winter storms. This salt hydrate transition may well amplify the freeze-thaw effects of plain water in concrete and rocks.

A further possibility with hydrates is that stress may develop merely upon moving through the transition temperature, without change in water content, if the densities of the hydrate and the equivalent free water plus salt differ and porosity is too low for ready dissipation of pressure. The ability of $CaCO_3$ to form a hexahydrate, $CaCO_3 \cdot 6H_2O$, at about 0°C and develop pressure to break concrete upon dehydrating (warming) has been cited recently.* This may be the more important where carbonation can occur, as on highways.

Solubility-temperature. Solutes with large temperature coefficients of solubility could also have untoward effects on the durability of concrete. While NaCl solubility changes only slightly with temperature, that of salts like Na_2SO_4, $MgSO_4$, $NaHSO_4$, $MgCl_2$, Na_2CO_3 and many others, increases markedly with temperature. As concrete pores filled with such salts cool, as from day to night, crystals could grow rapidly at the expense of liquid solution in surrounding fine pores, stressing the structure. Perhaps extensive supersaturation from such cooling could be suddenly relieved by vibration from a passing heavy vehicle. This could explain extensive "popping" of a concrete highway surface noted in Utah after temperature dropped to -13°F (-25°C) over one night.†

Some salts have inverse solubility-temperature relations or change to such relations above certain temperatures; i.e. solubility decreases as temperature rises. This is notably true of Na_2SO_4. When pores containing crystals of these salts and drawing upon solution available from nearby pores become warm, as in sunshine or summer days, further crystallization again may cause disruptive effects.

Carbonation. Another aspect of concrete deterioration related to deicing pavements used by autos may be carbonation, i.e. the taking up of atmospheric CO_2 and its reaction with the $Ca(OH)_2$ of concrete. While harmful to freshly poured concrete, carbonation in cured concrete generally improves strength and reduces permeability by deposition of $CaCO_3$ in pores (Neville 1973). However, as Neville observed, by using up the excess $Ca(OH)_2$ that normally maintains high pH and passivity of steel in concrete, carbonation neutralizes the protection of rebars from corrosion.

Since carbonation is a function of CO_2 concentration, this action must be greater on busy thoroughfares where many vehicles are discharging CO_2-rich exhaust gases at or close to the pavement. Moreover, the deicer salts may be enhancing this action in several ways:

1) Melting of snow by salt makes the pavement bare and wet.

2) Salt's hygroscopic action keeps the pavement wet longer, so it is

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*Oral comment of Carl Crumpton, Kansas Department of Transportation, in TRB Committee A2E01 discussion, 1980.

†Personal communication with Derle Thorpe, Utah State University, Logan, 1979.

more saturated and vulnerable to crystallization pressure, whether of ice, salt or salt hydrate on cooling or drying, and the resulting microcracking enhances access of CO_2.

3) Wet concrete would absorb and transmit CO_2 to the interior (rebars) more readily than dry by virtue of solubility, diffusion and pH effects in the pore water.

4) Salt solutions enhance the "aggressiveness" of CO_2 on concrete, i.e. its ability as an acid with H_2O to interact with concrete components (Lea 1956).

5) The $CaCO_3$ formed can form a hydrate, with possible effects as cited above.

Supplemental information

Completeness of vacuum saturation. The apparent permeation rates of the short Period I, even without air flow, were much greater than in the longer Periods II and III with air flow (Tables 4 and 5). Solution take-up or "apparent permeation" rates were also greater for samples with less time since preparation, and also for 3-in. disks.

Comparison of permeation rates between 1-in. and 3-in. disks in the same solution suggested less complete saturation for 3-in. and for shorter times since preparation. One must conclude, then, that saturation was not complete when the tests were started. This agrees with other experience* suggesting that nearer 12 hours is required for saturation of evacuated concrete.

Possible concrete evaluation. By measuring permeation and/or crumbling under standardized conditions, perhaps adding cyclic wet-dry, freeze-thaw, temperature and humidity variations, the present test might be adapted for evaluating permeability, quality or durability of concrete.†

Thoughts for the future

Implications. Results here suggest how salt crystallization effects can enhance the deterioration of concrete structures and roadways. The tiny cracks and surface chipping generated must facilitate salt penetration as cycles of freeze-thaw in winter and wet-dry all year continue the action. Ultimately, when salt, water, CO_2 and oxygen reach the rebars, depassivation

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*At informal presentation of this work in TRB Committee A2E01 in January 1977, comment by a listener, believed to be Carl Crumpton, Asst. Engineer, Planning and Development, Kansas DOT.

†Personal communication with Harry A. Smith, Project Engineer, National Cooperative Highway Research Program, 1976.

and galvanic action induce corrosion of the steel and the well-recognized spalling ascribed to growth pressure of corrosion products. Impairment of the trafficability and integrity of the concrete surface or structure follow.

Much deicer testing on pavement materials has seemed to involve freeze-thaw with salt exposure under liquid solution, i.e. always wet, or only briefly drained without really drying. Such tests do not simulate field conditions: the dry and warm periods of winter or summer when salt crystals may develop and grow internally; thus, salt action could hardly arise. As Powers (1956) suggested, such climate variations should be considered in designing future testing of deicer effects on concrete. Their neglect is unfortunate.

<u>Clogging reactions</u>. Reduced exudation with seawater and Na_2SO_4 may be due to chemical precipitation in concrete pores. This implies the possibility of control of salt action by use of an additive or treatment in deicer or concrete. This could react with the $Ca(OH)_2$ of the cement paste to produce a highly insoluble, pore-blocking precipitate, lessening penetration, internal crystallization and rebar corrosion. This intriguing possibility should be pursued; success could be highly rewarding.

<u>Thermal expansion</u>. The large differences between coefficients of expansion for concrete, steel and some rock vs ice and salts must be important in field conditions. Thermal expansion effects should be examined in developing investigations.

<u>Hydrate formation</u>. As temperatures and humidities change, volume changes in salt hydrate transitions must play a part in salt and freeze-thaw action. These, particularly hydrates of NaCl and $CaCO_3$ that appear below freezing and those of $CaCl_2$, need to be investigated further.

<u>Solubility-temperature relationships</u>. Large solubility changes of some solutes (and their hydrates) with temperature, small and even inverse for others, must enter into salt action. These should be considered in future work.

<u>Carbonation</u>. Depassivation of steel by lowered pH promotes rebar corrosion, and the penetration of CO_2 can lower pH. The role of carbonation (and of other atmospheric acids) should be looked into, particularly where vehicular or other pollution (e.g. acid rain) occurs.

<u>Crystallization pressure</u>. The crystallization pressure of growing crystals of salt and of ice has been demonstrated and calculated. Evidences of such pressure are commonly available, as in frost action, rebar corrosion,

lifting of paint by metallic corrosion, ASTM (1977) test for aggregate quality, and separation of fossils. However, a direct measurement of salt crystallization pressure might help convince skeptics of its role in concrete deterioration.

Possible methods include:

1) That of Knacke and von Erdberg (1975), already reported for $Na_2SO_4 \cdot 10H_2O$ pressure.

2) That of Cody (1977), already being applied to crystal growth pressures of gypsum that cause heaving of black shale.

3) Adaptation of the familiar frost heaving test by feeding salt solution instead of water to the bottom of a cell packed with soil and evaporating rather than freezing through a porous cover plate, where displacement and pressure might be measured.*

4) Growing crystals in a cell with a porous bottom contacting a saturated solution, by imposing a temperature differential or by evaporation of solvent through an upper semipermeable membrane passing water but not salt molecules, and measuring volume and pressure increase by a strain gauge or loading on a flexible top cover or piston.

Other considerations. Future research might also consider:

1) Cycling wet-dry, freeze-thaw, temperature and humidity.

2) The relation of permeation and exudation to concrete properties, including porosity and pore size.

3) The influence of entrained air.

4) Ionic radii and hydration.

5) Chemical reactivity of deicers with concrete: Which ions in deicer are bad, innocuous or helpful, e.g. Mg^{++}? What components of concrete are good or bad, e.g. dolomitic vs siliceous aggregate?

6) Hygroscopicity.

7) Effects of mixtures (are some synergistic?).

8) Chemical analysis and more sophisticated means for surface study to diagnose interaction, plugging, cracking, particle lifting, etc.

9) The status of salt-exposed concrete in the field might be evaluated routinely by simple portable microscope or hand lens examination for tiny cracks, chipping and (where sheltered from rain) exudation and particle lifting.

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*Personal communication with Dean Freitag, former Technical Director, CRREL.

SUMMARY AND CONCLUSIONS

1) Disks of several concretes were partially immersed in deicer and other solutions. Air flow on the surface promoted evaporation and the growth of crystalline exudations.

2) The crystalline salt exudation is reminiscent of frost action at the surface of soil, i.e. needle ice, whose columns similarly entrain and lift particles. Like salt weathering of rocks, the mechanism is analogous to that of frost action: liquid from finer pores migrates to loci of crystallization, which then grow and develop disruptive pressure.

3) Tiny cracks, dislodged chips and insoluble particles lifted by exudate crystals developed in a number of cases, particularly upon 1-3 years drying in storage, and in a later, simpler test, strikingly demonstrated salt-caused deterioration.

4) Drastic cracking of one concrete occurred with $CaCl_2$ and with $Ca(NO_3)_2$. In long storage of two disks in contact with $CaCl_2$ high, complete disintegration followed in three years. This must relate in part to particular properties of the concrete (it had a "non-reactive" siliceous aggregate, whereas others had dolomitic fillers), but also must involve hygroscopicity, hydrate formation and humidity effects of $CaCl_2$.

5) The lack of exudation with seawater and Na_2SO_4 suggests there may be a chemical reaction depositing highly insoluble precipitate to block pores and reduce migration of salt to the surface, e.g.

$$MgCl_2 + Ca(OH)_2 \rightarrow \underline{Mg(OH)_2} + CaCl_2 \qquad (2)$$

Somewhat similarly

$$CaCl_2 + MgCO_3 \rightarrow \underline{CaCO_3} + MgCl_2 \qquad (1)$$

may have helped inhibit $CaCl_2$ attack on other concretes tested (which had dolomitic aggregate).

6) Hypothetically, adding Mg^{++} to deicers or concrete might plug pores with $Mg(OH)_2$ and impede penetration of salt, water, CO_2 and oxygen, thus reducing salt effects damage per se and consequent corrosion of rebars. Zn^{++} might work even better.

7) Thermal expansion, salt hydrate transitions, solubility-temperature relations, and carbonation are discussed. All may play significant roles in salt action on concrete.

8) Exudations varied from none to heavy, were a few mm to several cm long, and took forms that were hair-like, filamentous, columnar, chunky, in plant-like clusters or crusty.

9) Exudation of crystalline solids varied with concrete properties and nature of the solution. There was none with $CaCl_2$ and $Ca(NO_3)_2$, due to their hygroscopic-deliquescent properties at existing humidities.

10) Exudation of urea was particularly great, likely due to its physical-chemical properties as well as higher concentration.

11) Liquid permeation rate relates to concrete properties. Its decrease with time suggests blocking by crystal deposits on the surface or in pores, and/or by chemical precipitation within pores.

LITERATURE CITED

Ahlhorn, G.A. and H.C. Poehlman (1976) Environmental Protection Agency 600/2 to 240, December (Ball Bros. Corp.).

ASTM (1977) Test method C-88, soundness of aggregate by use of Na_2SO_4 or $MgSO_4$. Annual Book of ASTM Standards, vol. 14, pp. 40-53; vol. 15, pp. 6-12.

Axon, E.O., L.T. Murray and R.M. Brucher (1969) Laboratory freeze thaw tests vs. outdoor exposure tests (for concrete). Highway Research Record, 268: 35-45.

Beaumont, P. (1968) Salt weathering on the margin of the Great Kavir. Geological Society of America Bulletin, 79: 1683-1684.

Becker, A. and A. Day (1905) The linear force of growing crystals. Proceedings of the Washington Academy of Sciences, 7: 283-288.

Ben-Yair, M. (1974) The effect of chlorides on concrete in hot and arid regions. Cement and Concrete Research, 4: 405-416.

Bergstrom, S.G. (1959) Deterioration of concrete pavements due to salting in wintertime. Swedish Concrete and Research Institute, Translation FSTC-HT-375-69.

Berman, H.A. and B. Chaiken (1972) Techniques for retarding the penetration of deicers into cement paste and mortar. FHWA Report RD-72-46.

Beskow, G. (1935) Soil freezing and frost heaving with special application to roads and railroads. Swedish Geological Society Series C, No. 375, 26th Yearbook, No. 3, translated by J.B. Osterberg, Northwestern U. (with supplement for 1935-46), November, 1947.

Blight, G.E. (1976) Migration of subgrade salts damages thin pavements. Transportation Engineering Journal of ASCE, 102(TE4): 779-791.

Browne, F.P., T.D. Larson, P.D. Cady and N.B. Bolling (1970) Deicer sealing mechanisms in concrete. Pennsylvania State University. (PHD contract 44242).

Burd, R.M. (1976) Seawater analysis. ASTM Standardization News, January, pp. 30-32.

Civil Engineering - ASCE (1982) Summary of Carl Crumpton and G.P. Jayaprakash informal presentation to the Corrosion Committee (A2G05) at the Transportation Research Board, January 1982 Meeting, May.

Clear, K.C. and W.C. Ormsby (1975) Concept of internally sealed concrete. FHWA Report RD-75-21.

Cody, R.D. (1977) Prevention of heaving in structures built on black shales by prevention of crystal growth within the shales. Research proposal to Army Research Office. Iowa State University, Ames.

Coleman, J.M., S.M. Gagliano and W.G. Smith (1966) Chemical and physical weathering on saline high tidal flats, northern Queensland, Australia. Geological Society of America Bulletin, 77: 205-206.

Concrete Construction (1975) Chemical attack on hardened concrete. Aug., pp. 322-333, 350.

Concrete Research Lab (1974) Aalborg portland cement R&D seminar on alkali silica reaction. Summary, Karlstrup, Denmark.

Cooke, R.U. (1979) Laboratory simulation of salt weathering process in arid environments. Earth Surface Processes, 4: 347-349.

Cooke, R.U. and I.J. Smalley (1968) Salt weathering in deserts. Nature, 200: 1226-1227.

Cordon, W.A. (1966) Freezing and thawing of concrete - Mechanisms and control. American Concrete Institute, Monograph MC-3.

Correns, C.W. (1949) Growth and dissolution of crystals under pressure. Transactions of the Faraday Society, 5: 267-271.

Ellis, W.J. and R.E. Colson (1980) Cathodic protection of concrete bridge structures. National Cooperative Highway Research Program (NCHRP) Project 12-19, Final Report (Corrosion Engineering Research Co.).

Everett, D.H. (1961) The thermodynamics of frost damage to porous materials. Transactions of the Faraday Society, 57: 1541-1551.

Fookes, P.G. and L. Collis (1975a) Problems in the Middle East. Concrete, 9(7): 12-17.

Fookes, P.G. and L. Collis (1975b) Cracking and the Middle East. Concrete, 10(2): 14-19.

Fookes, P.G. and W.J. French (1977) The Highway Engineer. Journal of Institute of Highway Engineers, December, pp.10-20.

Franklin, R.E. (1967) Frost scaling on concrete roads. Road Research Laboratory (Britain), Report LR 117.

Gille, F. (1960) Depth of carbonation layer in old concrete. Beton Herstellung-Verbindung (Dusseldorf), 10: 320-330.

Glaessner, M.F. (1948) Principles of Micropaleontology, Melbourne, Australia: Melbourne University Press.

Grattan-Bellew, P.E. and W.J. Eden (1975) Concrete deterioration and floor heave due to biogeochemical weathering of underlying shale. Canadian Geotechnical Journal, 12(3): 372-378.

Griffin, D.F. and R.L. Henry (1961) Integral sodium chloride effect on strength, water vapor transmission and efflorescence of concrete. Journal of the American Concrete Institute, 38-35: 751-771.

Hansen, W.C. (1963) Crystal growth as a source of expansion in portland-cement concrete. Proceedings, ASTM, 63: 932-945.

Hay, R.E. (1976) The bridge deck problem - An analysis of potential solutions. Public Roads, 39(4): 142-147.

Helmuth, R.A. (1960) Capillary size restrictions on ice formation in hardened portland cement pastes. Fourth International Symposium on the Chemistry of Concrete, Washington, D.C.

Henry, R.L. and G.K. Kurtz (1963) Water vapor transmission of concrete and of aggregate. United States Navy Civil Engineering Laboratory, Technical Report 244.

Hillansbrand, B.F. (1977) Inadequate structurally deficient bridges, A crisis. AASHTO Quarterly, 56(4): 5.

Hoekstra, P. (1969) Water movement and freezing pressures. Soil Science Society of American Proceedings, 33(4): 512-518.

Hoekstra, P., E. Chamberlain and A. Frate (1965) Frost heaving pressures. U.S.A. Cold Regions Research and Engineering Laboratory, Research Report 176.

Hudek, P.P. and S.G. Rigbey (1976) The effect of sodium chloride on water sorption characteristics of rock aggregates. Bulletin of the Association of Engineering Geologists, 13(3): 199-211.

Idorn, G.M. (1969) Durability of Concrete Structures in Denmark, Study of Field Behavior and Microscopic Features. Copenhagen, Denmark: Technical University of Denmark.

Jenkins, G.H. and J.M. Butler (1975) Internally sealed concrete, FHWA Report RD-75-20 (done at Monsanto Research Corp.).

Jones, J.C. (1977) Inadequate structurally deficient bridges, A national problem. AASHTO Quarterly, 56(4): 4-5.

Khaimov-Mal'kov, V.Ya. (1956) Growth of crystals. Interim report between 1st and 2nd Conference on Crystal Growth, Institute of Crystallography, Academy of Sciences, USSR (Transl. by Consultants Bureau, NYC).

Knacke, O. and R. von Erdberg (1975) The crystallization pressure of sodium sulfate decahydrate. Ber. Bunsen Gesellschaft f. phys. Chem., 79(8): 653-657.

Lankard, D.R., J.E. Slater, W.A. Hedden and D.E. Niesz (1975) Neutralization of salt in concrete. FHWA Report RD-76-60.

Lea, F.M. (1956) The Chemistry of Cement and Concrete. London: Edward Arnold.

Litvan, C.G. (1976) Freezing effects in concrete. ACI Journal, April, pp. 234-235.

Malin, M.C. (1974) Salt weathering on Mars. Journal of Geophysical Research, 79(26): 3888-3894.

Mather, B. (1975) Durability of concrete construction - 50 years of progress. Journal of the Construction Division, ASCE, 101(CO 1): 5-14.

McGreevy, J.P. (1982) Frost and salt weathering: Further experimental results. Earth Surface Processes and Landforms, 7: 475-488.

Mullin, J.W. (1961) Crystallization. London: Butterworths.

Murray, D.W. (1977) An economic analysis of the environmental impact of highway deicing. Paper presented at TRB meeting (done at Abt Associates, Cambridge, Massachusetts).

NCHRP (1982) Research Reports Digest No. 132, National Cooperative Highway Research Program.

Neville, A.M. (1973) Properties of Concrete, Second Ed. New York: Wiley.

New Civil Engineer (1975) Sun and salt - The scourge of concrete in the Gulf. 19 June, pp. 32-33.

OECD Research Group (1972) Winter damage to road pavements. Road Research, May, p. 19.

Pfeifer, D.W. and M.J. Scali (1982) Concrete sealers for protection of bridge structures. NCHRP Project 12-19A, Final Report, NCHRP 244 (Wiss, Janey, Elstner & Associates, Inc.).

Portland Cement Association (1951) What resulted from basic research studies: Influence of cement characteristics on the frost resistance of concrete. pp. 28-43.

Powers, T.G. (1956) Hardened concrete - Resistance to weathering - freezing and thawing. ASTM Special Publ. No. 169, Portland Cement Association Bulletin 64.

Powers, T.G. and A.R. Collins (1945) Discussion on: A working hypothesis for further studies of frost resistance of concrete. Journal of the American Concrete Institute, 41 (supplement): 272-314.

Price, C.A. (1975) Stone - Decay and preservation. Chemistry in Britain, 11(10): 350-353.

Radd, F.J. and D.H. Oertle (1966) Experimental pressure studies on frost heave mechanics and the growth-fusion behavior of ice in soils and glaciers. Continental Oil Co., Ponca City, Oklahoma, Report No. 515-4-2-66.

Radd, F.J. and D.H. Oertle (1968) Melting point behavior of glacier ice. Nature, 218: 1242.

Sayward, J.M. (1966) Miniature tests re frost heaving and needle ice. U.S.A. Cold Regions Research and Engineering Laboratory, Internal Report 19.

Sayward, J.M. (1979) Small scale testing of soil for frost action and moisture migration. U.S.A. Cold Regions Research and Engineering Laboratory, Special Report 79-17. Also in ASTM Geotechnical Testing Journal, 2: 223-231, December 1979.

Sayward, J.M. (1980) Some thoughts and results on deicer action in concrete. U.S.A. Cold Regions Research and Engineering Laboratory, Technical Note.

Schaffer, R.J. (1932) The weathering of natural building stones. Department of Sciences and Industrial Research (Britain), Building Research, Special Report No. 18.

Scotto, E. (1975) Do different levels of service for winter road traffic in Italy really exist? A fact-finding study in provincial administration. Neve Inter.,: 21-24 (in Italian).

Selby, M.J. and A.T. Wilson (1971) The origin of the labyrinth, Wright Valley, Antarctica. Geological Society of America Bulletin, 82(2): 471.

Snyder, M.J. (1965) Protective coatings to prevent deterioration of concrete by deicing chemicals. NCHRP Report 16 (done at Battelle Memorial Inst., Columbus, OH).

Steiger, R.W. and M.W. Hurd (1980) The durability of concrete. Concrete Construction, January, pp. 35-39.

Stevens, E.R. (1977) Electrochemical evaluation of bridge decks. Maine Department of Transportation, Tech. Paper 77-5.

Stewart, P.H. and R.K. Schaffer (1974) Investigation of concrete protection sealants and curing compounds. Highway Research Record, No. 268.

Stratful, R.S. (1974) Experimental cathodic protection of a bridge deck. FHWA Report RD-74-31.

Stumm, W. and J.J. Morgan (1970) Aquatic Chemistry. New York: John Wiley.

Taber, S. (1916) The growth of crystals under external pressure. American Journal of Science, 51(4): 532-556.

Timms, A.G. (1968) Detrimental effects of common salt and calcium chloride on concrete surfaces. Modern Concrete, March, p. 29.

Verbeck, G.J. and P. Klieger (1957) Studies of "salt" scaling on concrete. Highway Research Board, Bulletin No. 150, pp. 1-13.

Vrähle, J.B. (1977) Cathodic protection for reinforced concrete bridge decks--laboratory phase. National Cooperative Highway Research Program, Report 180.

Wellman, H.W. and A.T. Wilson (1965) Salt weathering, a neglected erosion agent in coastal and arid environments. Nature, 205: 1097-1098.

Whiting, D. and D. Stark (1981) Galvanic cathodic protection for reinforced concrete bridge decks - Field evaluation. National Cooperative Highway Research Program, Report 234.

Williams, R.B.G. and D.A. Robinson (1981) Weathering of sandstone by the combined action of frost and salt. Earth Surface Processes, 6: 1-9.

Winkler, E.M. and P.C. Singer (1972) Crystallization pressure of salts in stone and concrete. Geological Society of America Bulletin, 83: 3509-3514.

Woods, H. (1968) Durability of concrete construction. American Concrete Institute, Monograph No. 4.

APPENDIX A. BACKGROUND

Salt Action

Salt action, called salt weathering, fretting or wedging, occurs when salt solution, from ground water or the sea, evaporates near the surface of rocks (Wellman and Wilson 1965) and concrete (Winkler and Singer 1972). As in frost action in soils (Beskow 1935), in finer pores the capillary walls in close proximity exert forces that inhibit both nucleation and crystal growth. A growing crystal (salt or ice) must expend work extending its surface against interfacial tension as well as increasing its volume against ambient pressure (Wellman and Wilson 1965):

$$dP = P_s - P_\ell = \frac{\sigma dA}{dV} \qquad \text{(A1)}$$

where P_s and P_ℓ = pressures in growing solid and in the liquid, respectively

σ = interfacial tension of the crystal to the surrounding liquid

$\frac{dA}{dV} = \frac{\text{(area increase)}}{\text{(volume increase)}}$ for the crystal.

Hence energetics will favor large and equidimensional crystals, where dA/dV is small. Thus, as in frost action, a crystal grows where it is rather than into fine pores (of larger dA/dV), being fed by liquid that can diffuse to it through the fine pores, via a "liquid-like" layer, to the crystallization front. The resulting growth pressure may well exceed the relatively low tensile strength of the surrounding matrix. These processes have been reviewed by Hansen (1963).

Salt weathering occurs in arid areas, where groundwater that is relatively rich in salts (hardness) migrates into rock outcrops. Upon evaporation, crystallization of dissolved salts disrupts the surface layers, gradually undercutting the rock above the ground line. Fine rock meal on or below the affected surface is a symptom. I have observed this in the heated, non-waterproofed cellar of my house, where rock meal has fallen from walls of shaly rock and mortar.

Deicer salts have brought about the deterioration of concrete on many bridges (Fig. 1) and other structures. Roughened pavements occur where winter salt has caused crumbling and spalling at the surface, but rebars may not yet be involved. Salt-caused erosion of a brick and mortar wall (no rebars) is shown in Figure 2. Damage to street-side structures by deicers has been pictured and warned of by Winkler and Singer (1972).

Salt weathering also occurs under wet-dry seashore conditions (Fig. 6), as noted by Wellman and Wilson (1965). It may be an erosion factor in the dry valleys of Antarctica (Selby and Wilson 1971) and is considered possible on Mars (Malin 1974). An open rock cut in the Lebanon, N.H., area seemed to exhibit salt weathering.* The splintering erosion of wood utility poles in Great Salt Lake,† where highly saline water rises and falls annually, may be of related nature.

Coleman et al. (1966) discussed chemical and physical weathering on saline, high tidal flats in Queensland, Australia, ascribing the fracture of gravel and crumbling of granite to the growth of salt crystals during dry periods. They cited similar observations of others in Australia, Manitoba and Egypt. Beaumont (1968) described the role of salt weathering in the formation of fine-grained material from pebbles in the Grand Kavir, Iran.

The large bulk of concrete in dams, large bridges, airstrips or fortifications could contain considerable soil-water salts if prepared (or perhaps even if flushed or in contact) with local water of high mineral content and in areas of little rainfall. Perhaps salt action could occur as such salts move to the surface by evaporation during arid periods over many years.

Salt hydrate formation and temperature changes, as well as evaporation, may contribute to pressure due to crystals in porous materials (Cooke and Smalley 1968, Wellman and Wilson 1965, Winkler and Singer 1972, Sayward 1980). Paleontologists use this principle in breaking up the more porous, shaly rock surrounding fossils by soak-dry with Na_2SO_4 or $MgSO_4$ solutions (Wellman and Wilson 1965). A similar technique is employed in testing the suitability of aggregate for concrete (Neville 1973, ASTM 1977); the acceleration of damage by alternate wet and dry is ascribed to crystallization of salt or its hydrates in the pores. Neville (1973) noted that $CaCl_2$ reduces the resistance of concrete to sulfate attack.

Some incidents

Crystallization pressure is a possible factor in spalling at Minot Air Force Base, N.D., after the first near 0°F night in October 1972,** and at Fort Carson, Colorado Springs, Co.†† The same occurred in Utah for sudden

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*Personal communication, Austin Kovacs, Research Civil Engineer, CRREL.

†Personal communication, Roger Berger, Research Physicist, CRREL.

**Personal communication, Col. William Orth, Offutt Air Force Base, 1973.

††Personal communication, Stephen Lotterhand, Plans and Programs Engineer, CRREL, 1977.

pop-outs of interstate pavement on a very cold night (-15°F),* and for bad degrading of city pavements and curbs where salt exposure may be greater than on interstate highways.

Crystallization pressure

Crystallization pressure, the ability of a growing crystal to exert force, i.e. to lift a weight, was demonstrated by Becker and Day (1905) and again by Tabor (1916), a highway geologist. It may amount to many atmospheres, as discussed by Khaimov-Mal'kov (1956) and Winkler and Singer (1972).

The consequences of crystallization pressure in frost action are familiar (Fig. 3 and 4) and long studied by many workers, e.g. Beskow (1935). In soils, where water is free to migrate through capillaries to the freezing front, the theoretical pressure is only limited by the ice-water phase transition, or at -10°C (14°F) about 1200 atm (Hoekstra et al. 1965, Hoekstra 1969); pressures as high as 100 atm have been measured experimentally (Radd and Oertle 1966, 1968).

The pressure exerted by crystals growing upon relief of super-saturation in salt solution as water evaporates (and/or solubility changes upon temperature change) has been considered by Winkler and Singer (1972). Their approach was based on the work of Correns (1949), who used the Riecke principle:

$$P = \frac{RT}{V_s} \ln \frac{C}{C_s} \qquad \text{(A2)}$$

where P = crystal growth pressure (atm)
R = gas constant (0.082 liter-atm/mol K)
T = absolute temperature (K)
V_s = molar volume of solid (L/mol)
C and C_s = existing and saturated concentrations, respectively.

Thus, a crystal under linear pressure melts at a lower than normal temperature, which explains glacier flow and the slipperiness of ice. Conversely the growth of crystals develops pressure, as in frost heaving.

Referring to Mullin (1961) and Stumm and Morgan (1970), Winkler and Singer (1972) calculated crystallization pressure for a variety of salts and degrees of supersaturation; Table A1, for example, shows 554 atm from two-

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*Personal communication, Derle Thorpe, Utah State University, 1979.

fold supersaturated NaCl. Such pressures far exceed the tensile strength of concrete and rock and thus explain salt weathering. As Winkler and Singer (1972) also pointed out, the crystallization pressure of rapidly hydrating $MgSO_4$ is the basis of the ASTM (1977) C-88 test for soundness of aggregates.

Knacke and von Erdberg (1975) have reported on the transition

$$Na_2SO_4 + 10H_2O \rightleftarrows Na_2SO_4 \cdot 10H_2O \qquad (A3)$$

which involves a 300% expansion as crystals of the hydrate replace the anhydrous form, i.e. by take-up of water present as vapor in air. Thermodynamics suggests a pressure of 200 kp/cm^2 (19.6 MN/m^2 or 193 atm). In limited trials, pressures reached 19 atm (1.9 MN/m^2), i.e. above the tensile strength of many stones and ceramics.

Grattan-Bellew and Eden (1975) reported on damage to a church floor in Canada. Biological oxidation of contained pyrite in underlying shale formed gypsum. Its growth in the shale caused heaving.

Price (1975) asserted that crystallization of salts in pores is most important in stone decay and preservation in Britian. It was frequently cited in an older survey (Schaffer 1932), which is considered a classic.

Sun and salt effects on concrete in the Middle East were discussed in New Civil Engineer (1975). It suggested that the cyclic wet-dry of dew and sunshine and cyclic temperature changes might enhance the salt weathering pressure. Both are factors in concrete deterioration in that arid, hot and salty area, where even asphalt is affected (Fookes and French 1977). Damage to fairly good concrete has shown up within two to five years, with as much as 15-30 mm (0.6-1.2 in.) erosion (Fookes and Collis 1975a,b).

Salt weathering is an accepted factor in the deterioration of stone and brick and concrete structures in urban areas (Fig. 1 and 2) where salting is heavy (Schaffer 1932, Winkler and Singer 1972). In Portland cement concrete, Woods (1968) cited the detrimental action of salts, whether extraneous or formed by reaction, in developing destructive crystallization pressure upon evaporation or hydration. Blight (1976) noted blisters and cracks when soluble salts in the aggregate of base or in the underlying material leach upwards by evaporation of water through the surfacing.

Practical aspects

In the deicer-salt-concrete problem, salt action may continue year-round. Granite, too, is not immune, according to Winkler and Singer

(1972). While freeze-thaw stresses occur only in winter, those of salt action may well be greater in the more extreme wet-dry and warmer conditions of summer. Hosing down bridges in the spring has been proposed; Browne et al.(1970) recommended it for $CaCl_2$. Lankard et al. (1975) found back-flushing ineffective, and it was supposedly abandoned. Brief hosing, or even heavy rain, seems unlikely to cause much salt to diffuse to the surface in a limited time and be washed away. However, hosing is still being done.*

Economic penalties of deicing with salt appear in a comprehensive report for the Environmental Proctection Agency (Murray 1977). This estimated that damage and economic losses to the country as a whole are many times the cost of salt spreading by highway departments.

<u>Corrosion aspects</u>

The alkalinity (high pH) of concrete tends to passivate embedded steel reinforcement (rebars). Probably it was earlier thought this would continue to protect the steel from corrosion when salts were applied to concrete pavements. However, lowering its pH from 13 to 11.5, as by penetration of atmospheric CO_2, is enough to disrupt the protective film and depassivate the metal. On good, normal, uncracked concrete, CO_2 reportedly does not penetrate beyond 1.3 cm (1/2 in.) even in long exposure (Gille 1960). Other stronger atmospheric acids like nitric and sulfuric could also play a part.

Rebar attack at greater depths implies that salt loosens up concrete and enhances penetration of salt, CO_2, oxygen, atmospheric pollutants, etc. The thesis of this report is that salt affects concrete by causing microcracks and crumbling, thus increasing penetration.

Free CO_2 reacts with $Ca(OH)_2$ in concrete (carbonation):

$$CO_2 + Ca(OH)_2 \rightarrow \underline{CaCO_3} + H_2O \quad . \qquad (A4)$$

Some free CO_2 is necessary to stabilize bicarbonate formation in the equilibrium next resulting:

$$CaCO_3 + CO_2 + H_2O \rightleftarrows Ca(HCO_3)_2 \quad . \qquad (A5)$$

The CO_2 requirement increases with $Ca(HCO_3)_2$ concentration. Only CO_2 above this level is aggressive, i.e. capable of dissolving more $CaCO_3$ and lowering the pH, and thus also depassivating steel and enhancing its corrosion. More free CO_2 is needed to stabilize a given amount of $Ca(HCO_3)_2$ when calcium

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*The Vermont Highway Department, for example, feels hosing down bridges since about 1970 has been worthwhile, according to Russell Snow, Engineer (Montpelier) and Thomas Tatro, Asst. District Engineer (White River Jct.), personal communication, 1977. It is still being practiced in 1984.

salts like $CaSO_4$ are present. However, when salts of other bases, such as NaCl, are present, the free CO_2 needed for eq A5 is less (Lea 1956). By leaving more CO_2 to be aggressive, this must favor depassivation and corrosion when salts reach the rebars in concrete. Loss of the integrity of the concrete would hasten such penetration, e.g. due to cracks generated by mechanical, thermal or physical-chemical effects.

Deterioration of the concrete and eventual corrosion and weakening of steel bridge deck reinforcement or even of structural members are popularly ascribed to deicer or marine salt action on the reinforcing steel. In this, penetration of salt solution to the metal provides the electrolytic medium needed for galvanic corrosion in the presence of oxygen and water. These (as well as the CO_2) must also diffuse into the concrete. Certainly cracking and crumbling due to prior action of salt on concrete itself would favor this.

Typical corrosion reactions are:

$$Fe + H_2O + 0.5\ O_2 \rightarrow \underline{Fe(OH)_2} \qquad (A6)$$

$$2Fe + H_2O + 1.5\ O_2 \rightarrow \underline{2FeO(OH)} \qquad (A7)$$

$$2Fe + 3H_2O + 1.5\ O_2 \rightarrow \underline{2Fe(OH)_3} \qquad (A8)$$

$$3Fe + 2O_2 \rightarrow \underline{Fe_3O_4}\ . \qquad (A9)$$

These and other reactions produce solid products several times the volume of the original metal. Their formation and growth therefore develop pressures that increasingly stress the concrete. Being of low tensile strength, it cracks, scales and spalls, enhancing further access of salt, water, oxygen and CO_2. This could accelerate both salt action and corrosion, aggravating deterioration.

Freeze-thaw and salt

Freeze-thaw also deteriorates concrete. In cavities or pores over 91% full of water, the 9% volume expansion as water freezes may rupture the matrix if the rate of crystallizing exceeds permeability (Portland Cement Assn. 1951), i.e. rate at which excess water can escape through pores. The forming ice may also act as a plunger to produce hydraulic pressure, transmitting stress through liquid-filled pores to other zones.

Diffusion of water from pores to a relatively few loci of ice growth can cause dilation of concrete (Neville 1973), just as in soil frost action. This mechanism is an important cause of frost damage in concrete (Everett 1961, Helmuth 1969, Neville 1973, Litvan 1977). Ice crystals have actually been seen to aggregate in layers and to rupture concrete (Neville 1973, Powers and Collins 1945).*

Deicing salts are a participating and aggravating factor in freeze-thaw effects on concrete (Concrete Construction 1975), sandstone (Williams and Robinson 1981) and limestone (McGreevy 1982). Thus, salts cause "osmotic" pressure that helps induce water to move from below toward the salt solution (which it dilutes) and the colder surface, where it can freeze (Helmuth 1969, Neville 1973).

Damage is greatest at low, 2-4% salt concentrations (Verbeck and Klieger 1957, Neville 1973, McGreevy 1982), suggesting that the action is more physical than chemical. Higher salt concentrations [Williams and Robinson's (1981) were saturated] would, of course, be less subject to freezing. Hudek and Rigbey (1976) found that immersion of rocks in 3% NaCl increased the amount of water subsequently taken up at high humidity or upon immersion. Such enhanced water content (the pores are more full) increases the susceptibility to deterioration for aggregates exposed to deicing salts. As experimental data on these processes are lacking for concrete and the mechanism of deicer effects has not been determined (Neville 1973), extension of the present work into the freezing area would be doubly of value.

Miscellaneous

Other recognized causes of deterioration of concrete include cyclic wet-dry, sharp thermal changes, corrosion of reinforcing iron (in which salt is seen a prime factor), sulfate attack, leaching and the alkali-silica reaction. Mather (1975) has recently reviewed some of these.

The summary (Concrete Research Lab 1974) of a 1971 seminar in Denmark concerned the alkali-silica effect on concrete but not salt weathering. The damage by deicing salts was discussed at the Transportation Research Board meeting of January 1975. So was possibility that chlorides aggravate the more familiar sulfate attack. The need for more study of salt effects was evident. Ben-Yair (1974) showed that chlorides penetrate concrete much more than sulfates. (Perhaps sulfates tend to be blocked in the process by their own precipitation as $CaSO_4$.) Thus, chlorides may enhance sulfate attack in arid regions.

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*However, one informant suggested that the affected concrete may have been "green," i.e. incompletely cured, although it seems logical that water migration, freezing and lens segregation, so well recognized in fine-grain soils, might occur to some degree in concrete (personal communication George Verbeck, former director of Portland Cement Association, 1977).

Interest in crystallization pressures for the writer arose in 1962 upon seeing Khaimov-Mal'kov's (1956) report. It grew in studies of frost action needle ice (Fig. 7) (Sayward 1966, 1979). Salt weathering (a manifestation of such pressure), its similarity to frost action in soil, and the possibility that it might logically apply to concrete exposed to deicing salts first became of concern in 1965 after Wellman and Wilson's (1965) note made evident the similarity of salt weathering and frost action.

Building and maintaining highways involves many responsibilities and distractions. It is hardly considered a physical-chemical activity. However, just as corrosion has become a concern, so interest in salt action mechanism per se is developing. A note in Civil Engineering - ASCE (1982) summarized a presentation to the Corrosion Committee (A2G05) of the Transportation Research Board by Carl Crumpton and G.P. Jayaprakash, of Kansas DOT and Kansas State University. By sophisticated means, they demonstrated the growth and stress by deicer salts and corrosion products in concrete and exudation from pores as columns and fibers like those described here and informally by the writer at TRB Committee A2E01 meetings in 1977 and 1980. The Kansas workers also observed lifting of particles by salt fibers, as noted here. Arrangements for a sophisticated environmental chamber for such studies in Britain and discussion of pressure development by growing crystals are being made by Cooke (1979). Recent studies on salt-freeze-thaw action on rocks have also been made by Williams and Robinson (1981) and McGreevy (1982).

Table A1. Calculated crystallization pressures (Winkler and Singer 1972).

Salt	Formula	Crystallization pressure at 0°C, atm		
		C/C_s* = 2	10	550
anhydrite	$CaSO$	335	1120	1900
epsomite	$MgSO_4 \cdot 7H_2O$	105	350	595
gypsum	$CaSO_4 \cdot 2H_2O$	282	938	1595
halite	$NaCl$	554	1845	3135
kieserite	$MgSO_4 \cdot H_2O$	272	910	1543
tachhydrite	$2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$	50	166	282

*C/C_s = concentration/solubility = degree of supersaturation.

Table A2. Seawater analysis (Burd 1976).

Ion	mw	%	Molarity $\frac{\text{mol}}{\text{L solu.}}$
Na^+	23.0	1.0561	0.4711
Mg^{++}	24.3	0.1272	0.0537
Ca^{++}	40.1	0.0400	0.0103
K^+	39.1	0.0380	0.0100
Cl^-	35.5	1.8980	0.5485
$SO_4^=$	96.1	0.2649	0.0283
HCO_3^-	61.0	0.0140	0.0024
Total		3.4382	1.1243
Other		0.0118	
Total		3.500	

pH = 8.1 - 8.3
sp. gr. (17.5°C) = 1.026

Table A3. Seawater makeup.

Salt	mw	$\frac{g}{L\ H_2O}$
$NaHCO_3$	84.0	0.20
Na_2SO_4	142.1	4.05
KCl	74.6	0.75
$CaCl_2$	111.0	1.14
$MgCl_2$	95.2	11.585*
$NaCl$	58.5	24.3

*$MgCl_2 \cdot 6\ H_2O$

Table A4. Chronology: Periods of tests and activities.

Period	Length and dates	Air flow (mL/min)	Remarks
I	5-11 days 5/14-5/25/76	0	Prepn. during 5 days Stand (no air, 5-11 days) Exudations on 15 Drastic cracking of F4-4- photos 5/25 and 27/76 Photos: at end 5/25/76 At end: disks scraped
II	66.3 (5/25-7/30)	360	Exudation on 27 Drastic cracking of F11-4' in few days -- photos 7/6-12/76 Photos: midway 6/30/76 (angle) at end 7/22-24/76 At end: disks scraped (heavier exudations in two portions) and swabbed
A	37.8 (5/25-7/2)		
B	28.5 (7/2-7/30) A/B ratio 1.33		
III	48.5 (7/30-9/17)	630	Exudations on 19 Photos: at end 9/17/76 At end: disks scraped and double-swabbed
A	27.7 (7/30-8/27)		
B	20.8 (8/27-9/17) A/B ratio 1.36		
IV			
A	7 weeks (9/17-11/5)	-	Storage Under cover breaker in petri dish with solution (renewed occas.) F3-3 badly cracked - photos Photos: 9/22-24/76 all; 11/5 and 11/76
B	9 weeks (11/5-1/5/77)	-	Under cover, solutions drying out (no longer renewed) F3-3 very badly cracked
C	8 months (1/5- 9/1/77)	-	Under cover, solutions dried F3-3 very badly cracked F10-10 badly cracked By microscope (photos) Cracks: B2-1, D2-1(?) F1-1, F2-2, B1-3, D7-3(?), D3-5(?), E3-7, F19-7, E4-9, F9-9, F14-x, Chips or particles: B2-1, F1-1, C1-2, E1-2, B1-3, C1-3, E7-3, E3-7, D4-8, F14-x

Table A4 (cont'd).

Period	Length and dates	Air flow (mL/min)	Remarks
D	2 years (9/1/77- 9/15/79)	-	Cracks: D2-1(?), A2-5, F18-5, F14-x Chips or particles: D3-5, F14-x By microscope: Cracks: B2-1, D2-1, F1-1, C1-2(?), E1-2, E5-4, A2-5, D3-5, E2-5, F5-5, F18-5, A4-8, D4-8, F9-9, F14-x Chips or particles: D2-1, C1-2, E1-2, D1-3, A2-5, D3-5, E2-5, F5-5, A3-7, F14-x Photos: 9/17/79 F4-4, F11-4', F14-x
E	2-1/2 months (9/15/79- 2/1/80)	-	F4-4 and F11-4' deterioration continued further--expanding mealy condition, many crystal filaments (beaker only half full) F14-x more swelling and cracks and gray powder lifted on exudation (beaker dry) Photos: 2/1/80, F4-4, F11-4'
F	5 months (2/1/80-6/25/80)	-	F4-4 and F11-4' mealy mass somewhat collapsed due to hygroscopicity and higher summer humidity Photos: 6/25/80, F4-4, F11-4'
V	18 weeks (11/23/79-3/31/80)	0	Special later test (no air) using 13 disks, with NaCl low and high, also 3 NaCl/1 $CaCl_2$, also water. By microscope: Cracks in all with salts Chips or particles in several (see text) Photos: 1/8/80, photomicros 3/27/80