J. M. Pitt, R. A. Carnazzo, J. Vu, M. Seshadri

Final Report

Control of Concrete Deterioration Due to Trace Compounds in Deicers

May 1992

Sponsored by the Iowa Department of Transportation,
Highway Division, and the
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Iowa DOT Project HR-299
Project 3071
ISU-ERI-Ames-92229

Iowa Department of Transportation

report

College of Engineering
Iowa State University

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Highway Division of the Iowa Department of Transportation.

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ABSTRACT

This reports work on three facets of rock salt deicer action on freeze-thaw resistance of portland cement concrete. The first deals with improvement of mortars where it is demonstrated that a 10 to 15 percent replacement of cement with fly ash can more than double the life of concrete by reduction of porosity and stabilization of calcium hydroxide. Excessive fly ash was found to counter this benefit. Secondly, this research defines behavior and performance of aggregates displaying different service lives in concrete subjected deicers. Freeze-thaw in water produced failure in the aggregate while in deicers damage was exclusive to the mortar-aggregate interface or the mortar. Aggregate porosity appeared to be a good but not infallible predictor of concrete service life. Low porosity aggregates were best. The third feature of this research was development of a test method capable of modeling the freeze-thaw process and predicting life performance. This was done by adaptation of the ASTM C 666 test to include a reliability based design. Essential to this test method was objective definition of failure and a realistic model linking laboratory tests to the temperature environment observed in the field. The methodology was compared to performance of a pavement in central Iowa. The model predicted life of 25 years while the pavement failed at 26 years. This predictive method was also used to contrast the life of a pavement subject to different deicing materials follows: no deicer-life = 25 years, low sulfate NaCl-life = 19 years, and high sulfate NaCl-life = 14 years.

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PART 1: BACKGROUND AND REVIEW

Introduction

The placement of deicing salts on portland cement concrete has been known to be destructive but the rate, amount, and cost of this damage has not been defined. Though much is known about the effect of freezing and thawing with deicers on portland cement mortar, management of highway systems might be enhanced with better knowledge of deicers and frost action on whole concrete. This means evaluation of aggregates and admixtures commonly used in concrete.

This project is intended to advance the work done with deicers operating on the mortar phase of concrete to include aggregate, air entrainment, and pozzolans. An objective of this work is to develop a predictive test which includes all phases of concrete.

Literature Review

<u>Freeze-thaw in water</u> Freezing and thawing of water in porous materials has been described by several theories. One of the earliest theories was based on a 9% increase in volume as ice forms from water. If there is not an adequate amount of empty voids to accept the increased volume, the ice forming in the pores will expand against pore walls causing destructive pressures to develop in the material. This implies that a critical saturation level, 91% satura-

tion, above which a frozen sample will incur damage. Experiments on frost susceptible material such as concretes and other porous materials indicate that not all "saturated" materials, and some "unsaturated" materials, are damaged by freezing. Thus, the theory errors in requiring the expansion of water during freezing to produce damage. As stated by Everett (1961), "It was recognized many years ago that the damage has no necessary connection with the expansion which occurs when water freezes: similar damage to stone and consolidated earth can be produced by organic liquids which contract on freezing."

Other theories have been presented to explain the process of frost damage in concrete. Theories by Powers (1945, 1949, 1965), Litvan (1972b, 1974, 1976), and Everett (1961) have been proposed. Of these theories, only Powers' and Litvan's proposals attempt to explain the effect of salts on freeze-thaw activity.

In 1945, Powers introduced a hydraulic pressure hypothesis which was based on the 9% expansion of water previously described. To better describe frost action in concrete, Powers presented modifications to this hypothesis in a number of articles: Powers and Brownyard (1947), Powers (1949), Powers and Helmuth (1953). In these articles the reduction in volume of porous material that occurs during the initial stage of freezing was explained. In

modifying his theory, Powers included an osmotic pressure term with the hydraulic pressure.

Powers' theory, as modified, is described in the Stanton Walker Lecture Series (Powers, 1965). The theory considers water in the pores of concrete to contain a "considerable" amount of soluble material in solution. During freezing, the solution in capillary pores freezes differentially, pure water alone forms ice, concentrating solutes until a fully saturated level is reached. As the capillary pore solution becomes more concentrated, its equilibrium with the surrounding solution contained in unfrozen gel pores becomes unstable. The solutions attempt to equilibrate; water diffuses from gel pores to capillary pores and solutes diffuse from the capillaries to the gel pores. Water molecules being smaller than solute molecules diffuses more quickly (Litvan, 1972a) creating an osmotic pressure in the capillary pores capable of damaging the material. The flow of water out of the gel pores into the capillary pores causes the initial reduction in volume in concretes observed in experiments.

Expansion of the material, in Powers' theory, occurs when temperatures drop low enough to freeze the solute saturated solution in the capillary pores causing the solution to expand. Expansion also occurs when low surface

pressure over ice, as compared to water, causes gel water to flow into already frozen capillaries where it freezes and expands (Powers and Helmuth, 1953; and Pickett, 1953). This expansion is harmful when capillary pores are concurrently filled with ice. Hydraulic pressures occur as described in Powers' initial hypothesis when conditions as outlined at the beginning of the discussion are met.

The theory extended by Litvan (1972a, 1972b) for frost action in a porous material is based on the vapor pressure of water (P_l^o), ice (P_s^o) and, the relative pressure of the system (P/P_l^o). The pressure of the system is relative to the vapor pressure of water (P_l^o) as opposed to ice (P_s^o). In a porous material, the relative pressure (P/P_l^o) is usually less than unity as pressure of the system (P) cannot exceed the vapor pressure of ice (P_s^o), and the vapor pressure of water (P_l^o) exceeds that of ice (P_s^o). When the pressure of the system exceeds the vapor pressure of ice, ice will form to return the system to equilibrium. As temperature lowers during cooling, the difference between the vapor pressures of ice (P_s^o) and water (P_l^o) increases, causing the relative pressure to decrease. When relative pressure lowers to a value equal to that of a pore meniscus, the meniscus becomes unstable and water flows to the surface or a larger pore where it will freeze.

Litvan's theory predicts stress will occur in a material when more water is released from unstable pores than the sample permeability is able to allow to flow to the surface or larger pores where the water can freeze. As more water is released, stress will increase to potentially damaging levels for the material. Stress will also increase as sample permeability is reduced by water freezing in the pores. Damage can also occur as temperatures fall, lowering the relative pressure until water in smaller pores flows into blocked pores and freezes. Water freezing in the already filled pores causes expansive pressures with its 9% volume increase.

The theory by Litvan does not acknowledge freezing of water in pores without "rearrangement of the absorbate" (Litvan 1973). This rearrangement can occur by flow as discussed above or by desorption from the meniscus to the surface of the material or to an ice front where the water can freeze. The desorption of water from the meniscus is a continuous process that equilibrates the pressure over the meniscus to the relative pressure (P/P_1^o). This process continues until the relative pressure reaches the meniscus pressure and allows the pore water to flow.

<u>Freeze-thaw in deicers</u> The theories by Powers and Litvan are given for the case of normal pore solutions in portland

cement hydrate. Damage done to porous material by freezing, though, is accelerated in the presence of deicers. Both Powers' and Litvan's theories are able to explain this increase in damage.

Powers outlines the effects of deicers in the Stanton Walker Lecture Series (Powers, 1965). As discussed earlier, pore water in a porous material such as concrete, is already "concentrated" with salts. When deicers are placed on the surface of porous materials, some of the melt water drains into the porous material carrying salt with it. Capillary pores being larger than gel pores saturate more quickly with the deicing solution. Due to differential freezing of water in the pores, at the next freezing cycle, the salt will be much more concentrated than before the deicer was added, causing an increase in osmotic pressure.

Litvan, in a series of papers (Litvan 1973, 1974, and 1976) described the effects of deicers on porous material. He related the increase in damage with a differential freezing, similar to Powers (1965). Pore water, now containing dilute salt solution, differentially freezes pure water ice, initially, in the manner described by Litvan's theory above. Initial freezing occurs at slightly lower temperatures than would be accounted for by pore size. This is caused by salt changing the vapor pressure of water ($P_1^{o\prime}$). As pore water freezes, it concentrates the deicer. Increased damage

occurs when the flow of water to the surface, or larger pores, is slowed by the increasingly viscous deicing solution. Ice, produced by differential freezing, also increases the damage by reducing permeability of the sample and blocking the flow of water. The presence of salt in the pores also increases the amount of water held within the pores at a given relative humidity. The increase in water requires more water to flow out of the sample when the relative pressure drops with the lowering temperature.

In Powers' and Litvan's theories, the effects of deicers on the freezing of porous material are physical in nature. This is in agreement with studies done by Verbeck and Klieger (1957) and Whiting (1974). Experimental data indicate that a potential for maximum damage to porous materials occurs at deicer solution concentrations of approximately 5%. Less damage occurs at increasing concentrations. This trend is not indicative of chemical action which would show an increase in damage at increased concentrations of deicer.

Evidence has also been shown that salt solutions cause changes in properties of porous materials such as concrete. Kawadker and Krishnamoorthy (1981), Hoffmann (1984) and Ftikos and Parissakis (1985) all have shown that salt stressed concretes undergo chemical reactions. Increased expansive reactions of ettringite formation, ettringite

carbonation, penetration of chloride ions into C-S-H gels, are some of the reactions. One well known reaction due to chloride penetration into concretes is the leaching of calcium hydroxide.

Studies have also shown that salt action in concretes affects the freezing resistance. Schluter (1986) showed that an increase in the deicer impurity, calcium sulfate, increased damage to cement mortars. Beddoe and Setzer (1988) showed that increased chloride content from deicers can be related to increased specific internal surface of samples. The proceeding reactions can be related to reductions in strength and increased permeability of concretes, and decreased freezing strength of cement pastes. Although these theories serve as guides to evaluating the problem, they also serve to illustrate the lack of attention given to freezing and thawing on the composite concrete.

Deicer Usage in Iowa

Amount Purchase records indicate sodium chloride usage in Iowa changed significantly in 1963. Prior to this date annual usage for the state averaged slightly less than 19,000 tons per year. After 1963 usage averaged about 66,000 tons per year, with a high in 1974 of 123,500 tons, Figure 1-1. One objective of this research is to measure and evaluate the impact of deicer usage on longevity por-

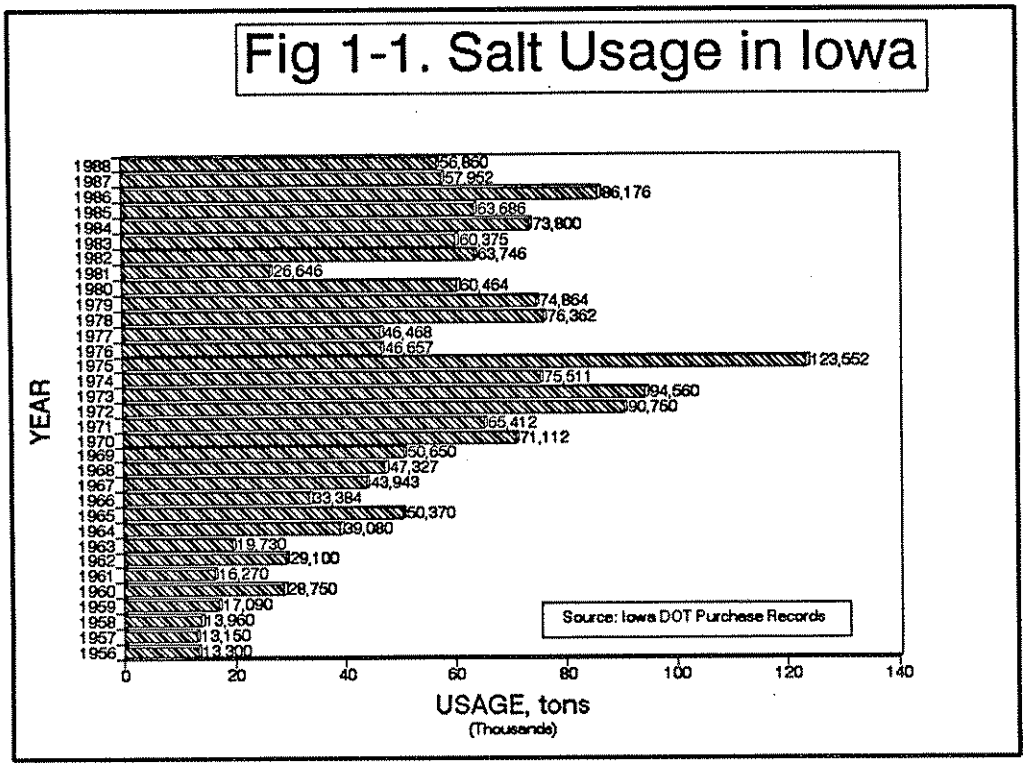


Fig 1-1. Salt Usage in Iowa
YEAR
1988 56,860
1987 57,952
1986 86,176
1985 63,686
1984 73,800
1983 60,375
1982 63,746
1981 26,646
1980 60,464
1979 74,864
1978 76,362
1977 46,468
1976 46,657
1975 123,552
1974 75,511
1973 94,560
1972 90,760
1971 65,412
1970 71,112
1969 50,650
1968 47,327
1967 43,943
1966 33,384
1965 50,370
1964 39,080
1963 19,730
1962 29,100
1961 16,270
1960 28,750
1959 17,090
1958 13,960
1957 13,150
1956 13,300
Source: Iowa DOT Purchase Records
0
20
40
60
80
100
120
140
USAGE, tons
(Thousands)

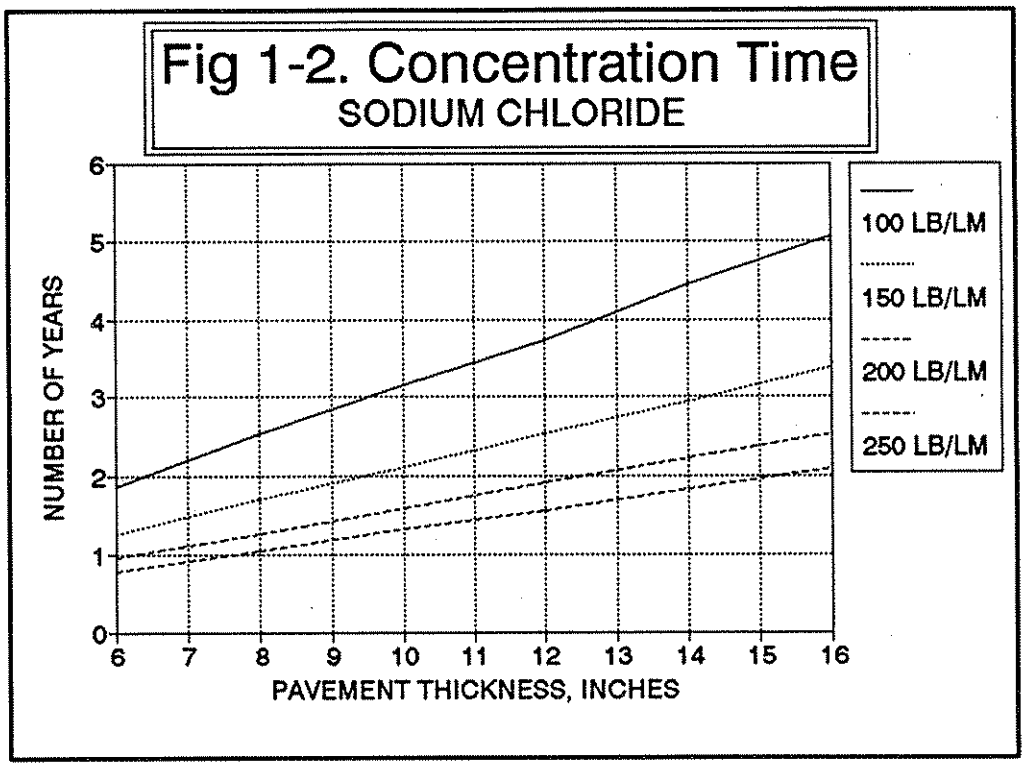


Fig 1-2. Concentration Time
SODIUM CHLORIDE
NUMBER OF YEARS
0
1
2
3
4
5
6
6
7
8
9
10
11
12
13
14
15
16
PAVEMENT THICKNESS, INCHES
100 LB/LM
150 LB/LM
200 LB/LM
250 LB/LM

tland cement concrete pavements.

There are about 8,400 lane miles of Service Level A and B and 5,200 lane miles of Service Level C pavements are routinely deiced by the Iowa DOT each winter [2]. If the A and B pavements receive 250 pounds of deicer per lane-mile and level C pavements get 150 pounds per lane mile, the quantity of deicer required to cover the entire road system is 1,440 tons. If the average annual purchase is 66,000 tons, there is enough sodium chloride to make 45 applications to the road system each year.

Presuming that the salt applied to the pavement surface enters the concrete uniformly, the number of applications to reach critical salt concentration of 0.18 percent by weight of concrete (Pitt et. al, 1987) can be estimated as a function of pavement thickness. As approximately 45 applications are made each year, the time at which critical concentration can be reached can be estimated. Results of such computations are summarized in Figure 1-2.

It can be reasoned that deicer assimilation into concrete is not uniform but will be concentrated at joints and cracks. Also, it is doubtful that concrete can accept sodium chloride as fast as it is applied. Thus these simplification to an upper bound on time it takes to accumulate enough salt to cause damage to a pavement. Nevertheless, there will be some delay which is dependent on pavement thickness and service class of the road. For example, a 12

inch pavement may have four years to accumulate enough salt to cause damage where a minimum application rate of 100 lb/lm. The time to critical concentration is reduced in proportion to the rate. As deterioration phenomena are viewed being due to volumetric assimilation of salt, concentration time for thin pavements is significantly less than that for thick sections. It only takes a year with little sensitivity to application rate to spread enough salt to cause problems to six-inch pavement. For a twelve-inch pavement concentration can take as much as four years or as little as 1.5 years, depending on rate. This factor should be considered when assessing pavement life.

Salt Composition In Iowa DOT Project HR-271, it was demonstrated that natural rock salt can contain enough sulfate as an impurity to reduce the strength of portland cement mortar by as much as sixty percent of specimens subject to the same freeze-thaw regimen in water. A least desirable two percent calcium sulfate concentration in the salt percent produced the most alteration of pores and made the mortar most vulnerable to frost attack. The mechanism for deterioration differs from that of classic sulfate attack in that it is coincident only with freeze-thaw and is the consequence of chemical products and crystallization of salts. Internal stress and specimen disintegration are from freezing a liquid in a network of pores incapable of accommodating

expansion. Mortar subjected to sulfate tainted salt brines has been reduced to rubble in 120 freeze-thaw cycles, about one-third of the life in water. Specimens in water survived to at least 300 cycles while those in pure sodium chloride had an intermediate life.

Results of laboratory tests on twenty two rock salt samples taken from Iowa DOT stockpiles throughout the state are in Appendix A. With exception of sulfate expressed as gypsum, the ions were combined by order of solubility to form compounds presumed to exist in the solid. Sulfate as gypsum is presented to facilitate reference to past work.

The salt source was not documented for some samples; nonetheless, the dta serve the intent of a brief survey of rock salts in stockpiles the Spring of 1988. If damage were to be limited to 70% of that occurring in water, sulfate as gypsum would have to be limited to 0.5% (Pitt, et al 1987). It follows from Appendix A that all but the source in Mexico would have to be eliminated. Thus deicer selection is not an option.

As alternative to rock salt are more costly, the decision to change should be balanced against the cost of damage from the salt. This means a need for predicting life expectancy.

PART 2: MORTAR

Introduction

Past research concentrated on the influence of deicers and their trace compounds on plain portland cement mortar. The intent of this phase is to establish behavioral characteristics of mortar with pozzolans, curing conditions, and post hardening treatments to delay deterioration of existing pavements.

Pozzolans

Fly ash is produced as a waste product in coal burning power plants throughout the Midwest. As such, fly ash is a readily available product that can vary from plant to plant and on a daily basis. This produces many different fly ashes used to partially replace portland cement in concrete. The amount of fly ash used to replace cement is also variable. Thus, the scope of this investigation was to determine how source, fly ash type, and percent replacement of portland cement by fly ash affect freeze-thaw resistance of fly ash concretes in saturated salt brines.

There were two objectives to this investigation. First, determine how fly ash source could affect the freeze-thaw resistance of portland cement mortars in saturated salt brines. Five different fly ashes were used, ranging from a borderline Type C or Type F to a highly cementitious Type C fly ash. Second, determine how percent replacement of

cement by fly ash affects resistance. Six levels of replacement of a single fly ash source were used ranging from 5% to 50%.

Experimental Design Test design for this investigation was based on the use of ASTM standard C666 Procedure A, for rapid freezing and thawing with slight modifications. Molded 2 x 4-inch cylindrical specimens were placed upright in a saturated salt brine, inundated to their midpoints. Prior to placement in the solutions, the specimens were measured for length and pulse time to derive a pulse velocity (ASTM C597) instead of a dynamic modulus. Pans containing the specimens were then placed in a freeze-thaw cabinet. At approximately 25 freeze-thaw cycle intervals, the specimens were again measured to attain pulse velocities. At 300 cycles, the specimens were removed from the cabinet and again measured to attain pulse velocities, then tested for tensile strength by the split cylinder test (ASTM C496). Control groups in distilled water were run concurrently.

Materials Mortar specimens for this investigation were made with Type I portland cement, Ottawa sand meeting specifications for cube tests (ASTM C190), and distilled water. Doravair-R, a commercial air entraining agent was used to attain a 9% by volume entrained air void content in the mortar. This approximated a 6% by volume entrained air void content in concrete (1" max. size). Fly ashes used for

partial replacement of the cement were Neal #3, Neal #4, Weston K. C., Lansing, and Ottumwa. Elemental oxides of the cement and fly ashes are tabulated in Tables 1-2a and 1-2b, respectively.

Solutions in which the specimens were placed during freezing and thawing were made using reagent grade chemicals of sodium chloride and calcium sulfate dihydrate. Solutions were mixed to produce an approximate 26% NaCl solution by weight of solute, with 2.0% by weight calcium sulfate as an impurity. The solutions as used, and their chemical composition were: Control, 100% distilled water; test solution, 33.0 g/100g H_2O of sodium chloride, 0.650 g/100g H_2O of calcium sulfate dihydrate. Distilled water was used as the solvent.

Procedure A total of 12 batches of concrete mortar were produced, each containing 10 specimens. One set of six batches consisted of a control batch and five batches of differing fly ash sources and types. The second set of six consisted of a control batch and five batches with differing concentrations of Neal #4 fly ash only.

Batch quantities for materials of the non-fly ash mortar specimens were derived for mortar content from Iowa D.O.T. mix design C-3 for pavements. Appendix B shows the mix proportions. Fly ash mortar specimens used the same mix proportions as non-fly ash mortar specimens; fly ash replac-

Table 2-1a. Elemental and compound composition of portland cement

Element (or Oxide)	PC	PC (Compounds) Percent by weight	
SiO_2	20.6	C_3S	55.3
Al_2O_3	4.34	C_2S	17.3
Fe_2O_3	3.24	C_3A	6.0
CaO	62.3	C_4AF	9.9
SO_3	2.78		
MgO	2.19		
K_2O	0.71		
TiO_2	0.24		
Na_2O	****		
P_2O_5	****		
BaO	****		
SrO	0.18		
LOI	3.08		

Table 2-1b. Elemental composition and classification of fly ashes

Element (or Oxide)	N4	N3	WST	LAN	OTT
			(Percent by weight)		
SiO_2	32.7	39.0	34.8	31.3	34.3
Al_2O_3	19.9	19.6	18.0	16.6	19.3
Fe_2O_3	5.51	10.1	5.34	5.75	5.24
Total	58.1	68.7	58.1	53.7	58.8
Type	C	F/C	C	C	C
CaO	26.7	19.8	26.6	30.1	25.1
SO_3	2.58	2.45	2.59	3.72	3.30
MgO	4.70	5.41	5.53	5.94	5.03
K_2O	0.40	1.30	0.35	0.26	0.41
TiO_2	1.55	0.83	1.41	1.42	1.50
Na_2O	2.98	0.18	1.41	1.95	3.78
P_2O_5	1.22	1.96	1.23	1.25	1.08
BaO	0.78	0.31	0.81	0.79	0.72
SrO	0.42	0.14	0.34	0.45	0.39
LOI	0.37	0.17	1.15	0.92	0.39

N4 = Neal #4 fly ash
N3 = Neal #3 fly ash
WST = Weston K. C. fly ash
LAN = Lansing fly ash
OTT = Ottumwas fly ash

ing the cement by weight. Batch quantities were designed with a constant water/cement ratio; no attempt being made to maintain a constant consistency of the mixes.

Specimens were molded in split 2-inch diameter by 4-inch length PVC pipe in accordance with ASTM C192. Each mold was held closed by a single ring clamp and capped at the base with plastic wrap. All specimens were cured in a humid room for 24 hours, the mold removed, and then cured in a lime bath for 28 days. Each specimen was marked with its batch number and lettered A through J. A waterproof mark was placed on the top of each specimen for length measurement positioning.

All specimens were removed from the lime bath after the 28 day curing period and rinsed clean of the excess lime. The length and pulse time for each specimen was then measured to derive pulse velocities in accordance with ASTM C597.

Length measurements were to the nearest 0.001 inch using a dial gauge positioned on a portable platform. The dial gauge was standardized using a brass cylinder of known height. Pulse times were measured to the nearest 0.1 microsecond using a James V meter. Specimens were immersed in water to attain a better coupling between specimen and meter heads.

The specimens were placed in pans from the freeze-thaw

cabinet after length and pulse time measurements were completed, each batch was placed in a separate pan. The freeze-thaw cabinet met specifications of ASTM C666. Batch specimens marked A, B and C were placed in the control pans. Pans were then filled with solution to the mid-points of the specimens. Control pans were filled with distilled water.

The test solution was made by weighing the appropriate quantities of sodium chloride, calcium sulfate and distilled water into a container, shaken vigorously, and allowed to equilibrate over night.

The filled pans were placed into the freeze-thaw cabinet and cycled according to ASTM C666. After approximately 25 freezing cycles, the specimens were removed from the cabinet, during the thaw half of the cycle. The length and pulse time of the specimens were tested again, as described earlier, and the specimens replaced in the cabinet. This was repeated at approximate 25 freezing cycle intervals. At the 100 and 200 intervals, solutions in the pans were replaced with fresh solution to maintain a constant salinity, since salt was lost "climbing" the sides of the pans and off specimens as they were immersed during pulse time measurements. Specimens were run through a total of 300 cycles.

Mercury porosimetry tests was performed on mortar fragments with a Quantichrome SP-200 Scanning Porosimeter. One intrusion was made per specimen to a pressure of 60,000

psi.

Freeze-Thaw Results Figures 2-1 and 2-2 are of pulse velocity data normalized by each specimens initial value plotted against the number of cycles. Each data point in these graphs is for an average of seven specimens. Figures 8 and 9 show tensile strength data. From Figure 2-1 it can be seen that the source of fly ash was not important, but not using fly ash allowed the mortar to begin a reduction in pulse velocity at about 100 cycles and ended at 35% of the original value. Pulse velocity reduction is primarily an indication of crack formation within specimens and to a lesser extent void formation by dissolution of cement hydrates such as calcium hydroxide.

The graph in Figure 2-2 shows a decrease in pulse velocity for the treated non-fly ash control group to approximately 35% of the initial value. The treated 50% fly ash group produced a decrease in pulse velocity to nearly 55% of the initial value. The decrease in pulse velocity for the treated, control group started at about 150 cycles while the treated 50% fly ash group started to decrease around 225 cycles. Both continued to decrease throughout the test. Near the end of the freeze-thaw test, both treated 5% and 35% fly ash groups began to decrease in pulse velocity. The final value for the 5% fly ash was 95% of the initial value and, for the 35% fly ash, it was 98%. The

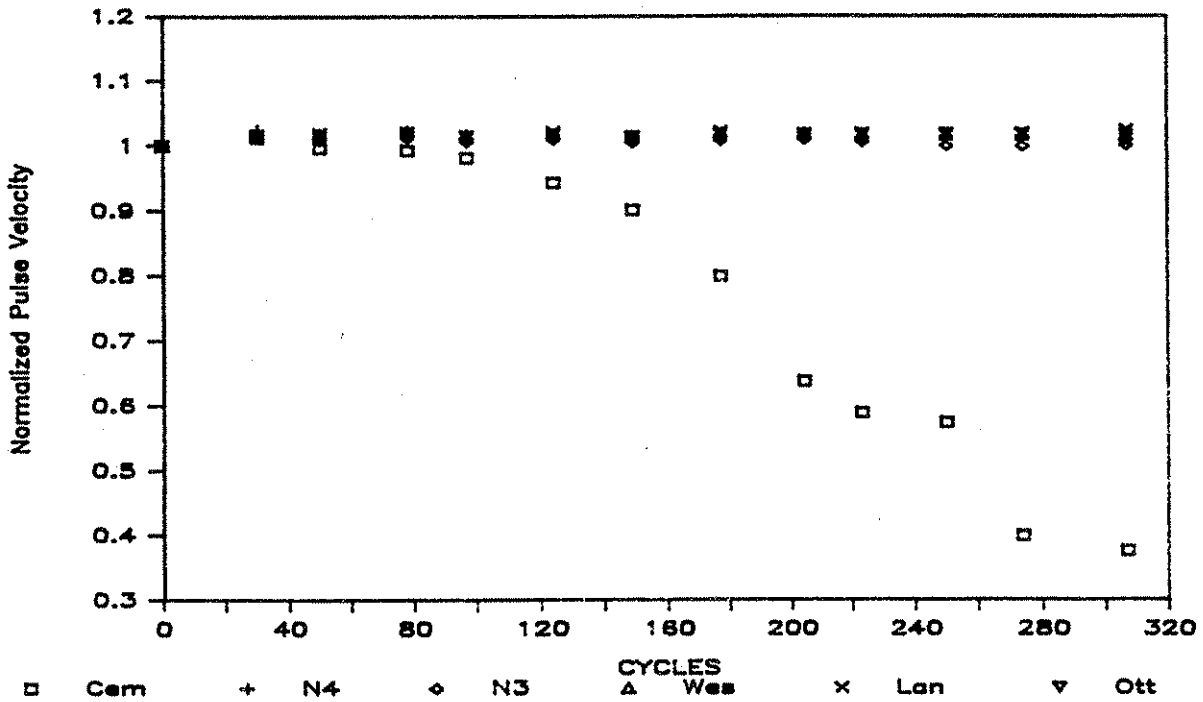


Figure 2-1. Pulse velocity data normalized. Test varied fly ash source at 15% fly ash content

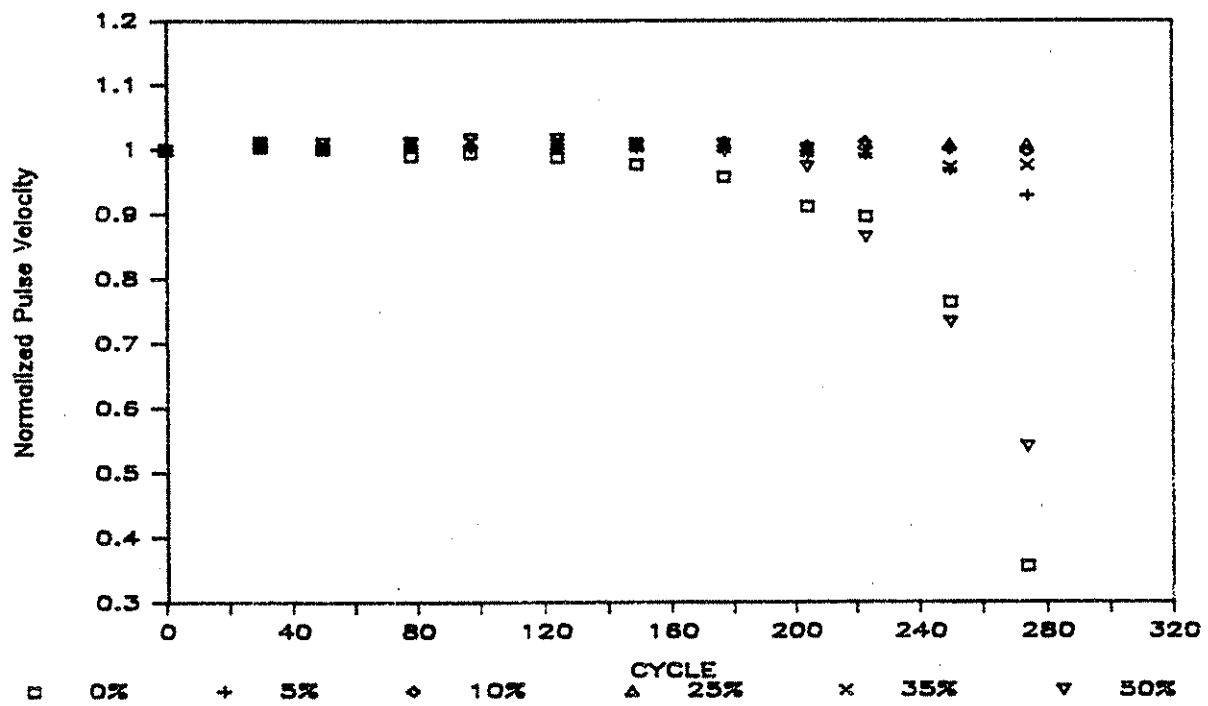


Figure 2-2. Pulse velocity data normalized. Test varied Neal #4 fly ash content

treated 10% and 25% fly ash groups showed no change in their pulse velocity. The reduction in pulse velocity again indicated the increase of open spaces produced by crack formation, loss of calcium hydroxide, or both.

A subjective evaluation of the specimens was also done during freeze-thaw cycling as is given in Table 2-2. A description of the amount of damage incurred by specimens of each batch mix is given. From Table 2-2 it can be seen that there was no physical damage evident on water control specimens, nor on 15% fly ash specimens. Non-fly ash specimens incurred the most damage with a total of four failed specimens between the two sets. Some damage was also evident on specimens with 5% fly ash content, 10% fly ash content, 35% fly ash content, and 50% fly ash content. The most damage occurred to the 50% fly ash specimens, the least damage to the 10% fly ash specimens.

Mercury Porosimetry Data Mercury porosimetry test results are Figures 2-3 and 2-4. The general distribution of pores for all of the specimens save the 10 and 15 percent fly ash replacement are about the same. The marked feature of these data is the significant reduction in pores in specimens with 10 and 15 percent fly ash. This suggests an optimum fly ash concentration of this magnitude which is probably due to the amount of amorphous silica that can be accommodated calcium by hydroxide from cement hydrates.

Table 2-2. Physical description of freeze-thaw specimens

Batch Mix	Treatment	Physical Description*
Fly ash source and type		
Non-fly ash	untreated	no damage
	treated	two failed samples, others failure, all scaled
15% Neal #4	untreated	no damage
	treated	no damage, slight scaling
15% Neal #3	untreated	no damage
	treated	no damage, slight scaling
15% Weston	untreated	no damage
	treated	no damage, slight scaling
15% Lansing	untreated	no damage
	treated	no damage, slight scaling
15% Ottumwa	untreated	no damage
	treated	no damage, slight scaling
Fly ash content		
non-fly ash	untreated	no damage
	treated	two failures, three near failures, one sample lightly cracked, heavy scaling
5% Neal #4	untreated	no damage
	treated	two cracked, two lightly cracked, two no damage, slight to heavy scaling
10% Neal #4	untreated	no damage
	treated	one lightly cracked, rest no damage, slight scaling
25% Neal #4	untreated	no damage
	treated	no damage, slight scaling
35% Neal #4	untreated	no damage
	treated	all show light cracking at top, moderate scaling
50% Neal #4	untreated	no damage
	treated	all show heavy cracking at top, moderate to heavy scaling

*Damage ratings are none, light cracking, cracking, heavy cracking, near failure, failure

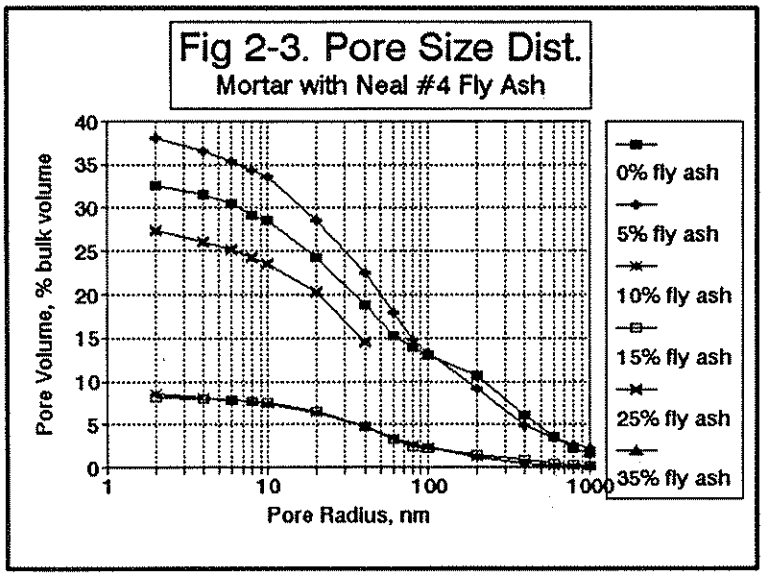


Fig 2-3. Pore Size Dist.
Mortar with Neal #4 Fly Ash
Pore Volume, % bulk volume
40
35
30
25
20
15
10
5
0
1
10
100
1000
Pore Radius, nm
0% fly ash
5% fly ash
10% fly ash
15% fly ash
25% fly ash
35% fly ash

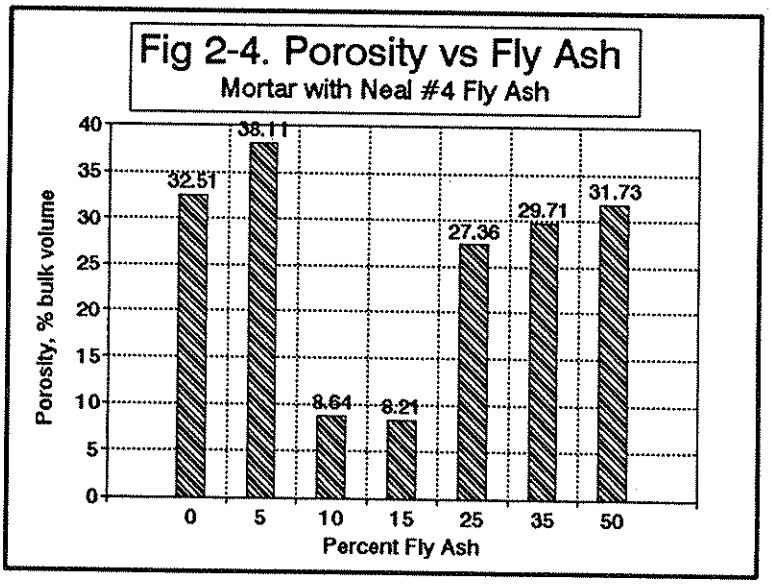


Fig 2-4. Porosity vs Fly Ash
Mortar with Neal #4 Fly Ash
Porosity, % bulk volume
40
35
30
25
20
15
10
5
0
32.51
38.11
8.64
8.21
27.36
29.71
31.73
0
5
10
15
25
35
50
Percent Fly Ash

This minimum in porosity corresponds to physical tests by no reduction in pulse velocity.

As deicers inter the mortar as a solution by motive of thermal gradient, capillary pressure, and osmotic pressure; any reduction in permeability which restricts entry of salts should be beneficial.

Curing Time

Proper curing is known to improve the normal service of concrete but there is yet to be an evaluation on curing with respect to first application of deicers. Thus sets of mortar specimens prepared as described earlier in this section were cast and allowed to cure 32, 90, 180, and 365 days prior to being subjected to freeze-thaw in deicing brines. Normalized pulse velocity vs. number of freeze-thaw cycles is plotted in Figure 2-5. Obviously the immature mortar degrades very quickly and as curing time increased, so did resistance to freezing and thawing.

Obviously one year of curing allowed the mortar to last longest, about 140 cycles. In applying the concept of maturity, defined as average daily temperature minus the freezing point of water, the likelihood of achieving a given amount of curing can be estimated from weather records. Figure 2-6 is a dual plot of monthly and cumulative degree-days for Ames. The cumulative data has been replotted in Figure 2-7 with construction dates from April to September.

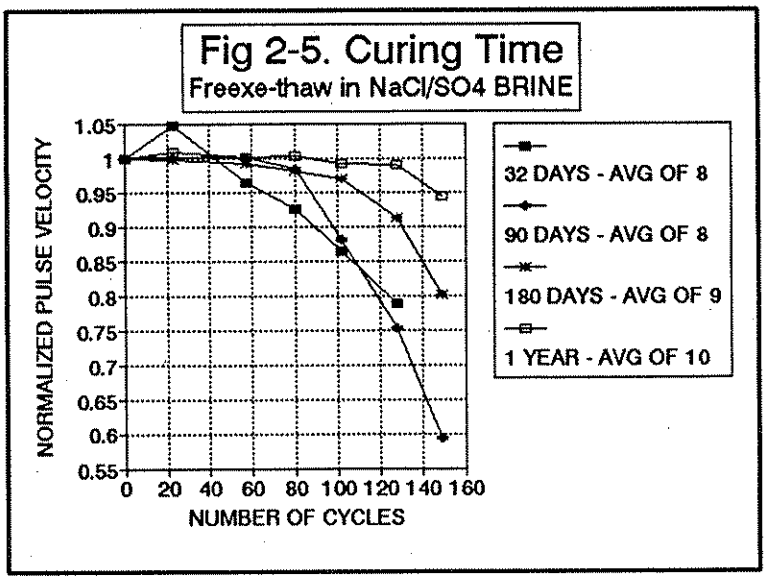


Fig 2-5. Curing Time
Freexe-thaw in NaCl/SO4 BRINE
NORMALIZED PULSE VELOCITY
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0 20 40 60 80 100 120 140 160
NUMBER OF CYCLES
32 DAYS - AVG OF 8
90 DAYS - AVG OF 8
180 DAYS - AVG OF 9
1 YEAR - AVG OF 10

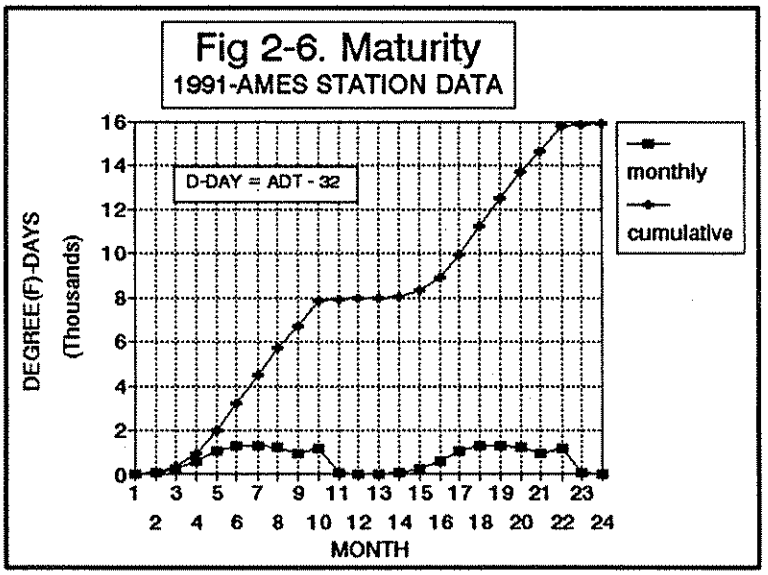


Fig 2-6. Maturity
1991-AMES STATION DATA
DEGREE(F)-DAYS
(Thousands)
16
14
12
10
8
6
4
2
0
D-DAY = ADT - 32
1 3 5 7 9 11 13 15 17 19 21 23
2 4 6 8 10 12 14 16 18 20 22 24
MONTH
monthly
cumulative

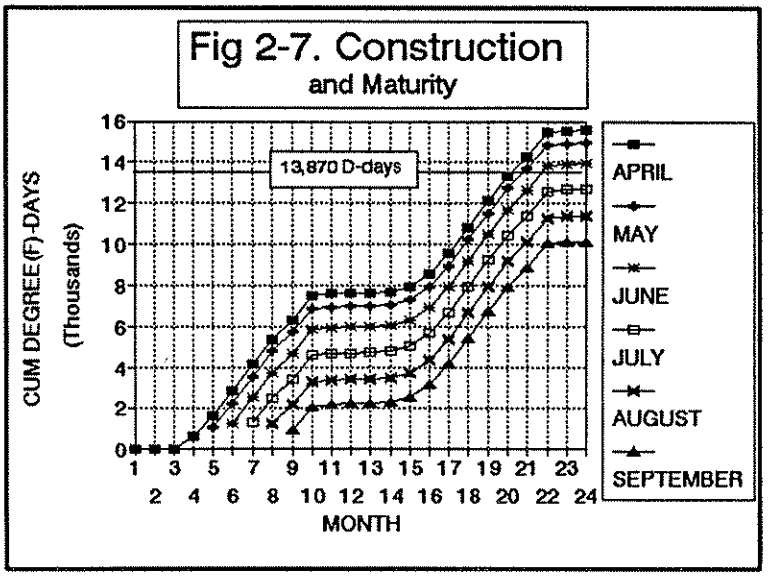


Fig 2-7. Construction
and Maturity
CUM DEGREE(F)-DAYS
(Thousands)
13,870 D-days
MONTH
APRIL
MAY
JUNE
JULY
AUGUST
SEPTEMBER

As the one year of curing corresponds to 13,870 degree-days, equivalent curing would only happen in 1991 for construction in April, May, and June.

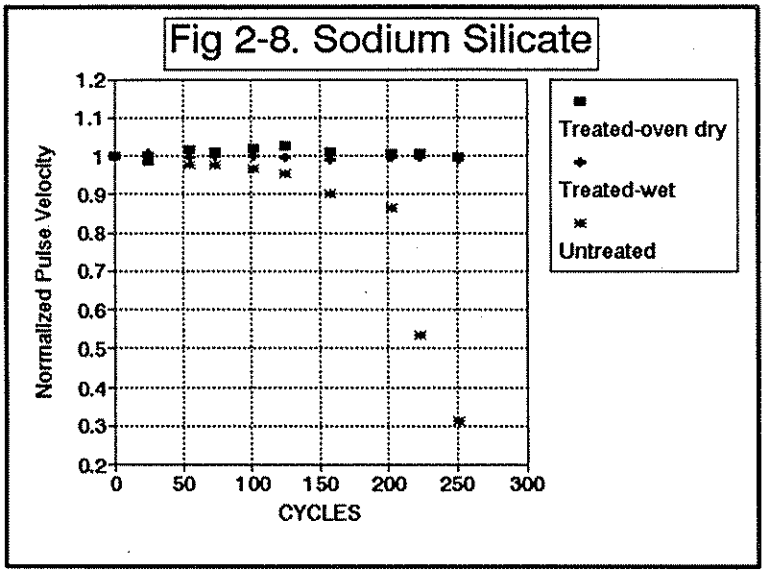
Looking back to the pulse velocity data for pozzolans in Figures 2-1 and 2-2, the use of 10 to 15 percent fly ash of 1064 degree-days of maturity would provide superior performance. In this case construction could be started through September.

This analysis was done for a single year. Several years' temperature records should be evaluated to make predictions more accurate.

Post Hardening Treatments

Liquid sodium silicate solution was painted on the surface of mortar specimens made and cured as described in the study on pozzolans. The idea is to find an inexpensive treatment that might prolong the life of pavements constructed without fly ash. Commercial grades of saturated sodium silicate cost about one dollar per gallon and could be used in conjunction with joint maintenance and sealing by simply filling the crack before sealing. The concept is application of a liquid pozzolan which could react with free calcium in hydrated cement, only after the concrete is hardened. Figure 2-8 are results of preliminary experiments where ten repetitions of wet and dry specimens were subjected to freeze-thaw in a brine. Obviously, the sodium sili-

cate specimens maintained their integrity far better than untreated mortar, probably because of reduced permeability.



PART 3: AGGREGATES

Background

The intent of this part of the research is to evaluate the influence of deicers on the aggregate fraction of concrete and to develop a test capable of predicting the life of aggregate-mortar composites.

Eight aggregates were selected with the advice of Iowa DOT staff to represent a spectrum in pore structure, chemistry, and performance capabilities observed throughout the state. These aggregates, identified by quarry name and life expectancy based on Iowa DOT staff observations are as followings:

Early Chapel - Limestone of Class 1 durability rating and expected life of less than 10 years.

Jabens - Dolomite of Class 2 durability rating and observed life of about 15 years.

Ames - Limestone of Class 2 durability rating and observed life of about 20 years.

Garrison - Dolomite of Class 2 durability rating and observed life of about 13 years.

Alden - Limestone of Class 2 to 3 durability rating, depending on bed and a service which can span from 20 to as much as 30 years.

Montour - Limestone with Class 2 durability rat-

ing, and a service life of about 20 years.

Weston Lamont - Dolomite of Class 3 durability rating and service life of about 30 years.

Waucoma - Limestone of Class 3 durability rating and a service life of about 30 years.

Chemical Composition

Table 3-1 is a summary of chemical composition of the subject aggregates determined by x-ray fluorescence analysis. The first objective of this testing is to verify consistency of the rock type used in this experimentation with that of the general description provided by the Iowa DOT. These aggregates from sources identified as limestones are consistent with the general identification owing to concentrations of calcium carbonate in excess of 97 percent. Likewise, the dolomites used in this study are consistent with the typic rock in that they have low calcium carbonate contents at the expense of more magnesium carbonate.

Pore Size

A common thesis is porosity and pore size distribution are dominant characteristics controlling the life of concrete subjected to cyclic freeze-thaw. As a base line in evaluating the test aggregates, pore size distribution was measured by mercury intrusion porosimetry. Results of these tests are presented in Figures 3-1 a and b where the cumulative volume of pores as a percentage of the bulk volume is

Table 3-1. Theoretical Composition of Aggregates

Composition,%	Alden	Waucoma	Ames	Garrison	Early Chapel	Montour	Weston Lamont	Jabens
Calcium Carbonate	97.47	98.42	97.98	58.48	96.21	98.11	55.57	72.89
Magnesium Carbonate	0.88	0.72	0.97	37.08	1.22	0.72	42.72	22.4
Iron Oxide	0.35	0.13	0.23	1.50	0.47	0.62	0.34	0.69
Silicon Dioxide	0.70	0.50	0.47	1.61	1.79	0.15	1.00	2.89
Aluminum Oxide	0.33	0.16	0.12	0.23	0.20	0.04	0.20	0.61
Potassium Oxide	0.08	0.05	0.05	0.11	0.04	0.00	0.07	0.24
Phosphorus Oxide	0.04	0.00	0.01	0.02	0.01	0.00	0.03	0.02
Mangenese oxide	0.01	0.00	0.01	0.07	0.03	0.02	0.02	0.04
Titanium Oxide	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.04
Strontium Oxide	0.03	0.01	0.04	0.02	0.04	0.02	0.02	0.02
Sulfur Trioxide	0.02	0.03	0.32	1.50	0.03	0.30	0.02	0.17
Alkalis	0.12	0.05	0.06	0.13	0.05	0	0.1	0.26
Life, years	20	30	20	13	10	20	30	15

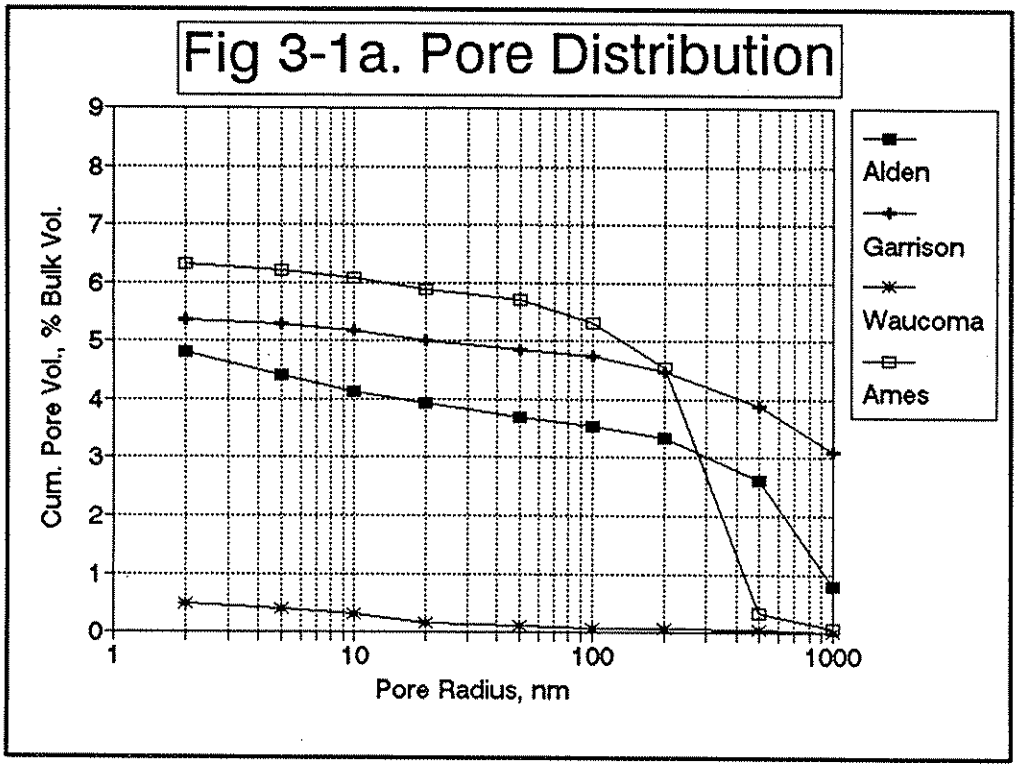


Fig 3-1a. Pore Distribution
Cum. Pore Vol., % Bulk Vol.
Pore Radius, nm
Alden
Garrison
Waucoma
Ames

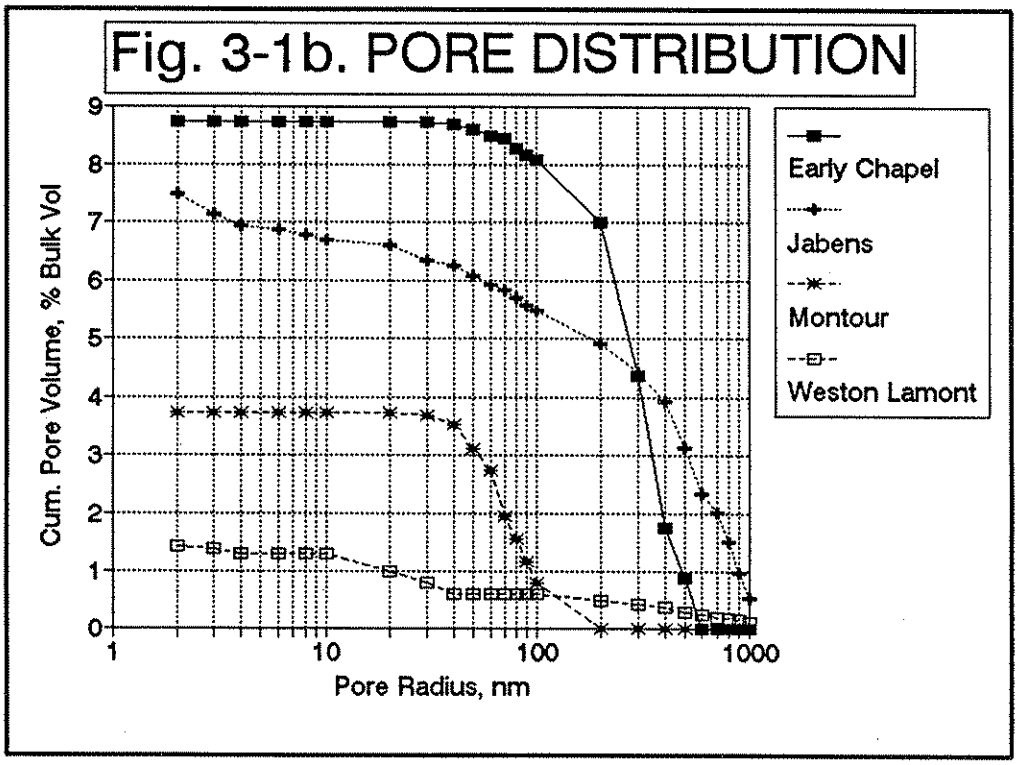


Fig. 3-1b. PORE DISTRIBUTION
Cum. Pore Volume, % Bulk Vol
Pore Radius, nm
Early Chapel
Jabens
Montour
Weston Lamont

plotted against pore radius.

Pore distribution of the five most porous stones are similar in that most of the pores are larger than 100 nm. The two least porous aggregates, Waucoma and Weston Lamont, also have similar distributions but with voids smaller than the 100 nm size. Montour aggregate is of intermediate porosity but differs from the companions in that most pores are smaller than 100nm radius

Total porosity of these aggregates is summarized in Figure 3-2 where it is apparent that a good representation of porosities was selected. Attempts were made to correlate several pore distribution characteristics such as median pore radius, porosity at 100 nm, and slopes of pore distribution curves. From this evaluation the only meaningful relationship that was apparent was that of total porosity and observed life. Figure 3-3 shows two linear models of life vs. porosity. The code identifying the aggregates is the first or first two letters of the quarry name. The lower solid line includes all eight aggregates and has a fairly respectable correlation coefficient, RSQ = 0.85, meaning that porosity accounts for 85% of the variation. Porosity is not the cause of the remaining 15% of variation required for a perfect fit. Garrison and Ames aggregates contradict the model the most in that they diverge from the average by at least five years. Variation from the expected

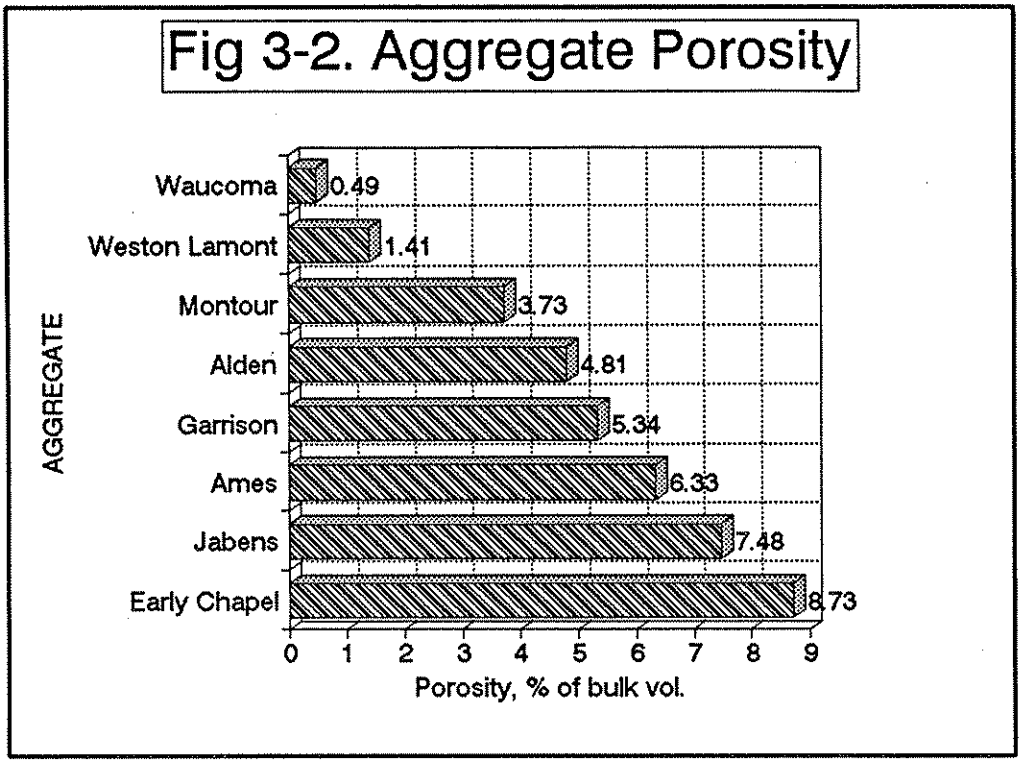


Fig 3-2. Aggregate Porosity
AGGREGATE
Waucoma
Weston Lamont
Montour
Alden
Garrison
Ames
Jabens
Early Chapel
0.49
1.41
3.73
4.81
5.34
6.33
7.48
8.73
0 1 2 3 4 5 6 7 8 9
Porosity, % of bulk vol.

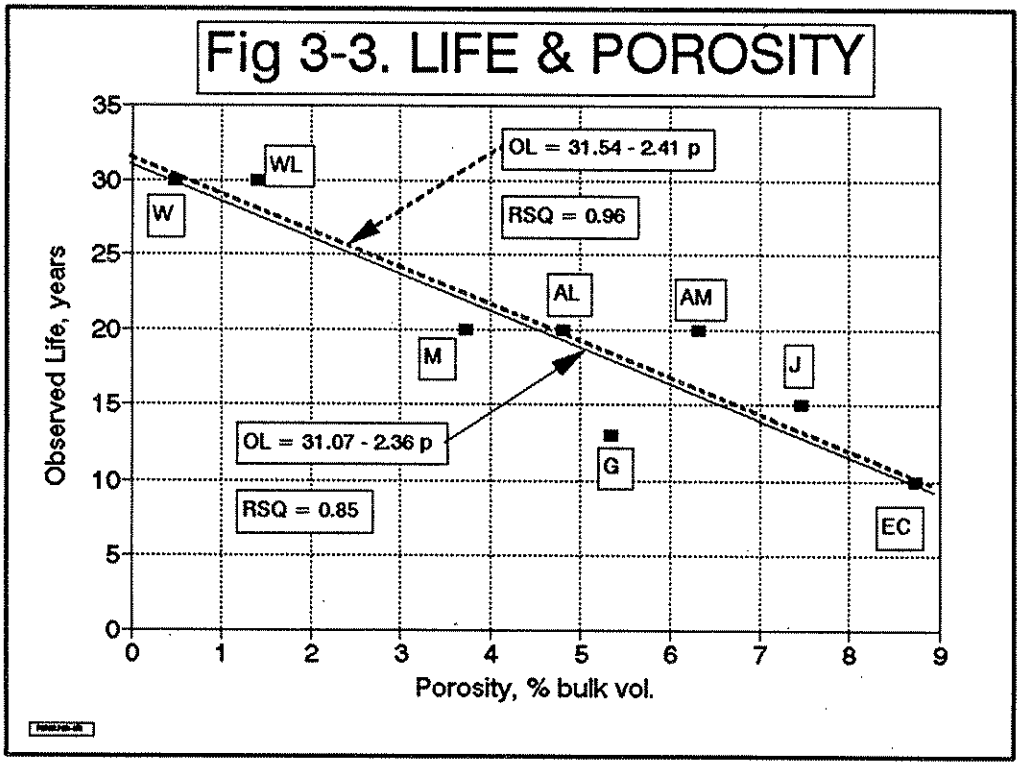


Fig 3-3. LIFE & POROSITY
Observed Life, years
0 5 10 15 20 25 30 35
0 1 2 3 4 5 6 7 8 9
Porosity, % bulk vol.
OL = 31.54 - 2.41 p
RSQ = 0.96
OL = 31.07 - 2.36 p
RSQ = 0.85
W
WL
M
AL
AM
J
G
EC

lives for the other six aggregates is two years or less, well within the limits of subjective life assessment.

A second linear model, the upper dashed line in Figure 3-3, was fit after eliminating the Garrison and Ames data. Although the relationship between life and porosity changed little, the improvement in correlation coefficient to RSQ = 0.96 is as good a fit as can be obtained. Based on porosity Garrison should have a twenty year life, rather than thirteen years. Ames should be good for about sixteen years, rather than twenty.

Trace Chemistry of Aggregates

Trace chemistry of the aggregates was evaluated by plotting oxide compositions of the elements listed in Table 3-1 against observed age of concrete and then looking for a divergence from compositions of companion aggregates. Figures 3-4 and 3-5 are plots of calcium and magnesium carbonate and serve to verify the fact that limestones and dolomites are being evaluated.

A general trend for the lesser elements is the more porous the material, the greater the quantities of trace elements. This stands to reason in that porous strata were more likely to contain deposits of extrinsic elements from percolation of mineral laden water. Whether or not extraneous elements are present also depends on elements in the ground water.

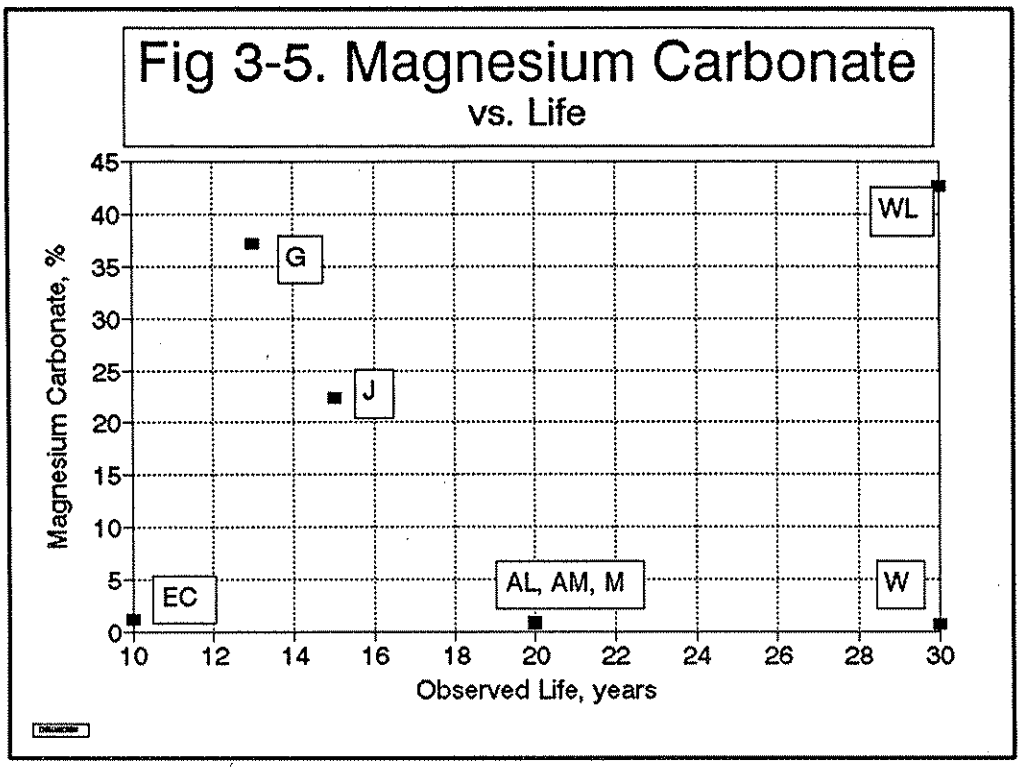


Fig 3-5. Magnesium Carbonate
vs. Life
Magnesium Carbonate, %
Observed Life, years
45
40
35
30
25
20
15
10
5
0
10
12
14
16
18
20
22
24
26
28
30
WL
G
J
EC
AL, AM, M
W

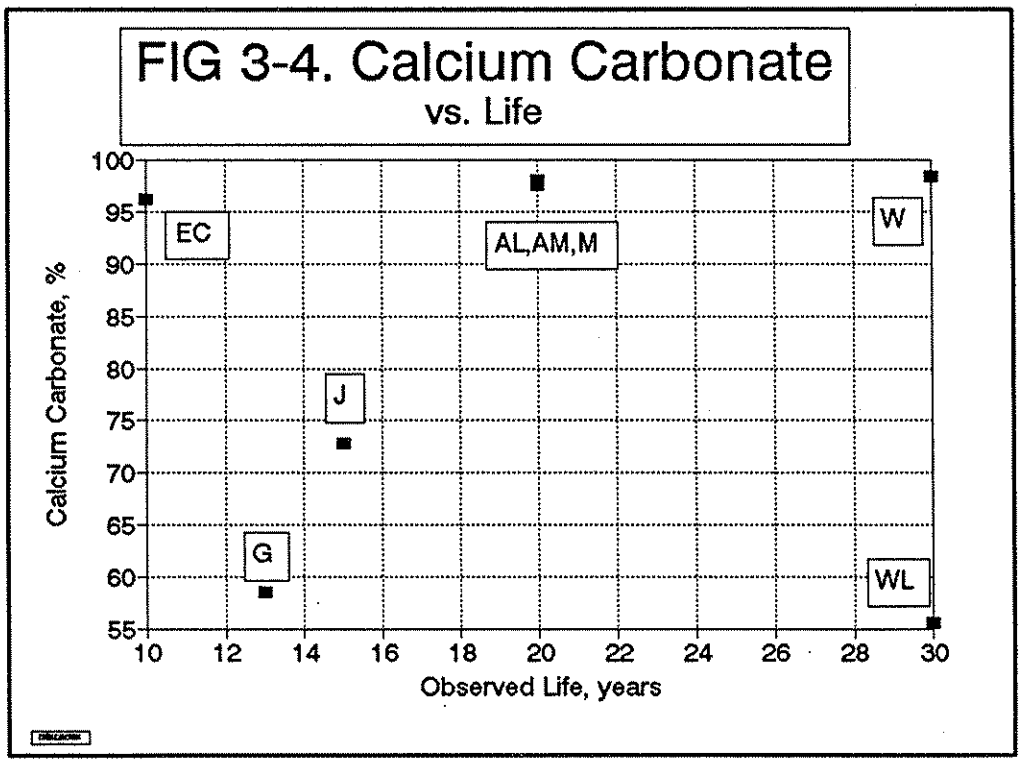


FIG 3-4. Calcium Carbonate
vs. Life
Calcium Carbonate, %
Observed Life, years
100
95
90
85
80
75
70
65
60
55
10
12
14
16
18
20
22
24
26
28
30
EC
AL,AM,M
W
J
G
WL

Garrison aggregate stands out from aggregates of similar porosity in that it contains more iron (Fig 3-6), silicon (Fig 3-7), manganese (Fig 3-10), and sulfur (Fig 3-13) than its companions. Iron and sulfur could be present as the mineral pyrite which is known to disassociate in chloride solutions. Silicon can occur in an amorphous form which is reactive with alkalis from portland cement. Both of these compounds are known to impair mortar-aggregate bonding, but disruption because of pyrite could be dominate with deicers. The role of manganese is unknown.

The predominant chemical feature of the Ames aggregate is more strontium than the companions, Alden and Montour in Figure 3-12. If strontium has an influence on concrete life, it would have to be positive in that the Ames concrete lasts longer than the porosity model predicts. Early Chapel has as much strontium as Ames but a much shorter life. Thus it is questionable whether strontium has any bearing on life.

Conventional Freeze-thaw testing

The most prevalent form of physical test used to evaluate the complete concrete system is ASTM C666, Procedures A and B. Results of IOWA DOT Procedure B (frozen in air) tests and ISU Procedure A (frozen in water) tests were pooled to take advantage of the large data base accumulated by the Iowa DOT. These results are summarized in Table 3-2

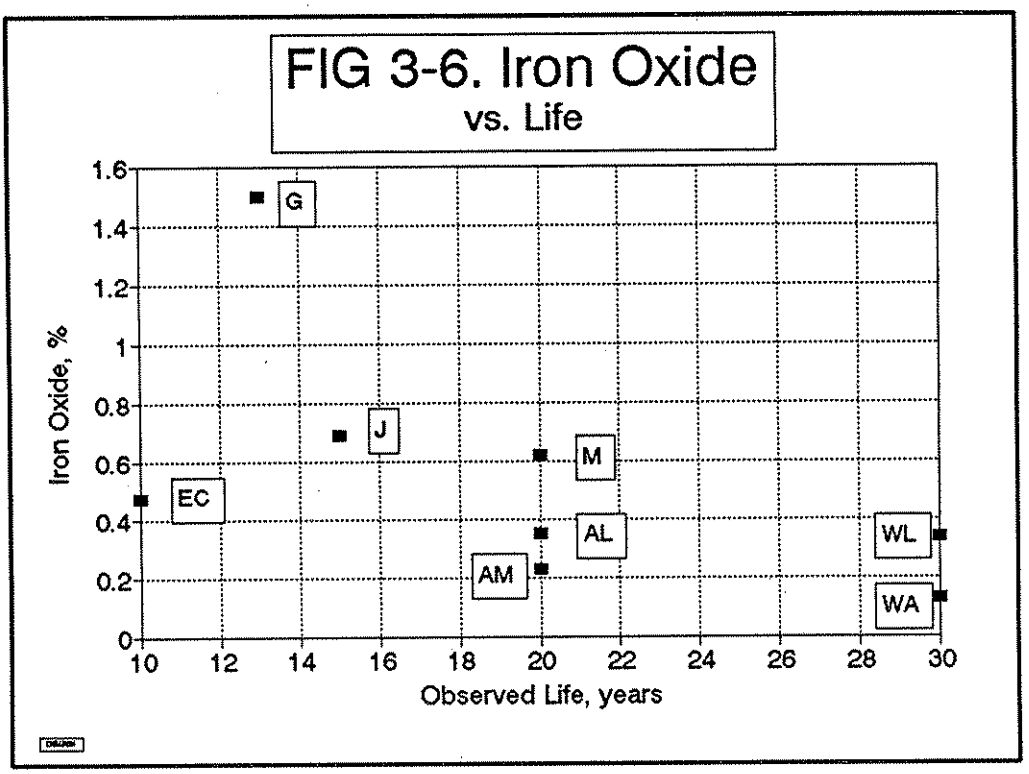


FIG 3-6. Iron Oxide
vs. Life
Iron Oxide, %
Observed Life, years
G
J
M
EC
AL
AM
WL
WA
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
10
12
14
16
18
20
22
24
26
28
30

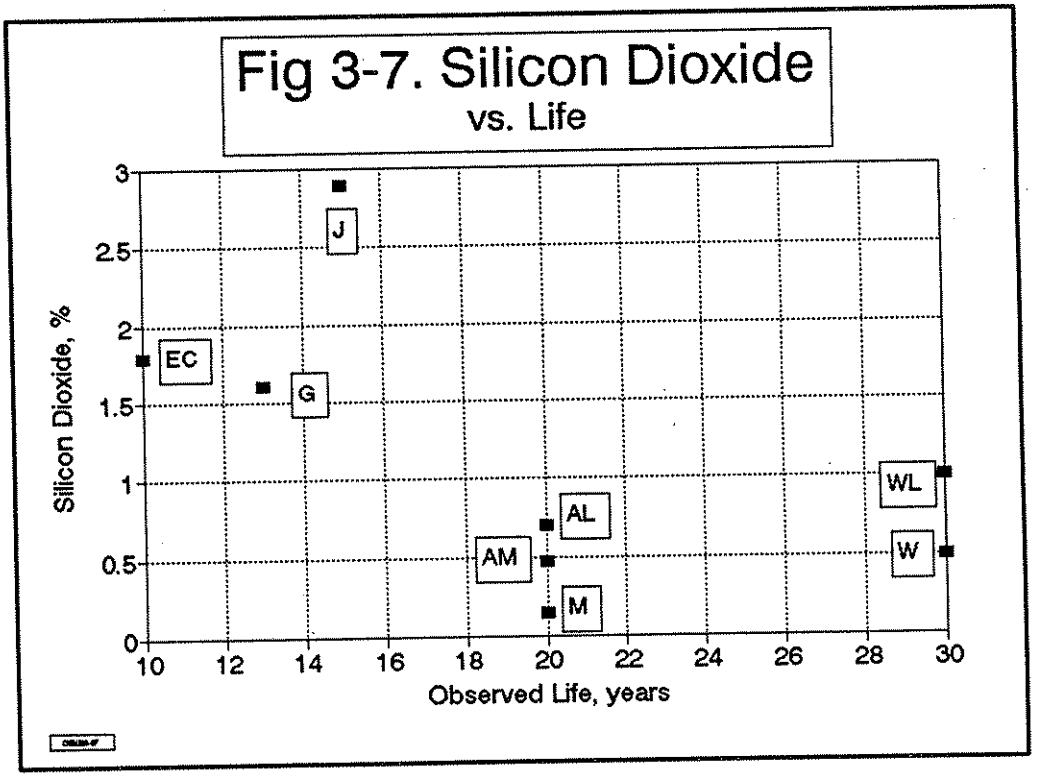


Fig 3-7. Silicon Dioxide
vs. Life
Silicon Dioxide, %
Observed Life, years
J
EC
G
AL
AM
M
WL
W
0
0.5
1
1.5
2
2.5
3
10
12
14
16
18
20
22
24
26
28
30

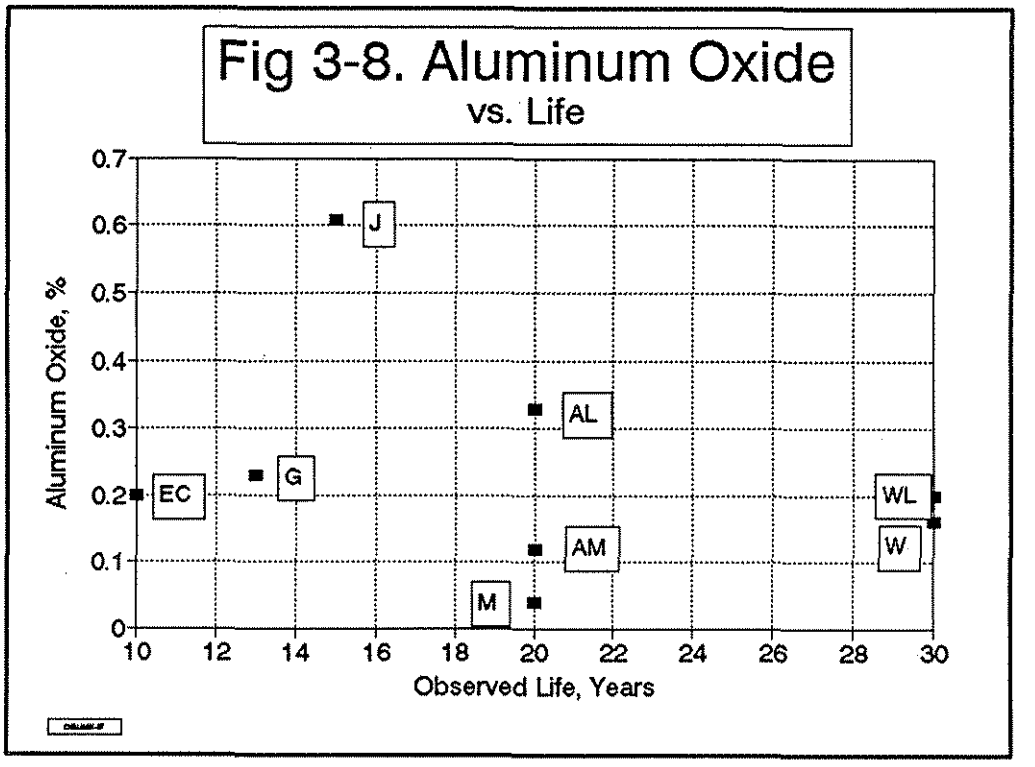


Fig 3-8. Aluminum Oxide
vs. Life
Aluminum Oxide, %
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
12
14
16
18
20
22
24
26
28
30
Observed Life, Years
J
AL
EC
G
WL
AM
W
M

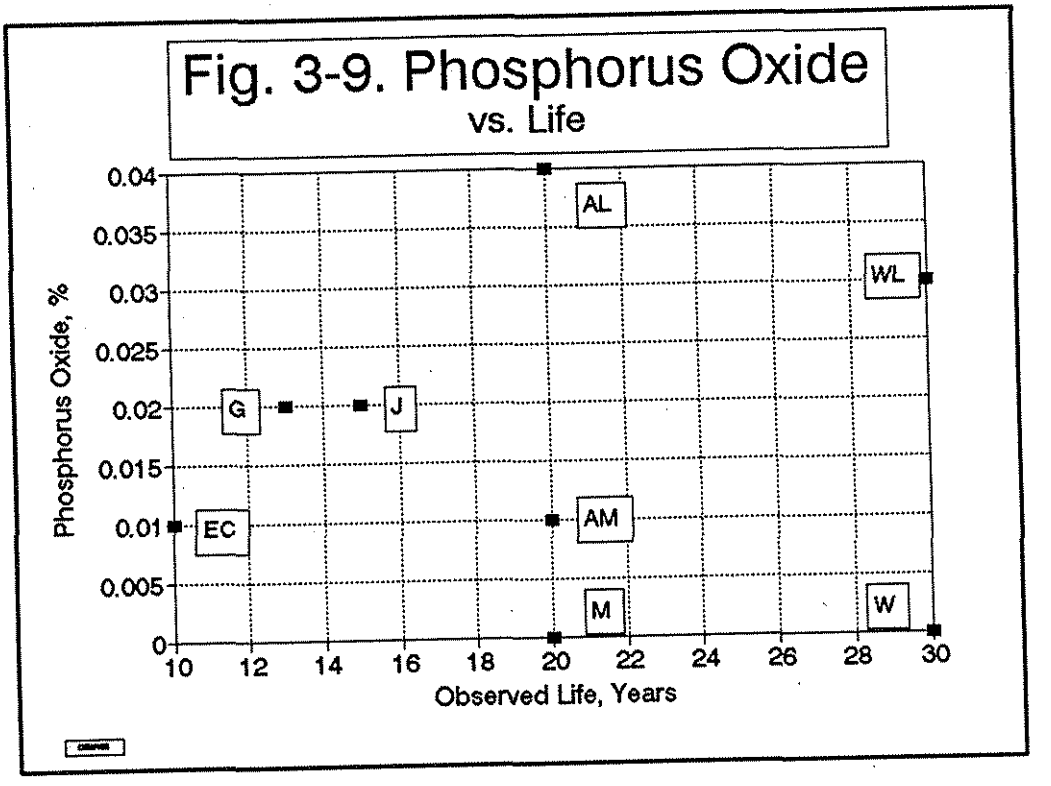


Fig. 3-9. Phosphorus Oxide
vs. Life
Phosphorus Oxide, %
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
10
12
14
16
18
20
22
24
26
28
30
Observed Life, Years
AL
WL
G
J
EC
AM
M
W

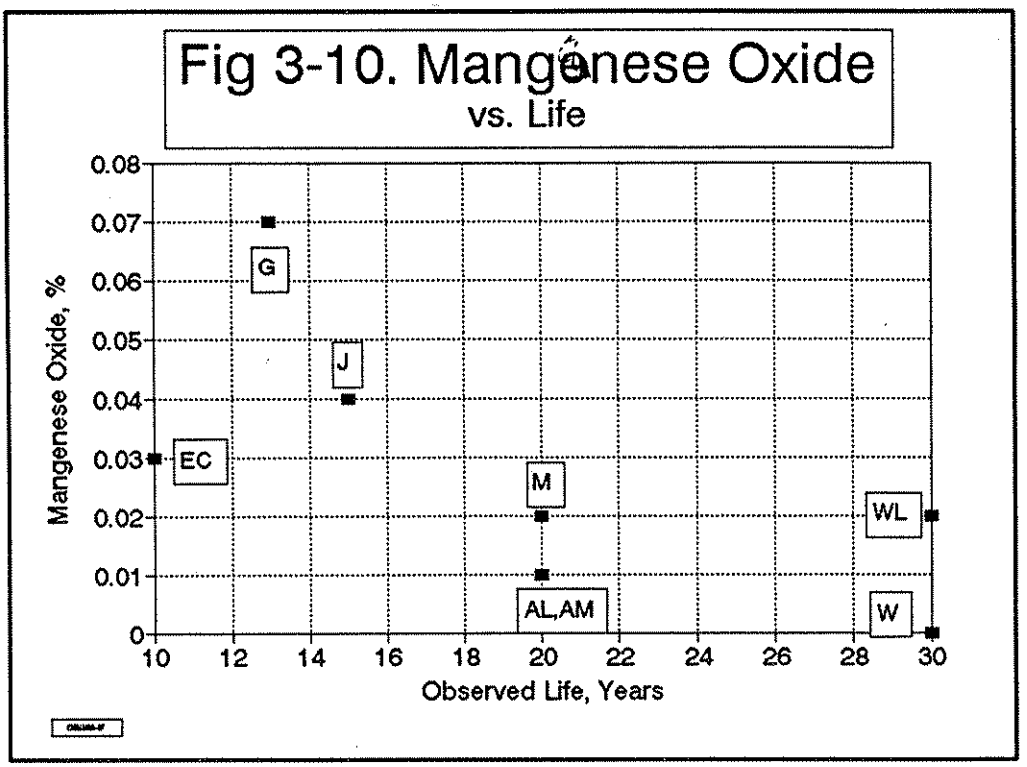


Fig 3-10. Manganese Oxide
vs. Life
Mangenese Oxide, %
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
10
12
14
16
18
20
22
24
26
28
30
Observed Life, Years
G
J
EC
M
WL
AL,AM
W

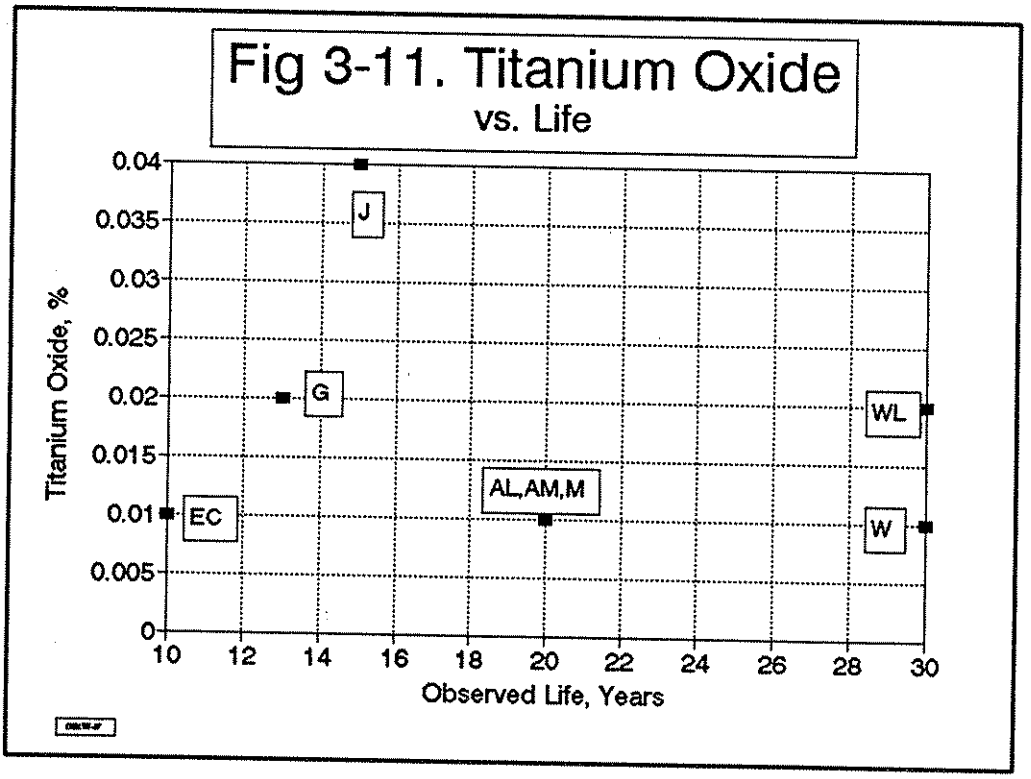


Fig 3-11. Titanium Oxide
vs. Life
Titanium Oxide, %
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
10
12
14
16
18
20
22
24
26
28
30
Observed Life, Years
J
G
WL
AL,AM,M
EC
W

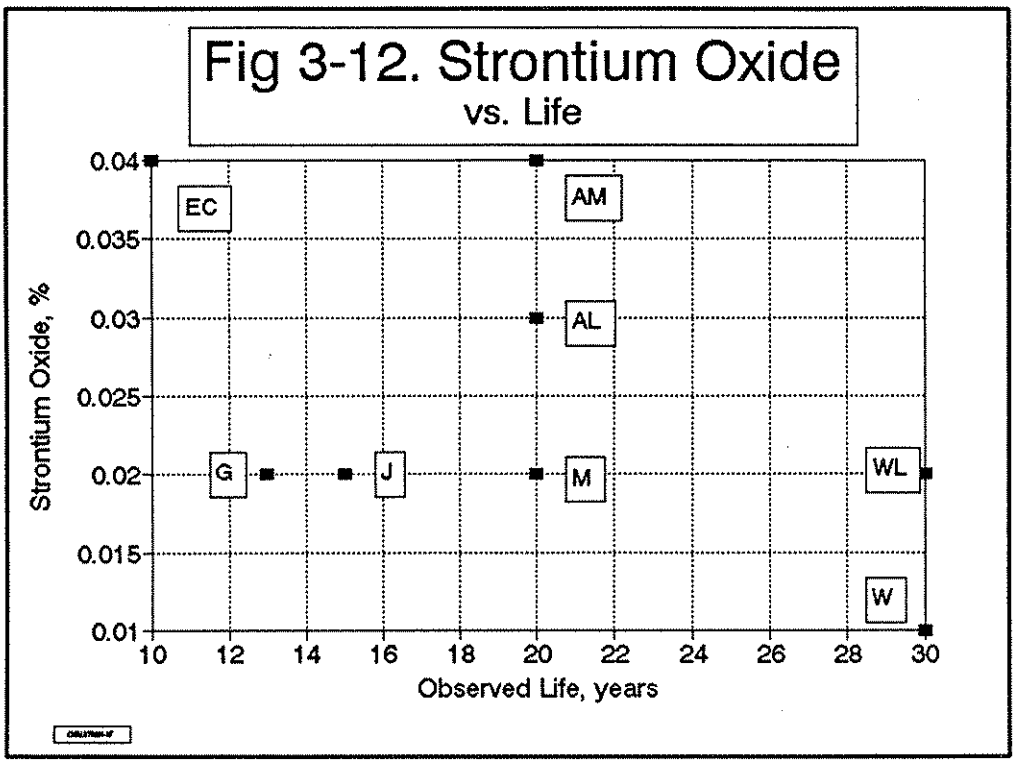


Fig 3-12. Strontium Oxide
vs. Life
Strontium Oxide, %
0.04
0.035
0.03
0.025
0.02
0.015
0.01
EC
AM
AL
G
J
M
WL
W
10
12
14
16
18
20
22
24
26
28
30
Observed Life, years

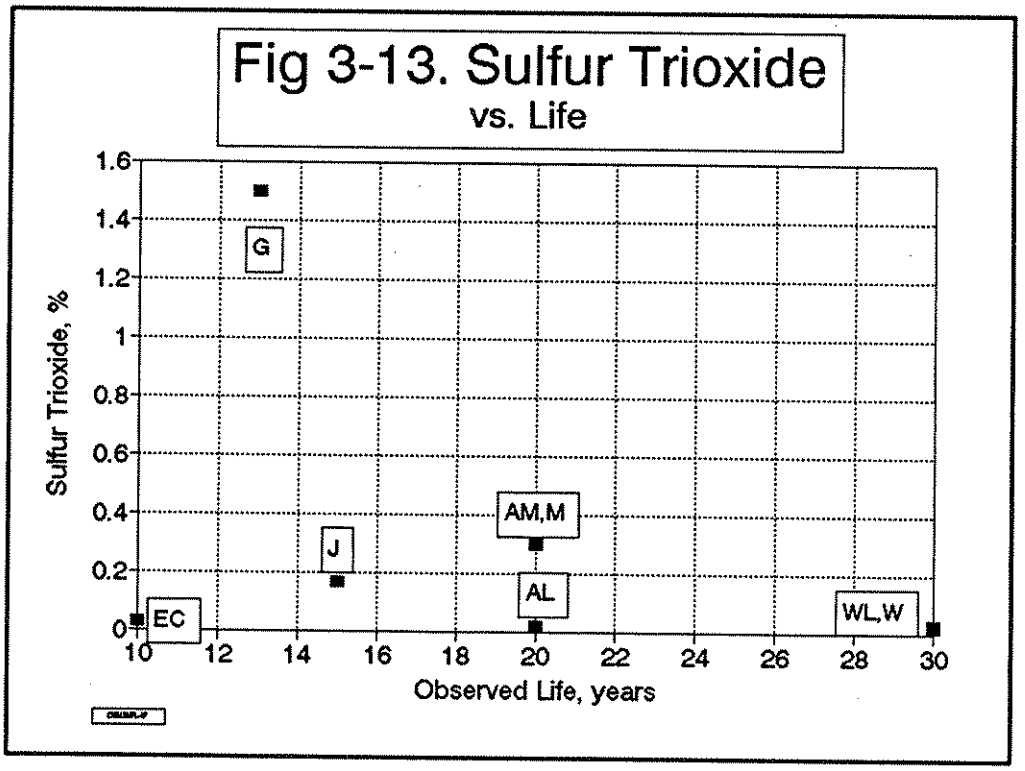


Fig 3-13. Sulfur Trioxide
vs. Life
Sulfur Trioxide, %
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
G
J
AM,M
AL
EC
WL,W
10
12
14
16
18
20
22
24
26
28
30
Observed Life, years

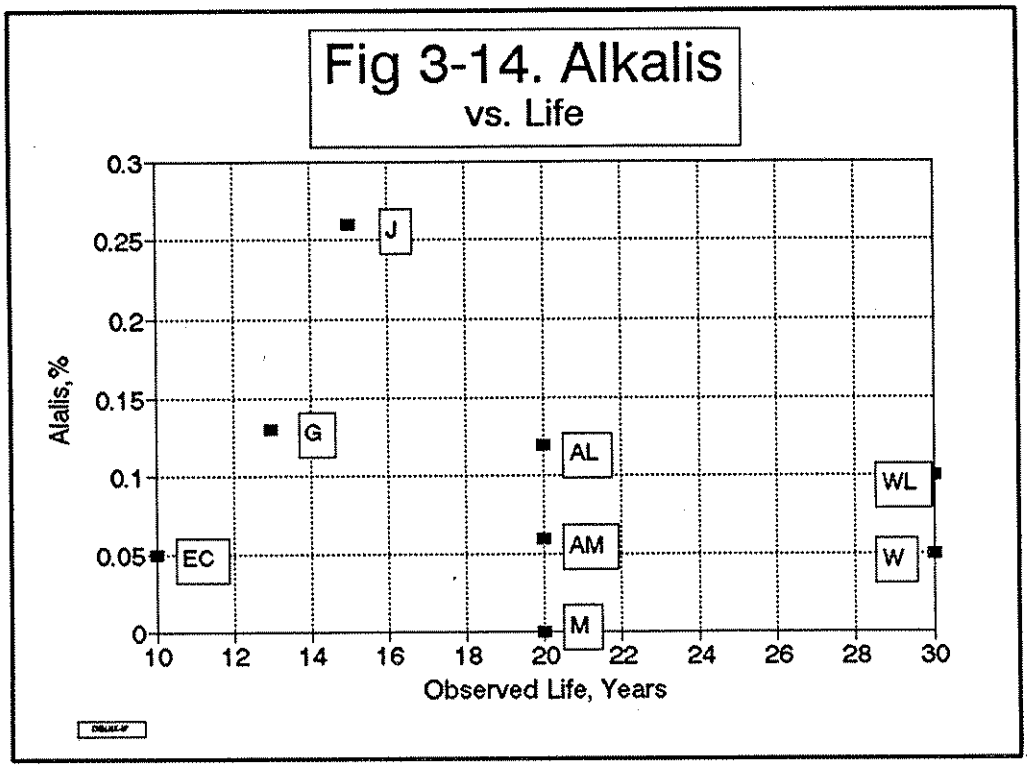


Fig 3-14. Alkalis
vs. Life
Alalis, %
0.3
0.25
0.2
0.15
0.1
0.05
0
10
12
14
16
18
20
22
24
26
28
30
Observed Life, Years
J
G
AL
WL
EC
AM
W
M

and Figure 3-15. With exception of Montour aggregate, the average durability factor for each aggregate when plotted against service life is hyperbolic and asymptotic to 100 percent durability factor. Montour is an outlier that does better in the field than indicated by the laboratory test, even when field observations include the influence of deicers.

The ASTM C-666 test discriminates between the very poor and the good aggregates but only separates 20 and 30 year stones by a few percentage points. If the trend is extended to more than 30 years, this type of test is of little value.

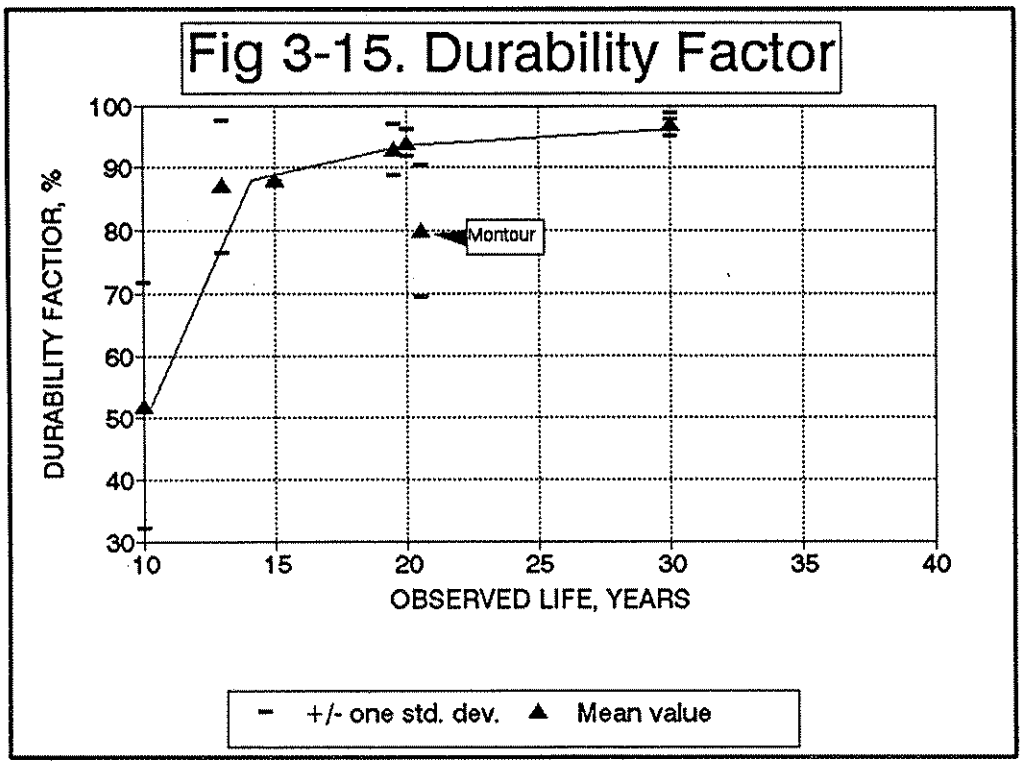


Table 3-2. Summary of Durability Tests

AGGREGATE	AVG. DURABILITY FACTOR, %	STD. DEVIATION	NO. TESTS	OBS. LIFE, YEARS
WAUCOMA	97	0.8	8	30
WESTON LAMONT	97	1.9	5	30
MONTOUR	80	10.6	39	20
ALDEN	94	2.1	31	20
GARRISON	87	10.6	14	13
AMES	93	4.1	30	20
JABENS	88		2	15
EARLY CHAPEL	52	19.8	6	10

Source: Iowa DOT

Mortar Bar Test at Elevated Temperature

The significant difference in service life between Montour and Early Chapel aggregates led Iowa DOT staff to speculate that longevity was influenced by chemical reactions between components of the coarse aggregates and deicers. Montour and Early Chapel were selected because they are both limestones, but the Early Chapel stone has higher concentrations of some trace elements. Early Chapel aggregate is also 2.3 times as porous as Montour stone, but this evaluation was done prior to the study on porosity.

Potential for chemical reactivity was enhanced by increasing surface area of the coarse aggregate and elevating the temperature as specimens were exposed to water and two types of brine. The objective was to measure bar length with expansion being an indication of chemical reactivity.

Coarse aggregate was crushed to a gradation specified in ASTM C-227 or the test for Potential Alkali Reactivity of Cement-Aggregate Combinations. Aggregate absorption was determined to allow for proper adjustment of water. The cement and aggregate were mixed in the proportion of 1:2 per Iowa DOT C3 mix design.

Mortar bars were cast in 1"x1"x10" molds and then placed in a humidity room for 24 hours. Next, the specimens were subjected to an accelerated curing process by immersion in water at 43 degrees Celsius for 28 days. This curing is

equivalent to 90 days at normal temperatures. After curing, the mortar bars were placed in containers as specified in ASTM C-490 with one of three types of fluid: 1. water, 2. saturated sodium chloride, saturated sodium chloride plus maximum calcium sulfate. The test involved controlled temperatures and periodic measurement of length and saturated surface dry mass.

Length and weight measurements as an average of ten specimens for each case are in Figure 3-16 a and b. Both aggregates immersed in brine increased in length and weight during the first week. Thereafter, there was little increase and stable dimensions were observed through the three month period. Dimensional and weight responses for both aggregates were the same in both brines, and the expansion that did occur was much less than the deleterious limit of 0.05 percent established in ASTM C-227. Neither aggregate showed much expansion or weight gain in water.

There were no visible sign of cracking or scaling over the three month test period. However, Montour specimens in deicers turned brown which is attributed to dissolution of pyrite. Apart from discoloration, the presence of pyrite in the aggregate may not cause harm. R. C. Mielenz (1963) showed pyrite can be present in aggregate in non detrimental forms. Since Montour aggregate is a good field performer for its porosity, the pyrite must be harmless.

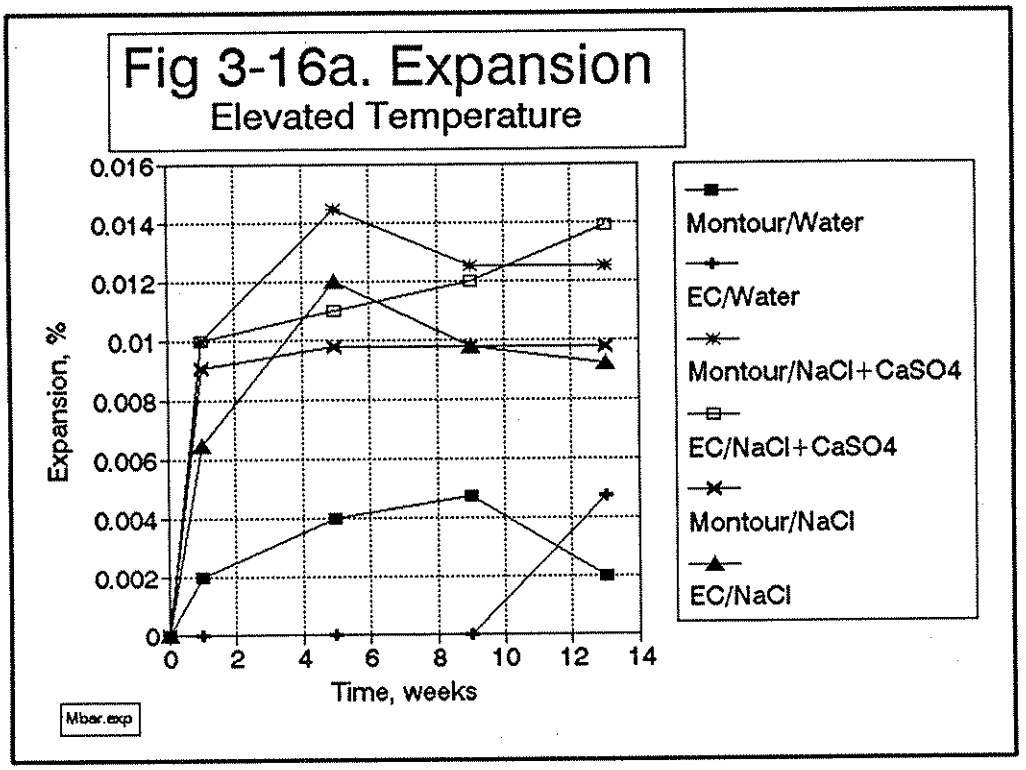


Fig 3-16a. Expansion
Elevated Temperature
Expansion, %
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0 2 4 6 8 10 12 14
Time, weeks
Montour/Water
EC/Water
Montour/NaCl+CaSO4
EC/NaCl+CaSO4
Montour/NaCl
EC/NaCl
Mbar.exp

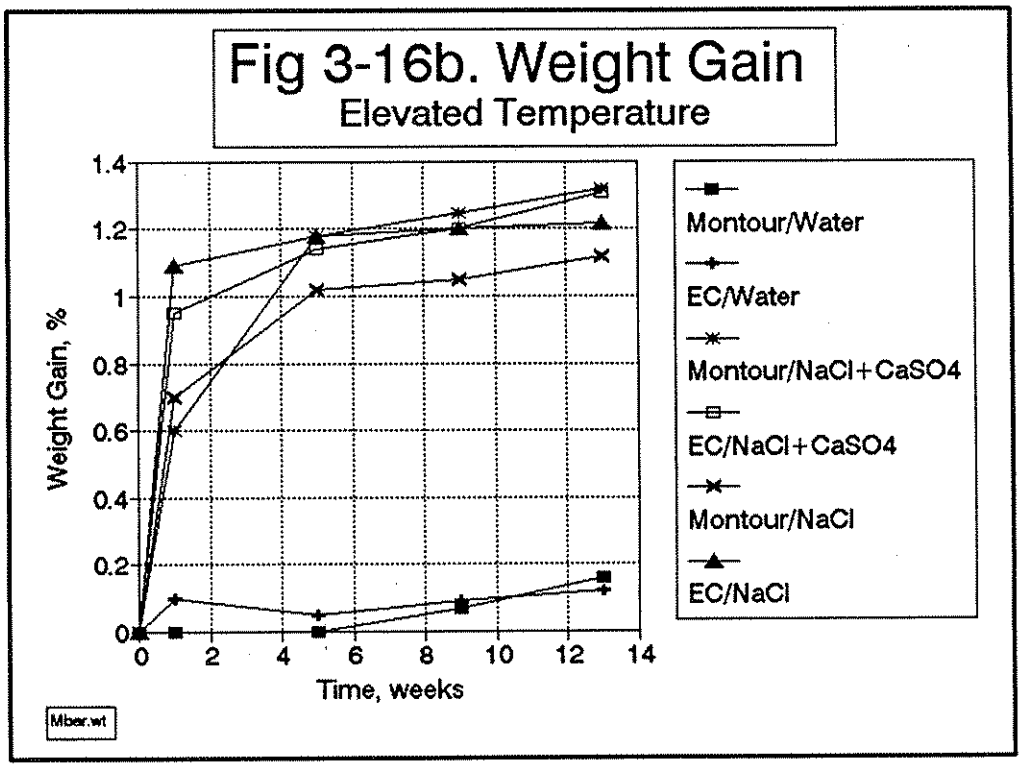


Fig 3-16b. Weight Gain
Elevated Temperature
Weight Gain, %
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0 2 4 6 8 10 12 14
Time, weeks
Montour/Water
EC/Water
Montour/NaCl+CaSO4
EC/NaCl+CaSO4
Montour/NaCl
EC/NaCl
Mbar.wt

Expansion of specimens in salt solutions were also accompanied by increase in weight. Hence, it may be concluded that expansions are due to diffusion of solute from the surrounding liquid into the specimen and not because of any chemical reactions among deicers, coarse aggregates, or cement paste.

Field performance in presence of deicers cannot be predicted from this test. This does not mean chemical reactions did not occur. In fact discoloration in the case of Montour aggregates means something is happening. Results from this experiment merely suggests any chemical reactions occurring are not expansive.

Because expansion did not differentiate service lives, this type of test was not continued.

Failure Mechanisms

To understand the mechanisms by which deicers acting in conjunction with cyclic freezing and thawing cause deterioration of concrete, specimens were cast in dog-bone molds, designed for tensile strength testing of mortar ASTM C-190. The intent of this configuration is to bring individual aggregate-mortar elements in contact with deicing brines while being subjected to freezing and thawing and observing modes of failure.

Fragments of Montour and Early Chapel aggregate, passing the one inch but retained on the 3/4 inch sieves, were embedded in the neck (1"x1" cross section) of dog-bone molds after they had been filled with portland cement mortar. The mortar was designed to represent that of an Iowa DOT C-3 paving mixture. Fine aggregate was ASTM C-192 ottawa sand. The formula for the mortar is in Appendix B. Non air entrained and 9% air entrained mortar was used with each aggregate. Curing involved 24 hours in a humid room followed by 28 days in a 43 degrees Celsius water bath.

The dog-bone specimens set upright freeze-thaw containers and submerged in fluid to the mid height or the center of the embedded aggregate fragment. Specimens were next subjected to freeze-thaw cycles and at selected thaw cycles, samples were inspected.

A simple but crude failure criteria was used. If a

specimen remained whole when lifted from the container, it passed; and specimens that broke when lifted from the container, failed. When failure was encountered, the type of failure and number of cycles to cause that failure were noted. Failure modes were classified as follows:

1. Aggregate failure - fracture passed through the aggregate
2. Bond failure - fracture occurs at the boundary between the aggregate and mortar
3. Mortar failure- no distinct fracture, mortar disintegrates in region away from aggregate

Failure mode observations are summarized in Figure 3-17a & b. When no air entrainment was used with Early Chapel aggregate, bonding and aggregate failures were nearly equally responsible for deterioration in water. Deicer caused a change in behavior with about 80 percent of failures in both Early Chapel and Montour specimens occurring at the bond.

Air entrainment caused aggregate failures to become more predominant in water with all of the Montour specimens failing in the aggregate. Failure of air entrained specimens in deicer was mainly in the mortar of Montour specimens and in the mortar and at the bond of Early Chapel specimens.

The fact that deicers change the mechanism by which concrete fails from that of failure of centered at the ag-

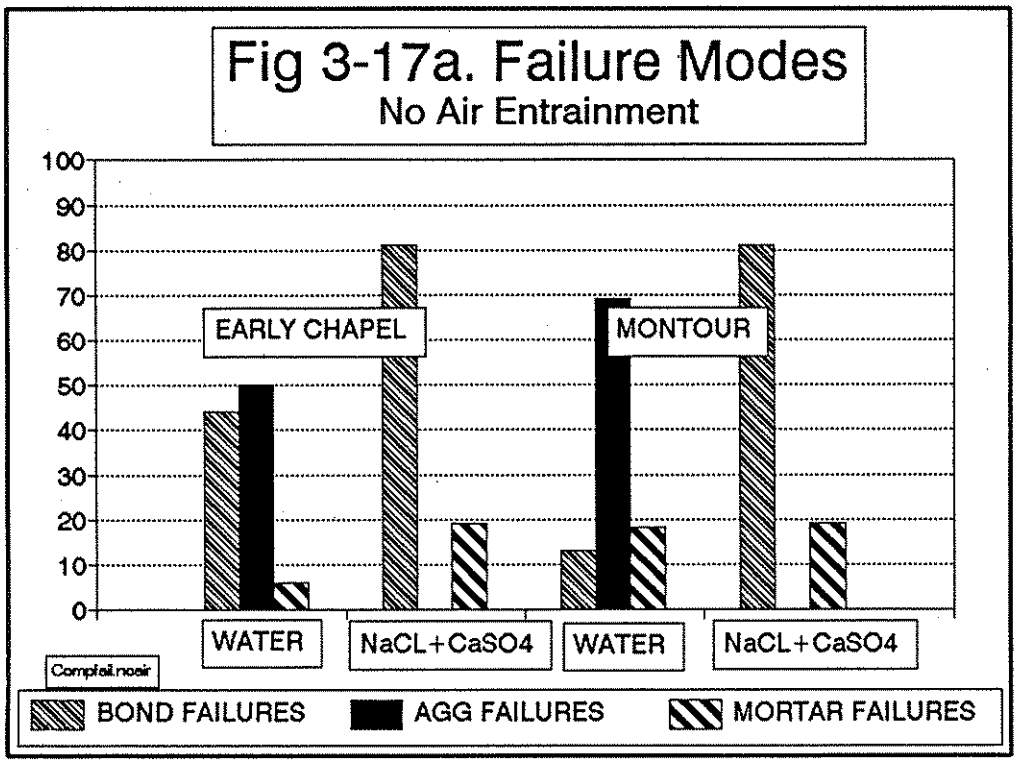


Fig 3-17a. Failure Modes
No Air Entrainment
100
90
80
70
60
50
40
30
20
10
0
EARLY CHAPEL
MONTOUR
WATER
NaCL+CaSO4
WATER
NaCL+CaSO4
BOND FAILURES
AGG FAILURES
MORTAR FAILURES

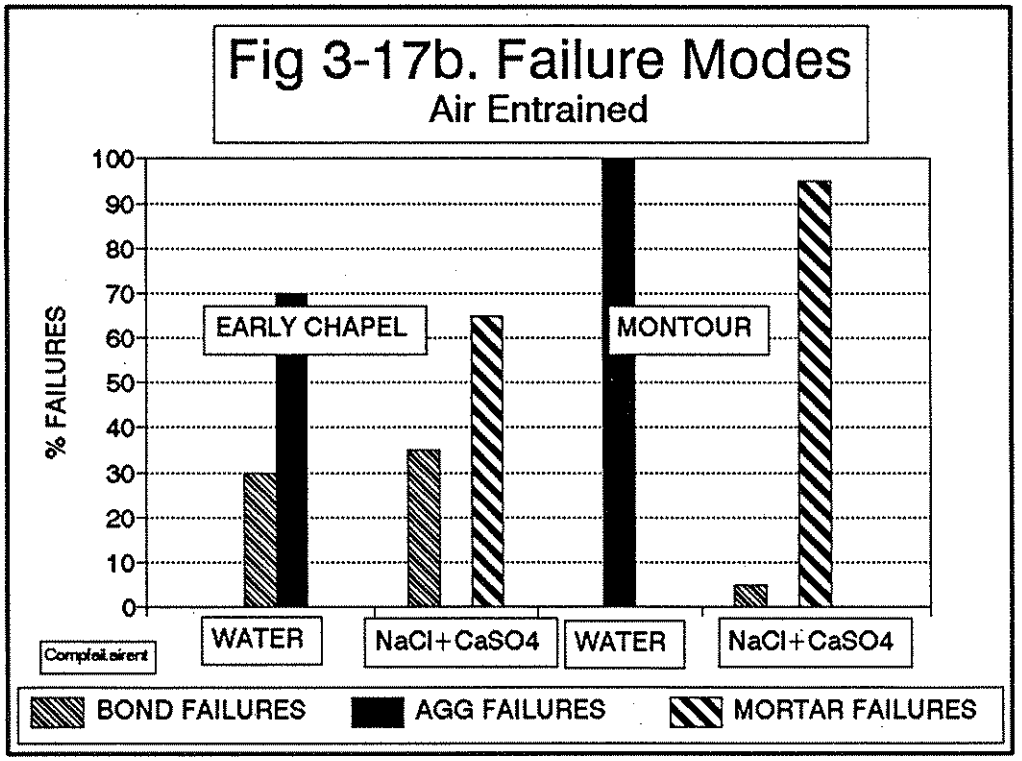


Fig 3-17b. Failure Modes
Air Entrained
% FAILURES
100
90
80
70
60
50
40
30
20
10
0
EARLY CHAPEL
MONTOUR
WATER
NaCl+CaSO4
WATER
NaCl+CaSO4
BOND FAILURES
AGG FAILURES
MORTAR FAILURES

Table 3-3. Summary of Subjective Life Cycle Tests

Aggregate	Early Chap.	Montour	Early Chap.	Montour	Early Chap.	Montour	Early Chap.	Montour
Air Entrainment	no	no	no	no	yes	yes	yes	yes
Fluid	water	water	brine	brine	water	water	brine	brine
Avg. Fail. Cycles	72	122	57	63	153	333	170	see note
Std. Dev.	37	26	10	19	78	108	89	see note
First Failure	37	80	48	37	77	158	17	129
Last Failure	134	160	78	91	287	497	245	see note

note: mortar failures without a difinitive point of failure

gregate to a tendency of failures occurring at the bond or in the mortar suggests conventional ASTM C-666 testing is inappropriate. ASTM C-666 is done in water and evaluates the aggregate whereas the problem lies elsewhere within the concrete. These data also suggest poorer aggregate such as Early Chapel, tends toward failure at mortar-aggregate interfaces while the mortar rather than the aggregate becomes the controlling factor for better quality stone. Thus better concrete might be had with low porosity aggregate by improving the mortar and improved mortar may have a lesser effect with highly porous stone.

Aggregate porosity and chemistry are two explanations for Early Chapel tending toward bond failure. Early Chapel is 2.3 times more porous than Montour. This means Early Chapel aggregate has fewer places to make bonds and more voids at the interface in which salt crystals can accumulate and grow.

The role of trace elements in the aggregates is less clear. It was observed that levels of trace elements in the aggregate correlates to porosity with more porosity indicating more contamination. Thus trace elements may either be causative or coincidental. If trace elements are causative, the elements found in significantly greater concentrations in Early Chapel than in Montour are silicon and strontium. There is a significant amount of silicon, about 2 percent as

an oxide, in the Early Chapel aggregate. If this silicon were in an amorphous form, a reasonable chemical mechanism could be some sort of delayed reaction such as an alkali-aggregate reaction. However, the mortar bar test ruled this out. The role of strontium in deicer-cement-aggregate reactions is unknown. Still, nothing showed in the mortar bar tests.

A second observation from these subjective life cycle tests is the fact that there was a significant difference in time or number of cycles to failure even within like specimens and treatments. Statistics of these tests are in Table 3-3 where it can be seen deicers and lack of air entrainment causes significant reductions in average life. These experiments also demonstrated that the inability of making subjective determinations of when mortar failed. This experience lead to refinements in life cycle evaluation.

Refined Life Cycle Tests

In an attempt to impose failure criteria that correlates to field performance, the ultrasonic pulse velocity criteria developed from the E-29 study was applied to dog bone shaped specimens described in the previous section. Specimen condition was monitored at frequent intervals during thaw cycles. Fifty kHz transducers of a James V-meter were mounted in a plexiglass tank to maintain constant spacing and allow consistent water coupling. Failure was defined as the number of cycles at which two-thirds of initial specimen pulse velocity was reached.

Figure 3-18 a through g are a statistical representation of failure occurrence for seven of the aggregates included in this evaluation. Ames aggregate was not tested because of limited space in the freeze-thaw machines. A linear plot of cumulative percent of failures vs. number of cycles indicates a consistent failure mechanism with the average being interpreted as the expected number of cycles it takes for the population to fail and the slope being an indicator of failure rate. Waucoma, Weston Lamont, Montour, and Alden show a tendency toward linearity, suggesting a single failure mode, probably in the mortar. The slight bow in the plots may result from some interspersed bond failures.

Garrison, Jabens, and Early Chapel have bimodal distri-

butions suggesting two distinct failure modes, bond and mortar. These more porous aggregates started failing sooner than the first four aggregates mentioned.

Although failure mode can be used as a clue to improving composite concrete behavior, the objective of this research is a predictive test. If the process of freeze-thaw in concrete is controlled by the law of averages, the average number of cycles to failure should correspond to field observations. Figure 3-19 is a linear model for this data with a correlation coefficient of 0.92. This high degree of correlation suggests the concept may be appropriate and what variation from this model could be attributed to such factors as: objectivity of the observed life estimates, pavement thickness, curing allowed prior to deicing, and time to reach detrimental deicer concentrations.

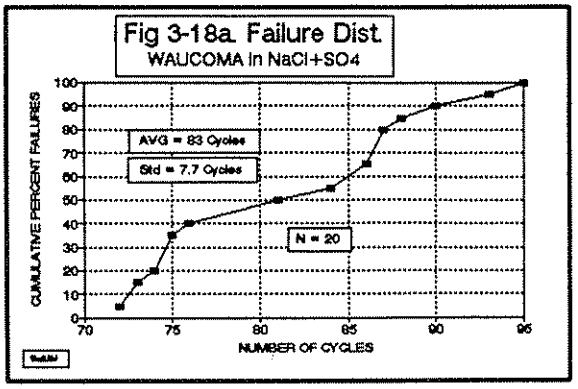


Fig 3-18a. Failure Dist.
WAUCOMA in NaCl+SO4
AVG = 83 Cycles
Std = 7.7 Cycles
N = 20
CUMULATIVE PERCENT FAILURES
NUMBER OF CYCLES

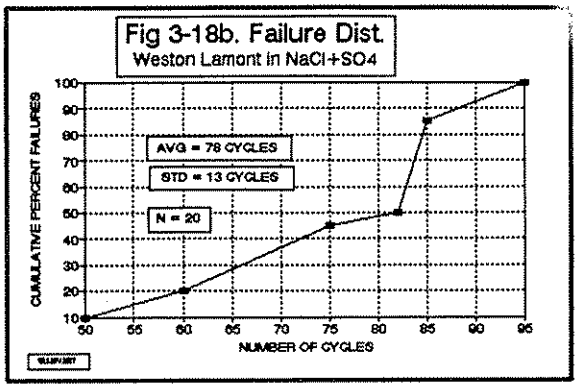


Fig 3-18b. Failure Dist.
Weston Lamont in NaCl+SO4
AVG = 78 CYCLES
STD = 13 CYCLES
N = 20
CUMULATIVE PERCENT FAILURES
NUMBER OF CYCLES

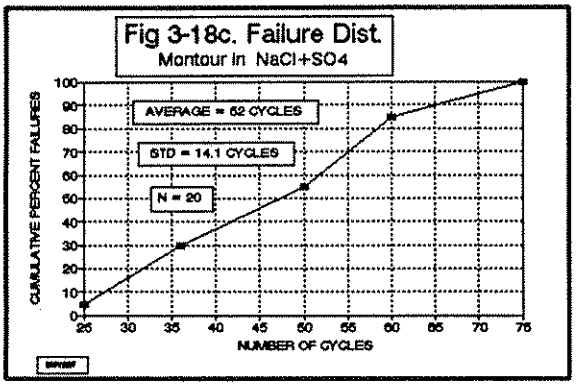


Fig 3-18c. Failure Dist.
Montour in NaCl+SO4
AVERAGE = 52 CYCLES
STD = 14.1 CYCLES
N = 20
CUMULATIVE PERCENT FAILURES
NUMBER OF CYCLES

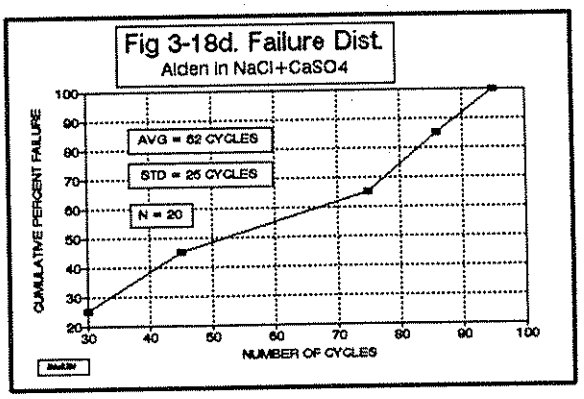


Fig 3-18d. Failure Dist.
Alden in NaCl+CaSO4
AVG = 52 CYCLES
STD = 25 CYCLES
N = 20
CUMULATIVE PERCENT FAILURE
NUMBER OF CYCLES

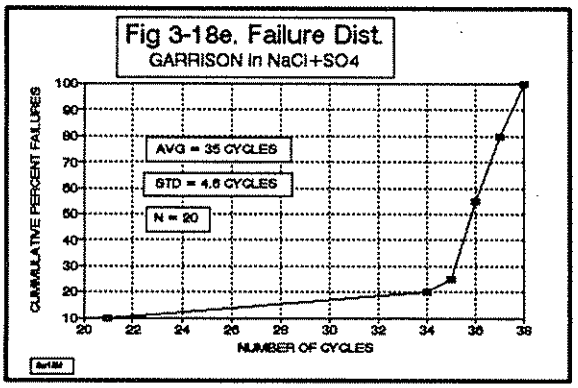


Fig 3-18e. Failure Dist.
GARRISON in NaCl+SO4
AVG = 35 CYCLES
STD = 4.6 CYCLES
N = 20
CUMULATIVE PERCENT FAILURES
NUMBER OF CYCLES

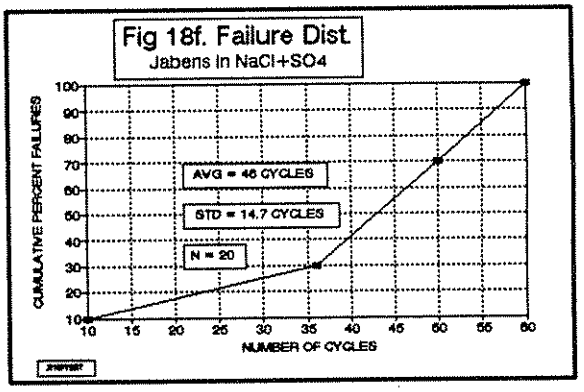


Fig 18f. Failure Dist.
Jabens in NaCl+SO4
AVG = 46 CYCLES
STD = 14.7 CYCLES
N = 20
CUMULATIVE PERCENT FAILURES
NUMBER OF CYCLES

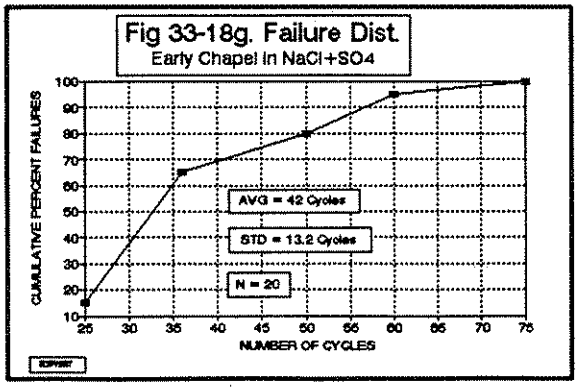


Fig 33-18g. Failure Dist.
Early Chapel in NaCl+SO4
AVG = 42 Cycles
STD = 13.2 Cycles
N = 20
CUMULATIVE PERCENT FAILURES
NUMBER OF CYCLES

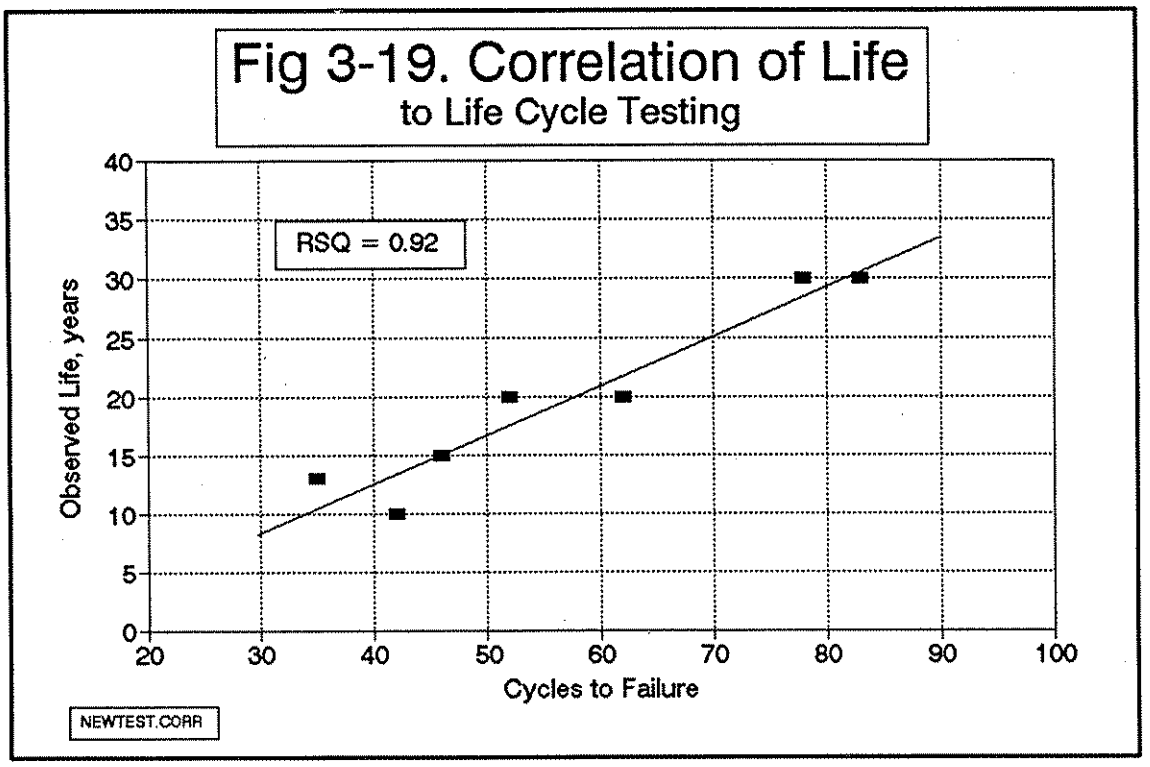


Fig 3-19. Correlation of Life
to Life Cycle Testing
RSQ = 0.92
Observed Life, years
Cycles to Failure
0
5
10
15
20
25
30
35
40
20
30
40
50
60
70
80
90
100
NEWTEST.CORR

PART 4: RELIABILITY TESTING

Background

Part 3 of this report illustrates the inadequacy of attempting to correlate such characteristics as pore size, chemistry, or expansion to performance of pavements. In such correlations significant, yet unknown factors are often overlooked because the deterioration process is not well understood. The greatest danger is in attempting correlations which concentrate on a single facet of a complex system with neglect of the total process that contributes to deterioration. Thus test systems that model as many of the field processes as possible are attractive. The ASTM C-666 freeze-thaw test comes close, but in its conventional form neglects the effects of deicers. However, the greatest shortcoming of this or any other test in use is failure to address the primary question of such design: a measure of expected life.

Another way to improve design is through historical observation. Certainly every advantage must be taken of past successes and failures, but undue reliance on history is nothing more than long term, expensive experiments.

A significant body of statistical science, life testing or reliability analysis, has been applied to many areas of engineering. The technique is simple in concept and in many

cases direct in application. Reliability analysis requires three elements: 1. a definitive criteria for success or the converse, failure; 2. a test process that accurately simulates the prototype processes; and 3. a sufficient number of specimens to define the statistical variability of the prototype population. The classic application of life testing is for electrical components. Light bulbs, resisters, and computer chips either work or they do not. Such components are relatively inexpensive, thus many can be tested under prototype conditions. The result is an estimate of expected time to failure or the probability of failure occurring within a specified time.

One difficulty in applying reliability analysis to concrete durability is an objective definition of failure. Durability factor of ASTM C-666 is determined by vibrating concrete prisms to determine the fundamental resonate frequency before and after freeze-thaw deterioration. This is objective and may measure appropriate physical properties, but it lacks direct linkage to concrete condition in the field when failure occurs. A test to bring concrete pavement slabs to their resonate frequency is not practical because of scale and need for support conditions consistent with those in the field.

Ultrasonic pulse velocity tests, ASTM C-597, has potential for linking measures of the field performance to the

laboratory, because it can be performed on concrete in both laboratory and field settings. This test measures the time it takes a low level stress pulse to pass through a specimen. It has been found that pulse transmission time is quite sensitive to cracks because these flaws reflect and refract the pulse wave energy, thus delaying transmission velocity. Theoretically ultrasonic pulse testing can be interpreted as being dependent on modulus of elasticity but the physical attribute measured as freeze-thaw progresses is development of fractures which interfere with the time it takes to pass a low level energy pulse through a solid.

E-29 Case Study

In a previous report (Pitt, et.al.1987), Story County Road E-29 near the U. S. Highway 65 intersection was evaluated because D-cracking was noticed near the intersection, but the distress systematically decreased with distance from the intersection, until damage was not apparent some 300 to 400 feet to the east of the intersection. As the roadway features are the same regardless of distress, it was speculated that the D-cracking may have been the result of deicers being tracked from U. S. 65. Story County policy is not to deice such pavements.

Core samples from joints were analyzed for chloride concentration. Near the intersection, the concrete contained 0.20 chloride by weight of the concrete. Chloride

concentration then decreased systematically with distance from the intersection until a concentration of 0.08 percent was found at 600 feet. The smaller percentage of sodium chloride corresponded to absence of visible distress while the greater amount corresponds to joints that were replaced the same year as the test, 1987.

An observation from this evaluation is that deicer concentrations in concrete with joint failure is between 0.20 to 0.08 percent sodium chloride by weight of concrete. This amount of chloride might be interpreted as representing a range of deleterious substance required to cause failure.

To illustrate application of field to laboratory link for reliability analysis, pavement near a deteriorated joint at station 6+50 to the east of the U. S. Highway 65 intersection was tested with a James V-METER in April 1992. This section of Story County E-29 is a six inch thick pavement of Iowa DOT B-3 concrete mix constructed in 1966. The coarse aggregate is gravel. A condition survey made in 1986 showed extensive D-cracking near the intersection, but damage decreased with distance to the East of the intersection until no surface cracking could be observed at station 4+50 and beyond. The damaged joints nearest the intersection were sawed out and replaced a few months after the 1986 survey.

Observations from the 1992 survey are as follows:

1. The most easterly joint of the 1986 study, near station 6+50, now shows visible distress.

2. Reinspection of the 6+50 core specimen taken in 1986 revealed minor cracking at the bottom but no damage was visible at the surface.

3. The joint near station 6+50 was so badly deteriorated in 1992 that cores could not be taken.

4. Old concrete at the repaired joints showed signs of initial distress but the patch material was sound.

These observations suggest the pavement at the station 6+50 joint had begun failing at the bottom in 1986, and that it took six years for the damage to reach the surface. Additionally, old concrete at joint repair sites is prone to rapid deterioration and continuation of the process.

Results of ultrasonic pulse traverses near the station 6+50 joint are in Figure 4-1. Transmission time is plotted against distance between piezoelectric sender and receiver. The reciprocal of slope is the pulse velocity, given in the legend in feet per second. Two measurements of uncracked concrete were taken at the center of the slabs bordering the failed joint. Both plots of time vs. distance are similar and diverge from linearity at 15 inches on the traverse, indicating response to the base course. Pulse velocity for the uncracked concrete was found to be 8,370 fps.

Pulse velocity from the two tests on fractured material

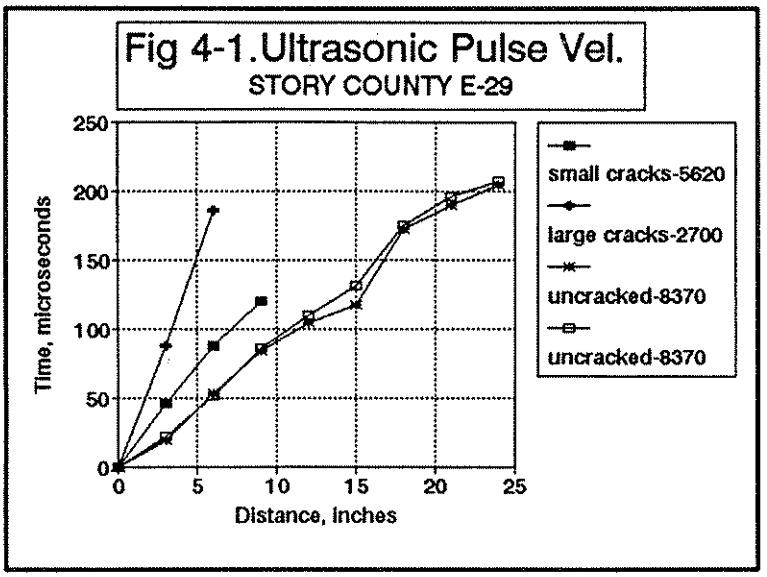


Fig 4-1.Ultrasonic Pulse Vel.
STORY COUNTY E-29
Time, microseconds
250
200
150
100
50
0
0
5
10
15
20
25
Distance, inches
small cracks-5620
large cracks-2700
uncracked-8370
uncracked-8370

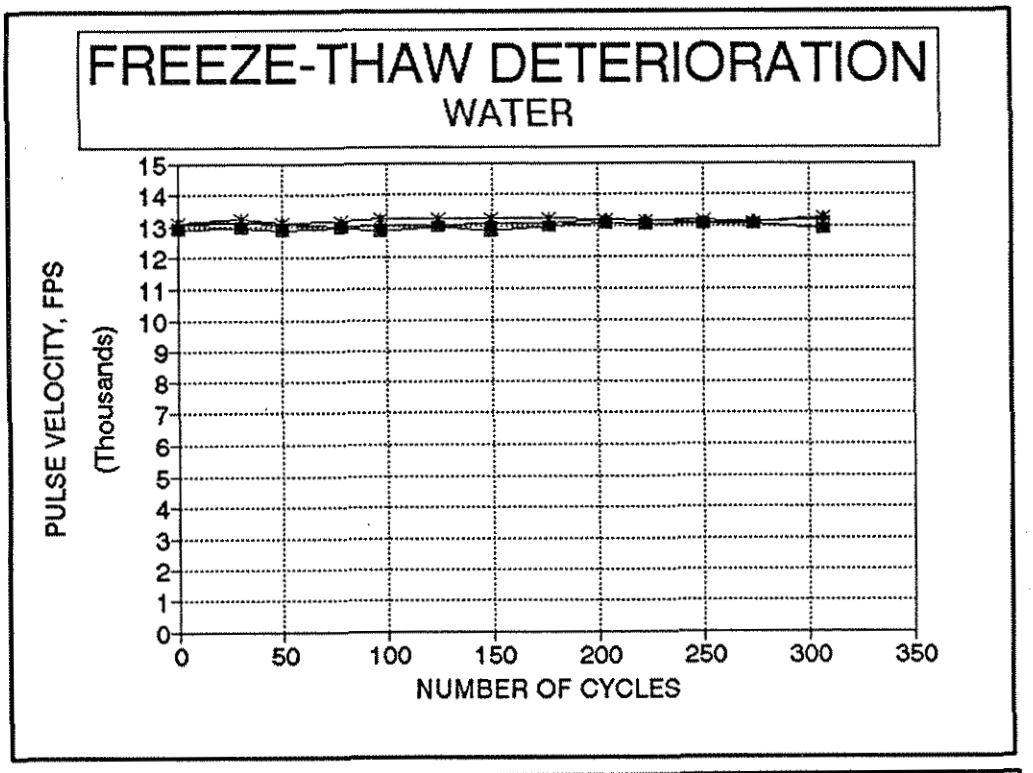
was more variable and ranged from 2,700 to 5,600 fps, depending on the size of cracks. If pulse velocity of deteriorated concrete is normalized by that of serviceable material, unserviceable concrete has 37 to 67 percent of the velocity of good material.

Laboratory Test

The test method described in Part 2 of this report was used to evaluate an equivalent material in the laboratory to test the validity of the proposed prediction method. Because observations of failed E-29 cores suggest deterioration was in the mortar, mortar specimen were made to simulate the Iowa DOT Class paving mix used in the road. Twelve specimens cured for 28 days were subjected to freeze-thaw in water and in saturated brine solutions from low and high sulfate salt samples number 22 and 7 in Appendix A.

Representative plots of pulse velocity vs. cycles are in Figure 4-2a and b. There was no decrease in pulse velocity of specimens in water out to 300 plus cycles. Unfortunately, design of this experiment was blinded by convention, and the test was limited to the standard 300 cycles. Thus life of this mortar in water can only be established at something more than 300 cycles.

The typical response of specimens in brine was a severe decrease in pulse velocity after the onset of deterioration. The two-thirds failure criteria can be used to establish the



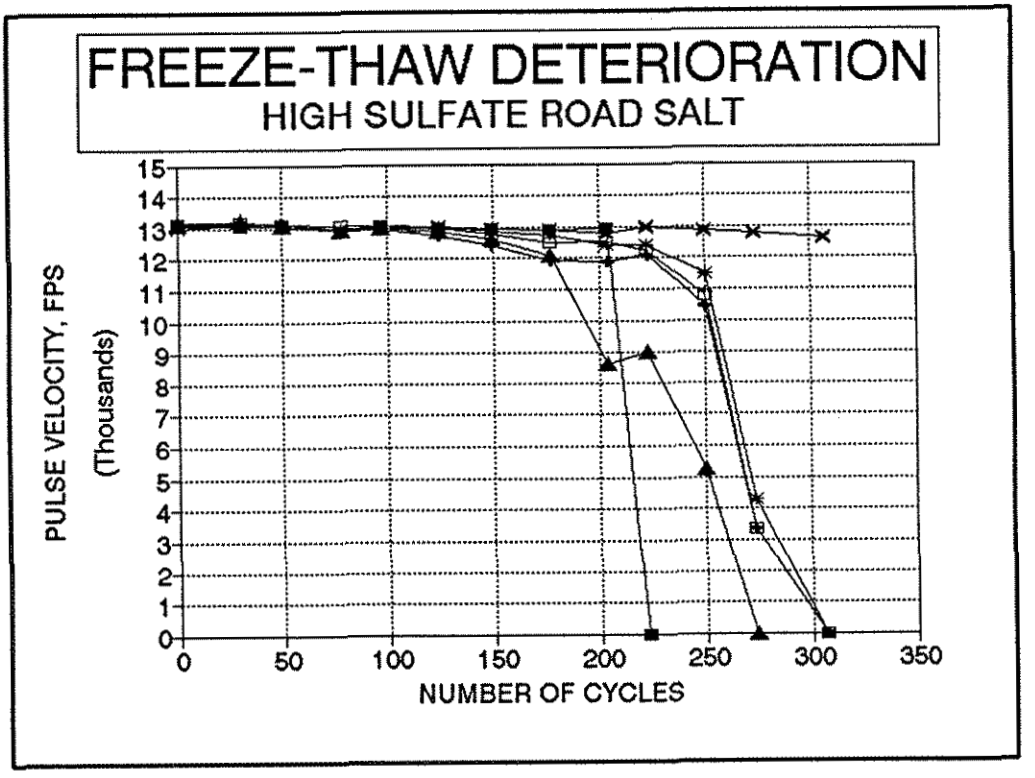


Fig. 4-2a and 4-2b. Typical Pulse Velocity Plots

cycles at which failure occurs and the result can be portrayed by a graph of cumulative failures vs. number of cycles, Fig 4-3a and b. The linear trend of these data suggest a consistent failure process with the average time to failure in high-sulfate brine occurring about 50 cycles sooner than the low-sulfate salt.

There is also a substantial spread in the occurrence of first to last failure. Such variation in specimen life suggests first emergence of joint failure will appear to be random. These randomly occurring failed joints were observed during the Spring of 1992 on the west-bound lanes of U.S. Route 30, just west of Ames. That is before the joints were sawed out and the pavement overlaid.

Converting Cycles to Time

Knowing the cycles it takes to fail a specimen has little meaning unless a rational approach is developed to relate this to real time. This means knowledge of the number of freeze-thaw cycles a pavement undergoes at different depths is needed. An 8' by 8' concrete slab twelve inches thick was constructed near the Spangler Geotechnical Laboratory with thermistors at the surface and embedded at 2, 4, 6, 8, and 12 inch depths, near the center of the slab. Temperature was measured every thirty minutes with a computer based logging system during the winter of 1989-90. Figure 4-4 is a plot of the number of times the pavement

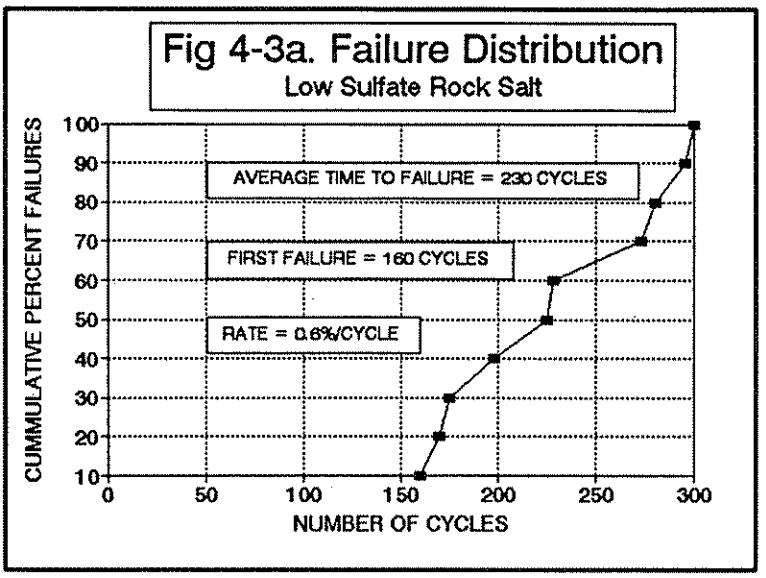


Fig 4-3a. Failure Distribution
Low Sulfate Rock Salt
AVERAGE TIME TO FAILURE = 230 CYCLES
FIRST FAILURE = 160 CYCLES
RATE = 0.6%/CYCLE
CUMMULATIVE PERCENT FAILURES
NUMBER OF CYCLES
100
90
80
70
60
50
40
30
20
10
0
50
100
150
200
250
300

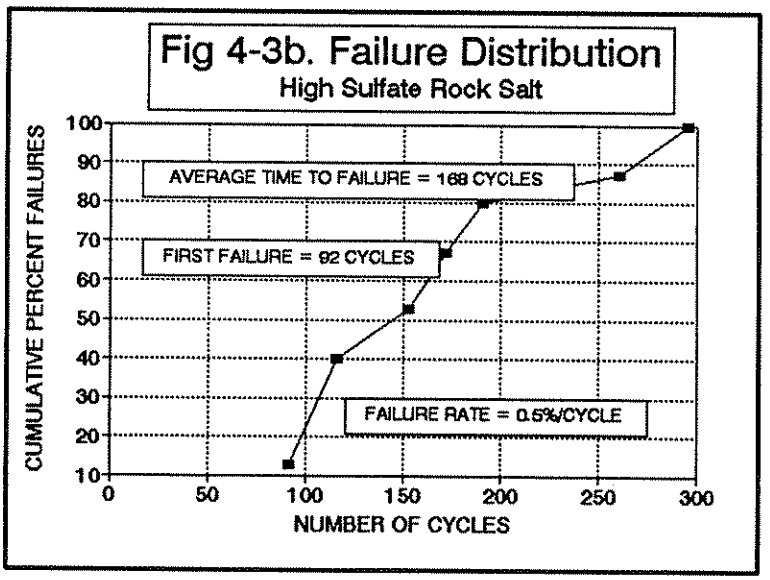


Fig 4-3b. Failure Distribution
High Sulfate Rock Salt
AVERAGE TIME TO FAILURE = 168 CYCLES
FIRST FAILURE = 92 CYCLES
FAILURE RATE = 0.5%/CYCLE
CUMULATIVE PERCENT FAILURES
NUMBER OF CYCLES
100
90
80
70
60
50
40
30
20
10
0
50
100
150
200
250
300

cycled between freezing and thawing.

Observations of partially deteriorated pavements suggest the deterioration process begins at the bottom of the slab near joints where moisture and salt accumulates and progresses upward and outward because the damaged material allows ingress of more water. This process may be approximated by the following:

$$L = \text{SUM } [l/C_i] \ , \ i = 1, 2, \ldots n$$

where: L = total life expectancy of the pavement, years
l = expected value of laboratory test life, cycles
C_i = average number of annual freeze-thaw cycles for each layer.
n = number of layers as determined by pavement thickness and lab specimen size.

For the 2 X 4 inch cylinders used in this study, the effective test size is two inches because specimens were immersed to one-half their heights and failure occurs in the lower one-half of the four inch long specimens. Pavement life for the E-29 sections can be estimated in the following manner: n = 3 and l = 168 for the high sulfate brine. The number of freeze thaw cycles for each layer are is follows:

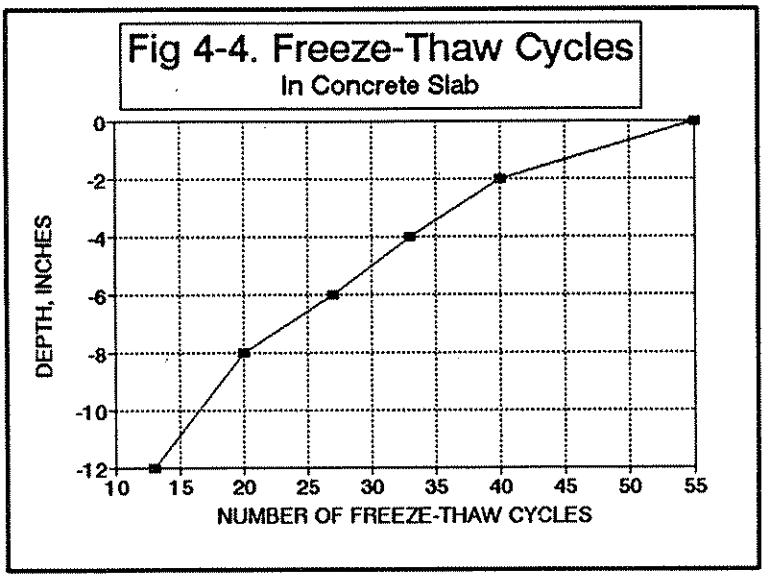


Fig 4-4. Freeze-Thaw Cycles
In Concrete Slab
DEPTH, INCHES
0
-2
-4
-6
-8
-10
-12
10
15
20
25
30
35
40
45
50
55
NUMBER OF FREEZE-THAW CYCLES

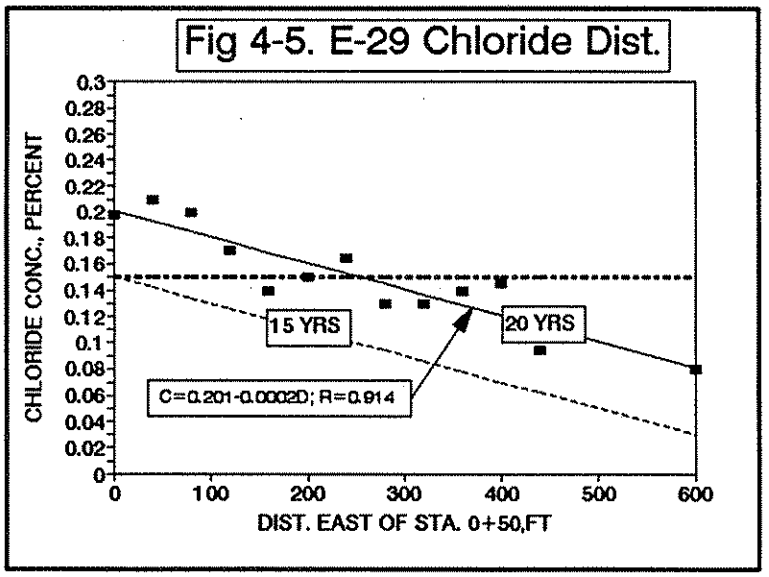


Fig 4-5. E-29 Chloride Dist.
CHLORIDE CONC., PERCENT
0.3
0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
15 YRS
20 YRS
C=0.201-0.0002D; R=0.914
0
100
200
300
400
500
600
DIST. EAST OF STA. 0+50,FT

DEPTH(in)	CYCLES	C_i	L_i
0	55		
		47.5	3.5
2	40		
		36.5	4.6
4	33		
		30.0	5.6
6	27		
		SUM	13.7

Similar computations for the low-sulfate brine and the mortar in water lead to lives of 19 years and more than 25 years, respectively.

Next, accuracy of this prediction will be considered by evaluating data in Figure 4-5, a plot of chloride concentrations vs. distance from the intersection. In this unique situation where salt was applied by tracking from a known source, inferences can be drawn from the good correlation of chloride concentration and distance. The dashed horizontal line represents the chloride concentration for the outer limit of deterioration observed in 1986 or at 20 years of age. If it is assumed that chloride concentration at any point is also linear with time, the time at which the first joint should have shown distress is 15 years. The difference between 15 years to fail the pavement and 14 years (rounded up) to fail the material leaves one year to reach critical salt concentration. Figure 1-2 shows a six inch thick pavement can reach critical deicer concentration in a year for 150 to 200 pound/lane mile rates anticipated at such a location.

At the 20th year of life, the fourteen year material means it should have taken six years of tracking to reach critical concentration. By plotting time to critical concentration against distance an estimated time to concentration at 600 feet can be taken as 11 years. Thus the joint at distance 600 ft should have failed at 11 + 14 = 25 years after construction. Actual failure was observed at 26 years.

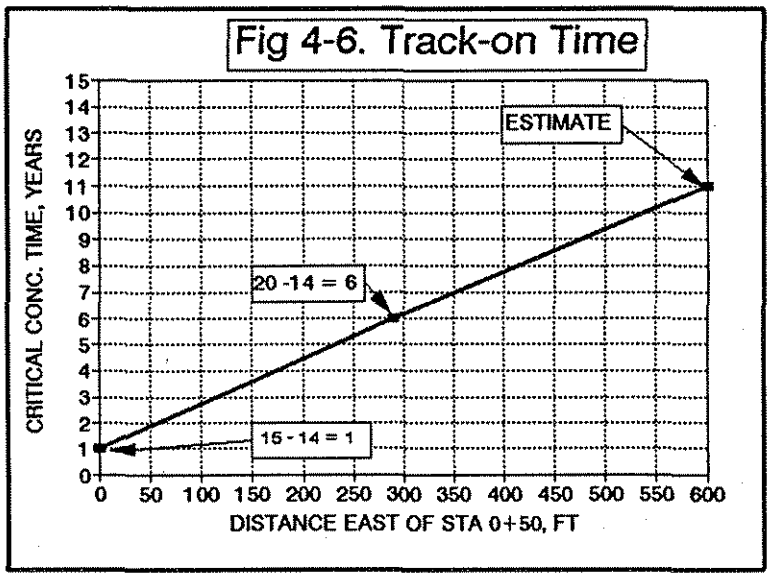


Fig 4-6. Track-on Time
CRITICAL CONC. TIME, YEARS
DISTANCE EAST OF STA 0+50, FT
ESTIMATE
20 -14 = 6
15 - 14 = 1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
50
100
150
200
250
300
350
400
450
500
550
600

PART 5: SUMMARY AND CONCLUSIONS

This research on the action of deicers on porltland cement concrete leads to the assessment that much of the damage results from ingress and collection of salt in the pores of mortar and near aggregate-interface boundaries. Forces causing entrance of salt solutions are in excess of those from diffusion, capillaries, and osmosis. This is substantiated by mortar bar tests in which no detrimental result occurred. Thus the key factor controlling ingress of deicers must be thermal gradient present during freeze-thaw. Deicers are accumulated in concrete by crystallization from repeated drying of the fluid until the pore system cannot accommodate expansion from freezing or crystal growth. This is supported by the fact that deterioration in deicers does not occur unless a portion of the specimen is exposed to air.

Pore systems of mortar and aggregate pay an important role in preventing damage to concrete with less porous materials being less vulnerable. Mortar can be made more effective with optimum amounts of pozzolanic admixtures such as fly ash and possibly post hardening treatments of sodium silicate. Both treatments reduce porosity and thus ingress of deicer solution which delays the destructive process.

Deicers change the mechanism of freeze-thaw from one centered on the character of the aggregate to the character of the aggregate-mortar boundary or the mortar itself. Many aggregates can be used in improved concrete by improving the mortar and bonding at the aggregate-mortar interface.

An evaluation of several existing techniques for assessing pavement life in the presence of deicers demonstrated most were successful but to a limited extent. Correlation to aggregate porosity and ASTM C-666 durability testing all produced outliers for the eight aggregates selected for this study. An adaptation of an alkali-aggregate reaction test proved useless and chemical analysis opened the door for more speculation rather than answers.

Reliability testing was adapted to evaluate concrete by using ultrasonic pulse velocity to define failure from field experience and a variation on ASTM C-666 testing in which deicers were introduced and tests were run define cycles to failure. This test produced a good correlation to observed service life.

Reliability test results were adapted to pavement life prediction by development of a simple model which sums the life of individual pavement layers which is determined from the laboratory life of concrete specimens and the number of freeze-thaw cycles occurring at different depths within a pavement. This model compared favorably with a field evaluation. Also, the model provides an estimate on the number of years of pavement life deicers can cost. A test material subjected to freeze-thaw in water was found to last more than 25 years. Life was reduced to 19 years in a low sulfate deicer and 14 years in a high sulfate deicer. The rock salts used in Iowa are usually of the high sulfate variety.

PART 6: SUGGESTIONS FOR IMPLEMENTATION

Frown this research it is suggested that fly ash at 10 to 15 percent replacement of portland cement should be required in all concrete subjected to deicers. The data suggest that high levels of fly ash are undesirable and should be avoided.

Curing requirements for new construction may also be reduced 1,064 degree-days if fly ash is used. Otherwise, concrete without fly ash should have 13,870 degree days for similar degrees of deicer resistance.

Consideration should be given to treating joints of those pavements constructed without fly ash with sodium silicate in conjunction with normal joint maintenance. Deterioration of these materials might be arrested and major rehabilitation delayed.

If long lived pavements, those lasting longer than thirty years, are desired the reliability based testing scheme developed in this project should be refined and used to identify those combinations of materials capable of producing the desired performance.

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APPENDIX A: DEICER COMPOSITION

Table A-1 Composition of rock salts used in Iowa.

ID	Sulfate as %GYPSUM	$\%CaSO_4$	$\%MgSO_4$	$\%NaSO_4$	$\%SO_4^{--}$
1	4.381	3.465	0.182	0.050	2.630
2	1.385	1.095	0	0	0.773
3	1.450	1.147	0	0	0.809
4	4.467	3.533	0.197	0	2.650
5	1.407	1.113	0	0	0.785
6	1.156	0.914	0	0	0.645
7	3.410	2.697	0.046	0	1.945
8	2.414	1.909	0.154	0	1.470
9	4.106	3.247	0.249	0	2.490
10	3.781	2.990	0	0	2.110
11	1.693	1.339	0	0	0.945
12	0.568	0.449	0	0	0.317
13	5.326	4.212	0.254	0.074	3.234
14	2.921	2.310	0.200	0	1.790
15	3.329	2.633	0.074	0	1.917
16	7.731	6.114	0.246	0.314	4.764
17	7.044	5.571	0.243	0.140	4.238
18	1.366	1.080	0.026	0.005	0.787
19	5.000	3.954	0	0	2.790
20A	3.582	2.833	0.005	0	2.003
20B	5.928	4.688	0.311	0.125	3.657
20C	3.930	3.108	0	0	2.193
20D	5.025	3.974	0.254	0	3.007
21	0.993	0.785	0	0	0.554
22	0.370	0.293	0	0	0.207

[a]Supplier
[b]Site

I	%$MgCl_2$	%$CaCl_2$	%NaCl	Source
1	0	0	96.30	Independence Salt Co., Kansas[a]
	0.013	0.220	98.67	DOMTAR[a]
3	0.007	0.173	98.67	MORTON[a]
4	0.002	0	96.27	Forest City[b]
	0.062	0.530	98.30	Waterloo[b]
	0.033	0.371	98.68	West Union[b]
7	0.183	0	97.07	Independence Salt Co., Kansas[a]
	0.040	0	97.90	Independence Salt Co., Kansas[a]
	0.009	0	96.50	Independence Salt Co., Kansas[a], Linn Co.[b]
10	0.163	0.986	95.88	Independence Salt Co., Kansas[a]
11	0.025	0.442	98.19	Rock Island[a]
1	0.009	0.365	99.18	Cargil[a]
13	0	0	95.46	Independence Salt Co., Kansas[a], Crawford Co.[b]
14	0.003	0	97.49	Independence Salt Co., Kansas[a], Carroll Co.[b]
1	0.181	0	97.11	Independence Salt Co., Kansas[a]
1	0	0	93.33	Independence Salt Co., Kansas[a], Calhoun Co.[b]
17	0	0	94.05	Independence Salt Co., Kansas[a], Calhoun Co.[b]
1	0	0	98.89	Louisiana[a]
	0.147	0.017	95.88	Unknown
0A	0.387	0	96.78	Independence Salt Co., Kansas[a]
0B	0	0	94.88	Independence Salt Co., Kansas[a]
0C	0.199	0.512	96.18	Independence Salt Co., Kansas[a]
0D	0.101	0	95.67	Independence Salt Co., Kansas[a]
21	0.010	0.102	99.10	Unknown
2	0.363	0.079	99.27	Mexico, Com Kare Group U.S. LTD[a]

APPENDIX B: MIX PROPORTIONS

Table B.1. Mortar mix proportions for ten specimens

Non-fly ash control specimens

Portland Cement: 1509 grams
Ottawa Sand: 3080 grams
A/E agent (Doravair-R): 0.5 milliliters
H_2O: 679 grams

W/C = 0.45
Entrained air voids = 9% by volume

Fly ash specimens

Portland Cement: 1283 grams
Ottawa Sand: 3080 grams
A/E agent (Doravair-R): 0.5 milliliters
H_2O: 679 grams

W/C = 0.45
Entrained air voids = 9% by volume