Chloride Penetration and the Effect on Porosity in a Pavement

R. A. MILLER, B. KROUSKOP, I. A. MINKARAH, AND A. BODOCSI

A concrete pavement 230 mm (9 in.) thick was studied for chloride penetration and porosity. The pavement was subjected to an estimated 4600 kg/km (16,000 lb/mi) of deicer annually. Three types of cores were removed from the pavement: cores through sound areas, through sealed joints, and through cracks. Cores were taken in 1985 and 1990. Chloride concentrations were measured in the cores at depths of 25, 76, 127, and 178 mm (1, 3, 5, and 7 in.). The chloride concentrations in whole cores—that is, the cores taken from intact areas of the pavement containing no visible cracks or joints—fall under the corrosion limit at depths below 76 mm (3 in.), although higher chloride contents were detected near the surface. The steel mesh [located between 76 mm (3 in.) and 102 mm (4 in.) below the surface of the concrete] showed no indication of corrosion in these cores. Cores taken through cracks and joints showed much higher chloride concentrations than cores taken from sound concrete. The chloride in the cracked and joint cores was usually above the corrosion limit for steel, and the mesh in the cracked areas had completely corroded, showing that the chloride penetration is mainly through cracks and joints and not through sound concrete. Data from literature suggest that flexural cracks may be enough to admit chlorides. The porosity of the samples was measured using mercury porosimetry. There was no correlation between porosity and chloride content, confirming that damage is more important than porosity in chloride intrusion.

Deicer (NaCl and CaCl₂) penetration in concrete can have an adverse effect on the performance of pavements and bridges. Specifically, chlorides penetrating the pavement or joints can corrode steel reinforcing mesh or dowel bars. It has also been suggested that the presence of deicers in the pore structure can cause scaling of the surface during freeze-thaw cycles (1,2). Brown and Cady also suggested that high concentrations of CaCl₂ may chemically attack the concrete (1).

This study examines a 20-year-old jointed concrete pavement in Chillicothe, Ohio. Like most pavements in Ohio, the pavement was often subjected to deicing materials and freeze-thaw cycling during the winter. The freeze-thaw resistance may be especially critical since the pavement is in southern Ohio, where nighttime temperatures below freezing are common but daytime temperatures are often above freezing. The Ohio Department of Transportation (ODOT) uses NaCl, sometimes prewet with CaCl₂, for deicing. ODOT was interested in knowing the extent to which the deicers were penetrating the concrete and if the penetration was associated with possible deterioration of the reinforcing mesh, dowel bars, and concrete.

R. A. Miller, I. A. Minkarah, A. Bodocsi, Department of Civil and Environmental Engineering, University of Cincinnati, ML 0071, Cincinnati, Ohio 45221. B. Krouskop, Barge, Waggoner, Sumner and Cannon, 8755 Gander Creek Road, Miamisburg, Ohio 45342.

DESCRIPTION AND CONDITION OF TEST PAVEMENT

The test pavement is a 1-km (3,218-ft) section of southbound Route 23 near Chillicothe, Ohio. Route 23 has two lanes in each direction. In each direction, the slab is 7.3 m (24 ft) wide and 230 mm (9 in.) thick. The pavement was constructed in 1972 to test four variables in pavement construction: stabilized (asphalt) versus granular base, 12-m (40-ft) slabs versus 6.4-m (21-ft) slabs, coated versus uncoated dowels, and saw-cut configuration.

All of the 12-m (40-ft)-long sections were cracked in three or four places, usually near the center of the slab. The 6.4-m (21-ft) sections on granular base were also cracked at the center of the slabs, but the 6.4-m (21-ft) sections on stabilized base were not cracked. Virtually all the damage in the pavement was mechanical, that is, appeared to be caused by traffic, pumping, shrinkage, or other stress-related distress. The concrete surface was in excellent condition, and there was very little scaling or spalling of the concrete.

PETROGRAPHIC ANALYSIS OF CONCRETE

Concrete from the pavement was subjected to petrographic analysis. Cores from the pavement revealed a sound, angular coarse aggregate of 19-mm (¾-in.). The coarse and fine aggregates appeared well-graded. Air entrainment was used, and air contents varied from 2 to 12 percent, but most values were near the average of 7 percent. There was no sign of alkali-aggregate reaction or any chemical attack.

TEST SAMPLES

The test pavement was cored to remove samples for material analysis. One set of cores had been taken in 1985 and stored in the Materials Laboratory at the University of Cincinnati. The cores were stored at room temperature in air. A second set of cores was taken in 1990 and immediately used for analysis. The locations of the 1985 cores were carefully recorded, and the 1990 cores were taken as close as possible to the original core locations. Table 1 matches the sample numbers from the two sets of cores and indicates whether a core was taken from sound areas of the pavement or through a joint or a crack. In this paper, cores are numbered by sample number and the year the core was taken: for example, Sample 1 (1990).

TABLE 1 Identification of Concrete Cores

Sample # 1985 Cores	Sample # 1990 Cores	Location	Type of Core
4	6	bet. joints 25 & 26	Whole
N/A	10	bet, joints 56 & 57	Whole
N/A	12	bet, joints 95 & 96	Whole
5 & 6	4	joint 25	Joint /
8	14	joint 42	Joint
18	8	joint 56	Joint
9	N/A	joint 78	Joint
13	1	15' N of Joint 15	Crack
7	2	13' S of Joint 46	Crack
21	3	18' S of Joint 56	Crack

N/A = Not Available - No Corresponding Core

CHLORIDE CONTENTS

ODOT estimates that the pavement was subjected to 4600 kg/km (16,000 lb/mi) of NaCl each year. Since the CaCl₂ is sprayed on the NaCl, accurate estimates of CaCl₂ contents are not available. Using these numbers, the use of deicers is 0.6 kg/m² (0.13 lb/ft²) annually. This is not a large number, but it may be enough to cause corrosion. If the chloride from this amount of salt was absorbed uniformly through the 230-mm (9-in.) thickness of the slab, the chloride content would be about 700 ppm, which is above the 250-ppm lower-bound corrosion limit for steel.

Tests were performed to determine the penetration of chlorides into the concrete. Samples were taken from the cores at depths of 25, 76, 127, and 178 mm (1, 3, 5, and 7 in.) below the pavement surface.

A sample of the concrete was removed from the cores using a hammer drill. Because the cores were cut with water, there was a concern that chlorides may have been washed out of the surface concrete, so any sample from the first 3 mm (1/8 in.) of penetration of the hammer drill bit was discarded. To prevent bias, several holes were drilled at each location in the core and the resulting powder was combined. From the powder, a 10-g sample was removed for analysis.

The chloride content tests were performed in accordance with ASTM C114. To the 10-g sample, 75 mL of water, 25 mL of dilute nitric acid, and 3 mL of hydrogen peroxide (30 percent solution) were added. The solution was heated in accordance with the specification. Samples of the resulting solution were removed for titration after the solution had cooled. Chloride contents are given as parts per million, which is milligram/kilogram, by weight of concrete.

Figures 1 through 4 show the chloride contents plotted against the depth of the sample from the road surface. The data points are marked "1985" and "1990" to indicate the year in which the core samples were taken. The data are separated into three graphs: one for whole cores, one for cores taken through joints, and one for cores taken through cracks. Figure 4 shows the average chloride contents for each type of core. Data from literature suggest that the corrosion limit for steel is a chloride content of between 250 and 510 ppm by weight of concrete (3). AASHTO specifications for bridge decks state that chloride contents of 3,000 ppm by weight of cement or less are acceptable and that bridge decks should be replaced if the chloride contents exceed 6,000 ppm by weight of cement. Assuming that the concrete is 20 percent cement, the limits are 600 and 1,200 ppm by weight of concrete. A line indicating a concentration of 250 ppm is marked as the lower-bound corrosion limit on Figures 1 through 4.

The data in Figures 1 and 4 show the chloride concentrations in whole cores—those cores that were taken from intact areas of the pavement containing no visible cracks or joints. The chloride concentrations fall within the corrosion limits at depths below 76 mm (3 in.), although higher chloride contents were detected near the surface. It is interesting to note that although the pavement was almost 20 years old, the chloride concentrations in the intact areas 76 mm (3 in.) below the surface were just reaching the lower-bound level required for corrosion. The steel mesh in the pavement [located between 76 and 102 mm (3 and 4 in.) below the surface of the concrete] showed no indication of corrosion in these cores. The 1985

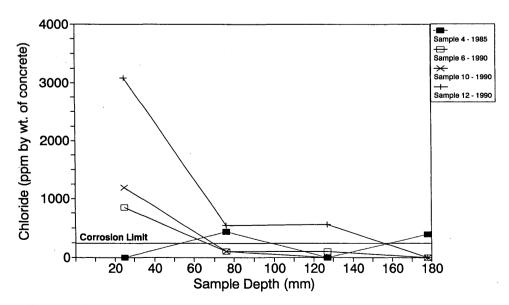


FIGURE 1 Chloride contents on whole (sound) cores.

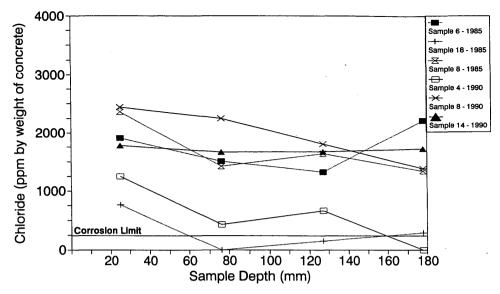


FIGURE 2 Chloride contents in cores through joints.

core (Sample 4) displays an unusual behavior. The chloride contents are 0 at 25 and 127 mm (1 and 5 in.) but 300 ppm at 76 and 178 mm (3 and 7 in.). The reason for this is not clear. Part of it may be the accuracy of the test (\pm 100 ppm), but this does not completely explain the difference. Perhaps the core was contaminated either during construction or while stored in the lab.

Figures 2 and 4 summarize cores taken through the joints in the pavement. Except for Sample 4 (1990), these cores all have chloride contents above the corrosion limits. It is of interest that Sample 4 (1990) has a lower chloride content than the 1985 cores, including Sample 6 (1985), which was taken from the same joint. The data from Sample 4 (1990) suggest that if the joint remains sealed, it will prevent the intrusion of chlorides, but the data from the other joints suggest that most of the joints did not remain sealed. Figure 2 also shows that the chloride contents are somewhat uniform

along the depth, perhaps indicating that chloride-laden water collected in the joints and allowed a more uniform penetration. The 1985 cores have a substantial chloride content, possibly indicating an early seal failure. However, the difference in chloride contents between the 1985 and 1990 cores is generally small, which probably indicates that the seal was partially effective so that chloride-laden water was admitted slowly over time.

Figures 3 and 4 show the chloride contents for the cracked specimens. The 1990 specimens show the highest chloride content, whereas the 1985 cores generally have chloride contents below those of the joints. Two of the cracks, represented by Samples 13 (1985) and 1 (1990) and Samples 21 (1985) and 3 (1990), were old cracks first noted in a survey in March 1974. The third crack, represented by Samples 7 (1985) and 2 (1990), is relatively new and was first discovered in a survey in May 1985. The older cracks show a large difference between

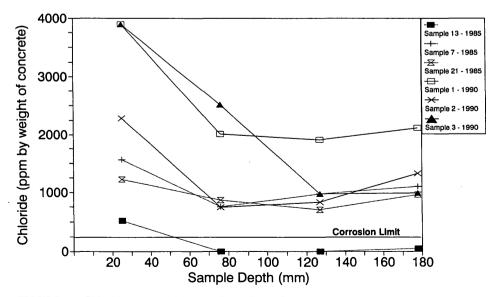


FIGURE 3 Chloride contents in cores through cracks.

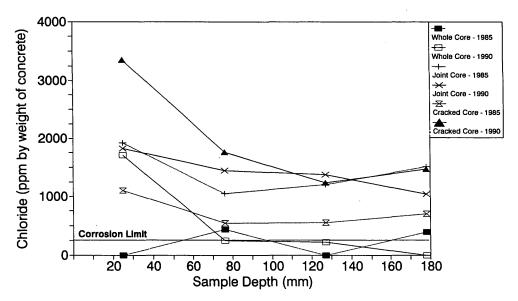


FIGURE 4 Average chloride contents.

1990 and 1985 core chloride contents. The low initial reading indicates that the chlorides penetrate more slowly at first, perhaps because the crack is not widely opened. However, the two older cracks are now open wide and the chlorides are being admitted more easily, as can be seen by the large change in the chloride content. The newer crack [Samples 7 (1985) and 2 (1990)] does not show a large change in chloride content between 1985 and 1990, except at the top. This was a smaller crack that probably did not easily admit chlorides. In the cracked cores, the wire mesh had completely corroded, as would be expected.

RESULTS FROM OTHER STUDIES

The results from the pavement cores are consistent with other studies on chloride penetration. Heckenmueller studied chloride penetration in a 37-year-old reinforced concrete bridge deck (4). The deck had extensive deterioration along the shoulder and side areas, but the driving lanes were in very good condition. Unfortunately, it is not possible to trace the exact sequence of deterioration, but the results of petrographic analysis lead to a probable sequence. First, the concrete deck was covered by an asphalt layer. Snow and ice pushed to the bridge shoulders by traffic and plows melted and saturated the asphalt and concrete beneath. The concrete was damaged by freeze-thaw because of a lack of air entrainment in the paste and a poor-quality aggregate susceptible to freeze-thaw cracking. Also, alkali-aggregate reactions took place in the shoulder regions, further damaging the concrete. The freeze-thaw cycling and alkali-aggregate reaction cracked the concrete and allowed entrance of the deicers.

Figure 5 compares the deteriorated areas of the bridge with the sound areas. The chloride contents are much higher. The chloride contents are not as high as for the cracked areas of the pavement, but the bridge was covered by an asphalt layer that would have slowed the migration of the deicers. Note that Core LL has a higher chloride content at 305 mm (12 in.); this is probably because the shoulder slab had cracked

horizontally and chlorides could penetrate from the side of the bridge through these horizontal cracks. Also note that Core L showed a high chloride concentration, even though it was removed from the sound roadway area. However, this core was removed from the area over the pier line that was subjected to negative moment. It is possible that flexural cracking on the top of the slab admitted the chlorides.

As with the pavement, cores in the sound areas revealed no corrosion of the reinforcing steel, except in the previously noted Core L. The fact that a rebar in Core L had corroded indicates that the bridge deck had been exposed to enough chlorides to cause corrosion. The fact that bars in other places in the intact concrete did not corrode indicates that the chlorides did not penetrate the sound area.

Coggins and French measured chloride penetration into prestressed concrete beams and the bridge deck that covered the beams (3). The prestressed beams were designed not to crack under service flexural loads, and no cracking was seen. Although chloride contents in the beams 13 mm (½ in.) below the surface were as high as 1,000 ppm, the chloride contents dropped below the 250-ppm corrosion limit at depths below 25 mm (1 in.). In the bridge deck that covered the prestressed beams, chloride contents 25 mm (1 in.) below the surface were as high as 5,000 ppm but in most cases dropped to 350 ppm or less at a depth of 76 mm (3 in.). The bridge deck data are consistent with results of whole cores taken from the pavement.

The usual theory of chloride penetration in concrete is the "concrete sponge" analogy, which states that the concrete absorbs chloride-laden water like a sponge. The results for the whole cores show this type of behavior, but only in the top 75 mm (3 in.). The amount of chloride actually absorbed is so small that it barely exceeds the lower bound for corrosion at a depth of 76 mm (3 in.) after almost 20 years.

The results clearly show that chlorides penetrate through the cracks and joints. The highest chloride concentrations appeared in the samples taken from cracks and joints in the pavement. The referenced bridge study confirms this since chloride contents were highest where there was extensive freeze-

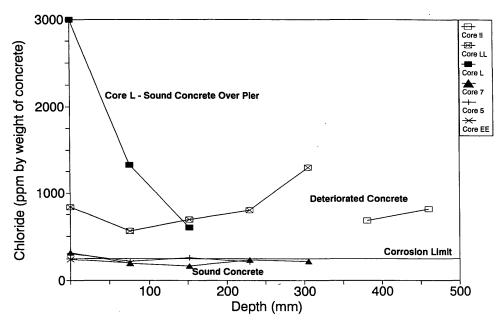


FIGURE 5 Chloride contents in a reinforced concrete bridge deck (4).

thaw cracking (4). Perhaps even flexural cracking is enough to admit chlorides since Heckenmueller (4) found higher chloride contents in a sound area over a pier where there was probably flexural cracking, and Coggins and French (3) found low chloride contents in beams designed not to crack under service flexural loads.

POROSITY

Previous laboratory studies have indicated that penetration of chloride ions does not change the pore structure of hardened cement pastes (5-7). However, introduction of chlorides during curing or into improperly cured concrete may result in a change in pore structure (7). Another possible problem with deicer intrusion occurs during freeze-thaw cycling. Studies on freeze-thaw deterioration have shown that deicers may aggravate scaling of concrete by increasing the osmotic pressure in the pore structure (1,2,8). The deicers themselves may not alter the pore structure of the paste, but it is possible that the presence of deicers in solution during freeze-thaw cycles will damage the concrete and alter the pore structure.

Samples of the pavement concrete were tested by mercury intrusion porosimetry. In this method, mercury is forced into the pores of a material by pressure. Because mercury is non-wetting (it is not absorbed by the porous material), there is a definite relationship between the pressure and the size of the pore. The relationship is

$$d = \frac{-4 \gamma \cos \Theta}{n}$$

where

d = pore diameter,

 γ = mercury surface tension,

 Θ = contact angle (usually taken as 130 degrees), and

p = pressure.

By measuring the volume forced into the specimen under a certain pressure, it is possible to determine the volume of all the pores in the structure of a certain size.

For the pavement, samples were taken from one set of whole cores, one set of joint cores, and two sets of cracked cores, where a set is a 1985 and a 1990 core from the same location. For each core, a sample was taken from the top, the middle, and the bottom. When the samples were taken, great care was used to ensure that pieces of coarse aggregate were not in the sample.

Core Type	Sample Number (1985)	Sample Number (1990)
Whole	4	6
Joint	8	14
Crack	13	1
Crack	7	2

Figures 6, 7, and 8 are typical results of the porosity tests. The graphs show the total amount of mercury intruded into pores of a given size and larger. For example, consider the plot for Sample 6 (1990), Bottom, in Figure 6. The graph indicates that a total volume of 0.032 cm³/g was intruded for a pore size of 1 micron, which means that it takes 0.032 cm³ of mercury per gram of sample to fill all the pores 1 micron in diameter and larger. If the line connecting the data is closer to the top and right sides of the graph, the material is more porous. If the line is closer to the bottom and left sides, the material is less porous.

The first comparison was made between samples with low and high chloride contents. Several cores showed little or no chloride intrusion, and the porosity of these cores is plotted in Figure 6 along with the porosity for the top of Core 1 (1990). The top of Core 1 (1990) had the highest chloride content, at 3,850 ppm. The results in Figure 6 show that there is no relationship between chloride content and pore size or total intruded volume, indicating that the presence of chlorides has not altered the pore structure.

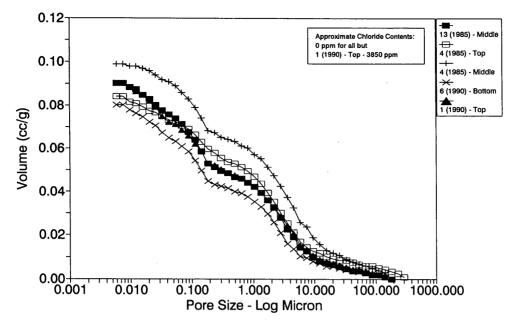


FIGURE 6 Porosity for samples with chloride contents of 0 ppm compared with a sample with high chloride content.

The next comparison was between cores taken from the same location. An example is shown in Figure 7, which compares Cores 13 (1985) and 1 (1990) taken from a crack. It was thought that cores taken from approximately the same location in the pavement would have roughly the same porosity at the time of casting and that if there were a change in pore structure it would show up in a comparison of these cores. However, the results in Figure 7 again indicate no correlation between chloride content and pore size or intruded volume. Also note that for the top and bottom samples, the graphs of the 1985 and 1990 cores fall very close together, indicating that there has been no damage to the pore system with time.

Finally, Figure 8 is a plot of the porosity of samples taken from the top of the cores. Assuming that deicers are uniformly distributed, all of these samples should have been exposed to the same amount deicers. Therefore, one would expect that the most porous samples would absorb the most chloride. However, this is not true: Core 4 (1985) has the highest porosity but a low level of chloride intrusion where Core 1 (1990) has the highest level of chloride intrusion and its porosity is in the midrange for the samples.

Again, the only correlation is between chloride content and the condition of the core (whole, jointed, or cracked). The cracks and joints clearly have the highest chloride content

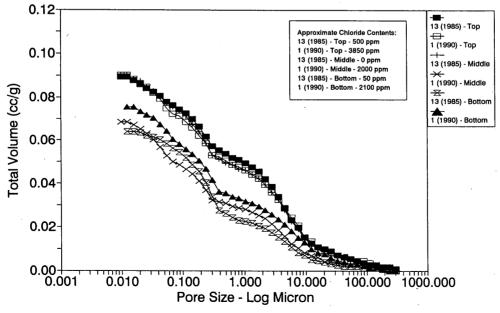


FIGURE 7 Porosity for samples taken from same position in pavement.

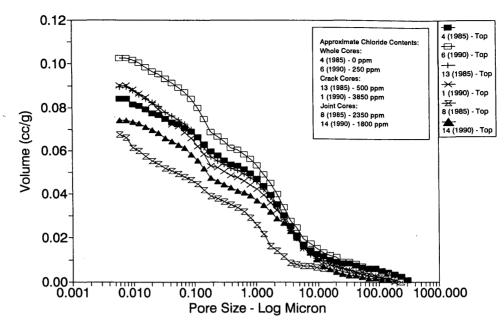


FIGURE 8 Porosity for samples taken from top of pavement.

regardless of porosity. This can be explained by two factors. First, there was probably standing water in the cracks and joints. The deicer-laden water would leak into the cracks and joints and evaporate more slowly than from the pavement surface. This additional time of contact would increase absorption of deicers (chlorides). Second, there was probably extensive microcracking around the cracks and joints (recall that the joint are partially saw-cut, which may induce damage, and then allowed to crack through the reminder of the pavement thickness). The microcracks would be too big to show up as additional porosity in the mercury intrusion process. The results of the porosity study confirm that although porosity is an important factor, damage is a more critical factor for chloride intrusion than porosity.

CONCLUSIONS

Much of the current thinking on chloride penetration assumes that the concrete acts like a sponge and that chlorides penetrate through the porous paste. The results of this study and others (3,4) indicate that such penetration in sound concrete is very slow. Most chloride penetration is through cracks and joints in the concrete. Even flexural cracking may be sufficient to allow the penetration of chlorides.

The pavement on Route 23 in Chillicothe was subjected to an estimated 4600 kg/km (16,000 lb/mi) of deicer a year, so that each 12-m (40-ft) slab was subjected to 54 kg (120 lb) of deicer a year. Yet, after 20 years the chloride contents in the sound concrete had barely reached the lower-bound corrosion limit of 250 ppm by weight of concrete at a depth of 76 mm (3 in.). The reinforcing mesh, located at a depth of 100 mm (4 in.), showed no signs of corrosion in the whole cores. However, in the cracks and joints, the chloride contents were usually well above the corrosion limit. The reinforcing mesh

in the cracked regions of the pavement was completely corroded.

The study also shows that damage to or breaks in the pavement play a much bigger role in chloride intrusion than porosity. There was no correlation between porosity and amount of chlorides absorbed by the concrete, which indicates that absorption of chlorides is not governed solely by porosity.

Finally, the deicers did not appear to have any effect on the concrete. Studies have shown that the presence of deicers can aggravate freeze-thaw deterioration by increasing the osmotic pressure in the pores (1,8). However, there was no sign of scaling in the pavement and the porosity studies showed that no damage had been done to the pores. This indicates that air entrainment of 7 percent was sufficient to protect the pavement against freeze-thaw cycling even if there was additional osmotic pressure from deicers.

ACKNOWLEDGMENTS

This research was funded by ODOT and FHWA.

REFERENCES

- F. P. Brown and P. D. Cady. Deicer Scaling Mechanisms in Concrete. In ACI SP-47: Durability of Concrete, American Concrete Institute, Detroit, Mich., 1975, pp. 101-120.
- T. C. Powers. Freezing Effects in Concrete. In ACI SP-47: Durability of Concrete, American Concrete Institute, Detroit, Mich., 1975, pp. 1-12.
- F. L. Coggins and C. W. French. Chloride Ion Distribution in Twenty-Year-Old Prestressed Bridge Girders. ACI Materials Journal, Vol. 87, No. 5, Sept. - Oct. 1990, pp. 479-488.
- 4. M. A. Heckenmueller. Deterioration Analysis of a 37-Year-Old Reinforced Concrete Bridge Deck. Master's thesis. University of Cincinnati, Ohio, June 1992.

- C. L. Page, N. R. Short, and A. El Tarras. Diffusion of Chloride Ions in Hardened Cement Paste. Cement and Concrete Research, Vol. 11, No. 3, May 1981, pp. 395-406.
 H. G. Midgely and J. M. Illston. Penetration of Chlorides into
- H. G. Midgely and J. M. Illston. Penetration of Chlorides into Hardened Cement Paste. Cement and Concrete Research, Vol. 14, No. 4, June 1984, pp. 546-558.
 O. A. Kayyali. Strength and Porosity of Portland Cement Paste
- O. A. Kayyali. Strength and Porosity of Portland Cement Paste Subject to Chloride Penetration. *Journal of Materials in Civil Engineering*, Vol. 1, No. 1, Feb. 1989, pp. 10-18.
- 8. D. F. Adkins and V. T. Christiansen. Freeze-Thaw Deterioration

in Concrete Pavements. Journal of Materials in Civil Engineering, Vol. 1, No. 2, May 1989, pp. 97-104.

The contents in this paper reflect the views of the authors, who are responsible for the facts and accuracy of the data presented herein. This paper does not necessarily reflect the views or policies of ODOT or FHWA and does not constitute a standard, specification, regulation, or recommendation.

Publication of this paper sponsored by Committee on Corrosion.