

The Relationship of Ferroan Dolomite Aggregate to Rapid Concrete Deterioration

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Some of Iowa's 13,200 miles of portland cement concrete (pcc) pavement have remained structurally sound for more than 50 years, while others have suffered premature deterioration. Research has shown that the type of coarse aggregate used in the pcc is the major cause of this premature deterioration. Some coarse aggregates for concrete exhibit a nonuniform performance history. They contribute to premature deterioration on heavily salted primary roadways while providing long maintenance-free life on unsalted secondary pavements. This inconsistency supports the premise that there are at least two mechanisms that contribute to the deterioration. Previous research has shown that one of these mechanisms is a bad pore system. The other is apparently a chemical reaction. The objective of this research is to develop simple rapid test methods to predict the durability of carbonate aggregate in pcc pavement. X-ray diffraction analyses of aggregate samples have been conducted on various beds from numerous quarries producing diffraction plots for more than 200 samples of dolomitic or dolomite aggregates. The crystalline structures of these dolomitic aggregates show maximum-intensity dolomite/ankerite peaks ranging from a d -spacing of 2.884 angstroms for good aggregates to a d -spacing of 2.914 angstroms for nondurable aggregates. If coarse aggregates with known bad pore systems are removed from this summary, the d -spacing values of the remaining aggregates correlate well with expected service life. This may indicate that the iron substitution for magnesium in the dolomite crystal is associated with the instability of the ferroan dolomite aggregates in pcc pavement.

Of the 13,200 miles of pcc pavement in Iowa, some have remained structurally sound for more than 50 years while others have suffered premature deterioration. For years, Iowa has had a quality assurance program based upon frequent testing of the cement and aggregate used in pcc. The oldest of these quality control tests is a 16-cycle water and alcohol freeze and thaw test for the coarse aggregate. This test effectively excludes argillaceous (shaley) materials and has been a part of the standard specifications for 40 years.

In general, Iowa has had good performance from pcc pavement. One of the major problems in Iowa with some pcc pavements has been a rapid deterioration, referred to as D-cracking, usually beginning at the joints (1). The life of these pcc pavements in Iowa has been severely reduced by D-cracking (Figure 1), necessitating extensive full-depth patching. Research in the 1960s identified the major factor in D-cracking as nondurable coarse aggregate. This research further revealed

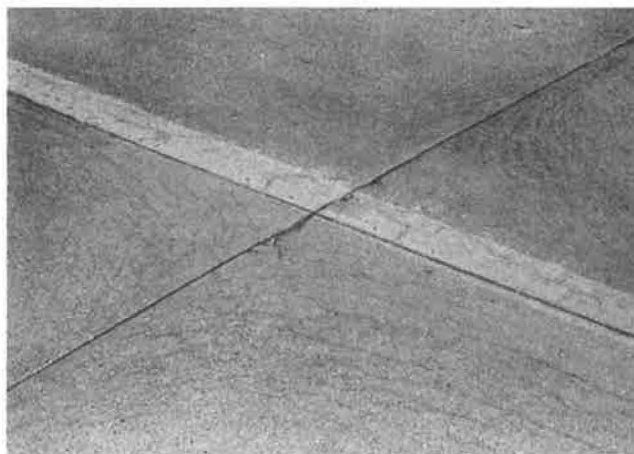


FIGURE 1 A close-up of D-cracking at the intersection of the transverse and longitudinal joints.

that the mechanism causing the cracking was freezing and thawing of water within the concrete. Iowa began using an ASTM C666, Method B (freezing in air, thawing in water) test in 1962 to further identify nondurable coarse aggregates. A 90-day moist-cure preparation before the ASTM C666, Method B testing produced results that correlated relatively well with the performance history of pcc pavements in Iowa. Research beginning in 1978 revealed a relationship between the freeze and thaw failure of carbonate aggregates and their pore systems (2, 3). The Iowa Pore Index was adopted and again was relatively reliable in identifying nondurable carbonate coarse aggregate.

Unfortunately, there were still notable exceptions in trying to categorize all aggregates that result in rapid deterioration as being caused by adverse pore systems (substantial pores in the 0.02- to 0.2-micron diameter range). Some nondurable aggregates with very good pore systems (pore sizes predominately larger than 0.2-micron diameter) contribute to rapid deterioration in a concrete system. This would indicate that there is another mechanism of failure. John Lemish of Iowa State University conducted substantial research on carbonate rocks as concrete aggregates. In research carried out in June 1962 he identified rim reactions with particular nondurable aggregates and noted that the aggregate "had reacted chemically with its concrete environment" (4).

In July 1967 D. L. Biggs of Iowa State University referred to the ferroan nature of a D-cracking Iowa coarse aggregate in

research on compositional and mechanical properties of carbonate rocks, which was some of the earliest Iowa work conducted with X-ray diffraction analysis of carbonates (5). The mineralogical characteristics of carbonate rocks from 13 different Iowa quarries were analyzed. Acetic acid was used to remove the calcite for a better diffraction evaluation of the crystallinity of the dolomite aggregates. Using Norelco X-ray diffraction equipment, a maximum-intensity dolomite peak was determined for a sample from Pints quarry, bed 5B (Coralville) as having a d -spacing of 2.895 angstroms. Biggs noted that some dolomite aggregates "contain an excess of magnesium and probably iron in solution." While no further pursuit of that portion of the research was conducted, current research shows this finding to be relevant to the performance of dolomitic aggregates.

ENVIRONMENTAL EFFECT ON RATE OF PAVEMENT DETERIORATION

The Iowa Department of Transportation's Office of Materials geologists evaluate pcc pavements to identify aggregate-related failures. Continued observation of pcc pavement indicates that the rate of deterioration is quite often dependent on environmental conditions. In some instances, this varied rate relates to the pore system of the coarse aggregate contained in the concrete (1). Nondurable aggregates with an undesirable pore system seem to be affected by the availability of water. Between 15 and 20 years of age, some pcc pavements will exhibit moderate joint deterioration throughout the length of the project, but accelerated joint deterioration is often found where perched water tables are intercepted through cut areas. It also appears that the permeability of the base affects the rate of D-cracking deterioration with an increased rate of deterioration occurring in PCC placed on relatively impermeable bases.

Joint seal research was incorporated into a 1966 project (Montgomery County Road H-54 at M-63) to compare preformed neoprene seals with the standard (in 1966) low-grade bituminous sealing material. The low-grade bituminous sealing material failed very quickly and water was allowed into the bituminous sealed joints. The preformed neoprene seals functioned relatively well, and even though there was some loss of seal, they functioned much better than the bituminous sealed joints. The bituminous sealed joints exhibited rapid joint deterioration much earlier and the deterioration progressed more rapidly than did the joints sealed with preformed neoprene. To date, joint deterioration at the bituminous sealed joints is much more severe than at the neoprene-sealed joints.

Substantial D-cracking deterioration (aggregate with a bad pore system) was identified on a section of pcc pavement at an interstate interchange (I-80 and US-71) that remained closed and received no deicing salt applications for a number of years. The section with no traffic exhibited approximately the same rate of D-cracking deterioration as that open to traffic. This D-cracking was caused by an aggregate with a bad pore system.

Primary roadway concrete has a higher cement content than the secondary roadway concrete. Laboratory research on the freeze and thaw durability of concrete has shown that with the use of the same materials the higher cement content produces a

concrete with better durability than a concrete with a lower cement content.

There is one additional environmental difference between primary and secondary concrete pavements. There are some carbonate aggregates that have a good pore system and yet exhibit rapid D-cracking on primary roadways. However, these same aggregates cause little or no D-cracking on secondary roadways that received limited or no applications of deicing salts. A pavement containing a Pennsylvanian crushed limestone from the Lemley-Exline quarry was incorporated into a pavement on primary highway US-34 in southern Iowa in 1962. Today, it exhibits severe D-cracking. A secondary road containing the same Lemley-Exline aggregate constructed in 1964 exhibits only staining and no visible D-cracking deterioration. A D-cracking susceptible gravel containing 70 percent carbonate was used in primary highway US-30 in central Iowa in 1965. Severe D-cracking of this pcc pavement has made it necessary to resurface a section with asphalt concrete. A secondary road containing the same gravel aggregate was constructed in 1966 and exhibits no indication of D-cracking today. In general, the secondary pavements do not receive applications of deicing salt for wintertime maintenance. The primary roadways receive substantial amounts of sodium chloride deicing salts. Many secondary highway departments use selective deicing salt applications at stop signs, on bridges, and at railroad crossings. This, in conjunction with salt brine being tracked from primary roadways, results in substantial salting on the secondary roadways at primary road intersections. The serious joint deterioration prevalent on Story County road E-29 at the intersection with US-65 decreases rapidly to no deterioration a short distance from US-65. This inconsistency in the performance of carbonate aggregates in pcc pavement was one of the factors that led to the current research on the instability of ferroan dolomites.

Another situation where nonuniformity in the rate of joint deterioration may occur is where a pcc roadway constructed with a nondurable aggregate passes under a bridge. There are cases where joint deterioration is extensive except where the road passes under the bridge (US-30 under I-35 and US-34 beneath city street overpasses in Burlington). The joints that are essentially beneath the overpass bridges will exhibit little or no joint deterioration. This variation could result from fewer freeze and thaw cycles or from being protected from the effects of the sun (temperature and evaporation) or rainfall. Despite much speculation, the mechanism that causes this variation has not yet been identified.

OBJECTIVE

The objective of this research is to develop simple, rapid test methods to predict the durability of carbonate aggregate in pcc pavement. The test methods include analyses of the pore systems and chemical compositions of aggregate sources.

DETERIORATION MECHANISMS

Past research and performance histories have provided conclusive evidence that the major property of one type of nondurable

aggregate is an undesirable pore system. The mercury porosimeter, the Iowa Pore Index test, and a recently developed ice porosimeter will identify very adequately aggregates containing undesirable pore systems. Other deterioration mechanisms would apparently be chemically related. A sodium chloride salt treatment (6) before ASTM C666, Method *B* freeze and thaw testing, causes rapid loss of durability with some aggregates while exhibiting very little effect on other aggregates. Research regarding the NaCl effects on aggregate appears to point toward an alteration of the crystalline structure. This alteration weakens the aggregate, rendering the concrete susceptible to deterioration by freeze and thaw cycles.

Another relatively simple test was used in an effort to determine the chemical reaction that was taking place with the carbonate aggregates. A slice of rock was sawed from a piece of Garrison ferroan dolomite. One side of this slice was polished. The polished slice was broken into three pieces, which were boiled in three different liquids for 2 hours. One liquid was distilled water, the second was a calcium chloride solution, and the third was a sodium chloride solution. Scanning electron microscope photomicrographs were taken of each sample (Figures 2, 3, and 4). The piece boiled in distilled water showed no appreciable change. The section boiled in calcium chloride

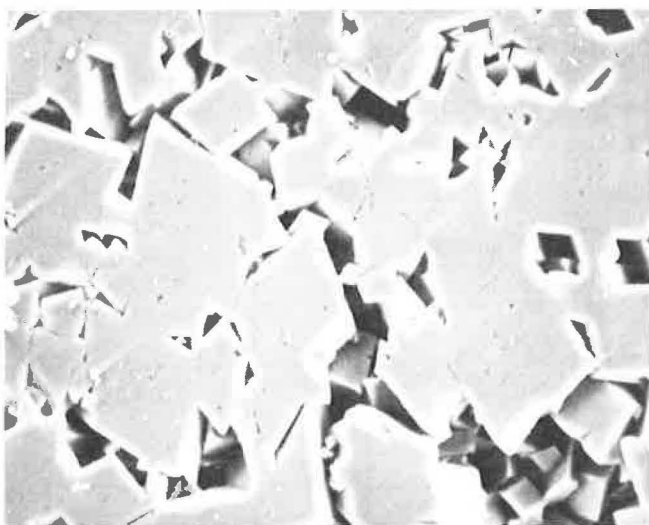


FIGURE 2 SEM photomicrograph of a polished Garrison dolomite surface after boiling in distilled water.

solution exhibited only minor etching and discoloration. The section that was boiled in sodium chloride showed substantial etching and discoloration (an apparent disruption of the crystal surface). X-ray diffraction analysis of material boiled in the calcium chloride solution showed changes that were not visually evident (Figure 5). Before boiling the material in the calcium chloride solution, there was no maximum-intensity calcite peak. There was a strong dolomite maximum-intensity peak at 2.904 angstroms. After boiling in calcium chloride there was still a strong maximum-intensity dolomite peak at 2.904 angstroms, but there was also a maximum-intensity calcite peak at a *d*-spacing of 3.039 angstroms. This would indicate that some of the iron and magnesium was replaced by calcium, but this apparently did not change the appearance of

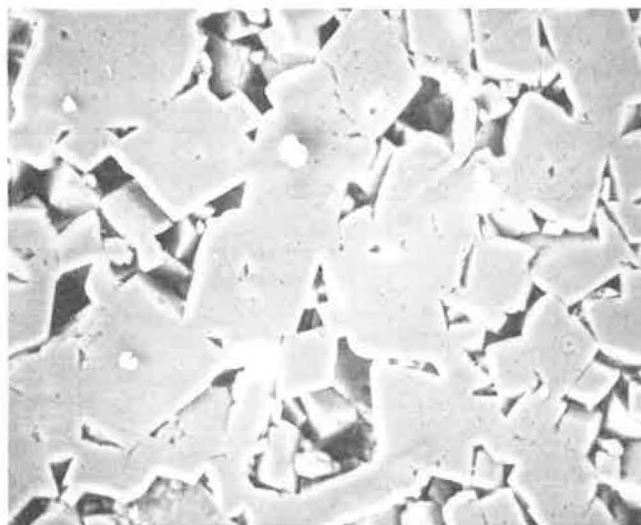


FIGURE 3 SEM photomicrograph of a polished Garrison dolomite surface after boiling in a calcium chloride solution.

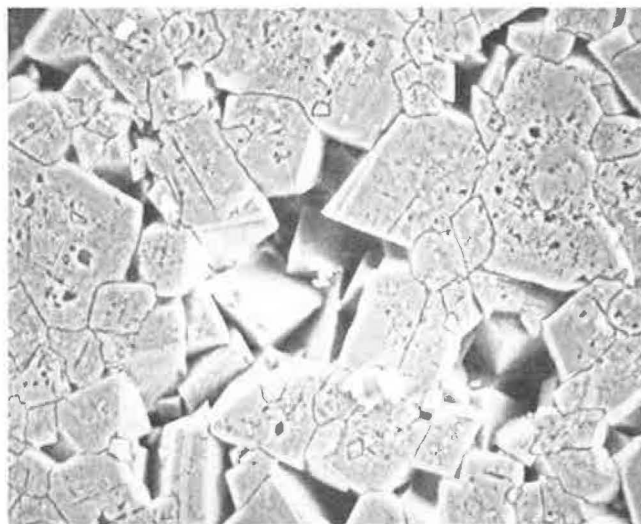


FIGURE 4 SEM photomicrograph of a polished Garrison dolomite surface after boiling in a sodium chloride solution.

the polished surface to any extensive degree. After boiling in water, sodium chloride, or magnesium chloride, the diffraction plots of the Garrison dolomite showed no significant change (Figures 6, 7, and 8). Boiling of a Maryville non-ferroan dolomite in calcium chloride also produced a calcite peak (Figure 9). While this study does not prove the aggregate is weakened by deicing salts, it does suggest that deicing salts produce chemical and crystallographic changes within the aggregate that may lead to deterioration.

X-RAY DIFFRACTION STUDY OF THE DOLOMITE/ANKERITE PEAK

A Siemens D-500 computer-controlled X-ray diffractometer was used for the analysis of all crushed carbonates. The diffractometer is controlled with a PDP-11-03 microcomputer. The

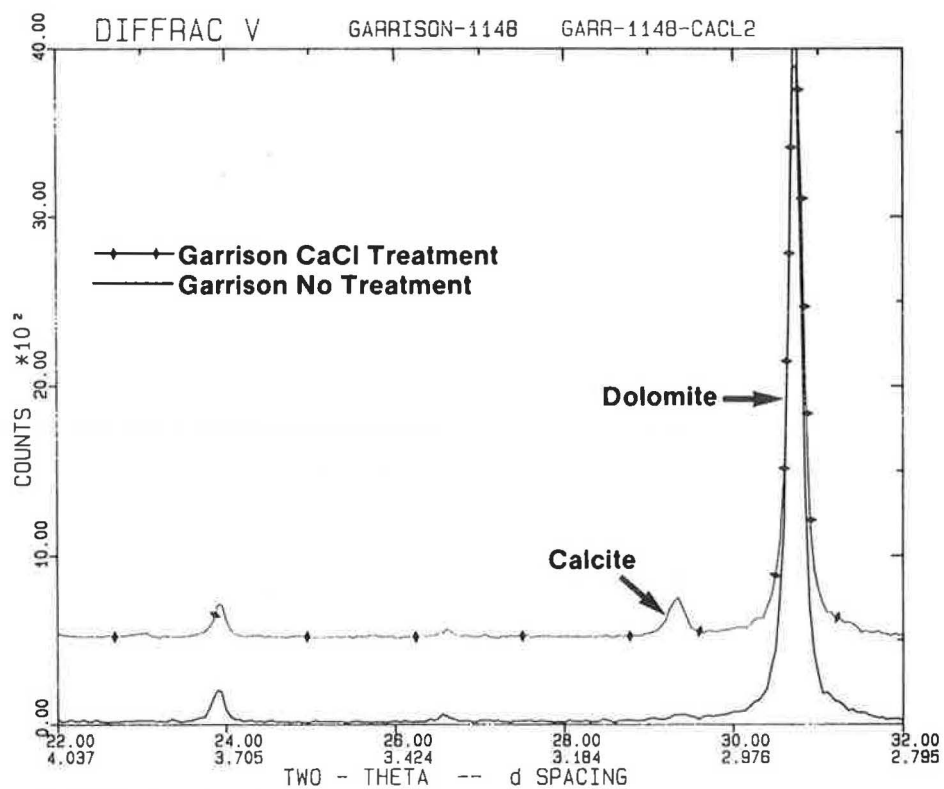


FIGURE 5 Garrison X-ray diffractogram—no treatment and boiling in a calcium chloride solution.

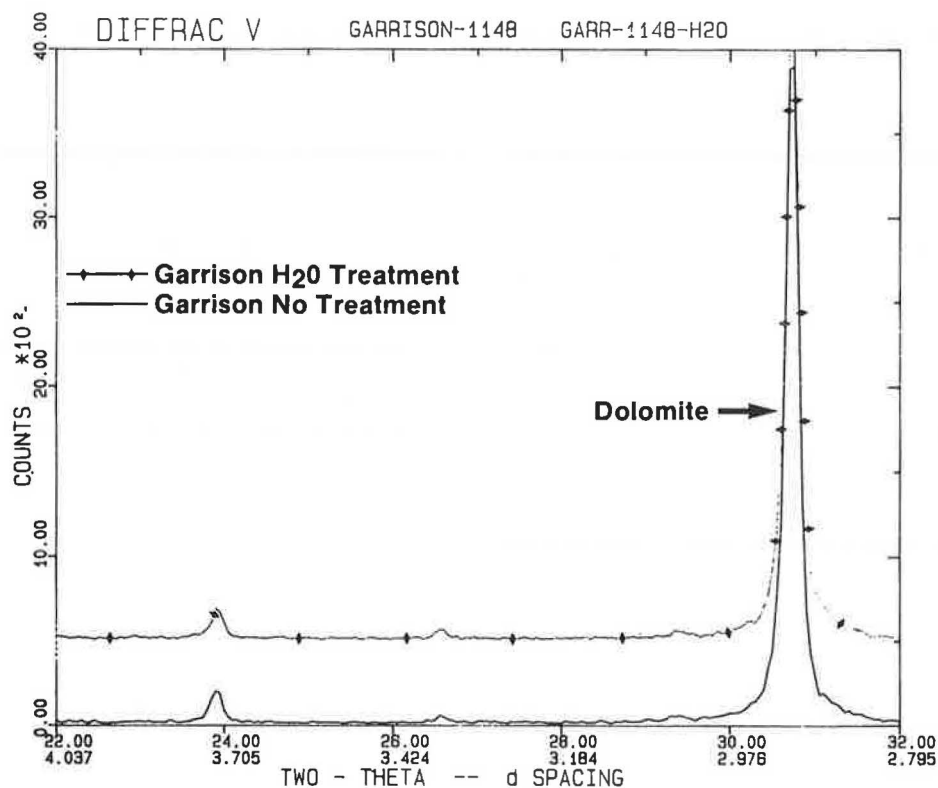


FIGURE 6 Garrison X-ray diffractogram—no treatment and boiling in distilled water.

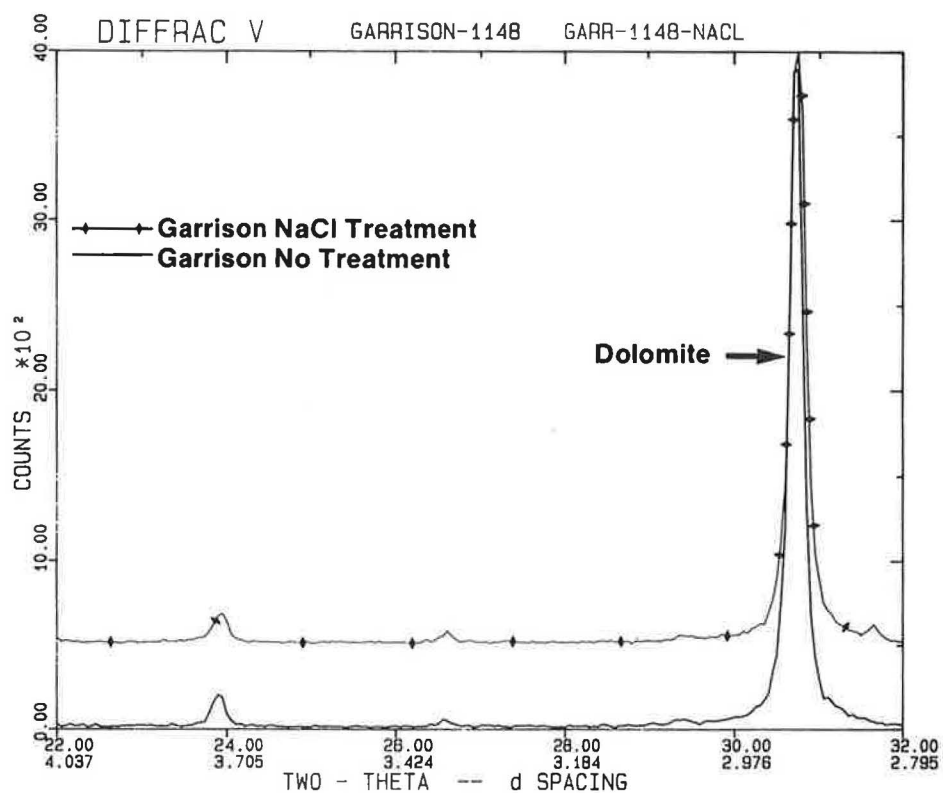


FIGURE 7 Garrison X-ray diffractogram—no treatment and boiling in a sodium chloride solution.

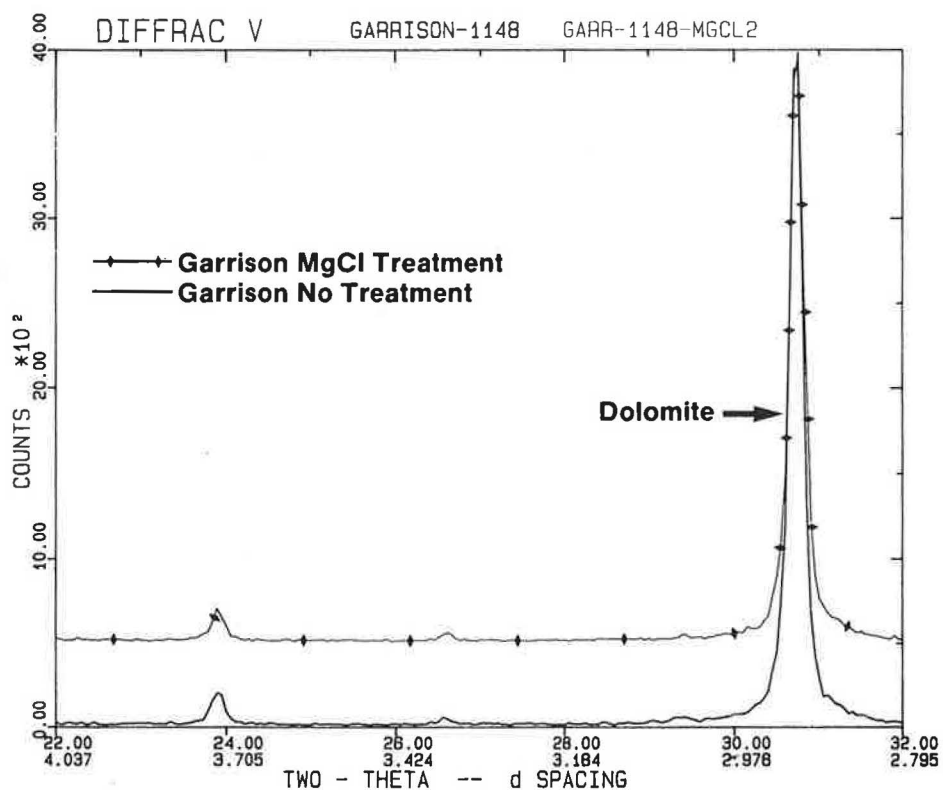


FIGURE 8 Garrison X-ray diffractogram—no treatment and boiling in a magnesium chloride solution.

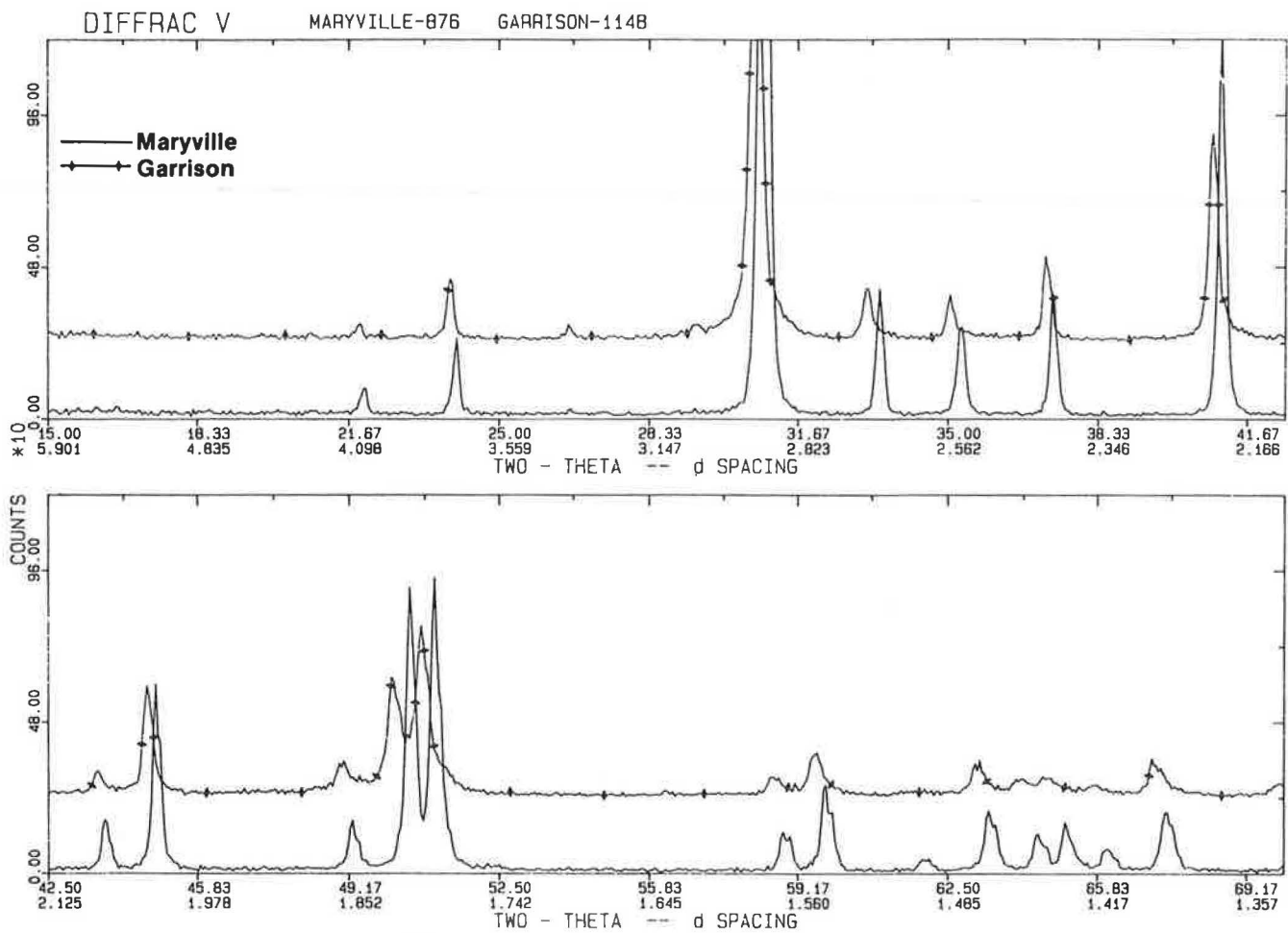


FIGURE 10 X-ray diffraction plots of Maryville and Garrison dolomites.

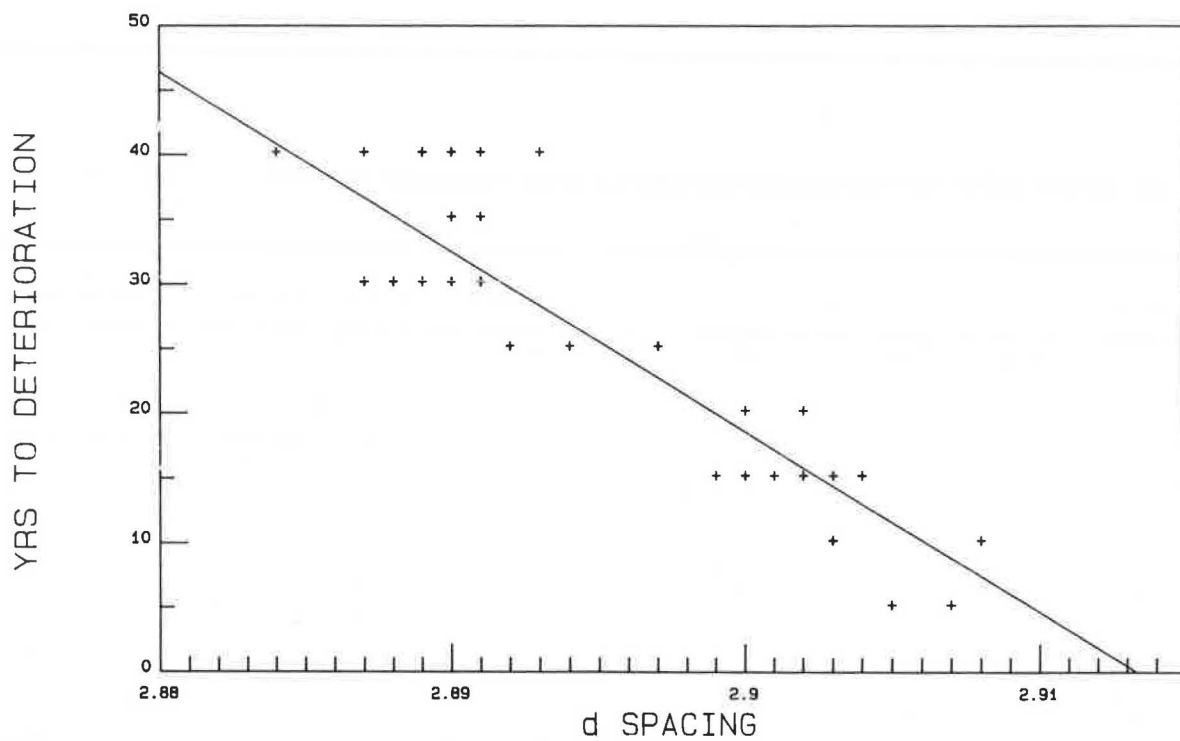


FIGURE 11 Graph of d -spacing of maximum-intensity dolomite peak versus years to visible deterioration of the concrete.

ankerite peak does correlate well with expected service life, and, therefore, may be an excellent indicator of the potential durability of that aggregate in pcc pavement.

An X-ray diffraction analysis was conducted on a sample made by combining 50 percent of the Garrison ferroan dolomite with 50 percent of an Aurora (Silurian Age, very similar to Maryville) non-ferroan dolomite (Figure 12). It did not result in 1 maximum-intensity dolomite peak but yielded 2 peaks of approximately $\frac{1}{2}$ the intensity of the individual samples.

Most researchers attribute the deterioration mechanism of the Kingston, Canada, dolomitic-limestone aggregate to alkali-carbonate reactivity. The dolomite in the Kingston aggregate produces a maximum-intensity dolomite/ankerite peak at a d -spacing of 2.908 angstroms.

It is interesting to note that the Pints Coralville maximum-intensity dolomite/ankerite peak occurs at a d -spacing of 2.895 angstroms, which exactly duplicates the d -spacing determined by Biggs in the 1967 research (5).

The Stanzel aggregate is predominantly a limestone but does have a maximum-intensity dolomite/ankerite peak occurring at 2.907 angstroms. The Stanzel aggregate has a good pore system but has a poor service record. Based on the correlation of performance histories to dolomite peak shifts, carbonates (dolomites and dolomitic limestones), having greater maximum-intensity dolomite/ankerite d -spacings, would be expected to exhibit poorer performance in pcc pavement than those dolomites with smaller d -spacings. This X-ray diffraction study would indicate that iron in carbonate aggregates could result in instability, causing premature deterioration when used in pcc pavements.

CONCLUSIONS

This research on the instability of some carbonate aggregates in pcc pavement supports the following conclusions:

1. Iron substituting for magnesium in the dolomite crystalline structure of coarse aggregate correlates with performance history in Iowa pcc pavement, especially when NaCl deicing salts are used.
2. For carbonate aggregates with good pore systems, a low maximum-intensity X-ray diffraction dolomite d -spacing would indicate a durable aggregate, whereas a high maximum-intensity dolomite/ankerite X-ray diffraction d -spacing would indicate a nondurable aggregate.
3. The determination of the d -spacing of the maximum-intensity dolomite/ankerite peak for dolomite or dolomitic limestone aggregates is a good screening test to predict dolomite-aggregate durability in pcc pavement.

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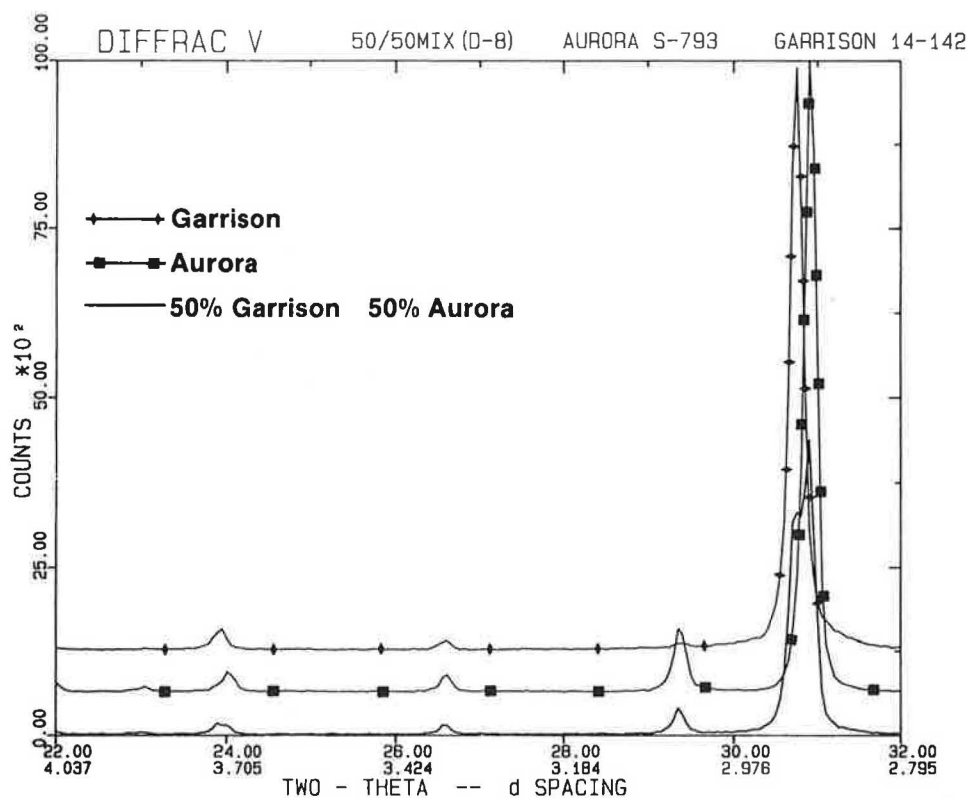


FIGURE 12 X-ray diffraction plots of Garrison and Aurora dolomite and a 50 percent Garrison-50 percent Aurora mixture.

REFERENCES

1. V. J. Marks and W. Dubberke. Durability of Concrete and the Iowa Pore Index Test. In *Transportation Research Record 853*, TRB, National Research Council, Washington, D.C., 1982, pp. 25-30.
2. J. Myers and W. Dubberke. *Iowa Pore Index Test*. Interim Report, Iowa Department of Transportation, Ames, Jan. 1980.
3. W. Dubberke. *Factors Relating to Aggregate Durability in Portland Cement Concrete*. Interim Report for Project HR-2022. Iowa Department of Transportation, Ames, Jan. 1983.
4. J. Lemish. *Behavior of Carbonate Rocks as Concrete Aggregates*. Department of Geology, Iowa State University, Ames, June 1962.
5. D. Biggs. *Compositional and Mechanical Properties of Carbonate Rocks*. Department of Earth Science, Iowa State University, Ames, July 1967.
6. W. Dubberke and V. J. Marks. The Effect of Deicing Salt on Aggregate Durability. In *Transportation Research Record 1031*, TRB, National Research Council, Washington, D.C., 1985, pp. 27-34.
7. R. Reeder. Carbonates: Mineralogy and Chemistry. *Reviews in Mineralogy*, Vol. 11. Mineralogical Society of America. 1983.

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Petrological Studies on Carbonate Aggregate Responsible for Pavement D-Cracking in Southern Manitoba, Canada

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Petrographic evaluation of aggregate in portland cement concrete from Winnipeg International Airport was conducted to determine the characteristic composition, texture, and porosity of nondurable carbonate aggregate associated with D-cracking. Aggregate in the concrete is from the glaciofluvial Birds Hill esker complex northeast of Winnipeg. Carbonate rocks (limestone and dolomite) constitute 75 to 85 percent (by volume) of aggregate in the recovered drill cores, with granite and basalt the only other significant rock types. Polarizing microscope, scanning electron microscope, and X-ray diffraction analyses of the carbonate aggregate resulted in the following conclusions: (a) All major fracturing in the concrete is associated with coarse carbonate aggregate greater than 1/4 in. in diameter. (b) Composition of nondurable carbonate aggregate is one of the following types: pure end member limestone, dolomite, or a chalky white silicified limestone. (c) Texturally, the carbonate rocks are massive, micritic-to-finely crystalline mudstone to packstone. Layering does not occur and clay minerals are noted in trace amounts only. (d) The uniform grain size and shape results in a narrow pore size range in the carbonate rocks mainly as intergranular porosity. (e) The expansive alkali-carbonate rock reaction is not a factor in the concrete deterioration as neither the composition nor the tex-

ture of the carbonate rocks corresponds to the documented characteristic of susceptible rock types. Also, the map-cracking characteristic of the deterioration does not occur on the apron. The few carbonate particles with reaction rims display a good bond between the cement and aggregate.

The current petrological study of carbonate aggregate was part of a wider engineering and geological investigation of D-cracking in portland cement concrete (pcc) in Manitoba (Figure 1). Research has been promoted and financed by Transport Canada following major D-cracking failure of an aircraft parking apron (Apron 1) at Winnipeg International Airport, Winnipeg, Manitoba. Laboratory petrographic analyses were conducted in 1984.

EVALUATION OF COARSE AGGREGATE

Macroscopic Petrography

Transport Canada supplied nine 6-in. (150-mm) diam drill cores recovered from Apron 1 at Winnipeg International Air-