

Evaluation of Carbonate Aggregate Using X-Ray Analysis

WENDELL DUBBERKE AND VERNON J. MARKS

Iowa has more than 13,000 miles of portland cement concrete (PCC) pavement. Some pavements have performed well for over 50 years, while others have been removed or overlaid due to the premature deterioration of joints and cracks. Some of the premature deterioration is classical D-cracking, which is attributed to a critically saturated aggregate pore system (freeze-thaw damage). However, some of the premature deterioration is related to adverse chemical reactivity involving carbonate coarse aggregate. The objective of this paper is to demonstrate the value of a chemical analysis of carbonate aggregate using X-ray equipment to identify good or poor quality. At least 1.5 percent dolomite is necessary in a carbonate aggregate to produce a discernible dolomite peak. The shift of the maximum-intensity X-ray diffraction dolomite d-spacing can be used to predict poor performance of a carbonate aggregate in PCC. A limestone aggregate with a low percentage of strontium (less than 0.013) and phosphorus (less than 0.010) would be expected to give good performance in PCC pavement. Poor performance in PCC pavement is expected from limestone aggregates with higher percentages (above 0.050) of strontium.

Over 13,000 miles of Iowa's 35,000 miles of paved highways are portland cement concrete (PCC). Many of the 22,000 miles of asphalt concrete pavement were originally PCC pavement that has been overlaid. The extent of the maintenance-free life of these PCC pavements is very dependent on the quality of coarse aggregate used. Some PCC pavements have performed well for over 50 years, while others have failed prematurely. The premature failures are predominantly deterioration of joints and cracks (Figure 1). This deterioration is generally referred to as D-cracking. In a recent synthesis (1), D-cracking is defined as "a form of PCC deterioration associated primarily with the use of coarse aggregates in the concrete that disintegrate when they become saturated and are subjected to repetitive cycles of freezing and thawing."

Iowa research in the 1960s identified many crushed stone aggregate sources that would, in a saturated condition, cause rapid deterioration of PCC due to freezing and thawing. Initial testing and identification was based on ASTM C666, Method B. Research beginning in 1978 established a relationship between the freeze-thaw failure of carbonate aggregates and their pore systems (2,3).

Within the last 10 years, poor performance of many miles of PCC pavement has been determined to be related to the use of carbonate aggregates with open, large pore systems not prone to critical saturation and subsequent freeze-thaw disintegration. These aggregates cause adverse chemical reactivity, resulting in pavement deterioration visibly similar to D-cracking. The amount or rate of deterioration is directly related to the amount of deicing salt used on the pavement

(4). This finding suggests that there are at least two types of rapid joint deterioration: the classical D-cracking failure as defined in the recent synthesis (1), and another type that can be related to the trace elements in the carbonate aggregate. The trace elements contribute to chemical reactions that alter and weaken the crystalline structure of the carbonate aggregate and the cement paste.

High-quality aggregates are essential to durable concrete. Iowa is using the Mercury Porosimeter and the Iowa Pore Index Test to identify carbonate aggregates with pore systems that are susceptible to rapid freeze-thaw deterioration. Previous Iowa research (5) has shown that aggregates that exhibit a predominance of pore sizes in the 0.04- to 0.2-micron diameter range are susceptible to critical saturation and subsequent freeze-thaw deterioration. Generally, aggregates that do not contain a predominance of these pore sizes are not prone to freeze-thaw (D-cracking) deterioration. Similar deterioration of some PCC pavements made using coarse aggregates with pore sizes larger than 0.2 micron in diameter prompted the research on premature failure associated with chemical reaction.

OBJECTIVE

The objective of this research was to demonstrate the value of chemical analyses using X-ray equipment to identify good or poor carbonate aggregate quality.

GEOLOGIC IDENTIFICATION OF IOWA CARBONATES

Beginning in the 1940s, Iowa geologists began developing geologic sections for quarries producing crushed carbonates for use in Iowa. The geologic sections describe the beds in all the ledges that are or at one time were approved for use in PCC pavement. These sections show the correlation of all concrete ledges with the geologic column for Iowa. Final acceptance of coarse aggregate for PCC pavement is based on quality testing of the aggregate produced.

Pavement history records, which include the quarry ledges by bed used to produce the coarse aggregate, have been maintained since 1940. Iowa geologists continually inspect pavements and record when visible deterioration of joints due to the aggregate is identified. A service record of years to visible deterioration is thereby developed for all the ledges of stone used in Iowa PCC pavement.

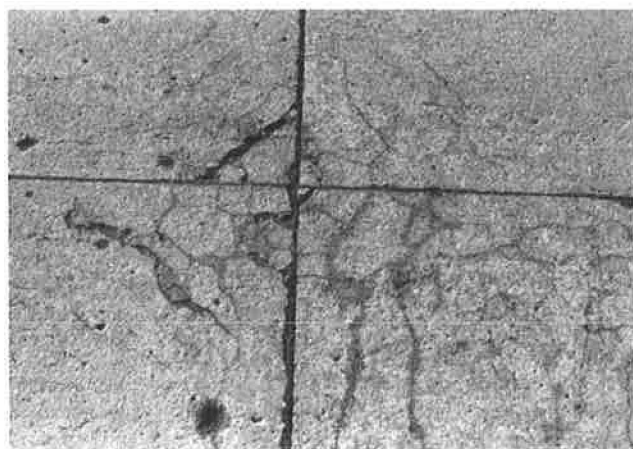


FIGURE 1 Close-up of premature deterioration at an intersection of the transverse and longitudinal joints.

Approximately 75 percent of the coarse aggregate used in Iowa PCC pavement is crushed carbonate. The other 25 percent is river gravel containing 20 to 70 percent carbonate particles. Geologically, the Paleozoic strata of Iowa are part of the Forest City Basin, which extends into Missouri, Kansas, and Nebraska (6). A cross-sectional view of the stratigraphic system is shown in Figure 2. With the exception of a small amount of sandstone and a very small area of gypsum the quarried bedrock is carbonate. The Pennsylvanian System generally yields poor quality stone. The Mississippian, Devonian, and Ordovician systems contain units that yield carbonate aggregates of poor to good quality. The best aggregates are obtained from the Silurian System.

X-RAY EQUIPMENT

The X-ray equipment used for elemental analysis of the carbonate aggregate is located at Iowa State University (ISU) (7). The ISU facilities include two scanning electron microscopes (SEMs), a sequential X-ray spectrometer, and an X-ray diffractometer. Since 1980, a software package providing automated image analysis has been added, thereby expanding the capabilities of the SEMs.

Electron microscopes scan across a specimen using a highly focused beam of electrons. When the beam strikes the surface of the sample, X-rays and secondary electrons are emitted. A positively charged detector attracts the negatively charged electrons and converts them into an electric current. An image of the sample is then displayed on a cathode ray tube. The newly obtained JEOL JSM-840A scanning electron microscope allows for easier operation and for observations with higher resolution of ultramicro surface structures than the JEOL JSM-U3, which was purchased in 1971. Both SEMs are equipped with an energy dispersive X-ray analyzer, which can identify elements present in the sample by the X rays they emit when the electron beam strikes them.

The SRS-200 automated sequential X-ray spectrometer analyzes elements by fluorescence. The spectrometer excites the samples using X rays and, by measuring the X rays emitted from the sample, elemental concentrations can be deter-

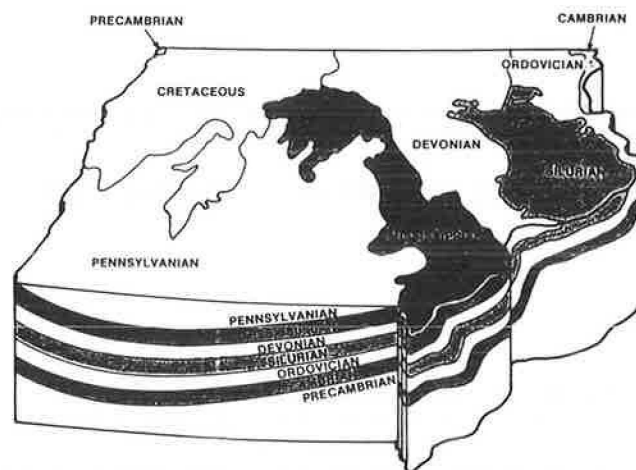


FIGURE 2 A stratigraphic cross-sectional view of Iowa geologic systems.

mined. The SRS-200 is capable of analyzing 10 samples at a time for up to 30 elements.

Using the Siemens D500 X-ray diffractometer, analysis of compounds is performed through the determination of spacings of crystallographic planes by diffraction of X rays. The D500/SRS-200 system uses two microcomputers for its analytical operations. The data can also be transmitted to the ISU mainframe computer for further evaluation.

SAMPLE SIZE AND PREPARATION

The new JEOL JSM-840A SEM will accommodate samples up to 4 in. in diameter and ½-in. thick. For initial evaluation, a broken piece with a relatively flat plane can be used without further preparation. A quick elemental analysis can be conducted to determine if further analysis is warranted. This also gives direction as to what elements should be selected for final analysis. Photographs are taken at relatively low voltage. Good-quality photographs can sometimes be taken without a special coating, but normally a gold, carbon, or silver coating is applied to prevent an electrical charge from occurring and interfering with the photograph. For final chemical analysis, the area of interest must be flat and polished. Rapid sawing with a diamond blade had been used to obtain a smooth flat face. This procedure is no longer used because it heats igneous and other hard particles and causes damage to the surface. Slow sawing with a lapidary diamond blade does not overheat the hard particles.

For X-ray fluorescence (XRF), the material to be analyzed is crushed for 2 min in a Spex Shatterbox (ring grinder) to produce material passing the Number 300 sieve. If a mechanical mixture is being prepared, care should be taken to try to obtain uniform particle size. Silica is a problem when crushed with the softer carbonate material. Grinding a mixture of harder and softer particles produces nonuniform particle sizes that do not allow for precise quantitative analysis. An extended period of grinding alleviates this problem. The sample holder is a 1-in.-diameter plastic cylinder. A plastic ring is used to attach a sheet of 6-micron-thick mylar to the bottom, making a cup. A ¼-in. layer of loose crushed dolomite or limestone

is poured into the cup. The top of the sample is covered with a sheet of 6-micron-thick mylar and fastened with another plastic ring.

The sample for X-ray diffraction (XRD) is crushed to the same size as for XRF. When the determination of a very exact d-spacing or a minor shift in a d-spacing is desired, approximately 10 percent crushed zirconia is mixed with the carbonate sample as a standard reference. Enough powdered sample material is placed in a 1-in.-diameter, 1/4-in.-deep plastic cup to overfill the cup. A strike off is used to remove excess material.

COMPOSITION OF AGGREGATE

There are times when the composition of an aggregate is an important factor in ascertaining its quality. Laboratory testing of the igneous fraction of Iowa river gravels always yields good performance in PCC. In some areas of Iowa, the carbonate fraction (up to 70 percent) of a river gravel produces premature failure in PCC pavement. In the past, it took an experienced petrographer to manually separate the various rock types.

With XRD, there is a much quicker, more accurate, and less labor-intensive method of conducting a petrographic analysis. The material to be analyzed is first crushed to pass the Number 4 sieve. This material is then split to yield a uniform representative sample. This representative sample is then ground in the Spex Shatterbox as previously explained. A software package has been obtained by ISU that will graphically display the percentage of each of the different rock types. Petrographic analysis of river sands is now being conducted. A sample of the computer output is shown in Figure 3.

A program to systematically determine the elemental analysis of Iowa carbonates began five years ago. During that time, percentages of various elements have been determined on over 1,700 samples. Some elements (Na and Cl) have shown no relationship to aggregate performance and are no longer included. The Iowa Department of Transportation (DOT) has recognized the benefits of using X-ray analysis of carbonate aggregate in determining quality of coarse aggregate for use in PCC pavement. Some carbonates from other

states, generally exhibiting poor performance, have been included in the X-ray analysis program. The X-ray analyses of this limited number (57 samples) do not conflict with the findings for Iowa carbonates.

Because the research is being conducted on dolomites, $\text{CaMg}(\text{CO}_3)_2$, and limestones, CaCO_3 , many of the elements are almost entirely contained as one compound. For instance, the calcium is almost entirely combined as CaCO_3 or limestone. Almost all of the magnesium would be in the form of $\text{CaMg}(\text{CO}_3)_2$ or dolomite. All of the X-ray chemical analyses for this research have been by XRF for elements, with an assumption as to the compounds. The percentages of calcium and magnesium provide information to determine the ratio of limestone to dolomite. XRD peak intensities can also provide this ratio information. Current research with XRD verifies the validity of the limestone-dolomite relationship determined using XRF elemental analysis.

Analysis by XRF yields the percentages of elements present in a sample. Prior to X-ray analysis the percentage of strontium found in a sample was usually expressed as strontium oxide. The authors do not believe that these elements are contained in the carbonates as oxides and, therefore, will not express them in that manner. All percentages expressed in this paper will refer to elemental strontium and elemental phosphorus. The conversion factor that may be used to determine how much strontium oxide this would represent is 1.1826. The conversion factor from elemental phosphorous to phosphorous oxide is 2.2913.

Currently the Iowa DOT uses a 16-cycle, water-alcohol freeze-thaw test (FTA) with a specified loss of not more than 6 percent of the total sample weight for acceptance of coarse aggregate for PCC. The percentage loss is directly related to the amount of clay in the carbonate. Most of the elemental aluminum and titanium are contained in clays and, therefore, they correlate with the results of the water-alcohol freeze-thaw test (Figures 4 and 5). Two factors that hinder this correlation are the presence of authigenic feldspar containing aluminum and titanium and the use of different gradations of aggregate in the freeze-thaw test. When the same gradation is used for the freeze-thaw test and the aggregate is from the same quarry (Festina), a high correlation ($r = 0.93$) is obtained (Figure 6). The correlation coefficient of elements (for 86 samples) with each other and with water-alcohol freeze-thaw is given in Table 1. Aluminum ($r = 0.65$) and titanium ($r = 0.62$) show the greatest correlation with the FTA. The elemental analysis of a few carbonates selected to give a range of limestone and dolomite aggregates from good to poor performance is given in Table 2.

The SEM is used to examine limestones, dolomites, and PCC. A deteriorated dolomite aggregate in PCC exhibited a dark rim (Figure 7). An initial assumption was that the rim would be high in iron. A SEM spot analysis showed no iron but a high sulfur, calcium, and silicon content. An investigation of the dark rim is continuing. Speculation is that a chemical reaction has occurred at the boundary of the dolomite particle, which adversely affects the bond.

EVALUATION OF DOLOMITIC AGGREGATE

XRD has become the principal Iowa method of identifying dolomitic aggregate that will result in poor performance in

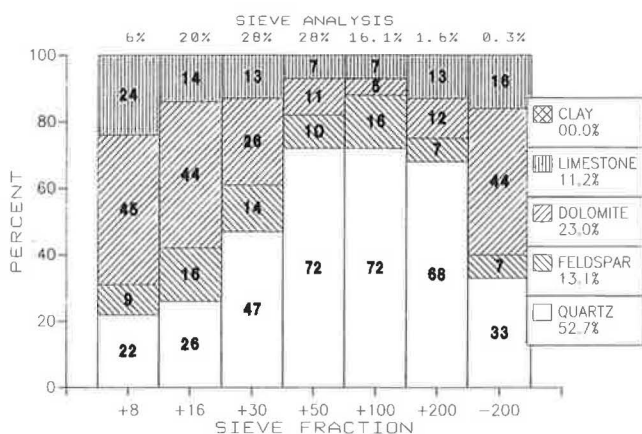


FIGURE 3 XRD petrographic analysis of river sand.

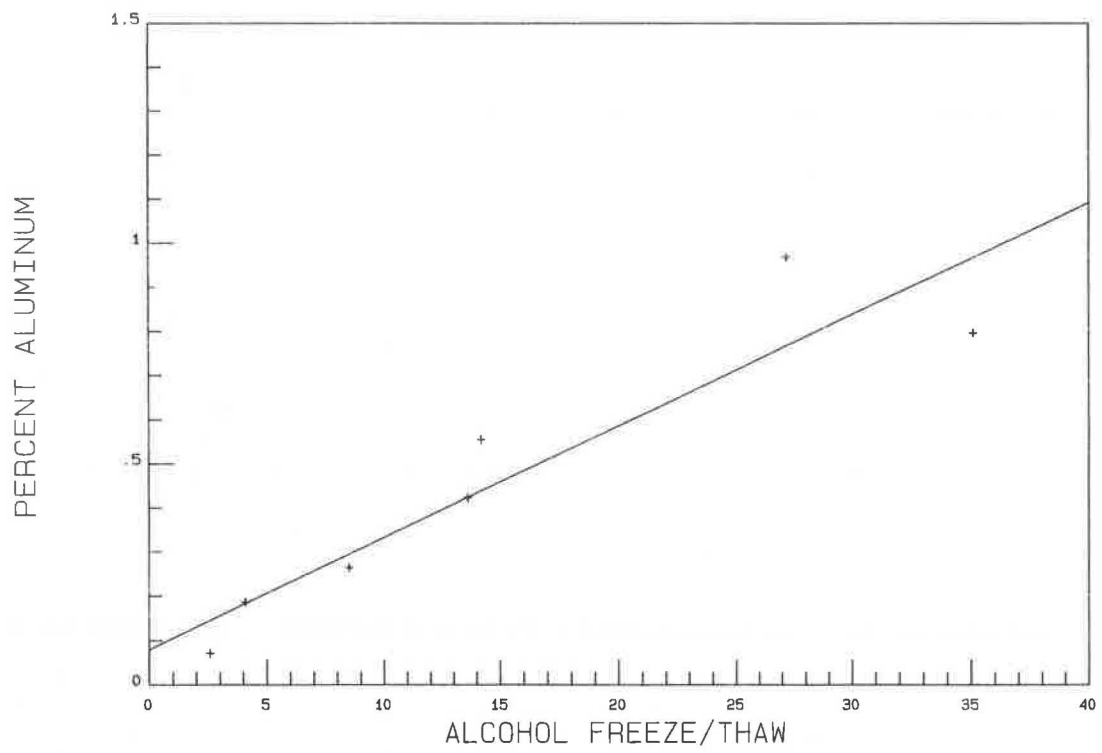


FIGURE 4 Alcohol freeze-thaw versus percent aluminum.

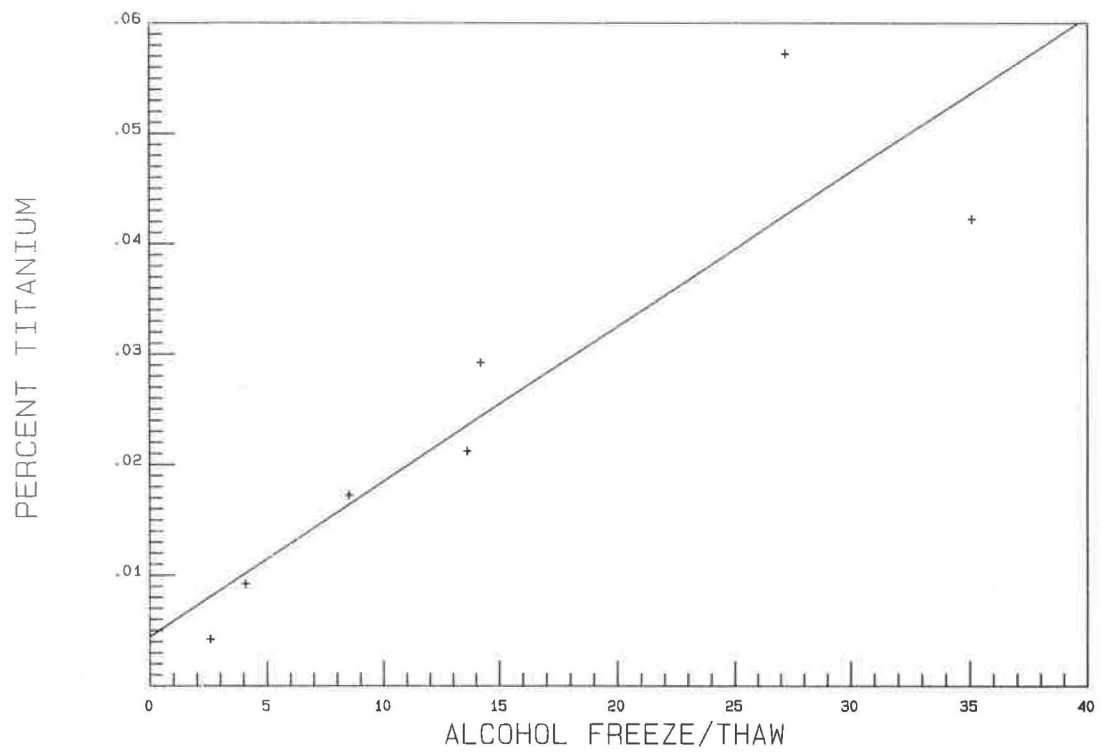


FIGURE 5 Alcohol freeze-thaw versus percent titanium.

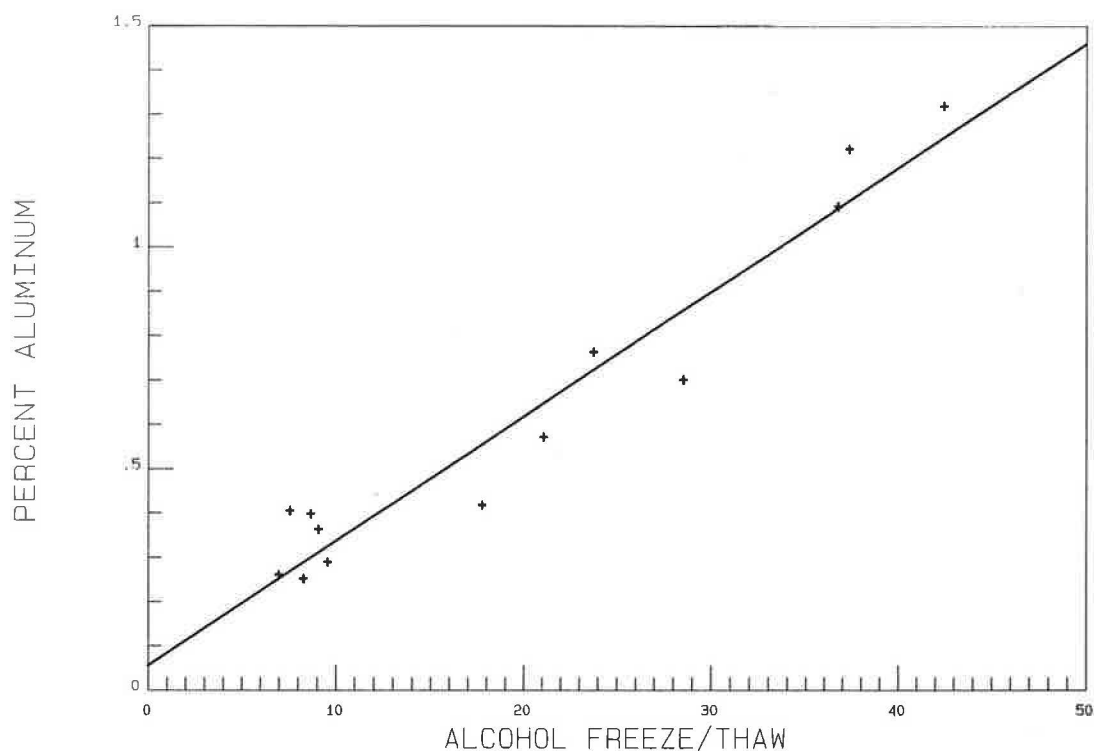


FIGURE 6 Alcohol freeze-thaw versus percent aluminum for the Festina Quarry.

TABLE 1 A SUMMARY OF CORRELATION COEFFICIENTS FOR ELEMENTS IN CARBONATES AND THE WATER-ALCOHOL FREEZE-THAW

	Sr	Mg	Fe	S	Ti	Mn	Si	Ca	K	P	Al
Mg	-0.30	1.00									
Fe	0.27	-0.05	1.00								
S	0.01	0.00	0.09	1.00							
Ti	0.34	-0.12	0.63	0.08	1.00						
Mn	0.10	0.05	0.32	0.04	0.16	1.00					
Si	0.21	-0.19	0.48	0.00	0.55	0.17	1.00				
Ca	0.07	-0.56	-0.41	-0.16	-0.36	-0.16	-0.54	1.00			
K	0.21	-0.11	0.33	-0.00	0.43	0.06	0.52	-0.44	1.00		
P	0.43	-0.24	0.44	0.00	0.58	0.11	0.34	-0.11	0.32	1.00	
Al	0.41	-0.21	0.59	0.03	0.73	0.21	0.80	-0.47	0.68	0.50	1.00
FTA	-0.08	-0.07	0.30	0.23	0.62	-0.10	0.60	-0.10	0.61	0.35	0.65

PCC pavement. In a stone consisting of a mixture of limestone and dolomite, at least 1.5 percent dolomite is needed to yield a discernible dolomite peak. If a discernible dolomite peak can be identified, poor performance in PCC pavement can be predicted by the maximum-intensity X-ray diffraction dolomite d-spacing (XRD d-s) (4). A high maximum-intensity dolomite-ankerite d-spacing (greater than 2.899) would iden-

tify a carbonate with poor performance in PCC pavement (Figure 8).

The pore system of the aggregate significantly affects the rate of adverse chemical reactivity. At this time, the relationship of the pore size effect on chemical reactivity has not been fully determined. This relationship is not intended to show that 1.5 percent poor-quality dolomite can cause rapid

TABLE 2 XRF ELEMENTAL ANALYSES OF A RANGE OF CARBONATES

Quarry	SR	XRD d-S	PERCENTAGES								
			Sr	Mg	Ca	Al	Fe	S	Ti	Si	P
Maryville	40	2.889	0.010	12.66	21.78	0.13	0.16	0.02	0.01	0.44	0.00
Aurora	40	2.887	0.011	11.72	22.51	0.17	0.19	0.02	0.01	1.04	0.00
Pape	30	None	0.011	0.22	38.32	0.28	0.12	0.04	0.01	1.22	0.00
Daley	30	2.887	0.008	12.59	21.36	0.22	0.58	0.07	----	0.63	----
Gil City	30	None	0.016	0.23	38.33	0.30	0.21	0.13	0.01	1.05	0.00
Kendall- ville	25	2.889	0.015	6.41	28.72	0.37	0.55	0.38	0.02	1.69	0.02
Skyline	25	2.891	0.024	3.42	30.84	0.58	0.43	0.19	0.03	3.87	0.03
Weeping Water	25	None	0.041	0.23	39.11	0.08	0.18	0.08	0.00	0.44	0.01
LeGrand	20	2.902	0.014	8.02	27.84	0.12	0.83	0.17	0.01	0.38	0.03
Smith	15	2.901	----	10.89	23.83	0.15	0.49	0.17	0.01	0.62	0.01
Logan	15	2.902	0.054	0.76	35.33	0.53	0.54	0.19	0.03	3.13	0.03
Garrison	15	2.904	0.021	10.67	23.53	0.16	1.06	0.65	0.01	0.71	0.01
Glory Rapid	10	2.903	0.016	9.86	19.40	1.48	1.05	0.43	----	5.47	----
Kingston, ONT	10	2.908	0.038	5.21	24.94	1.98	1.04	0.23	0.11	5.96	0.01
Ullin, IL	10	2.890	0.259	1.15	35.83	0.18	0.17	0.37	0.01	2.34	0.05
VA	?	2.903	0.033	1.34	36.36	0.35	0.39	0.19	0.02	1.34	0.01
Tyrone, KY	?	2.904	0.032	2.76	32.09	0.86	0.50	0.16	0.04	3.20	0.13
Jefferson	5	2.906	0.068	0.46	37.55	0.20	0.29	0.04	0.01	1.66	0.02
Stanzel	5	2.907	0.055	0.43	38.30	0.14	0.47	0.06	0.01	0.79	0.01
Ada, OK	?	2.908	0.017	0.18	38.16	0.22	0.28	0.10	0.01	0.74	0.54
C. Hill, TN	?	None	0.055	0.41	38.64	0.16	0.15	0.14	0.01	0.53	0.05



FIGURE 7 PCC containing a deteriorated dolomite aggregate with a dark rim.

deterioration of PCC pavement. Speculation is that the detrimental element, compound, or characteristic is also present in the limestone fraction of the carbonate particle.

X-ray analyses of over 120 samples have shown very low amounts (less than 0.025 percent) of strontium in dolomite aggregates.

EVALUATION OF LIMESTONE AGGREGATE

X-ray analyses have yielded data that will generally predict good or bad performance of limestone (CaCO_3) aggregate in PCC pavement. A good correlation for the full range has not been identified. There is a very small d-spacing shift of the maximum-intensity limestone (CaCO_3) peak as compared to the large d-spacing shift for dolomites. Zirconia was added to the carbonate sample to improve accuracy in the analysis

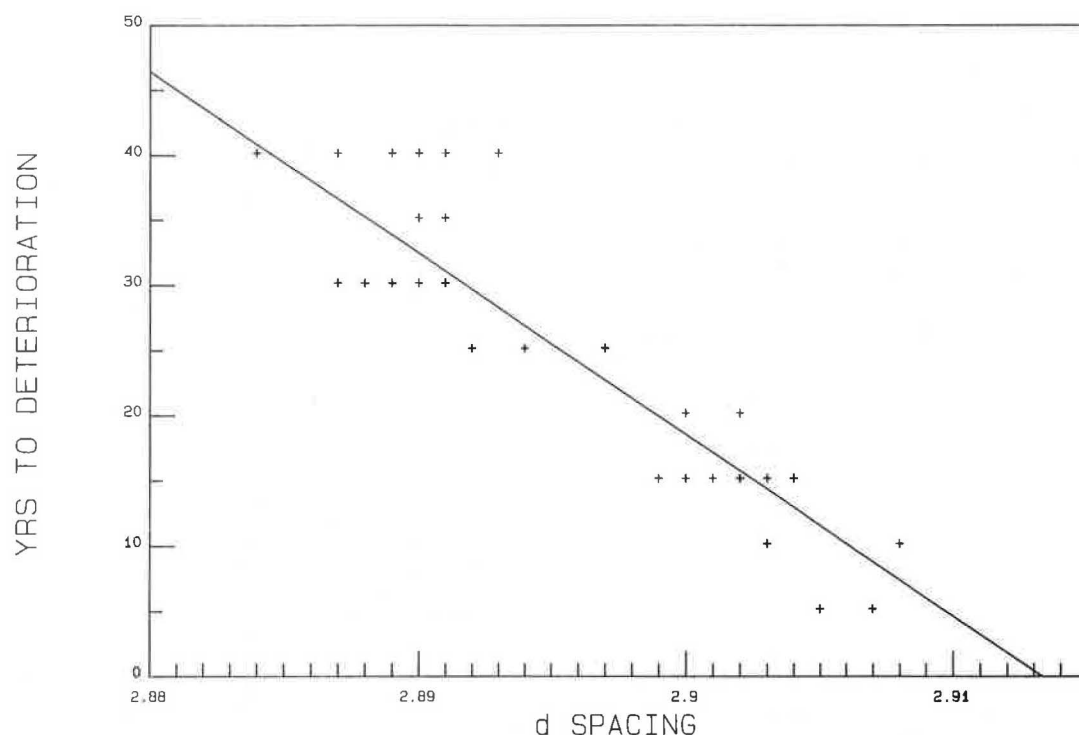


FIGURE 8 Graph of d-spacing of maximum-intensity dolomite peak versus years to visible deterioration of the concrete.

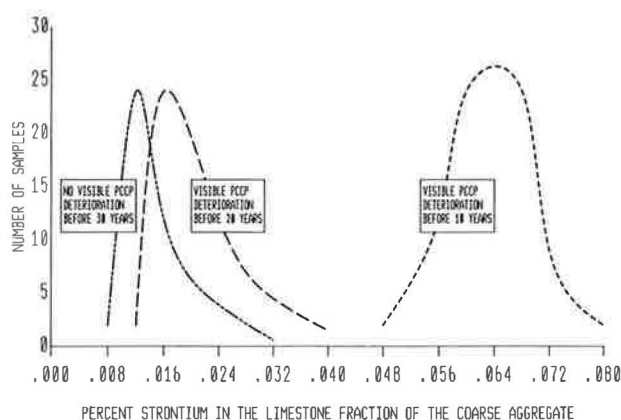


FIGURE 9 Relationship of percent strontium in the carbonate aggregate to service record when used in PCC pavement.

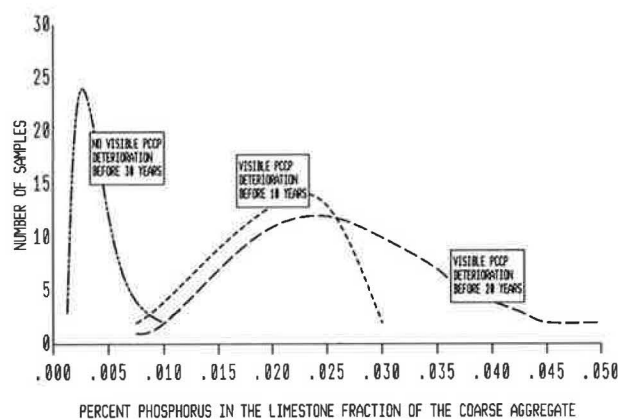


FIGURE 10 Relationship of percent phosphorus in the carbonate aggregate to service record when used in PCC pavement.

of peak shifts. Research to date has not shown a good correlation of this shift with limestone (calcite) performance records.

Strontium, an element not found in significant amounts in dolomite aggregates tested by the Iowa DOT, relates to performance of limestone aggregate in PCC pavement. Phosphorus is another element that exhibits a relationship to the performance of limestone aggregate in PCC pavement. If a limestone aggregate is low in strontium (below 0.013 percent) in the limestone fraction of the carbonate particle (Figure 9) and low in phosphorus (below 0.010 percent) in the limestone fraction (Figure 10), good performance in PCC pavement is expected. Poor performance is expected if the strontium in

the limestone fraction of the aggregate exceeds 0.050 percent. Iowa limestones from the Silurian System (less than 0.013 percent strontium) exhibit the best performance, while Pennsylvanian limestones (generally above 0.040 percent strontium) exhibit the poorest performance. Within the Pennsylvanian System, the Stanzel Quarry has the poorest performance and the highest percent strontium (0.055), while the Weeping Water Quarry has the best performance and the lowest percent strontium (0.041). The service record in years to visible deterioration of PCC pavement shows a correlation coefficient of $r = -0.38$ with strontium (for 367 samples), $r = -0.22$ with phosphorus (for 376 samples), and $r = -0.40$ with strontium plus phosphorus (for 367 samples).

CONCLUSIONS

This research on X-ray analysis of carbonate aggregates supports the following conclusions:

1. X-ray analysis of Iowa carbonate aggregates is an effective method of predicting their performance in PCC pavement.
2. For Iowa carbonate aggregates with more than 1.5 percent dolomite, the maximum-intensity X-ray diffraction dolomite d-spacing can be used to predict poor performance in PCC concrete.
3. Iowa limestone aggregates with large, open pore systems, strontium below 0.013 percent, and phosphorus below 0.010 percent exhibit good performance in PCC pavement.
4. Iowa limestone aggregates with strontium above 0.050 percent will exhibit poor performance when used in PCC pavement.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Turgut Demirel, Jerry Amenson, Scott Schlorholtz, and Glen Oren of Iowa State University for their assistance in X-ray analysis of aggregates and in the interpretation of the data. The use of ISU equipment made the research possible. Jim Myers,

Scott Graves, and Kathy Davis were very helpful in preparation of the report.

REFERENCES

1. D. Schwartz. *NCHRP Synthesis of Highway Practice 134: D-Cracking of Concrete Pavements*. TRB, National Research Council, Washington, D.C., October 1987.
2. J. Myers and W. Dubberke. *Iowa Pore Index Text*. Interim Report. Iowa Department of Transportation, Ames, Iowa, Jan. 1980.
3. W. Dubberke. Factors Relating to Aggregate Durability in Portland Cement Concrete. Interim Report HR-2022. Iowa Department of Transportation, Ames, Iowa, Jan. 1983.
4. W. Dubberke and V. Marks. The Relationship of Ferroan Dolomite Aggregate to Rapid Concrete Deterioration. *Transportation Research Record 1110*. TRB, National Research Council, Washington, D.C., 1987, pp. 1–10.
5. V. Marks and W. Dubberke. Durability of Concrete and the Iowa Pore Index Text. *Transportation Research Record 853*. TRB, National Research Council, Washington, D.C., 1982, pp. 25–30.
6. W. Anderson. *Geology of Iowa—Over Two Billion Years of Change*. The Iowa State University Press, Ames, Iowa, 1983.
7. J. Amenson and T. Demirel. *Materials Analysis and Research Laboratory: Capabilities*, Engineering Research Institute. Iowa State University, Ames, Iowa, September 1985.

The contents of this paper reflect the views of the authors and do not necessarily reflect the official views of the Iowa Department of Transportation. The paper does not constitute a standard, specification, or regulation.