Relationship of Physical Properties of Some Iowa Carbonate Aggregates to Durability of Concrete

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A study of carbonate rocks used for concrete aggregate is being made for the Iowa State Highway Commission to determine the factors in the aggregate causing distress in concrete and to establish criteria for recognizing potentially poor aggregates.

Devonian rocks from the Cedar Valley formation which is divided into the Solon, Rapid, and Coralville members, were sampled on a bed-by-bed basis in four quarries, one of which is the condemned Glory quarry. The Glory aggregate was produced from the Rapid member, which serves as a standard of comparison.

The aggregates were investigated by petrographic examination to determine insoluble residue, clay minerals present, porosity, pore size, and pore size distribution data. A petrographic study was also made of distressed concrete containing Glory aggregate. The results were correlated with freeze-thaw data and service records.

A petrographic study of the rocks from the Cedar Valley formation indicates that the Rapid member has a distinctive lithology which is easily recognized. Rocks with such a lithology have poor freeze-thaw resistance. The insoluble residue content of such rocks is considered an indication of durability. Rocks from this formation with high residue show poor freeze-thaw resistance and rocks with low residue show good freeze-thaw resistance and make serviceable concrete. The Rapid member is characteristically high in residue. Porosity data are on the whole variable and inconclusive but some correlation to freeze-thaw data is evident in rocks of uniform lithology. The only clay mineral present is illite which is restricted almost entirely to beds of Rapid lithology. Rocks from the concrete aggregate ledges are almost devoid of clay. Pore size distribution data and effective porosity are related to the lithology of the rocks and to freeze-thaw results. Pore size distribution data for the Rapid are distinctive and show that most of the pores are uniformly small and average 0.1 micron in radius. The Rapid aggregate has higher capillary pressures and more pore area available for reaction. Petrographic investigation of distressed concrete made from Glory aggregate showed the presence of reaction rims around pieces of rock of Rapid lithology.

It is concluded that impure carbonate rocks from the Cedar Valley formation characterized by high residue and clay content are deleterious. Pure rock types of high carbonate content, low residue, and little if any clay have a good service record. Because of higher capillary pressure, the Rapid aggregate would retain fluid more easily and provide more pore surface area for chemical activity. A study of reaction rims in Rapid aggregate in distressed concrete indicates that a reaction has occurred with the cement. The reaction probably causes a gradual weakening of the concrete which conditions it to later failure by freezing or external stresses.

● THIS PAPER is a progress report on an investigation of carbonate rocks as aggregate sponsored by the Iowa Highway Research Board with funds from the Iowa State Highway Commission. The objective of the project has been to delineate the factors in carbonate rocks causing distress in concrete and if possible to set up criteria for recognizing potentially poor aggregate.

An earlier study of some Mississippian carbonate aggregate was completed in 1954 by C. J. Roy and L. A. Thomas (15). The present project was begun in 1955 to continue research on the older systems of rocks used as aggregates.

Although rocks from the Mississippian, Devonian, Silurian, and Ordovician systems have been sampled as part of the project, only rocks from four quarries producing the Devonian Cedar Valley formation will be considered in this report. The quarries are the Glory, Newton, Pint, and Burton Avenue located in eastern Iowa (Fig. 1). Emphasis was placed on the Cedar Valley formation because this formation contains the Glory quarry which was condemned because of its poor service record. Each quarry was sampled on a bed-by-bed basis representing the lithologic variations present. Freeze-thaw tests were made on the samples whenever possible to provide a basis for comparison with the properties of the rock.

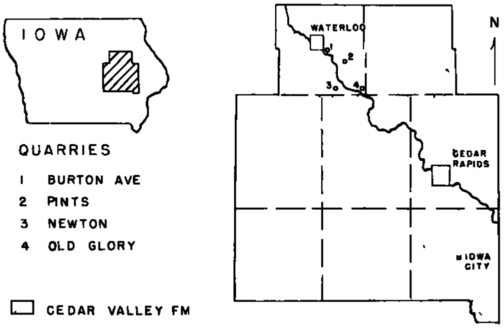

Figure 1. Index map showing distribution of the Cedar Valley formation and the location of the quarries.

The investigation is based on the premise that aggregate may create or contribute to stresses which cause concrete to fail. These stresses can be of physical nature, as caused by frost action, or result from chemical activity, such as the alkali-aggregate reaction. The properties of the aggregates discussed in this paper are the insoluble residue, type of clay mineral present, porosity, pore size and pore size distribution. The chemical properties of the aggregate which include the Ca and Mg content and determination of potentially deleterious constituents such as silica, sulphate, and clay content, are presented in the report by Bisque and Lemish (2). The information obtained has been correlated with (a) the freeze-thaw tests which are part of the present aggregate acceptance tests,[1] and (b) service records of concrete highways.

A study was also made of cores and pieces of distressed concrete taken from highways containing aggregate from the Glory quarry. The results of the petrographic study of the deteriorated concrete is presented here and the chemical investigation is discussed in the report of Bisque and Lemish (2).

Research on the behavior of other types of aggregates has been carried out by many investigators (10, 11). The investigation of carbonate aggregates, however, has not been carried on to the same degree. One of the first investigations of carbonate aggregates was made 30 years ago by Laughlin (4) and subsequent studies have been made by Sweet (17), Mather et al.(6), Mather (8), and others. In the attempt to study the suitability of carbonate rocks one of the biggest problems has been the lack of detailed knowledge concerning their petrography and properties. This is primarily due to the complex character of the carbonate rocks and the lack of suitable methods and techniques to provide adequate information. As a result of the present work, several new techniques and approaches to the study of carbonate rocks have been developed.

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[1] The present acceptance tests and standards for coarse concrete aggregate are described in the "Standard Specifications" Series 1956, Iowa State Highway Commission, Section 4107. Abrasion, soundness, former service, and amount of objectionable materials present are the main considerations in the specifications. The soundness tests consist of a water-alcohol freeze-thaw test as described in Section 4101-2C, of the "Standard Specifications." The freeze-thaw values, reported in the Appendix and used for the purpose of correlation with the various properties of the carbonate rocks, represent the percentages of material passing a No. 8 sieve after 16 cycles of freezing and thawing in a water-alcohol solution containing 0.5 percent alcohol (by weight). A maximum of 6 percent material loss is allowed for concrete aggregate.

GEOLOGIC SETTING

The rocks discussed in this report are part of the Cedar Valley formation of Devonian age and extend from Muscatine to Mason City in a NW-SE trending zone parallel to the Cedar River (Fig. 1). The Cedar Valley formation consists almost entirely of carbonate rocks varying from limestone to calcitic dolomite in composition. The detailed carbonate lithology of the group is highly varied both vertically and horizontally, and ranges from pure carbonate to highly argillaceous or cherty character.

The formation is divided into three members, the Solon, Rapid, and Coralville. The Solon member is a massive, fine-grained, light gray to buff limestone with characteristic zones of black fossil fragments. This is overlain by the Rapid member which consists mainly of a gray, argillaceous calcitic dolomite with abundant chert nodules. The Coralville is generally a buff-colored rock and varies in composition both spatially and vertically from calcitic dolomite to beds of very dense ultra-fine-grained (lithographic) limestone. The total thickness of the Cedar Valley is between 80 and 100 ft.

Figure 2 shows the stratigraphic range of rocks exposed in the various quarries in relation to a standard column for the Cedar Valley as accepted at present. It also shows which portion of the stratigraphic interval is or was used for concrete-aggregate (hereafter called the concrete aggregate ledge).

The Solon member yields acceptable concrete aggregate at the Burton Avenue quarry. The Coralville is acceptable at Burton Avenue, but not enough of it is present to be economical. The Coralville produces concrete aggregate at the Pint and Newton quarries and a small portion of the Coralville present at the Glory quarry will also pass acceptance tests. According to present acceptance tests, the Coralville is probably the best source of concrete aggregate in the Cedar Valley formation.

The Rapid member is found in all the quarries and generally does not pass present acceptance tests for concrete aggregate. Most of the face exposed in the Glory quarry is Rapid and it was used extensively as concrete aggregate throughout eastern Iowa but is unacceptable by present standards. The Rapid in these quarries is generally an argillaceous and cherty dolomite with well-defined bedding.

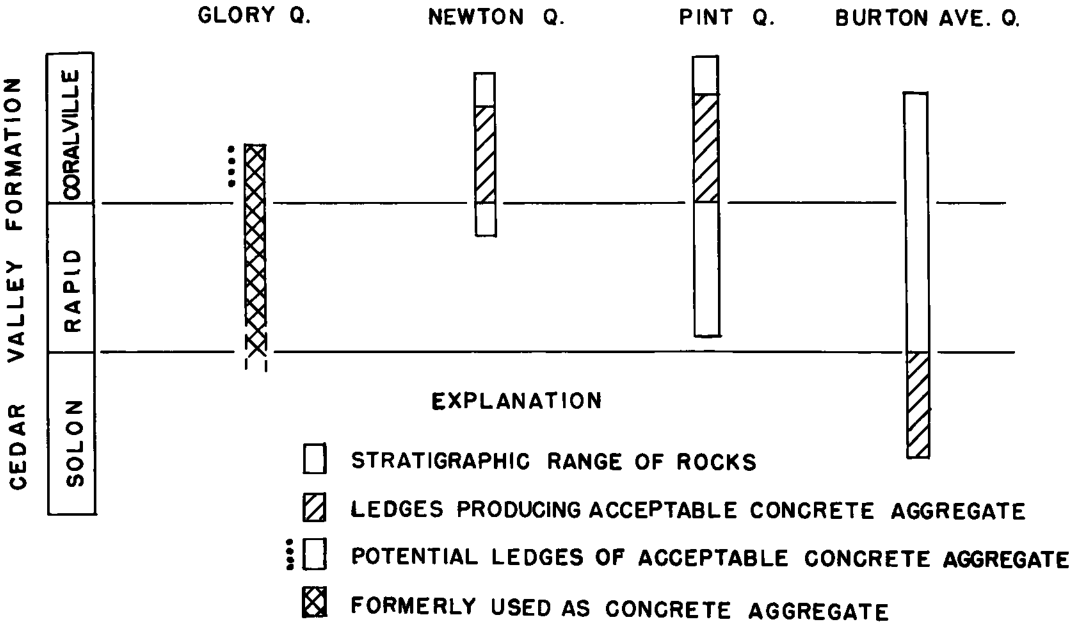

Figure 2. Stratigraphic range of the rocks exposed in the quarries and the position of the concrete aggregate ledges.

TABLE 1

CARBONATE ROCK PROPERTIES, CEDAR VALLEY FORMATION, GLORY QUARRY

Stratigraphic Unit	Sample No.	Lithology	Unit Thickness (ft)	Insoluble Residue (%)	Average Residue (%)	Clay Mineral Present	Powder Density	Bulk Density	Total Porosity (%)	Effective Porosity (%)	Freeze-Thaw (% loss)	Miscellaneous
Coralville	24	Lithographic limestone	1.5	2.0	-	-	2.70	2.63	2.5	1.2	6.9	
	23	Shale, calcareous	0.3	50.0		-	2.70	2.19	19.0	-	-	
	22	Lithographic limestone	2.1	1.0		-	2.69	2.63	2.2	0.3	1.8	
	21	Lithographic limestone	0.7	8.0	8	-	2.70	2.64	2.2	0.9	10.0	
	20	Lithographic limestone	1.5	2.0		-	2.70	2.66	1.5	0.3	5.4	
	19	Dolomitic limestone	1.0	12.0		illite	2.80	2.66	5.0	1.1	20.0	Weathered
Rapid	18	Shaly dolomite	0.4	50.0		illite	2.76	2.41	12.8	-	-	
	17	Calcitic dolomite	4.3	22.0		illite	2.80	2.20	21.4	-	95.0	Badly weathered
	16	Calcitic dolomite	4.3	16.0		illite	2.80	2.41	13.9	13.0	68.0	Badly weathered
	15	Dolomitic limestone	0.5	6.0		illite	2.73	2.68	1.8	0.1	-	Chert present
	14	Dolomite	2.4	16.0		illite	2.79	2.45	12.2	10.9	27.0	
	13	Calcitic dolomite	7.0	21.0		illite	2.80	2.40	14.2	11.5	30.0	
	12	Calcitic dolomite	7.0	22.0		illite	2.78	2.45	11.7	-	-	
	11	Calcitic dolomite	7.0	12.0	18	illite	2.79	2.50	10.4	-	42.0	
	10	Calcitic dolomite	1.5	10.0		-	2.76	2.55	7.6	5.8	25.0	
	9	Calcitic dolomite	2.6	15.0		illite	2.80	2.53	9.6	6.4	42.0	
	8	Calcitic dolomite	6.5	39.0		illite	2.68	2.55	4.8	4.6	29.0	
	7	Calcitic dolomite	6.5	12.0		illite	2.77	2.56	7.6	2.8	32.0	
	6	Calcitic dolomite	6.5	19.0		illite	2.76	2.54	8.0	4.2	33.0	
	5	Calcitic dolomite	3.7	15.0		illite	2.76	2.56	7.3	3.2	36.0	
	4	Calcitic dolomite	3.7	10.0		illite	2.68	2.54	5.2	3.4	42.0	
	3	Calcitic dolomite	1.7	22.0		illite	2.70	2.56	5.2	4.2	30.0	
	2	Calcitic dolomite	1.0	49.0		-	2.69	2.48	8.1	4.8	27.0	
	1	Calcitic dolomite	2.6	7.0		-	2.77	2.54	8.3	5.6	11.0	

TABLE 2

CARBONATE ROCK PROPERTIES, CEDAR VALLEY FORMATION, NEWTON QUARRY

Stratigraphic Unit	Sample No.	Lithology	Unit Thickness (ft)	Insoluble Residue (%)	Average Residue (%)	Clay Mineral Present	Powder Density	Bulk Density	Total Porosity (%)	Effective Porosity (%)	Freeze-Thaw (% loss)	Miscellaneous
Coralville	20	Lithographic limestone	2.5	1.0		none	2.67	2.57	3.7	-	19.0	
	19	Dolomite	2.8	14.0		illite	2.75	2.69	2.2	0.9	4.7	
	18	Dolomitic limestone	0.9	6.0		none	2.69	2.55	5.2	3.0	49.0	
	17	Dolomitic limestone	0.4	2.0		none	2.68	2.65	1.1	-	11.0	
	16	Lithographic dolomite	1.5	10.0	7	none	2.79	2.56	8.2	5.0	38.0	
	15	Calcareous dolomite	1.0	2.0		none	2.78	2.59	6.8	4.4	5.5	
	14	Calcareous dolomite	0.2	14.0		none	2.78	-	-	-	-	
	13	Dolomite	1.8	6.0		illite	2.79	2.47	11.5		7.5	
Concrete Aggregate Ledge	12	Calcareous dolomite	1.4	3.0		none	2.79	2.56	8.3		1.6	
	11	Calcareous dolomite	7.2	5.0		none	2.76	2.44	11.6	10.2	3.2	
	10	Calcareous dolomite	7.2	2.0		none	2.73	2.56	6.2	-	1.0	
	9	Calcareous dolomite	7.2	2.0		none	2.79	2.49	10.6	10.5	0.9	
	8	Calcareous dolomite	1.0	4.0		none	2.72	2.42	11.1	11.0	1.6	
	7	Dolomitic limestone	0.4	5.0	5	none	2.69	2.49	7.4	-	-	
	6	Dolomitic limestone	5.3	3.0		none	2.73	2.58	5.5	5.4	1.9	
	5	Dolomitic limestone	5.3	3.0		none	2.71	2.56	5.5	5.3	1.5	
	4	Calcareous dolomite	4.5	2.0		none	2.76	2.63	4.6	4.1	2.8	
	3	Calcareous dolomite	4.5	4.0		none	2.75	2.49	9.5	-	1.2	
	2	Calcareous dolomite	1.5	13.0		illite	2.80	2.58	7.9	1.5	31.0	
Rapid	1	Calcareous dolomite	4.4	10.0	10	none	2.76	2.59	6.2	4.3	16.0	

TABLE 3

CARBONATE ROCK PROPERTIES, CEDAR VALLEY FORMATION, PINT QUARRY

Stratigraphic Unit	Sample No.	Lithology	Unit Thickness (ft)	Insoluble Residue (%)	Average Residue (%)	Clay Mineral Present	Powder Density	Bulk Density	Total Porosity (%)	Effective Porosity (%)	Freeze-Thaw (% loss)	Miscellaneous
Coralville Concrete Aggregate Ledge	15	Calcitic dolomite	1.3	1.7		none	2.86	2.58	9.8	8.4	1.7	
	14	Calcitic dolomite	3.5	1.6		trace—illite	2.88	2.57	10.8	-	3.6	
	13	Calcitic dolomite	1.2	1.7		trace—illite	2.85	2.56	10.2	8.3	1.0	
	12	Dolomitic limestone	2.6	3.4		none	2.86	2.49	13.0	-	1.9	
	11	Limestone	1.7	2.4	2.3	none	2.83	2.59	8.5	3.8	2.3	
	10	Calcitic dolomite	3.8	2.3		none	2.84	2.56	9.8	6.1	1.7	
	9	Calcitic dolomite	3.2	2.7		none	2.85	2.54	10.9	9.1	1.5	
	8	Lithographic limestone	1.5	1.9		trace—illite	2.78	2.65	4.7	-	3.7	
Rapid	7	Shaly limestone	1.0	9.0		trace—illite	2.75	2.58	6.2	-	-	
	6	Lithographic limestone	1.0	0.8		none	2.78	2.68	3.6	-	2.3	
	5	Calcareous dolomite	5.0	18.9		illite	2.78	2.22	20.1	-	-	Extremely weathered. Very soft rock. Freeze-thaw losses are excessive
	4	Calcareous dolomite	2.6	16.7	16.6	illite	2.87	2.26	21.2	-		
	3	Calcareous dolomite	2.6	22.5		illite	2.81	2.31	17.8	-		
	2	Calcareous dolomite	3.5	17.5		illite	2.80	2.29	18.2	-		
	1	Calcareous dolomite	7.9	15.8		illite	2.87	2.14	25.4	21.6	58.0	

TABLE 4

CARBONATE ROCK PROPERTIES, CEDAR VALLEY FORMATION, BURTON AVENUE QUARRY

Stratigraphic Unit	Sample No.	Lithology	Unit Thickness (ft)	Insoluble Residue (%)	Average Residue (%)	Clay Mineral Present	Powder Density	Bulk Density	Total Porosity (%)	Effective Porosity (%)	Freeze-Thaw (% loss)	Miscellaneous
Coralville	28	Calcitic dolomite	5.0	8.8	8.6	illite	2.86	2.46	14.0	-	-	Weathered
	27	Limestone	2.5	1.6		trace—illite	2.75	2.55	7.3	1.6	48	
	26	Dolomitic limestone	0.5	27.5		illite	2.86	2.40	16.1		48	
	25	Limestone	2.5	0.7		none	2.78	2.57	7.5	1.7	48	
	24	Calcitic dolomite	2.0	11.2		illite	2.78	2.44	12.2	10.4	48	
Rapid	23	Calcitic dolomite	4.0	12.7	27.0	illite	2.85	2.44	14.4			
	22	Calcitic dolomite	6.5	47.6		illite	2.81	2.52	10.3			
	21	Calcitic dolomite	3.0	17.0		none	2.84	2.24	21.2			
	20	Calcitic dolomite	4.5	20.4		illite	2.82	2.41	14.6			
	19	Calcitic dolomite	4.5	35.0		illite	2.83	2.43	14.1			
	18	Calcitic dolomite	2.5	33.0		illite	2.83	2.43	14.1			
	17	Dolomitic limestone	0.5	34.0		illite	2.81	2.42	13.9		Avg 16-45	Cherty
	16	Calcitic dolomite	5.0	23.0		illite	2.79	2.55	8.6			
	15	Calcitic limestone	5.0	23.0		illite	2.88	2.57	10.8			
	14	Calcitic dolomite	7.0	24.0		illite	2.87	2.52	12.2			
	13	Limestone	7.0	16.0		illite	2.80	2.64	5.7			
Solon Concrete Aggregate Ledge	12	Limestone	10.0	5.2	6.5	none	2.77	2.63	5.1	1.1	Avg 0.8-3.0	
	11	Limestone	10.0	7.0		none	2.77	2.63	5.1			
	10	Limestone	10.0	4.0		none	2.80	2.60	7.1	1.3		
	9	Limestone	10.0	2.8		none	2.77	2.51	9.4			
	8	Limestone	8.0	4.3		none	2.81	2.66	5.4			
	7	Limestone	8.0	2.9		none	2.79	2.61	6.5	1.2		
	6	Limestone	8.0	12.8		none	2.79	2.52	9.7			
	5	Limestone	8.0	2.9		none	2.78	2.62	5.8			
	4	Limestone	2.3	4.5		none	2.77	2.59	6.5			
	3	Limestone	5.0	5.5		trace—illite	2.80	2.63	6.1	1.4		
	2	Dolomitic limestone	5.0	8.0		trace—illite	2.82	2.60	7.8	-		
	1	Dolomitic limestone	6.0	14.4		illite	2.81	2.54	9.7	1.9		

PHYSICAL PROPERTIES

Petrographic Description

The petrography of the rocks exposed in the four quarries under consideration was studied in thin section and megascopically. The following features were studied: texture, grain size, calcite and dolomite present, accessory minerals, and structure evident. A summary of these data is presented. For a more detailed review of the petrography, reference is made to the unpublished thesis of F. E. Rush (16). The three members of the Cedar Valley formation—the Solon, Rapid, and Coralville—have definitive lithologic characteristics.

The Rapid member is present in all four quarries, and where fresh is characterized by its gray color and fine-grained texture. Shaly seams or partings separate the beds into units ranging from 3 in. to 3 ft thick. Within these units bedding is generally well-defined due to laminations of black pyrite-rich streaks and films. The unit has an argillaceous appearance and nodules or bands of chert are common. In thin section the rock has a characteristic mosaic texture consisting of euhedral dolomite rhombs averaging 0.01 to 0.03 mm in diameter occurring in a finer-grained (0.001 mm) calcite paste or a recrystallized matrix averaging 0.01 mm. Chert and chalcedonic (fibrous) silica appear to preferentially replace calcite-rich areas such as fossil fragments. The dolomite generally has a dirty appearance caused by numerous tiny inclusions. Where the Rapid is intensely weathered, as at the Pint quarry, the over-all mosaic textural appearance is the same but some of the finer-grained matrix is missing. Larger pores are present and all the pyrite is converted to limonite.

The Solon is present at the Burton Avenue quarry where it forms the concrete aggregate ledge. Here it is a massive-bedded, buff-gray rock with few fossils. It is characterized by its dense appearance and its fine- to medium-grained, crystalline texture. A few calcite and chert nodules as well as sparsely distributed, darker gray fossil fragments are present. Thin sections of the ledge indicate that the rock is characteristically a crystalline limestone with grains from 0.03 to 0.5 mm in diameter. Some dolomite rhombs are present. Some pyrite and detrital quartz are present, and fossil fragments and oolites are sparsely distributed.

The character of the Coralville member varies from quarry to quarry. At the Glory and Burton Avenue quarries it contains numerous lithographic beds and is characteristically buff to tan in color. At the Newton quarry the lower portion of the working face forms the concrete aggregate ledge and it is a gray to buff, fine-grained, massive-bedded calcitic dolomite. The upper portion is highly variable, containing lithographic beds alternating with coral-rich beds and others of Rapid lithology. At the Pint quarry the lower portion of the Coralville forms the concrete aggregate ledge, and occurs as a tan to brown limestone and calcitic dolomite, containing fine- to medium-grained units of variable thickness. The Coralville in thin section shows the same variations. The lithographic beds are made up of a dense calcite paste with individual grains averaging less than 0.001 mm in diameter. Some oolites, sparse fossil fragments and occasional grains of pyrite are present. The thin sections indicate the concrete aggregate ledge at both the Newton and Pint quarries is composed essentially of rocks with fewer inclusions than the Rapid member. The limestone sections are generally very fine-grained but the dolomitic zones are coarser and consist of grains which average 0.06 to 0.08 mm in diameter.

Insoluble Residue

Insoluble residue content was determined for all the beds sampled by dissolving 100 gm of chip-size samples in a 3N hydrochloric acid solution, filtering, drying, and weighing. A wet sieve analysis was used to determine the coarse and fine fractions, both of which were studied mecroscopically. Pyrite is present in nearly every residue and as a rule silica in some form constitutes more than 95 percent of its composition. In all the samples it was found that the silt-clay size fraction makes up the major part of the residue.

The results for all the quarries studied are presented in Tables 1, 2, 3, and 4. High residue contents ranging from 17 percent to 27 percent are characteristic of the Rapid member in all the quarries. In sharp contrast to this are the low residue values averaging from 2.3 percent to 6.5 percent for those parts of the Solon and Coralville members forming the concrete aggregate ledges.

A correlation exists between the residue content and the freeze-thaw data for these rocks. Rocks with low residue have consistently low freeze-thaw values. It is also noted that concrete made from the Glory aggregate consisting almost entirely of the high residue Rapid member has a very poor service record.

Clay Minerals Present

An investigation was made of the clay minerals present in the carbonate rocks. An effective method of separating the clays from the limestone was developed (1, 16). Previous methods of analyzing clays from insoluble residues proved unsatisfactory because of the damage to the clays by acid treatment. In the technique developed for this project, the clays were separated as follows: 50 grams of powdered rock passing a No. 100 sieve was dispersed in water with a suitable wetting agent and transferred to a one liter graduate cylinder. After settling for 7 hours, a 60 ml sample is pipetted out and a coated slide is prepared for X-ray analysis. The presence of as little as 0.1 percent clay in a powdered carbonate rock sample has been separated by this technique, which avoids a harsh acid treatment. A quantitative estimate of the clay content can be made from the Al_2O_3 reported from chemical analysis (2).

The clay mineral data are presented in Tables 1 through 4. Without exception, the only type of clay mineral found in the carbonate rocks present in the four quarries was illite. Nearly every bed in the Rapid member contains illite which correlated very well with the argillaceous appearance so characteristic of this unit. In strong contrast to the Rapid are the concrete aggregate ledges of the Coralville and Solon members which are almost devoid of clay. This is a very significant relationship which correlates with the freeze-thaw results and service records of the respective units.

Porosity

The porosity of the carbonate rocks is another property investigated. The total porosity has been determined for all the beds and the effective porosity was measured on many of them. The results are presented in Tables 1 through 4.

The total porosity was calculated from values of the powder and bulk densities for the beds sampled in the four quarries. The powder density was determined by a fairly rapid combined volumetric flask-burette method which allows results reproducible within 1 percent. Powdered rock passing a No. 100 sieve is used in the determination (16). The bulk density is obtained by measuring the volume of mercury displaced by a weighed sample of limestone fragments. The total porosity was calculated from the following formula:

$$\text{Percent total porosity} = 1 - \left(\frac{\text{Bulk density}}{\text{Powder density}}\right)$$

The effective porosity was determined by means of the mercury capillary apparatus as part of the pore size determination procedure and represents the portion of the void volume filled with mercury at a pressure of 2,000 psi (see section on pore size distribution).

In analyzing the data, the porosity values of some of the lithologic units studied show no obvious relationship with freeze-thaw resistance. The Rapid member shows no apparent relationship of porosity values with freeze-thaw losses. This is true for those parts of the other members which do not make up the concrete aggregate ledges such as the upper part of the Coralville at the Newton quarry.

A closer relationship with freeze-thaw data is more readily seen in those beds which pass acceptance tests for concrete aggregate. This is perhaps due to the more uniform lithology generally present in a concrete aggregate ledge. The rocks with very dense lithographic textures common in the Coralville member at the Glory quarry generally show low total and effective porosity values which do relate to low freeze-thaw losses. The data available on the concrete aggregate ledge in the Coralville member of the Pint quarry indicate both a fairly high total and effective porosity which correlates well with the coarser textures present. Evidence available for the Solon ledge at the Burton Avenue quarry indicates contrasting high total porosity with a low effective porosity which in turn reflects the general crystalline texture characteristic of the concrete aggregate ledge. Where the Rapid has been weathered an extreme increase in total and effective porosity is evident in the Pint and Glory quarries.

Pore Size and Pore Size Distribution

One of the most important but difficult properties to determine in the carbonate rock is the size and distribution of pores. Sweet (17) and others believe that the relative size of pores in the aggregate with respect to the average size of pores in the cement matrix is the major factor controlling the amount and flow of moisture present in aggregate and hence is a vital factor in determining hydraulic pressure (12) generated in aggregate and concrete during a typical freezing cycle. The flow of fluids as controlled by pore size is directly involved in almost every type of distress of physical and chemical origin.

A great many investigators have stressed the importance of pore size but work has not progressed along this promising avenue of research because of the experimental difficulty of accurately measuring the size of pores (5). In papers published where an attempt was made to measure the pore size of aggregates, a correlation with the durability and freeze-thaw resistance has been indicated (3). Sweet (17) believes that if a large part of the total pore volume is made up of pores below 5 microns in diameter, poor freeze-thaw resistance is the result.

After a survey of the literature, a method was adopted which is believed to be a practical and fairly simple approach to the problem of size and distribution of pores in aggregates. A mercury capillary pressure apparatus made by the Ruska Instrument Corporation of Houston under license from the Shell Development Corporation was purchased for this investigation. The technique is the mercury capillary pressure method developed by Purcell (13) to measure the permeabilities of petroleum reservoir rocks from pore size distribution data. The determination of pore size is accomplished by measuring the pressure which must be applied to a non-wetting fluid (such as mercury) in order to bring the fluid into equilibrium with the capillary pressure exhibited by the pore size in question. The determination is based on the formula for capillary pressure in which:

$$r = \frac{-2a\cos\theta}{Pc}$$

where:
Pc = capillary pressure
r = pore entry radius
a = surface tension
θ = the wetting or contact angle

If the surface tension and wetting angle of a fluid are known, the pore entry radius can be calculated from the above relationship. Purcell devised a mercury pump and technique in which mercury is injected into specimens previously evacuated to a pressure of 5 microns. Mercury is then forced into the rock with increments of pressure over the range from 0 to 2,000 psi. The amount of mercury imbibed at any given pressure is equal to the pore volume filled. By measuring the amount of mercury injected into the rock at given increments over a wide pressure range, the range of pore entry sizes and the portion of the total void volume they occupy is measured. The procedure outlined above gives the effective porosity of the rock, its bulk volume, pore size distribution, and permits the calculation of relative permeability.

The size and distribution of pores in the Glory and Newton quarries and for several beds in the Pint and Burton Avenue quarries have been determined. Although this work is not complete, enough has been done to indicate that pore size distribution coupled with effective porosity data appear to have a definite relationship to freeze-thaw results.

Representative curves are presented for the different lithologies in Figure 3. The curves relate pore entry radius to the distribution function. The distribution function is defined in the equation below, taken from Ritter and Drake (14) who give a detailed mathematical analysis of pore size distribution in porous solids.

$$D(R) = \frac{p}{r}\,\frac{d(Vo-V)}{dp}$$

where:
$D(R)$ = distribution function
p = applied pressure
r = pore entry radius
Vo = total effective pore volume
V = volume of pores having radius less than r
$(Vo-V)$ = volume injected from zero to pressure p
$\frac{d(Vo-V)}{dp}$ = slope of $(Vo-V)$ versus pressure curve

The distribution curves represent the frequency of occurrence of any one particular size of pore. It should be understood that the term pore size is used synonymously with pore entry radius in the following discussions.

The Rapid member at the Glory quarry is characterized in Figure 3A by extremely high and sharp (steep-sloped) distribution curves which indicate that a large portion of the pores have an average size of 0.1 micron. The shape of the curve indicates the narrow limits of the range of pore size. These rocks also show a moderate to high total porosity and effective porosity. Rocks with a distribution curve of this type and with high effective porosity appear to be related to high freeze-thaw losses.

Where the Rapid is weathered, a typical bimodal distribution curve (Fig. 3B) results indicating a great increase in the number of pores in the larger size range. The weathered rock is characterized by extremely high total and effective porosities and very high freeze-thaw losses.

Several distribution curves of the Coralville concrete aggregate ledges at the Pint and Newton quarries are shown in Figure 3C and 3D. Both quarries have moderate total and effective porosity. The distribution curves are characterized by a broad range of pore sizes with a considerable proportion of the pores possessing a radius up to 1 micron. Freeze-thaw losses for both rock units are low. Lithologically the same stratigraphic horizons in both quarries are being correlated and it is interesting to note the general similarity of their distribution curves.

Rocks with lithographic texture show a typical distribution curve (Fig. 3E) consisting of a low peak and the highest frequency of pores in the 0.1 micron range. The gradual rise of the curve indicates that a significant portion of the pores are of larger size. These rocks have a low total and effective porosity and show excellent freeze-thaw resistance.

The Solon member which forms the concrete aggregate ledge at the Burton Avenue

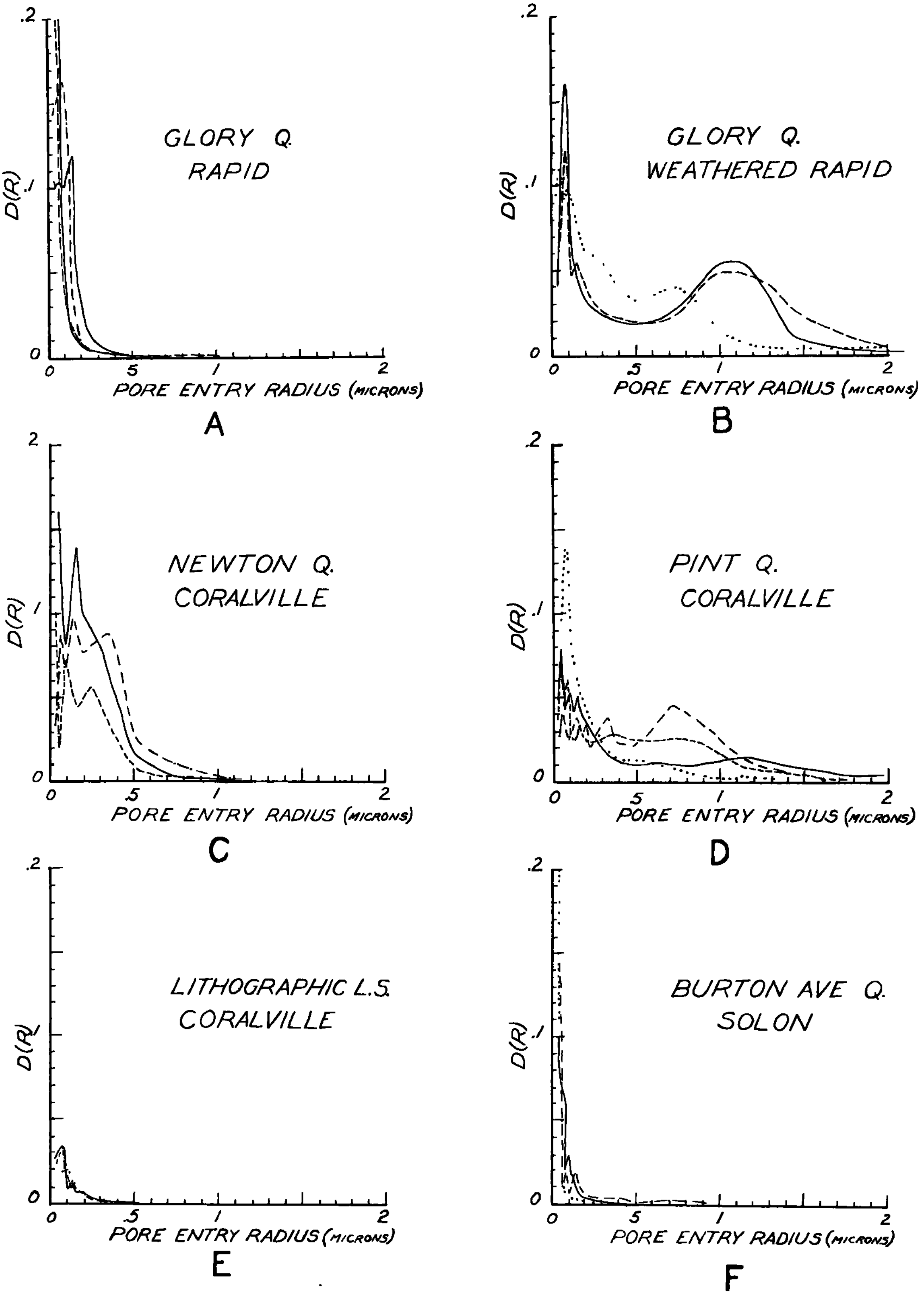

Figure 3. Some representative pore size distribution curves for carbonate rocks. The plot of the distribution function D(R) versus pore entry radius gives the frequency with which pores of a particular size occur in the rock.

quarry is characterized by a very narrow and sharp distribution curve (Fig. 3F) centered about a pore entry radius of 0.1 micron. However, the low effective porosity counters the detrimental effect of the very small pore sizes which are characteristic of the Rapid lithology. The Solon shows excellent freeze-thaw resistance. From thin section data the Solon is considered a crystalline limestone. The crystalline texture might indicate that non-connected pores are prevalent. This is substantiated by the high total porosity and low effective porosity.

The data summarized above point out the subtle relationship of pore size distribution, effective porosity, and freeze-thaw results. The present data also indicate the relationship of these curves to the distinctive types of lithology. This could have been predicted from the fact that pore size distribution is a function of rock texture, that is, the pattern or arrangement of the various sized particles making up the rock. More data and work will be necessary to confirm the present results.

It was interesting to note that most of the pores present in carbonate rocks are quite small. All of the rocks studied have a great number of pores below 0.2 microns. Some rocks in addition have appreciable amounts of even smaller pores. Variation in the relative abundance of pore sizes below 1 micron is considered significant. However in order to evaluate properly the role of the pore size in aggregate, the size and distribution of capillary pores in cement paste must be determined. The relationship of the pore size and pore size distribution of aggregate to that of the cement paste would be a critical factor in concrete durability.

The distribution curve for the Rapid shows that little variation exists in the pore sizes present. The majority of the pores occur in sizes at or below 0.1 micron. This is in contrast to the other lithologies which show a broader variation in pore sizes. The great abundance of uniformly small pores in the Rapid will cause extremely high capillary pressures to be exerted and this effect coupled with high effective porosity would correlate with the high freeze-thaw losses of the member. The rock would have a stronger tendency to retain moisture than the other lithologies characterized by a greater pore size variation. The presence of a greater number of uniformly small pores would also increase the amount of surface area available for chemical reaction in the Rapid lithology.

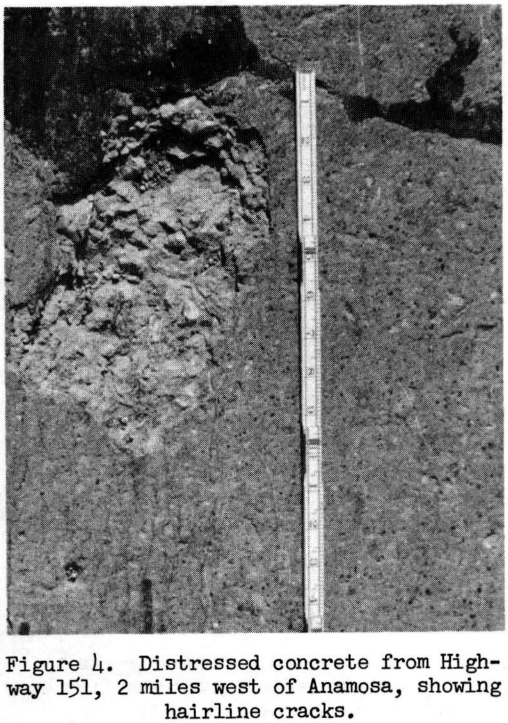

Figure 4. Distressed concrete from Highway 151, 2 miles west of Anamosa, showing hairline cracks.

Figure 5. Cores of distressed concrete showing the reaction rims. Taken at the same location on Highway 151 as Figure 4.

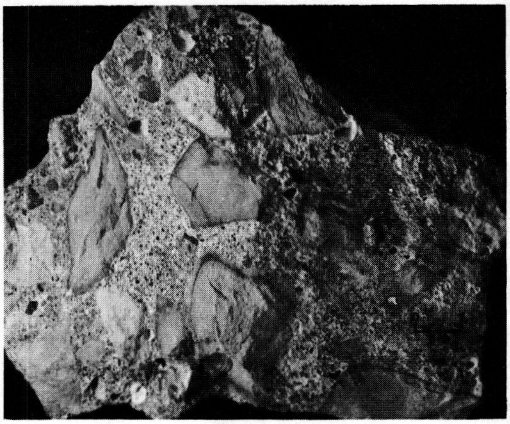

Figure 6. A piece of distressed concrete with reaction rims taken from a salvage pile along Highway 218 south of Waterloo.

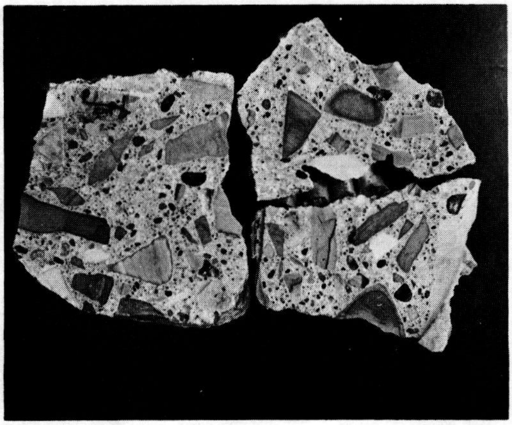

Figure 7. Sections of distressed concrete showing inner and outer rims about coarse Rapid aggregate.

Until more data on the quarries are obtained, conclusions other than those mentioned above would be premature. The approach to the problem through pore size distribution data is very promising and will be continued. It is hoped that an analysis of pore size distribution and effective porosity might lead to the prediction of freeze-thaw results.

CONCRETE INVESTIGATION

Introduction

The attempt to correlate the properties of carbonate aggregates with service records led to a study of concrete and concrete cores of highways with good and poor service records. Highways constructed with Glory aggregate have either been replaced or are in bad condition today (Fig. 4). Samples and cores of these highways were obtained and photographs of the distressed concrete are shown in Figures 4, 5, 6, and 7. For comparison purposes, cores were also taken of highways with good service records which were of similar age but were made from aggregate of different lithologies. The presence of dark reaction rims or zones about the periphery of the carbonate aggregate of the distinctive Rapid lithology (Fig. 5, 6, and 7) was noted in affected concrete. The rims were absent in specimens of concrete which had good service records and did not contain aggregate of the Rapid lithology.

A petrographic and chemical investigation of the concrete with reacted aggregate was initiated. The results of the chemical study are presented in the paper by Bisque and Lemish (2). The petrographic data obtained to date are presented below.

Petrography of Distressed Concrete

Hand specimen investigation of fragments and cores of distressed concrete disclosed some important observations which are noted below.

1. Two types of rims were noted: (a) a darker inner rim occurs within the aggregate and outlines its outer edge, and (b) an outer rim of light gray material occurs in the concrete matrix surrounding the affected aggregates (Fig. 7).
2. The dark inner rims show a distinct zonal arrangement which resembles diffusion banding commonly observed in altered or weathered rocks (Fig. 5, 6, and 7). As many as three concentric rings were observed in some specimens.
3. In samples collected from salvage piles of broken highway concrete, the matrix of the concrete is softer and disintegrates quite easily.
4. Some of the coarse carbonate fragments in cores of distressed concrete are fractured.

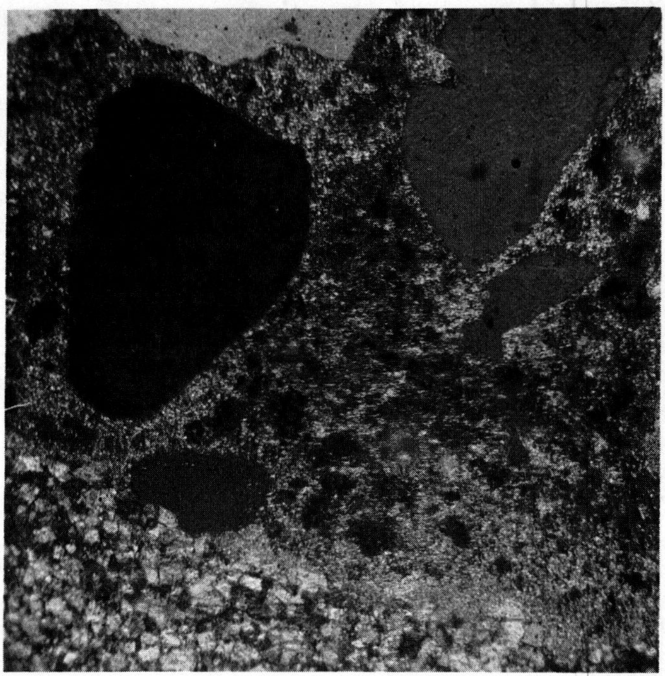

Figure 8. Photomicrograph of a typical specimen of distressed concrete showing abundant birefringent material in the matrix. (Crossed-nicols, 75X Mag.)

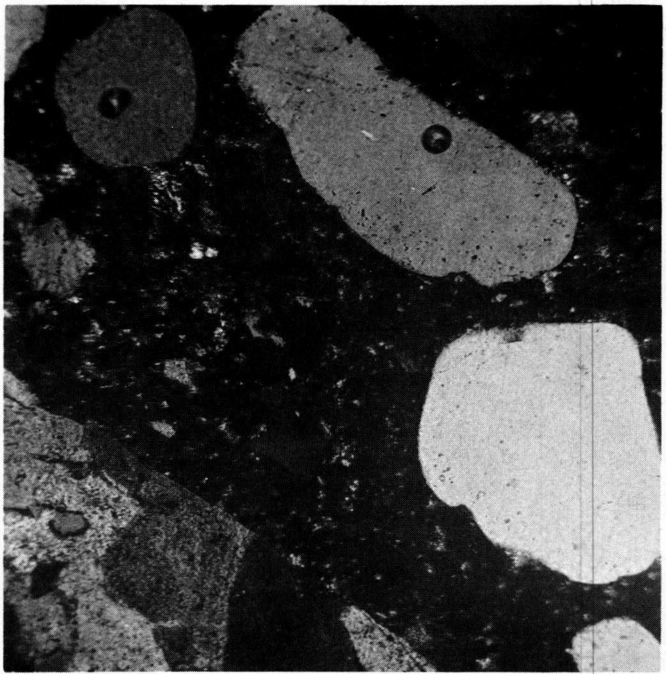

Figure 9. Photomicrograph of a specimen of good concrete from Highway 20 showing a darker and more uniformly isotropic matrix. (Crossed-nicols, 75X Mag.)

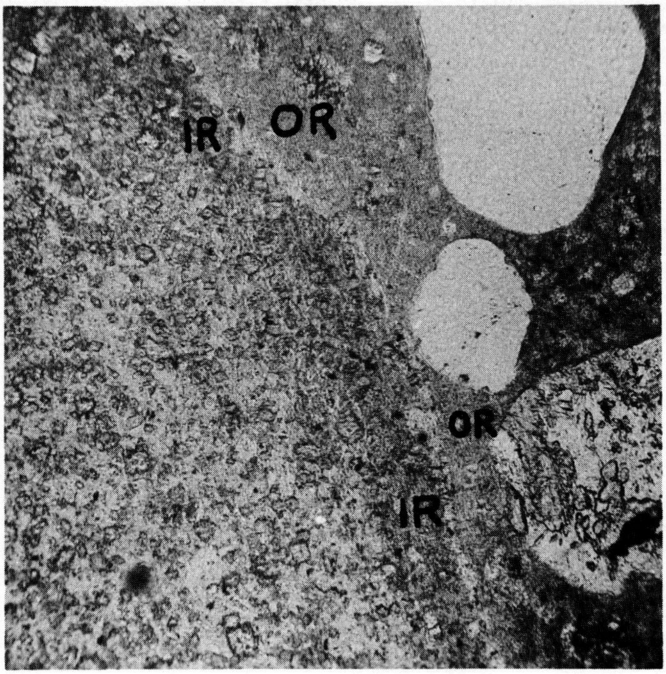

Figure 10. Photomicrograph showing a typical inner rim (IR) and outer rim (OR) seen in distressed concrete around coarse aggregate of the Rapid lithology. (Plane polarized, 75X Mag.)

Figure 11. Same as Figure 10. (Crossed-nicols, 75X Mag.)

5. The inner rims are controlled by the matrix-aggregate border and the rims cut across bedding planes of the aggregate indicating that the rims formed after the concrete was placed.
6. The inner reaction rims are characteristically related to the Rapid aggregate which may be either fresh or weathered.
7. Pieces of lithographic limestone from the upper part of the Glory quarry show no inner reaction rims. Some of these do show a slight outer rim of light-colored paste-like material (Fig. 7).
8. Specimens of broken concrete commonly show cavities lined with a white fibrous secondary mineral which was identified by oil immersion techniques to be calcium sulfo-aluminate.

Thin sections of the distressed concrete were studied and the observations made are summarized below.

1. A general aspect of thin sections of distressed concrete is the over-all appearance of the matrix which is characterized by a fair amount of birefringent material disseminated throughout as small clusters or larger aggregates (Fig. 8).
2. The inner rims are not readily apparent but where recognized they characteristically show a concentration of opaque material which forms an irregular border advancing toward the interior of the aggregate (Fig. 10 and 11). In reflected light the greater concentration of white opaque material in this zone is readily apparent. In some specimens a clarified rim commonly occurs between the darker rim and the periphery of the aggregate (9, 7).
3. The opaque material preferentially occupies the calcitic matrix of the aggregate.
4. The dolomite rhombs which make up the typical mosaic texture of the affected Rapid aggregate stand out in sharp relief in the area of the inner rim.
5. Under extreme magnification some evidence of very weakly birefringent to isotropic material with an index below balsam occurs interstitially among the carbonate grains within the inner rim zone. This may represent some form of silica or a silicate mineral.
6. The outer rim is very evident in thin section and consists of aggregates of low to moderate (0.012 - 0.020) birefringent material with poor crystal form. The index of refraction is about 1.55 to 1.57. This material is believed to be calcium hydroxide. The contact between the aggregate and outer rim may either be sharp or gradational. Occasionally a faint crack is evident along the border (Fig. 10 and 11).
7. In many specimens fine-grained irregular calcite appears to have formed at the expense of the calcium hydroxide.
8. The fine aggregate shows little or no evidence of any reaction with the matrix. Overgrowths on quartz sand grains are very uncommon.

From the evidence and observations made it appears that some type of exchange of materials between the paste and aggregate has probably occurred causing the outer and inner rims to form.

Petrography of Serviceable Concrete

Several thin sections were made from cores taken from highways with good service records. These contained aggregate from formations other than the Cedar Valley. Hand specimens of such concrete showed no reaction rims. Thin sections of these specimens verified the absence of inner rims in the aggregate. In some instances a very thin outer rim of calcium hydroxide has developed.

The characteristic feature of these sections of good concrete is the generally dark isotropic character of the matrix material (Fig. 9) which is in contrast to the greater abundance of birefringent material in the matrix of distressed concrete sections.

SUMMARY AND CONCLUSIONS

A summary of the data presented on the physical properties of the carbonate aggregates and the petrography of distressed concrete can be made.

1. The lithologic members of the Cedar Valley formation can be identified fairly well by their petrographic characteristics. Rocks with lithology similar to the Rapid member have poor freeze-thaw resistance and poor service records.
2. Rocks from the Cedar Valley formation with high insoluble residue content have poor freeze-thaw resistance.
3. Illite is the chief clay mineral present in the Rapid member. Clay minerals are rare or absent in the units with good freeze-thaw resistance which comprise the present concrete aggregate ledges.
4. Porosity data are on the whole inconclusive with regard to the service records or freeze-thaw data of these carbonate rocks. Where the rocks are more uniform as in some concrete aggregate ledges, porosity data may correlate with freeze-thaw data.
5. Pore size distribution data indicate that in these carbonate rocks most of the pores range in size from 1 micron to less than 0.1 micron. The shape of the pore size distribution curves and the effective porosities are significant and are related to (a) the lithology of the rocks and (b) the potential freeze-thaw performance. Pore size distribution data would indicate that the Rapid lithology has higher capillary pressures because of the great number of uniformly small pores averaging 0.1 micron in radius. Rapid rocks, therefore, have a stronger tendency to absorb and retain fluids and at the same time provide a larger surface area as a potential site for chemical reaction. This is not true of the rock types which form concrete aggregate ledges now being utilized for concrete.
6. Petrographic study of specimens of concrete with good and poor service records indicates characteristic differences between the two. A strong relationship is evident between the reaction rims on aggregate of Rapid lithology and concrete with a poor service record. This implies that the concrete has reacted with the aggregate.

A general conclusion warranted by the investigation to date is that carbonate rocks of the Cedar Valley formation that have high insoluble residue are unsatisfactory for use as aggregate in concrete pavement whereas pure limestone or dolomite with low residue and clay content makes satisfactory aggregate. Rocks of the impure type, which have higher capillary pressures and more pore surface area available for chemical activity, react with cement. The reaction probably occurs over a long period of time and causes a gradual weakening of the concrete matrix to a point where it can readily be destroyed by freezing or by external stresses.

A good description of the type of aggregate from the Cedar Valley formation which can cause distress in concrete is now evident. The exact mechanism by which it causes distress is still not completely understood. More work is necessary to clarify the manner in which the particular rock properties of certain types of carbonate rock have contributed to the poor service of concrete.

Another area of research necessary before any general classification of carbonate rocks as suitable aggregate can be carried out is to see how residue content, clay mineral content, pore distribution, and lithology are related to the geological origins of these rock types.

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