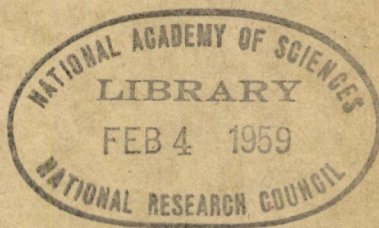


HIGHWAY RESEARCH BOARD

Bulletin 196

*Air Voids in Concrete  
And Characteristics of  
Aggregates*



**National Academy of Sciences—**

**National Research Council**

publication 622

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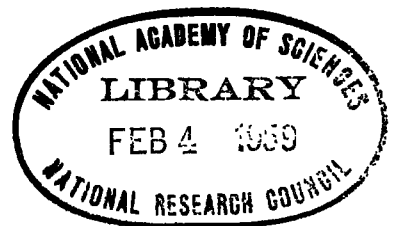
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## CHEMICAL CHARACTERISTICS OF SOME CARBONATE AGGREGATES AS RELATED TO DURABILITY OF CONCRETE

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

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F. EUGENE RUSH, Geologist, Phillips Petroleum Company, and  
CARL L. HILTROP, Research Graduate Assistant, Department of Geology,  
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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.

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,<sup>1</sup> 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.

<sup>1</sup>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.

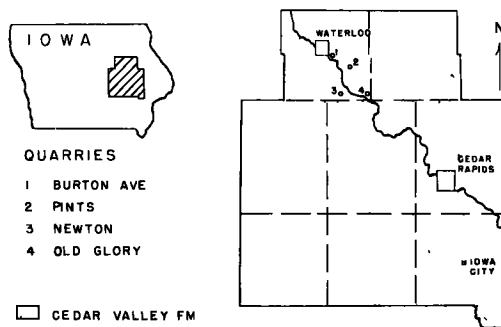


Figure 1. Index map showing distribution of the Cedar Valley formation and the location of the quarries.



## 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.

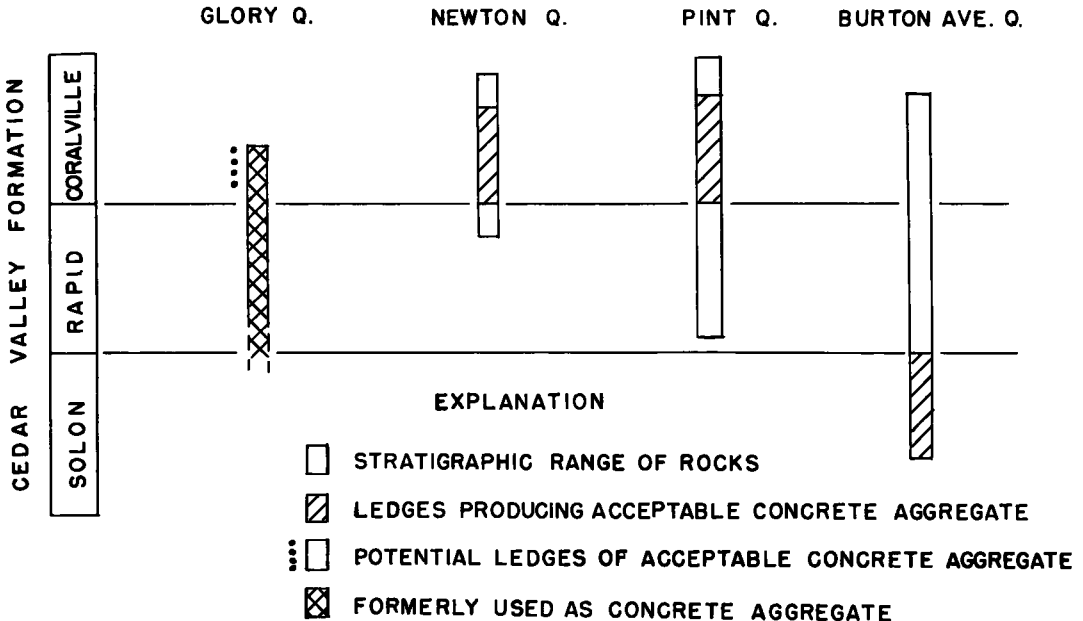


Figure 2. Stratigraphic range of the rocks exposed in the quarries and the position of the concrete aggregate ledges.

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	Calcareous dolomite	4.3	22.0	-	-	illite	2.80	2.20	21.4	-	95.0	Badly weathered
	16	Calcareous 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	Calcareous dolomite	7.0	21.0	-	-	illite	2.80	2.40	14.2	11.5	30.0	
	12	Calcareous dolomite	7.0	22.0	-	-	illite	2.78	2.45	11.7	-	-	
	11	Calcareous dolomite	7.0	12.0	18	-	illite	2.79	2.50	10.4	-	42.0	
	10	Calcareous dolomite	1.5	10.0	-	-	-	2.76	2.55	7.6	5.8	25.0	
	9	Calcareous dolomite	2.6	15.0	-	-	illite	2.80	2.53	9.6	6.4	42.0	
	8	Calcareous dolomite	6.5	39.0	-	-	illite	2.68	2.55	4.8	4.6	29.0	
	7	Calcareous dolomite	6.5	13.0	-	-	illite	2.77	2.56	7.6	2.8	32.0	
	6	Calcareous dolomite	6.5	13.0	-	-	illite	2.76	2.54	6.0	4.2	33.0	
	5	Calcareous dolomite	3.7	15.0	-	-	illite	2.76	2.56	7.3	3.2	36.0	
	4	Calcareous dolomite	3.7	10.0	-	-	illite	2.68	2.54	5.2	3.4	42.0	
	3	Calcareous dolomite	1.7	22.0	-	-	illite	2.70	2.56	5.2	4.2	30.0	
	2	Calcareous dolomite	1.0	49.0	-	-	-	2.69	2.46	8.1	4.8	27.0	
	1	Calcareous dolomite	2.6	7.0	-	-	-	2.77	2.54	6.3	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		
Rapid	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	15	Calcareous dolomite	1.3	1.7	-	none	2.86	2.58	9.8	8.4	1.7	
	14	Calcareous dolomite	3.5	1.6	-	trace-illite	2.88	2.57	10.8	-	3.6	
	13	Calcareous 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	Calcareous dolomite	3.8	2.3	-	none	2.84	2.56	9.8	6.1	1.7	
	9	Calcareous 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	-	-	
	4	Calcareous dolomite	2.6	16.7	16.6	illite	2.87	2.26	21.2	-	-	Extremely weathered
	3	Calcareous dolomite	2.6	22.5	-	illite	2.81	2.31	17.8	-	-	Very soft rock
	2	Calcareous dolomite	3.5	17.5	-	illite	2.80	2.29	18.2	-	-	Freeze-thaw losses are excessive
Rapid	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		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	8.6	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		illite	2.85	2.44	14.4			Cherty
	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	27.0	illite	2.83	2.43	14.1			
	17	Dolomitic limestone	0.5	34.0		illite	2.81	2.42	13.9			
	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		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	6.5	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 microscopically. 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 is 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:

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

where:  $P_c$  = capillary pressure  
 $r$  = pore entry radius  
 $a$  = surface tension  
 $\theta$  = 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.

$$D(R) = \frac{p}{r} \frac{d(V_0 - V)}{dp}$$

where:  $D(R)$  = distribution function  
 $p$  = applied pressure  
 $r$  = pore entry radius  
 $V_0$  = total effective pore volume  
 $V$  = volume of pores having radius less than  $r$   
 $(V_0 - V)$  = volume injected from zero to pressure  $p$   
 $\frac{d(V_0 - V)}{dp}$  = slope of  $(V_0 - V)$  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

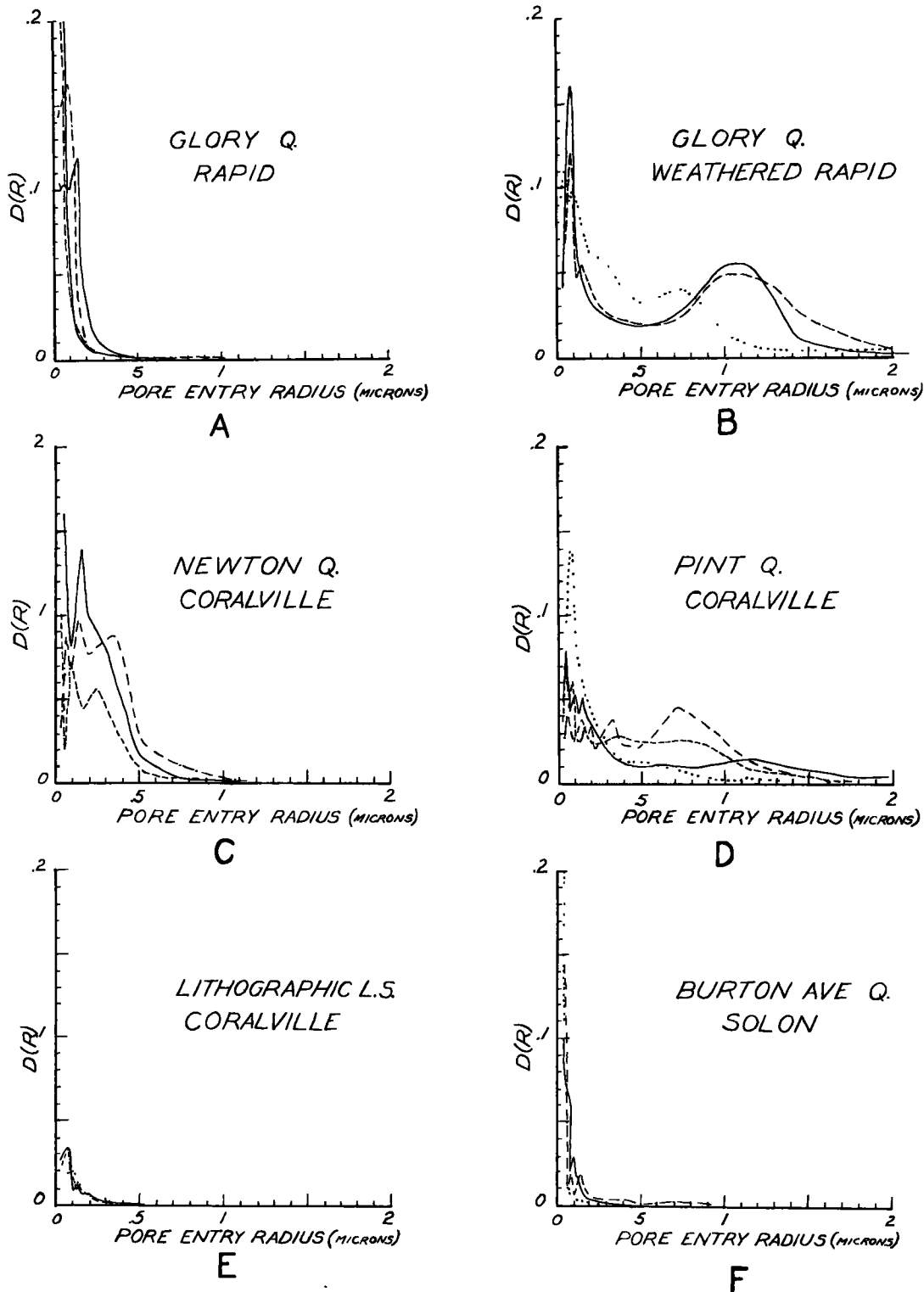


Figure 3. Some representative pore size distribution curves for carbonate rocks. The plot of the distribution function  $D(R)$  versus pore entry radius gives the frequency with which pores of a particular size occur in the rock.

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.

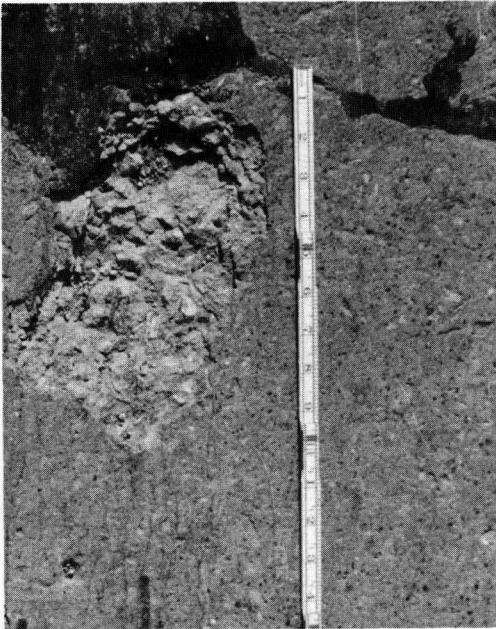


Figure 4. Distressed concrete from Highway 151, 2 miles west of Anamosa, showing hairline cracks.

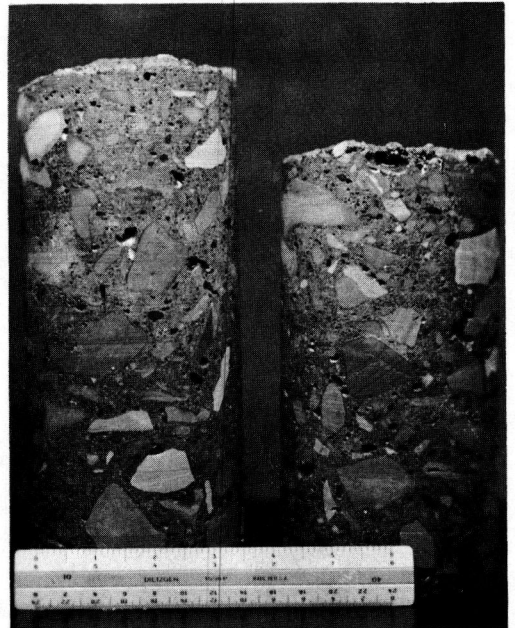


Figure 5. Cores of distressed concrete showing the reaction rims. Taken at the same location on Highway 151 as Figure 4.



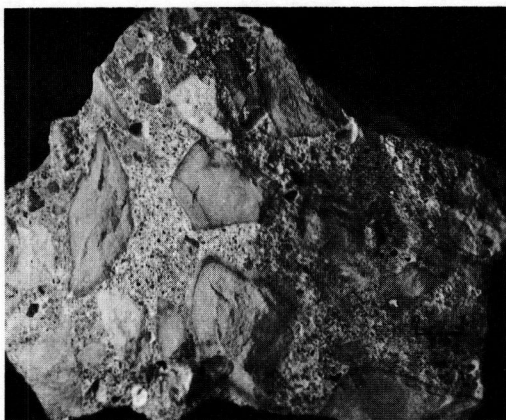


Figure 6. A piece of distressed concrete with reaction rims taken from a salvage pile along Highway 218 south of Waterloo.

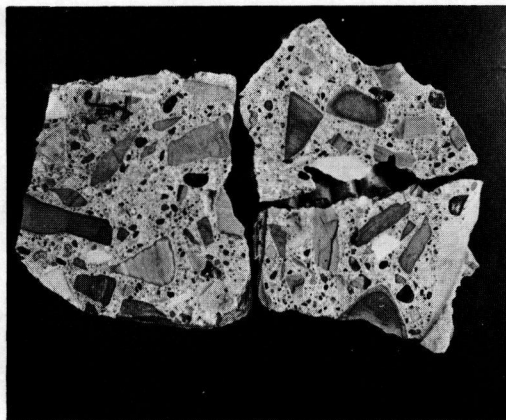


Figure 7. Sections of distressed concrete showing inner and outer rims about coarse Rapid aggregate.

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.

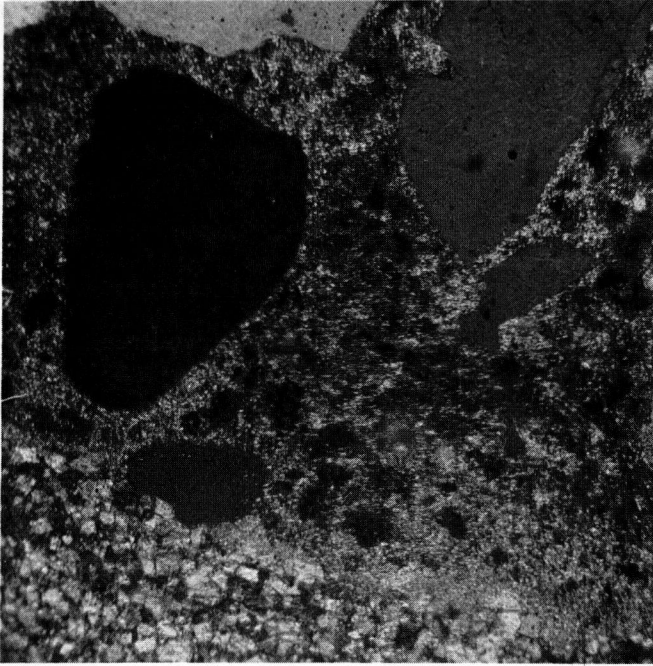


Figure 8. Photomicrograph of a typical specimen of distressed concrete showing abundant birefringent material in the matrix. (Crossed-nicols, 75X Mag.)

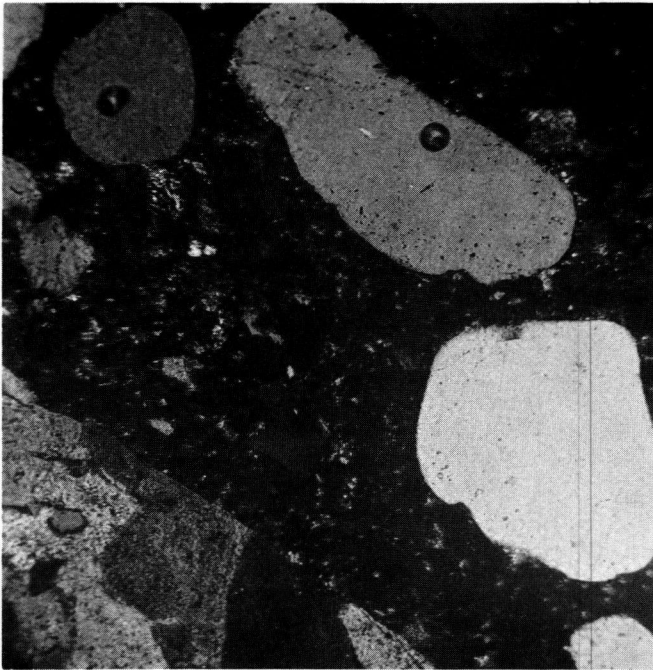


Figure 9. Photomicrograph of a specimen of good concrete from Highway 20 showing a darker and more uniformly isotropic matrix. (Crossed-nicols, 75X Mag.)

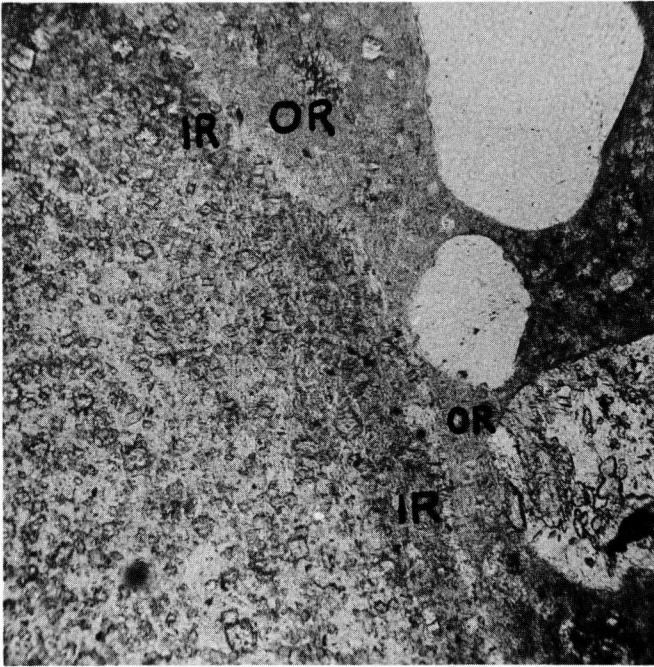


Figure 10. Photomicrograph showing a typical inner rim (IR) and outer rim (OR) seen in distressed concrete around coarse aggregate of the Rapid lithology. (Plane polarized, 75X Mag.)

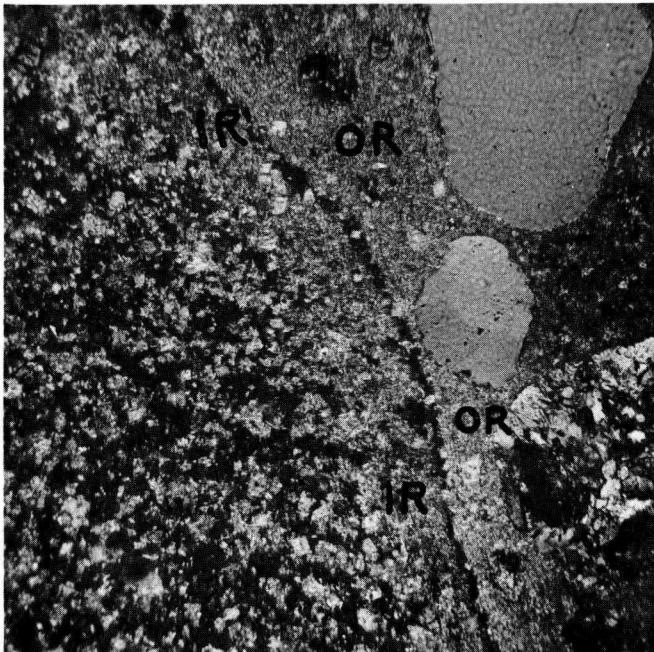


Figure 11. Same as Figure 10. (Crossed-nicols, 75X Mag.)

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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# Correlation Between Concrete Durability And Air-Void Characteristics

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The theory of the action of entrained air in producing frost-resistant concrete demonstrates the importance of the size and distribution of the air voids in the portland cement paste. The characteristics investigated were (a) air content, (b) number of voids intersected per unit length of traverse, (c) specific surface of the air voids, (d) number of hypothetical spheres of equal radius having the same volume of air per unit volume of concrete and the same specific surface as the actual system of random sized voids, and (e) spacing factor.

Statistical methods were applied to the study of the variability of the air content and number of voids per inch within a concrete beam. The analysis showed that the measurement of these characteristics for a particular beam may be considered as one long traverse without regard to the position or length of the individual traverses.

Thirty-eight beams from 19 mixes were used to study the correlation between each of the five air-void characteristics and durability. A durability factor was used to express the resistance of each beam to deterioration in a laboratory freeze-thaw test. The five air-void characteristics ranked in the order of their correlation with durability are (a) spacing factor, (b) specific surface, (c) number of voids per inch, (d) hypothetical number of voids per cubic inch, and (e) total air content.

The spacing factor and the specific surface were found to be of almost equal importance in producing durable concrete. Hence, either of these two characteristics may be used as a criterion for determining the air requirements for frost-resistant concrete.

● THE SUPERIOR performance of air-entrained concrete has been demonstrated in both the field and the laboratory (3, 4, 6, 8, 9, 10, 11). Most reports of research on air entrainment have dealt principally with factors which control the amount of air or with changes in properties of the concrete related to changes in the gross amount of air. However, the current theories of the action of entrained air in producing frost-resistant concrete show that the properties of the air voids themselves are important factors affecting the ability of concrete to withstand freezing and thawing (11, 12, 13, 14).

Considerable research on the effect of air entrainment on the durability of concrete beams as measured by resistance to deterioration under repeated cycles of freezing and thawing has been performed in the laboratories of the Joint Highway Research Project at Purdue University. At times, large differences in durability have been found between beams from the same mix and between mixes made from the same materials and having the same total air content as determined by measurements on the fresh concrete. The study reported in this paper was initiated to determine experimentally which property of the entrained air is most significant in producing durable concrete and to what extent the unexplained differences in durability could be attributed to differences in the characteristics of the void systems of the beams. The air-void characteristics which were investigated for correlation with durability were (a) total air content, (b) number of voids per inch, (c) specific surface, (d) hypothetical number of voids per cubic inch, and (e) spacing factor.

Equipment and procedures similar to those developed in the Portland Cement Asso-

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ciation laboratories and reported by Brown and Pierson (5) were used for measuring the air content and number of voids per inch. The other characteristics were computed from the equations presented along with their development in papers by T. C. Powers (12) and T. F. Willis (16). For ready reference these equations are given in the Appendix. As a preliminary study an investigation was made of the variability within a beam of the air content and number of voids per inch. This preliminary study is presented in the Appendix.

## MATERIALS

Concrete beams which were fabricated for use in another investigation conducted in the concrete laboratory of the Joint Highway Research Project were selected for examination in this study. These beams were chosen because of unexplained differences in durability between beams made from the same materials under similar conditions.

All beams used in this study were made with crushed limestone coarse aggregate. Data on the coarse aggregates are presented in Table 1. The six coarse aggregates from the sources in the Kokomo formation have poor durability records. The source from the Liston Creek formation has a good field performance record.

The fine aggregate used in all mixes was obtained from a river terrace deposit of glacial origin. This fine aggregate has been used in the Joint Highway Research Project concrete laboratory for years as a standard material and is considered to be a durable material in laboratory freeze-thaw weathering. The bulk saturated surface dry specific gravity of the fine aggregate was 2.65 and the fineness modulus for the gradation was 3.10. The absorption was 1.65 percent by weight.

Type I portland cement from a single clinker batch was used in all mixes. Darex was used as the air-entraining agent for the mixes made with coarse aggregates A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, and A<sub>4</sub>, while neutralized Vinsol resin solution was used for the mixes made with coarse aggregates A<sub>5</sub>, A<sub>6</sub>, and A<sub>7</sub>.

### Concrete Mixes

All coarse aggregates were vacuum saturated before being incorporated in concrete. Mixes were designed for a water-cement ratio of 0.46 by weight, a cement

TABLE 1  
COARSE AGGREGATES

Aggregate Designation	Aggregate Source Number	Laboratory Sample Number	Description	Geological Origin	Bulk Sp Gr	True Sp Gr <sup>a</sup>	Absorption after Evacuation and Saturation (% by wt)	Degree of Saturation <sup>b</sup> (%)
A <sub>1</sub>	9-2S	2033-A	Upper 25 ft Ledges 1, 2, 3, 4	Silurian (Kokomo formation)	2.63	2.86	2.69	90
A <sub>2</sub>	9-2S	2033-B	Lower 21 ft Ledges 5, 6, 7	Silurian (Kokomo formation)	2.53	2.86	4.66	98
A <sub>3</sub>	9-2S	2033-C	Stockpile sample	Silurian (Kokomo formation)	2.57		3.95	
A <sub>4</sub>	9-1S	2034	Ledge sample	Silurian (Kokomo formation)	2.45	2.86	5.85	100
A <sub>5</sub>	9-5S	2032-A	Upper 24 ft Ledges 1, 2, 3, 4	Silurian (Kokomo formation)	2.59	2.85	3.19	88
A <sub>6</sub>	9-5S	2032-B	Lower 24 ft Ledges 5, 6, 7	Silurian (Kokomo formation)	2.46	2.85	5.65	100
A <sub>7</sub>	1-1S	2037	Stockpile sample	Silurian (Liston Creek formation)	2.68	2.85	1.98	90

<sup>a</sup> True specific gravity values were determined by powdering a sample of the aggregate and then using the procedure for the determination of the specific gravity of soils.

<sup>b</sup> Ratio of the pore space filled with water to the total internal pore space of the aggregate particles.



TABLE 2  
AIR-VOID CHARACTERISTICS AND DURABILITY FACTORS—INDIVIDUAL BEAMS

Aggregate	Beam Designation	Durability Factor	Air-Void Characteristics of Hardened Concrete				
			Air Content, A (%)	Voids per Inch, n	Specific Surface, a (sq in./cu in.)	Voids per Unit Vol, N (voids per cu in.)	Spacing Factor, L (in.)
A <sub>1</sub>	A21	100	4.5	7.4	660	113,000	0.0075
	A22	99	4.9	9.1	740	178,000	0.0065
	A31	52	3.4	3.8	450	27,000	0.0128
	A32	34	3.2	3.5	440	24,000	0.0134
A <sub>2</sub>	B11	90	4.0	7.1	710	127,000	0.0074
	B12	27	3.7	6.4	690	108,000	0.0080
	B21	97	4.8	8.6	720	156,000	0.0068
	B23	58	4.2	7.6	720	141,000	0.0071
	B31	26	3.8	4.3	450	31,000	0.0119
	B32	23	3.2	3.5	440	24,000	0.0134
A <sub>3</sub>	C11	96	3.9	6.4	660	97,000	0.0081
	C13	91	4.3	7.2	670	114,000	0.0076
	C31	61	3.5	4.3	490	37,000	0.0114
	C32	87	3.2	4.7	590	57,000	0.0100
A <sub>4</sub>	422	62	4.5	7.2	640	104,000	0.0078
	423	85	4.8	8.1	670	130,000	0.0072
	432	60	2.9	3.8	520	37,000	0.0117
	433	100	3.2	5.2	650	78,000	0.0090
	441	19	3.3	3.4	410	20,000	0.0139
	442	38	3.7	3.4	370	16,000	0.0149
	443	38	3.7	3.4	370	16,000	0.0149
A <sub>5</sub>	SA11	80	3.7	5.5	600	69,000	0.0092
	SA13	99	4.2	7.1	680	115,000	0.0076
	SA21	94	5.0	9.2	740	176,000	0.0065
	SA23	95	4.6	9.3	810	214,000	0.0061
	SA32	90	4.4	7.0	640	100,000	0.0080
	SA33	92	4.2	7.2	690	120,000	0.0075
A <sub>6</sub>	SB11	100	10.3	22.2	860	584,000	0.0040
	SB12	95	9.9	20.5	830	498,000	0.0044
	SB21	88	5.5	11.5	840	285,000	0.0055
	SB22	83	5.5	10.7	780	229,000	0.0059
	SB31	57	3.8	4.9	520	46,000	0.0107
	SB33	38	3.8	5.1	540	52,000	0.0100
	SB41	62	4.4	8.6	780	186,000	0.0065
	SB43	45	4.6	8.3	720	153,000	0.0069
	SB52	97	6.3	12.7	810	293,000	0.0053
	SB53	52	6.2	12.8	820	308,000	0.0052
A <sub>7</sub>	711	100	3.7	6.3	680	103,000	0.0080
	712	100	3.7	5.6	600	73,000	0.0090

factor of six bags per cubic yard, and a slump of 3 to 4 in. The maximum size of aggregate was 1 in. The air content of the fresh concrete was measured gravimetrically according to ASTM Method C138-44 (1) except that a 0.1 cu ft measure was used because of the small size of the concrete mixes. The concrete used for making the air content determination was discarded. Three concrete beams, 3 x 4 x 16 in., were made from each mix. Curing was by immersion in water for 13 days following removal of the specimens from molds one day after casting.

#### MEASUREMENT OF DURABILITY

The relative durability of the beams was determined from their resistance to deterioration when subjected to repeated cycles of freezing and thawing. Automatic equipment was used with the freezing and thawing cycles corresponding to ASTM Method C291-52T (1) rapid freezing in air and thawing in water. Approximately seven cycles per day were obtained.

Periodic determinations of the dynamic modulus of elasticity were made to measure the amount of deterioration. Freezing and thawing were continued until a decrease in dynamic E to 50 percent of the original value occurred or until 200 cycles of freezing and thawing were completed.

The seven coarse aggregates described in Table 1 were represented by 19 mixes. The number of mixes using each coarse aggregate varied. Referring to the aggregate designations in Table 1, A<sub>1</sub> was used in two mixes, A<sub>2</sub> in three mixes, A<sub>3</sub> in two mixes, A<sub>4</sub> in three mixes, A<sub>5</sub> in three mixes, A<sub>6</sub> in five mixes, and A<sub>7</sub> in one mix. For use in

studying the air-void characteristics two beams were selected from each mix—the most durable and the least durable. Thus, a total of 38 beams from the 19 mixes was studied.

A durability factor was used to express the durability of each beam selected for measurement of the air-void characteristics. This factor was computed following the procedure suggested by Stanton Walker (15). It may be defined as the area under the curve (dynamic E as a percent of the original E plotted against cycles of freezing and thawing) to the left of the 200th cycle and above the 50 percent dynamic E line expressed as a percentage of the total area to the left of the 200th cycle and above the 50 percent dynamic E line. Table 2 gives the values for the durability factor and the five air-void characteristics for each of the 38 beams.

**CORRELATION STUDIES**

The durability of a given beam was affected by other variables in addition to the entrained air. In particular, the coarse aggregate could be expected to produce considerable differences in durability among the beams, since six of the coarse aggregates were from sources with poor durability records. For a single concrete mix there is a given number of deleterious particles and a large number of manners in which these particles may be distributed in beams made from the mix. Thus, within a mix, large variations in durability could exist as a result of differences in the distributions of deleterious particles in the beams. Variables such as efficiency of vacuum saturation, skill of labor, and location of beams within the freezer could have an effect on the durability. Hence, the beams examined in this study were regarded as a sample randomly selected from a universe of beams in which variables other than the entrained air exist. To determine the relative importance of the five air-void characteristics in producing durable concrete, the correlation technique was used to study the relationship between durability and each air-void characteristic.

**Linear Correlation—Individual Beams**

The scatter diagram in which the durability factor is plotted against air content is shown in Figure 1. The scatter diagrams using the other air-void characteristics are presented in Figures 2 through 5.

Although it is possible that some curve other than a straight line would give a higher correlation between durability and a given air-void characteristic, it is believed that for the purpose of this study a straight line fitted by the least-squares method is satisfactory. The results of the computations for slopes, correlation coefficients, and regression lines are summarized in Table 3. The t-value for testing the significance of the correlation coefficient is shown. The formula for t was taken from page 88 of "Statistical Theory in Research" by Anderson and Bancroft (2). The significance of the observed t for n-2 degrees of freedom is indicated in the table as well as the percentage of the variation in durability which is explained by the regression line. The regression lines have been plotted on the scatter diagrams.

Because of the large differences in durability which could be introduced by the

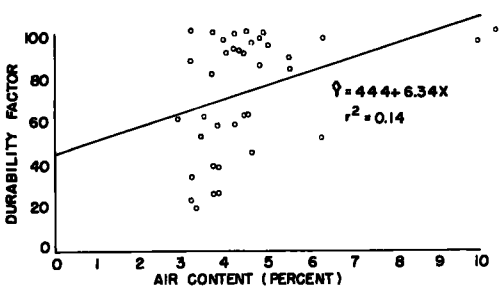


Figure 1. Scatter diagram for durability factor versus air content.

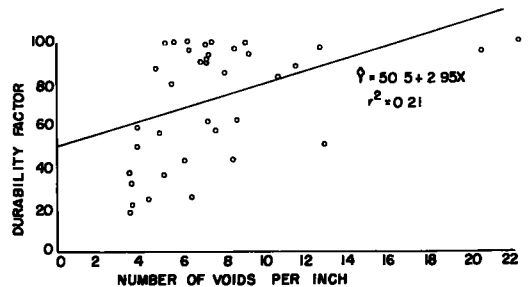


Figure 2. Scatter diagram for durability factor versus number of voids per inch.

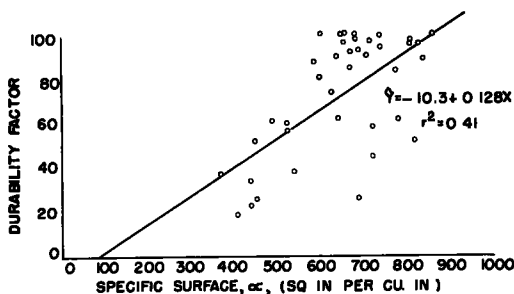


Figure 3. Scatter diagram for durability factor versus specific surface.

coarse aggregate and other variables these regression lines should not be used to predict the durability factor for a given value of an air-void characteristic. They should be regarded as indicating the trend in the change in durability factor with changes in an air-void characteristic.

#### Linear Correlation—Average Values for Each Mix

In order to study correlation between durability and air-void characteristics on a mix basis an analysis was made using the average values for each mix. Since freeze-thaw data were available on three beams from each mix, the durability factor for each mix was taken as the average for the three beams. Average values for the durability factor and five air-void characteristics for each mix are given in Table 4. The value for each air-void characteristic is the average for the two beams from the values given in Table 2. The results of this correlation study are summarized in Table 5.

#### Discussion of Correlation Studies

The graphs of the durability factor plotted against each of the five air-void characteristics (Figs. 1-5) show considerable scatter. Some of this scatter would be expected to result from the coarse-aggregate variable. Inspection of the scatter diagrams alone would lead one to conclude that little correlation exists between the total air content and durability for the beams examined. In the past the total air content has been the air-void characteristic most used in determining the air requirements for frost-resistant concrete.

The air-void characteristics (specific surface and spacing factor) which are computed from equations containing both air content and number of voids per inch show the smallest amount of scatter. This indicates the importance of the interaction of these two characteristics in producing durable concrete. Inspection of Tables 3 and 5 also shows the importance of the interaction of air content and number of voids per inch in producing durable concrete. The specific surface and spacing factor give considerably higher correlation coefficients than the other three characteristics.

Tables 3 and 5 show that the correlation coefficient obtained using the average values for each mix is noticeably higher for each air-void characteristic than the corresponding value computed from the data for individual beams. This results from eliminating the large differences in durability between beams within the same mix by means of averaging the individual values. A large part of this difference in durability within a mix can be attributed to the coarse aggregate, since differences in the combinations

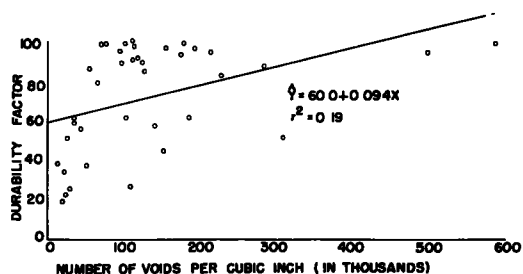


Figure 4. Scatter diagram for durability factor versus number of voids per cubic inch.

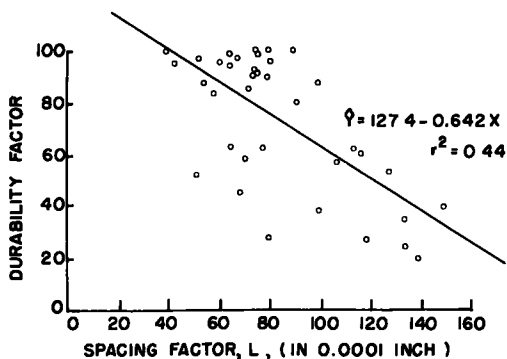


Figure 5. Scatter diagram for durability factor versus spacing factor.

TABLE 3  
SUMMARY OF STUDY OF LINEAR CORRELATION BETWEEN DURABILITY AND AIR-VOID CHARACTERISTICS  
INDIVIDUAL BEAMS

Air-Void Characteristic	$\bar{Y}$	$\bar{X}$	Slope (b)	Regression Line Y on X	Correlation Coefficient (r)	$t_{obs.} = \frac{r}{\sqrt{\frac{n-2}{1-r^2}}}$	Significance	Variation Explained by Regression Line (%)
Air content, A (%)	72.9	4.49	6.338	$Y = 44.4 + 6.34X$	0.3698	2.39	a	13.67
Number of voids per inch, n	72.9	7.62	2.946	$Y = 50.5 + 2.95X$	0.4542	3.06	c	20.63
Specific surface, a (sq in./cu in.)	72.9	648.2	0.1284	$Y = -10.3 + 0.128X$	0.6370	4.96	c	40.58
Voides per unit volume, N (thousands of voids per cu in.)	72.9	137.4	0.0941	$Y = 60.0 + 0.094X$	0.4349	2.90	b	18.92
Spacing factor, L (0.0001 in.)	72.9	84.9	-0.6416	$Y = 127.4 - 0.642X$	-0.6647	5.34	c	44.18
Note: Y = Durability factor		X = Air-void characteristic						
$t_{0.9875} = 2.34$		$t_{0.995} = 2.72$		$t_{0.9975} = 2.99$				
$a t_{obs.} > 2.34$		$b t_{obs.} > 2.72$		$c t_{obs.} > 2.99$				

TABLE 4  
AVERAGE AIR-VOID CHARACTERISTICS AND DURABILITY FACTORS FOR EACH LABORATORY MIX

Aggregate	Mix Designation	Durability Factor	Air Content as Measured on Fresh Concrete	Air-Void Characteristics of Hardened Concrete				
				Air Content, A (%)	Voides per inch, n	Specific Surface, a (sq in./cu in.)	Voides per Unit Volume, N (voids/cu in.)	Spacing Factor, L (in.)
A <sub>1</sub>	33-A2	99	4.3	4.7	8.3	700	146,000	0.0070
	33-A3	40	3.8	3.3	3.7	450	26,000	0.0131
A <sub>2</sub>	33-B1	70	3.6	3.9	6.8	700	118,000	0.0077
	33-B2	84	4.7	4.5	8.1	720	149,000	0.0070
	33-B3	23	3.0	3.5	3.9	450	28,000	0.0127
A <sub>3</sub>	33-C1	94	4.4	4.1	6.8	670	106,000	0.0079
	33-C3	78	3.8	3.4	4.5	540	47,000	0.0107
A <sub>4</sub>	34-2	74	4.4	4.7	7.7	660	117,000	0.0075
	34-3	70	3.5	3.1	4.5	590	58,000	0.0104
	34-4	30	3.3	3.5	3.4	390	18,000	0.0144
A <sub>5</sub>	SA-1	90	3.4	4.0	6.3	640	92,000	0.0084
	SA-2	94	4.7	4.8	9.3	780	195,000	0.0063
	SA-3	91	3.7	4.3	7.1	670	110,000	0.0078
A <sub>6</sub>	SB-1	96	9.9	10.1	21.4	850	541,000	0.0042
	SB-2	85	6.2	5.5	11.1	810	257,000	0.0057
	SB-3	51	3.9	3.8	5.0	530	49,000	0.0104
	SB-4	57	4.9	4.5	8.5	750	170,000	0.0067
	SB-5	82	7.5	6.3	12.8	820	302,000	0.0053
A <sub>7</sub>	37-1	100	3.9	3.7	6.0	640	88,000	0.0085

TABLE 5  
SUMMARY OF STUDY OF LINEAR CORRELATION BETWEEN DURABILITY AND AIR-VOID CHARACTERISTICS  
AVERAGE VALUES FOR EACH MIX

Air-Void Characteristic	$\bar{Y}$	$\bar{X}$	Slope (b)	Regression Line Y on X	Correlation Coefficient (r)	$t_{obs.} = \frac{r}{\sqrt{\frac{n-2}{1-r^2}}}$	Significance	Variation Explained by Regression Line (%)
Air content, A (%)	74.1	4.51	6.202	$Y = 46.1 + 6.20X$	0.4134	1.87	a	17.09
Number of voids per inch, n	74.1	7.64	2.903	$Y = 51.9 + 2.90X$	0.5138	2.47	c	26.40
Specific surface, a (sq in./cu in.)	74.1	650.5	0.1338	$Y = -12.9 + 0.134X$	0.7560	4.62	e	55.66
Voides per unit volume, N (thousands of voids per cu in.)	74.1	137.7	0.0940	$Y = 61.2 + 0.094X$	0.4952	2.35	b	24.53
Spacing factor, L (0.0001 in.)	74.1	85.1	0.6641	$Y = 130.6 - 0.664X$	0.7792	5.13	e	60.72
Note: Y = Durability factor		X = Air-void characteristic						
$t_{0.95} = 1.74$		$t_{0.975} = 2.11$		$t_{0.9875} = 2.46$		$t_{0.995} = 2.90$		
$a t_{obs.} > 1.74$		$b t_{obs.} > 2.11$		$c t_{obs.} > 2.46$		$d t_{obs.} > 2.90$		
						$e t_{obs.} > 3.22$		

of deleterious particles in the beams result in variations in durability.

Table 3 shows that 44 percent of the variation in durability can be attributed to differences in spacing factor based on the data for individual beams while Table 5 shows a corresponding value of 61 percent using average values for each mix. In Figure 6 durability factor is plotted against spacing factor using the mix values. Comparison with Figure 5 shows considerable reduction in scatter when mix values are used.

Although there may be a better way to express the size and distribution of the air voids in portland cement paste than the spacing factor used in this study, the results of the correlation studies emphasize the importance of size and distribution in producing frost-resistant concrete.

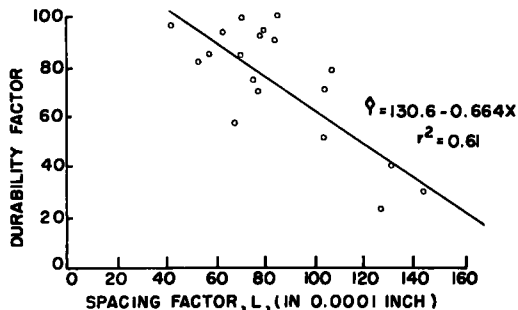


Figure 6. Scatter diagram for durability factor versus spacing factor, average values for mixes.

### SUMMARY OF RESULTS

The results of the work completed in this investigation may be summarized as follows:

1. The current theoretical explanations of the action of entrained air in producing frost-resistant concrete show the importance of the size and distribution of the air voids. The correlation studies of the relationship between each of the air-void characteristics and durability show the spacing factor to be most highly correlated with durability factor. Using the data on individual beams, 44 percent of the differences in durability can be explained by the differences in the spacing factor. Using average values for each mix, 61 percent of the differences in durability can be explained by differences in the spacing factor. Thus, the results of this investigation are in agreement with the current theories.

2. The specific surface is almost as highly correlated with durability as the spacing factor with 41 percent of the variation in durability being explained by the differences in the specific surface when the data on the individual beams are used. Using average values for each mix 56 percent of the variation in durability can be explained by differences in the specific surface.

3. The five air-void characteristics ranked in the order of their correlation with durability beginning with the one showing the best correlation are (a) spacing factor, (b) specific surface, (c) number of voids per inch, (d) hypothetical number of voids per cubic inch, and (e) total air content.

4. Since the specific surface is almost as highly correlated with durability factor as the void spacing factor, either of these two characteristics is probably a satisfactory guide for determining the air requirements for frost-resistant concrete. The correlation between each of these two characteristics and durability was found to be significant at the 99.75 percent confidence level.

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## Appendix

### FORMULAS FOR COMPUTATION OF AIR-VOID CHARACTERISTICS

The air-void characteristics which were investigated for correlation with durability were:

- A = air content, total volume of voids per unit volume of concrete, percent,  
 n = number of voids intersected per unit length of traverse, voids per inch,  
 $\alpha$  = the specific surface of the air voids, the surface area of the voids per unit volume of air, square inches per cubic inch,  
 N = number of hypothetical spheres all having the same radius  $r_h$  that would give a

volume of air equal to the actual air content of the concrete, voids per cubic inch, and

L = spacing factor, distance from void boundary to outer boundary of sphere of influence, inches.

Two of the characteristics, A and n, were measured directly with the linear traverse integrator shown in Figure 7. The remaining three were computed from these two measurements with the paste content being introduced in the computation of the spacing factor.

The equations that were used for the computation of  $\alpha$ , N, and L were presented along with their development in the paper "The Air Requirement of Frost-Resistant Concrete" by T. C. Powers (12) and a discussion of the same paper by T. F. Willis (16).

T. F. Willis (16) showed that regardless of the size distribution of the voids the true specific surface of the voids is given by the equation:

$$\alpha = \frac{4n}{A} \quad (\text{Eq. 1})$$

N and L are obtained by assuming that the voids are equal size spheres with the size determined by the specific surface. Powers (12) and Willis (16) show that the radius  $r_h$  of this hypothetical sphere is equal to  $\frac{3}{\alpha}$ . This hypothetical number of spheres, N, may be computed from the following formula:

$$N = \frac{A \alpha^3}{36 \pi} \quad (\text{Eq. 2})$$

To compute the spacing factor for the hypothetical void system, each sphere is considered to be at the center of a cube with the sum of the volumes of all such cubes and the enclosed spheres equaling the combined air and paste content of the concrete. The "sphere of influence" of each void is the radius of the sphere circumscribing the hypothetical cube. The spheres will overlap except at the corners of the cubes. The radius of the sphere of influence is equal to one-half the diagonal of the cube.

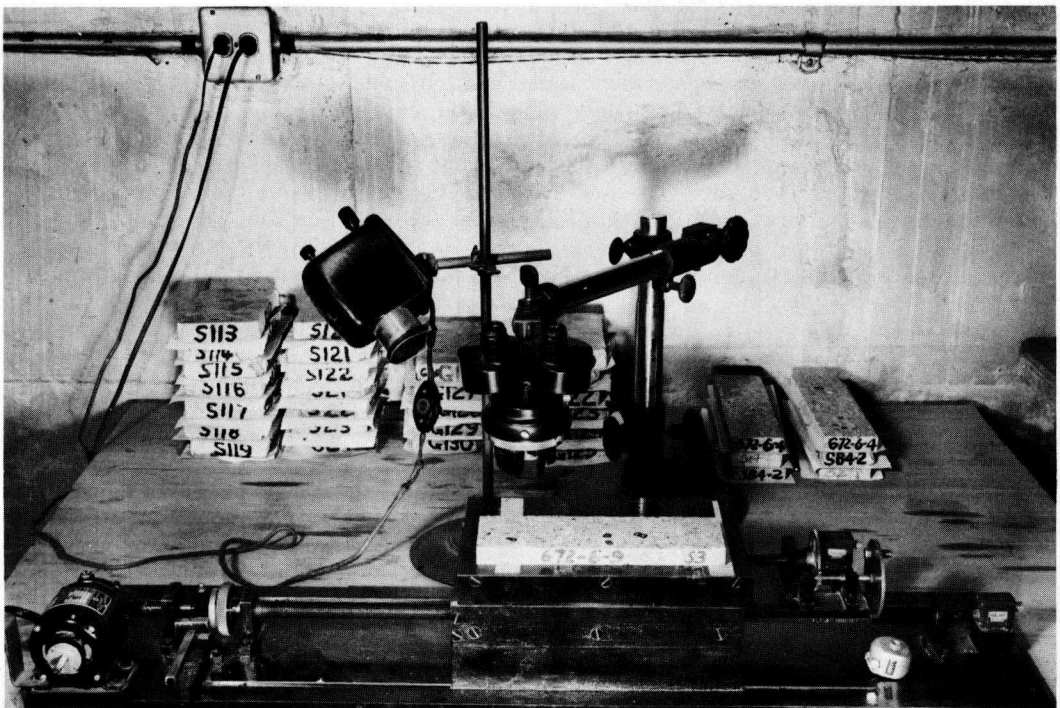


Figure 7. Linear Traverse Integrator.

The volume of the single hypothetical cube is  $\frac{p + A}{N}$  where  $p$  = paste content (sum of volumes of water and cement per unit volume of concrete). Hence, the length of one edge of the hypothetical cube is  $\frac{(p + A)^{1/3}}{(N)}$ .

And,

$$r_m = \frac{\sqrt{3}}{2} \frac{(p + A)^{1/3}}{(N)} \quad (\text{Eq. 3})$$

where  $r_m$  = radius of circumscribed sphere, the "sphere of influence."

The spacing factor  $L$  is equal to the difference between the radius of the sphere of influence  $r_m$  and the radius of the sphere  $r_h$ : that is,

$$L = r_m - r_h \quad (\text{Eq. 4})$$

### STUDY OF POSITION AND LENGTH OF TRAVERSE

The Rosiwal method of determining the percentage by volume of the constituents of a solid requires that a random line be passed through the solid. This principle is applied to a sample of concrete by first exposing a random section and then running a random traverse line in the plane of the section. In the actual application to a given beam the four surfaces of the beam are considered to have been randomly selected with respect to the concrete mix from which the beam was made.

In order to determine the effect, if any, of the position of the traverse within the beam an investigation of the variability of the air content and number of voids per inch within the beam was made. Also, the effect of the length of traverse on the reliability of the measurements was studied. For this investigation two beams from a concrete mix containing a durable coarse aggregate were selected for examination. Each of these beams had withstood 800 cycles of freezing and thawing without any loss in dynamic modulus of elasticity.

The original beam dimensions were 3 x 4 x 16 in. Three inches were removed from each end of the beams by sawing. Then three cuts were made longitudinally through the 3-in. dimension so that four slabs approximately  $\frac{3}{4}$ -in. thick were produced from each beam. Three surfaces from each beam were polished for examination by the linear traverse integrator. The three surfaces selected for examination were those which could be considered to represent three vertical planes spaced through the beam at approximately 1-in. intervals. These planes are designated 1', 2', and 3' in Figure 8.

To study the effect of using traverses of different lengths, determinations of the air content were made using traverses of four different lengths. Four equally spaced traverses were measured on each polished surface. Thus the twelve traverses in each beam could be considered to fall within either three vertical or four horizontal planes as shown in Figure 8.

An estimate of the air content of each beam was made using the first 4 in. of each

traverse starting at the right edge and moving the beam to the right. Estimates were then made using the first 6 in. of each traverse. Then the first 8 in. of each traverse were used. Finally all 10 in. of each traverse were examined. The estimates for each traverse are given in Table 6.

#### Statistical Analysis

The statistical procedure known as the "analysis of variance" (8) for testing for significant differences among two or more means was followed to determine if the measured air content is influenced by the position of the traverses with respect to

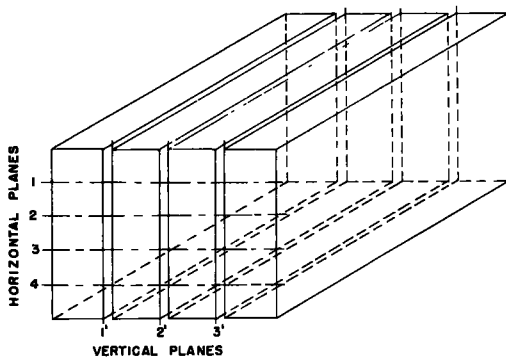


Figure 8. Position of traverses with respect to horizontal and vertical planes in beam.



horizontal or vertical planes within the beam. The results of this method of analysis are usually presented in an analysis-of-variance table such as Table 7. The F ratio is used to test for significance. It is formed in this case by taking the mean square found on the line whose effect is being tested and dividing by the mean square of the next lower subgroup in the sampling procedure. If this ratio is less than the F ratio at some chosen level of significance based on the Fisher variance ratio probability law, then it may be concluded that the particular factor being tested is not significant. The F ratios for a significance level of 5 percent are  $F_{0.95}(6, 16) = 2.74$  for horizontal planes and  $F_{0.95}(4, 18) = 2.93$  for vertical planes. Table 7 shows an F ratio of 0.83 for horizontal planes and an F ratio of 1.67 for vertical planes. Similar results were obtained in the study of the variability of the number of voids per inch. Hence, it may be concluded that air content and number of voids per inch may be determined without regard to the horizontal or vertical planes within which the traverses may fall.

A 90 percent confidence level for determining the air content of an individual beam within  $\pm 0.5$  percent of the true air content was selected. Table 8 presents the results of the study of the effect of the length of the individual traverse on the confidence limits for the mean air content. The standard error of the mean is shown to decrease as the length of the traverse is increased with the total number of traverses remaining the same. When the standard error of the mean is computed on the basis of a total of 120 in. of traverses, it is approximately 0.3 for traverses of all lengths. Very similar results were obtained for the number of voids per inch. Therefore, the total length of the traverses determines the confidence limits for the air content and number of voids per inch rather than the length of an individual traverse.

The individual traverses examined in the measurement of the air content and number of voids per inch of a beam may be considered as one long traverse. Table 8 shows that the length of this traverse should be approximately 135 in. to give the air content of a beam of the type studied within  $\pm 0.5$  percent of the true air content. In order to allow for some increase in variability when examining concrete from other mixes, 100 in. of traverses on each of two surfaces (200 in. total) were selected as

TABLE 6  
AIR CONTENT ESTIMATES (PERCENT)—INDIVIDUAL TRAVERSES OF DIFFERENT LENGTHS

Length of Traverses (in.)	Horizontal Planes	Beam I			Beam II		
		Vertical Planes			Vertical Planes		
		1'	2'	3'	1'	2'	3'
Four	1	3.47	2.68	7.50	6.17	4.03	3.22
	2	0.99	2.50	3.23	2.98	0.74	5.00
	3	0.75	2.99	3.46	3.70	1.27	1.76
	4	2.98	2.99	2.50	5.94	2.75	2.75
Six	1	3.17	2.32	6.25	5.47	4.13	3.65
	2	1.83	4.29	2.64	2.48	0.83	3.81
	3	1.17	3.17	3.82	3.50	2.15	2.32
	4	4.13	3.01	2.00	4.29	3.17	3.65
Eight	1	3.99	2.59	5.59	4.76	3.75	4.23
	2	2.25	3.94	3.26	2.74	2.99	5.90
	3	1.62	2.74	3.39	3.27	2.13	2.13
	4	4.35	2.62	3.91	5.47	3.75	3.75
Ten	1	4.10	2.63	6.64	4.38	3.71	3.66
	2	2.20	3.47	3.45	2.80	3.00	5.47
	3	3.00	2.66	3.29	2.98	1.85	3.90
	4	5.19	2.51	3.86	4.73	3.29	3.68

TABLE 7  
ANALYSIS OF VARIANCE—AIR CONTENT (PERCENT)

Planes	Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Ratio
Horizontal	Beams	0.0084	1	0.0084	0.01
	Pl. in Bm.	6.5401	6	1.0900	0.83
	Tr. in Pl.	21.0441	16	1.3153	
	Total	27.5926	23		
Vertical	Beams	0.0084	1	0.0084	0.00
	Pl. in Bm.	7.4788	4	1.8697	1.67
	Tr. in Pl.	20.1054	18	1.1170	
	Total	27.5926	23		
$F_{0.95}(4, 18) = 2.93$		$F_{0.95}(6, 16) = 2.74$			

TABLE 8  
CONFIDENCE LIMITS FOR AIR CONTENT (PERCENT)—TRAVERSES OF DIFFERENT LENGTHS

Length of Traverses (in.)	Error Mean Square	Std Error of Mean $S_{\bar{x}}$	Confidence Limits for Beam (90% confidence level)		$S_{\bar{x}}$ for 120 inches of Traverses	Total Length of Traverses Required for 90 Percent Confidence Intervals To Be 1 Percent Long (in.)
			Beam I	Beam II		
			Four	2.861		
Six	1.649	0.371	3.15 $\pm$ 0.63	3.29 $\pm$ 0.63	0.287	120
Eight	1.304	0.330	3.35 $\pm$ 0.56	3.74 $\pm$ 0.56	0.295	124
Ten	1.254	0.323	3.58 $\pm$ 0.55	3.62 $\pm$ 0.55	0.323	150
					Average 0.303	Average 133

standard procedure for the measurements. Thus the results of the study of the position and length of the traverse substantiate the procedure followed by other investigators (5) for the measurement of air in hardened concrete.

# Chemical Characteristics of Some Carbonate Aggregate as Related to Durability of Concrete

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This report includes a summary of the results of the chemical study of carbonate rocks from several quarries in northeast Iowa which produced carbonate aggregate for highway pavement concrete.

Rock from one of the quarries has proven to be definitely unsatisfactory for use as aggregate and is being used as a comparative standard. Comparison is based on the three following phases of investigation:

1. Analysis for major constituents (chemical description of rock types).
2. Determination of the type and quantity of potentially reactive deleterious constituents contained in the aggregates.
3. Chemical analysis and study of aggregate taken from samples of affected concrete.

An investigation of the equilibria established between certain carbonate rocks and silica solutions at pH 12 is being carried out to determine what reactions take place.

● THE RESEARCH described in this report was carried on as part of a broader project sponsored by the Iowa State Highway Commission, the goal of which is the determination of causes of premature deterioration in pavement concrete made with carbonate aggregate and the development of standard laboratory procedures to aid in recognizing aggregates with potentially poor service records.

Standard tests for predicting durability of aggregate have been shown to be inadequate (25, 14), and test results on materials without demonstrated service records are in no way conclusive or definitive. There is a definite need for research to determine the properties of aggregate which influence its performance in concrete and for the development of standard procedures for determining the properties which are important in this respect.

This particular investigation is based on the assumption that aggregate may be involved in deleterious chemical activity which accompanies normal aging and produces stresses in concrete. The influence of the aggregate material may be manifested in two distinct ways: (1) it may contain "active" substances which are available for subsequent slow reaction with the cement paste; (2) the aggregate particles may function as mere physical "centers" of reaction, leading to localization of activity and resultant weak spots. Physical characteristics of the material such as porosity and permeability are no doubt of prime importance in the latter case.

A considerable amount of literature concerning the possible types of chemical activity that might be initiated by constituents present in concrete aggregate has been published in the journals and in laboratory reports of highway commissions. Of those examined, only a relatively few deal with carbonate aggregate and none has been found which is concerned specifically with the quantity of chemical substances which is contained in the aggregate and actually "available" for reaction in concrete. Certain deleterious chemical substances are recognized in aggregates of other rock types and their role in promoting deterioration has been studied rather carefully. Since the presence of these same substances in limestone aggregate would lead to similar types of stress, their effects will be briefly reviewed.

Most published discussions of deleterious chemical substances in concrete emphasize the effects of excess sulfate ion and of free silica. Although gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

is added to portland cement as a retarding agent and in this capacity is both desirable and necessary, excess sulfate introduced with aggregate or by some outside source is definitely deleterious (13, 15, 19). Free or "reactive" silica is another undesirable constituent which may be introduced with the aggregate. Silica in certain forms is known to react with caustic from the cement and produce siliceous gels or sols which are believed to be a major cause of stress. This type of activity is commonly referred to in the literature as the "alkali-aggregate reaction" and extensive studies have been carried out to determine the exact nature of the reaction itself and the mechanism of the stress caused by the reaction products (3, 5, 7, 8, 17, 23, 26). Although the various papers pertaining to the alkali-aggregate reaction represent an impressive body of research, the exact mechanisms of the process have by no means been fully worked out. It is generally agreed, however, that certain forms of reactive silica definitely contribute to chemical activity which results in physical stress.

Another undesirable substance which may be introduced with carbonate aggregate and which may be involved in chemical activity is clay. Although the clay minerals are not chemically active constituents in the same sense as are the sulfate ion and silica, it has been postulated that clay particles may promote deterioration either by functioning as centers of activity or by swelling and movement of the clay particles themselves. It is reasonable to assume that a clay particle, which retains water and has available certain exchangeable cations, may contribute to or enhance chemical activity in concrete. Clay is not an uncommon constituent of limestone. Grim's analysis of 35 Paleozoic limestones from Illinois showed illite in all of them (6).

There are a number of other chemical substances which are not commonly present in aggregate in appreciable quantities but have been shown to be deleterious to concrete when introduced from some outside source (22). Among these are sodium and calcium chloride and numerous salts present in sea water.

### INVESTIGATION

The data used as the basis for the discussion in the first two divisions of this section (that is, Phase 1 and Phase 2) are taken mainly from an unpublished thesis (2) and have been supplemented by analyses run since the thesis was written. Carbonate rocks of Devonian age were sampled from five quarries on a bed by bed basis (12). The values reported in Tables 1 and 2 are averages arrived at by analysis of composite samples which were prepared by mixing powdered portions of each sample in proportion to their relative thickness in the formation member. The figures were since checked against values arrived at by averaging the results of analyses run on each lithologic unit (bed) of the same members. The differences in resultant values were not significant.

The Rapid member of Glory Quarry, now abandoned, has a notorious service

TABLE 1  
ANALYSES FOR MAJOR CONSTITUENTS (PHASE 1)

Members and Approximate Thickness in Feet	Calcium (as CaCO <sub>3</sub> ) %	Magnesium (as MgCO <sub>3</sub> ) %	Insoluble Residue %	Fe %
Glory Quarry				
Lower Rapid (19)	63.5	20.5	13.75	0.25
Upper Rapid (14)	54.0	20.0	16.16	0.28
Coralville (7)	90.5	5.5	2.86	0.08
Newton Quarry				
Total Rapid (28)	65.0	29.0	4.26	0.16
Coralville (20)	73.0	21.5	4.05	0.11
Burton Ave. Quarry				
Solon (31)	88.8	5.0	5.04	0.15
Lower Rapid (14)	58.5	22.5	16.45	0.22
Upper Rapid (22)	46.0	29.5	21.63	0.25
Coralville (12)	68.5	26.0	4.66	0.34
River Products Quarry				
Solon (22)	71.0	14.5	11.95	0.30
Total Rapid (13)	75.0	12.5	8.90	0.37
Coralville (42)	92.0	3.0	1.96	0.13
Pints Quarry				
Total Rapid (23)	56.0	27.5	5.45	0.13
Coralville (24)	75.0	23.0	1.44	0.19
Coralville <sup>a</sup> (24)	71.0	26.5	1.60	0.17

<sup>a</sup> Weathered

TABLE 2  
CONSTITUENTS EXTRACTED (PHASE 2)

Members and Approximate Thickness in Feet	Base Reacted %	SiO <sub>2</sub> Extracted (mg/100 gms)	Gypsum Extracted %
Glory Quarry			
Lower Rapid (19)	50	38.6	0.10
Upper Rapid (14)	72	49.0	0.25
Coralville (7)	22	9.7	0.02
Newton Quarry			
Total Rapid (28)	40	20.1	0.05
Coralville (20)	33	20.4	0.04
Burton Ave. Quarry			
Solon (31)	28	14.7	0.02
Lower Rapid (14)	64	52.0	0.14
Upper Rapid (22)	61	41.2	0.14
Coralville (12)	98	36.8	0.14
River Products Quarry			
Solon (22)	98	45.0	N. D. <sup>a</sup>
Total Rapid (13)	98	39.2	0.16
Coralville (42)	22	16.0	0.05
Pints Quarry			
Total Rapid (23)	32	28.9	Trace
Coralville (24)	28	9.8	Trace
Coralville <sup>b</sup> (24)	96	18.3	N. D.

<sup>a</sup> Non detected.

<sup>b</sup> Weathered.

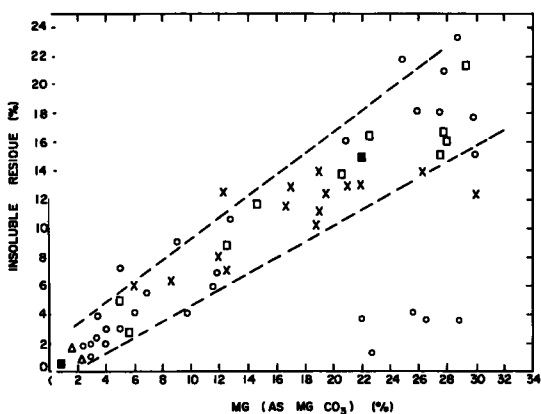


Figure 1. Relationship of insoluble residue and magnesium content. Data from Bisque (2) (composite samples of formation members) and results of analyses of lithologic units from four different quarries (Phase 1).

residue. These results are used as a "chemical description" of each lithologic unit and their values used to compare lithologic units as to "purity" based on implied carbonate content (that is, carbonate itself is not determined directly).

Powdered samples are dissolved by heating in 3N HCl at 80 C for 30 minutes. The remaining insoluble portion is separated by filtration with suction on a medium sintered glass filtering crucible. The dry weight of this portion (dominantly  $\text{SiO}_2$ , and in some cases small amounts of pyrite and clay) is the reported insoluble residue. The filtrate is transferred, diluted to volume in a volumetric flask and aliquots taken for determination of calcium and magnesium via a volumetric method utilizing the complexometric properties of Versene (ethylene-diamine-tetraacetic acid). The principles of this procedure are described by Cheng et al. (4) in a brief publication.

In examining the data of analyses of samples from six quarries it was observed that a definite correlation exists between the amount of insoluble residue and the magnesium content. This relationship is shown in Figure 1. The results of analyses of limestones from the five main quarries being considered are averaged in Table 1, and will be referred to in subsequent passages.

In instances where it was desirable to determine the iron and aluminum content of certain limestones (see Phase 2, Clay), Versene was again employed. The procedure involves first the determination of the sum of aluminum and iron in one aliquot and then the determination of iron alone in another. Aluminum is calculated by difference. The total is determined by causing both aluminum and iron to react with a known amount of Versene by boiling at low pH and then determining the amount of excess reagent by back titrating with standard zinc solution. Dithizone (diphenylthiocarbazone) is used as an indicator and the zinc-Versene back-titration must be buffered at pH 4.4 in a 1-1 methanol-water mixture. If present in appreciable amounts, iron may then be determined in another aliquot by titration with Versene solution to a salicylic acid end point at pH 3.5 as described by Cheng et al. (4). Small amounts of iron are best determined colorimetrically.

The method is applicable in cases where the aluminum content is desired to within 10 percent relative error. Its relative simplicity as compared with tedious gravimetric procedures which are themselves susceptible to numerous sources of error, makes the procedure desirable for routine analyses of this sort where relative values (that is, comparison of rock A to rock B) are more important than highly accurate, absolute determinations. Publication of the details of this procedure utilizing Versene for the determination of Ca, Mg, Fe and Al in limestones is forthcoming from this laboratory.

record as concrete aggregate and is being studied as a comparative standard.

The investigation may be divided into three phases, each of which will be treated separately in the following order.

Phase 1. Routine analysis of each lithologic unit for its major constituents.

Phase 2. Determination of the type and quantity of potentially "available" deleterious chemical constituents (including clay) in the samples.

Phase 3. Investigation of "affected" concrete samples from highways which have been constructed with poor aggregate from known sources. Limestones from these same sources are also treated in Phases 1 and 2 of the investigation.

### Phase 1

The "major constituents" determined were calcium magnesium and insoluble

## Phase 2

Since the pH of water in equilibrium with portland cement concrete is in the range of 11-12, only those constituents which might leach or "extract" into a basic solution were considered available for reaction. Powdered rock samples (50 gm) were agitated with 450 ml of a dilute solution (0.008 M, pH 11.4) of sodium hydroxide for 12 hours in polyethylene bottles. The mixture was then allowed to settle and the liquid separated by filtration. An aliquot of the filtrate was titrated to determine the decrease in basicity and the remaining portion analyzed for leached substances. Ions detected in appreciable amounts were  $\text{Ca}^{++}$ ,  $\text{SO}_4^{--}$  and  $\text{SiO}_4^{--}$ .  $\text{Mg}^{++}$  and traces of  $\text{Cl}^-$  were also common.

**Sulfate.** Although gypsum or other sulfate minerals were not detected in thin-section analysis of the rocks subjected to this extraction, the quantity of sulfate found in the filtrates is worth noting (Table 2). This sulfate was very readily dissolved from the powdered rock and easily detectable amounts were leached by placing the powdered sample in a filter funnel and merely allowing several hundred milliliters of distilled water to pass on through. To then determine whether the sulfate is readily leached from aggregate-sized particles, the extraction was modified. Approximately 50 pieces of these particles were placed in a separatory funnel and saturated with the same weakly basic solution. By allowing the solution to escape slowly from below and replenishing the supply from another separatory funnel at a comparable rate, it was possible, in two days time, to extract from 40 to 60 percent of the total amount of sulfate which was extracted from the same sample in powdered form. The results indicate that the sulfate present is not "locked" in the aggregate and may be available for reaction in concrete. The source of sulfate is assumed to be disseminated gypsum (10).

Sulfate was determined by the standard method of precipitating with barium ion in acid solution.

**Silica.** Larger samples of powdered rock were extracted in the manner described and the quantity of leached silica in the filtrate determined by the standard double dehydration procedure after removal of the dissolved sulfate by slow precipitation with barium. The amount of silica found correlated with the decrease in basicity is shown in Figure 2. When blanks were run it was found that a small amount of base "reacted" with reagent grade calcium carbonate or with powdered calcite rhombs. This amounted to 0.44 milliequivalents of the available 3.60 milliequivalents of base (that is, 450 ml of 0.008N NaOH) and is attributed to the complex equilibria involved in the hydrolysis of the carbonate ion.

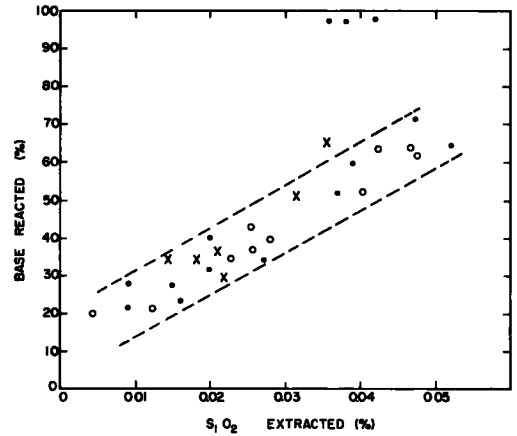


Figure 2. Relationship of the quantity of silica extracted to the amount of base reacted (Phase 2).

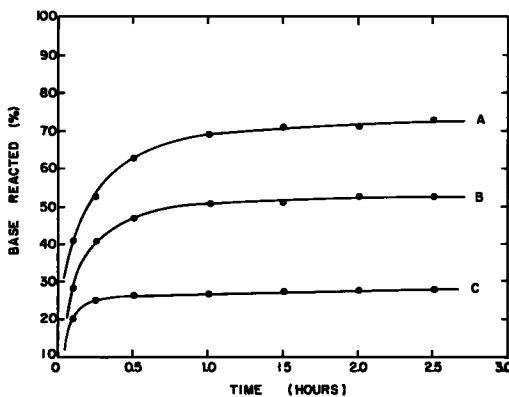


Figure 3. Rate of base reactivity for three samples from the Glory Quarry. Amount of base reacted after 12 hours; A, 76 percent; B, 54 percent; C, 29 percent.

Three interesting facts concerning this extraction procedure were noted. (1) The relatively rapid rate at which the base was consumed by those rocks which displayed base reactivity; 80 to 90 percent of the total amount which finally reacted had reacted in 30 minutes, Figure 3. (2) The

amount of silica extracted from samples of different lithologic units showed no relation to the abundance of chert nodules as observed in the respective units. (3) Finely powdered (passing No. 100 sieve) chert nodules taken from the limestone beds consumed considerably less base (1.0 meq of the available 3.6 Meq's) and yielded far less soluble silica than many of the limestone samples did.

These observations would support the postulation that the "available" or "reactive" silica extracted from the limestones is in some physical form distinct from that which it exhibits when aggregated to form chert. The concept of a reactive state of silica characterized by disrupted silicon to oxygen bonds and a general disorderly atomic arrangement which renders it more soluble is well recognized (21). Silica which is free to migrate or diffuse through carbonate rock must necessarily exist in some such physical state. The equilibria between soluble, amorphous and crystalline silica are little understood and the formation of authigenic silicates further complicates natural systems. For a recent publication concerning the dissolution and precipitation of silica at low temperatures the reader is referred to (9).

In connection with the discussion of reactive silica, another interesting fact was observed. This was a correlation between the amount of iron dissolved in Phase 1 and the amount of silica leached from the same rock in Phase 2 (Fig. 4). Since pyrite is insoluble in hydrochloric acid, the iron which was brought into solution via the procedure described in Phase 1 was assumed to originate from iron oxides present in the limestone. The correlation is at first puzzling but on further consideration is found to be compatible with the concepts reviewed in the following paragraph.

Conditions which tend to render silica mobile are conditions which would stabilize or "fix" dissolved iron as the oxide. Conversely, conditions which would mobilize iron would permit minimum activity of silica. These facts are borne out by numerous geologic processes such as laterization (18), residual concentration of iron (1), and the chemical nature of the elements themselves. Hence in the case of a rock whose recent history involved conditions which resulted in silica activity, and an increased proportion of reactive silica, stabilization and retention of any iron entering the environment in solution would occur. The observed correlation is at least harmonious with basic principles that are manifested in geologic processes.

**Clay.** A considerable amount of effort was expended in developing a suitable method for the separation and concentration of the clay fraction with a minimum amount of "damage" to the clay structure. A relatively simple and very satisfactory separation was effected as follows.

Fifty grams of finely powdered rock (passing No. 100 sieve), 50 ml of dispersing agent,<sup>1</sup> and several hundred ml of distilled water were agitated for five minutes in a mechanical laboratory stirrer. This suspension was then transferred into a 1,000 ml graduated cylinder and more water added. The system was again thoroughly agitated with a mixing plunger and allowed to stand for 7 hours at room temperature. A 50 ml aliquot was then taken at a depth of about 5 cm and placed in a centrifuge bottle. The aliquot was centrifuged for 15 minutes at 2,500 rpm and the supernatant decanted, leaving a heavy slurry clinging to the bottom of the bottle. Ten ml of distilled water were added and the slurry stirred into suspension. Exactly 4 ml of the resulting suspension were drained onto a 25 by 46 mm glass slide which was previously placed in an oven pre-heated to 60 C. After several hours the dry slide is found to be covered with a uniform coating suitable for X-ray diffractometer investigation.

The only clay type found in appreciable amounts was illite. Sixty percent of the rock from the Rapid member at the Glory Quarry which averaged 15 percent insoluble residue, contained appreciable amounts of the clay mineral. No trace of illite was found in the entire section of Mississippian rock exposed at the Alden Quarry which averages less than 1 percent insoluble residue. Alden Quarry aggregate has an exceptionally good service record (20). The Rapid member at Pints Quarry (average insoluble residue, 5 percent) contained appreciable illite whereas the overlying Coralville member (average insoluble residue, 1.5 percent) showed no trace of the mineral.

<sup>1</sup> Prepared by dissolving 40 gm of sodium meta silicate,  $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$ , and 7 gm sodium carbonate,  $\text{Na}_2\text{CO}_3$  in water and diluting the solution to one liter.

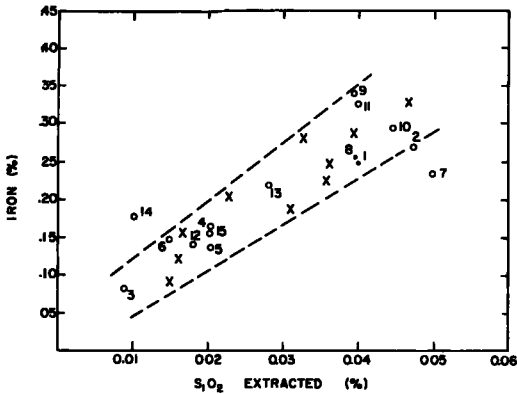


Figure 4. Relationship of the percent of soluble iron (Phase 1) to the quantity of silica extracted (Phase 2).

The Solon member at the Burton Ave. Quarry (average insoluble residue, 5 percent) showed only a trace of illite whereas the overlying Rapid member (average insoluble residue, 18 percent) yielded slides which gave excellent, intense diffraction patterns of the mineral. The Coralville member in this quarry (average insoluble residue, 4.5 percent) displayed less intense spectra via the same procedure. The diffraction patterns of the samples from the Rapid member in this quarry were so intense that the rate meter scale factor of the X-ray recorder (North American Phillips Co.) which was normally set at 4, had to be switched to 8 in order to record the intensity of the 10 angstrom reflection.

The X-ray diffraction pattern of a typical sample is shown in Figure 5 along with the diffraction pattern of a "clay mineral standard" from Fithian, Illinois.

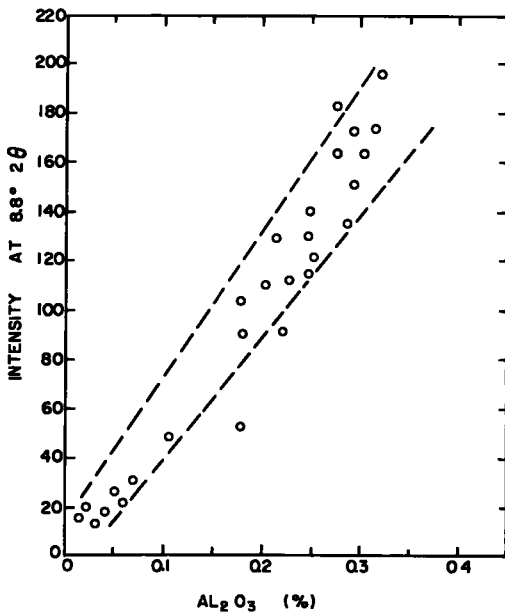


Figure 6. Intensity of 10 angstrom reflection from glass slides coated with illite separated from Burton Avenue samples (Phase 2) vs the quantity of aluminum found in the same rock (Phase 1).

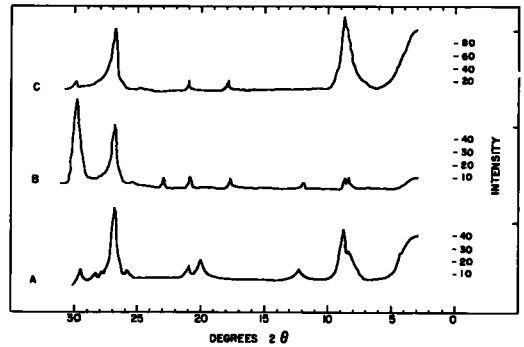


Figure 5. Relative intensity of major reflections of A, Fithian illite; B, Fithian illite-calcium carbonate mixture; and C, illite separated from a Burton Avenue Quarry sample (Phase 2).

A third diffraction pattern is included to show the effect of mixing the standard illite with calcium carbonate in a 1:1 ratio before depositing it on the glass slide in the manner previously described. The orientation of the clay particles has obviously been affected and the carbonate reflection at 29.45 deg 2  $\theta$  (dA, 3.03;  $\theta$ , 14.73 deg; hkl, 104) is very prominent. By comparing the intensity of this carbonate reflection in this diffraction pattern with the same reflection in the diffraction pattern of illite from a Burton Ave. sample it can be seen that an excellent separation has been effected. Glycolation caused no noticeable expansion of the illites separated from any of the samples being investigated.

To observe how the amount of dissolved aluminum (Phase 1) compares with the intensity of the illite diffraction pattern from the same rock (Phase 2), the samples from Burton Ave. Quarry were analyzed for aluminum via the method previously described, and these values plotted vs the recorded intensity of the clay pattern at 8.8 deg 2  $\theta$  (dA, 9.9 deg;  $\theta$ , 4.4 deg; hkl, 001). The resulting relationship shown in Figure 6 would imply



**TABLE 3**  
**ANALYSES OF AGGREGATE FROM SAMPLES OF AFFECTED CONCRETE**  
**(PHASE 3)**

Aggregate with No Visible Reaction Rims			Aggregate with Less Pronounced Reaction Rims			Aggregate with Pronounced Reaction Rims		
Insoluble Residue (%)	CaCO <sub>3</sub> (%)	MgCO <sub>3</sub> (%)	Insoluble Residue (%)	CaCO <sub>3</sub> (%)	MgCO <sub>3</sub> (%)	Insoluble Residue (%)	CaCO <sub>3</sub> (%)	MgCO <sub>3</sub> (%)
4.19	85.75	8.73	13.38	56.50	26.38	13.24	57.00	27.74
4.26	83.81	11.61	12.82	54.11	31.88	14.10	55.21	28.12
3.10	87.11	9.13	-	-	-	13.13	56.52	27.98

**TABLE 4**  
**ANALYSES OF REACTION RIM MATERIAL FROM AFFECTED CONCRETE (PHASE 3)**

Insoluble Residue (%)	CaCO <sub>3</sub> (%)	MgCO <sub>3</sub> (%)
A. 19.80	56.12	23.70
B. 17.41	61.00	23.85

that the illite is the main source of dissolved aluminum and that the quantity of illite separated, as indicated by the intensity of its basal reflection, is an approximate indication of the amount present in the rock. This plotted relationship would cease, however, when the optimum thickness of the illite layer on the glass slide was reached.

**Phase 3**

Considerable time was spent in examining the petrographic and chemical characteristics of the aggregate in affected concrete. Bulk samples of concrete were taken from the sites of highway repair in north-east Iowa. The sampled chunks were reduced to gravel size and examined for evidence of secondary deposits.

A white substance found lining small vesicles in the cement paste was removed by prying with a needle point. A portion of the quantity separated was analyzed by wet methods and the remainder subjected to spectrographic analysis. It was found to be almost pure calcium carbonate, the major impurity being magnesium. The migration of calcium carbonate in concrete is not uncommon (11). No evidence of silica gels as described in the literature (3, 15) was found. A few secondary deposits, presumably calcium sulfo aluminate, were found to contain sulfur. No visible effect of clay was expected to be observed, of course, but aggregate particles which had the chemical characteristics of limestone which frequently contains appreciable clay (that is, high insoluble residue and high magnesium content) were usually concentrated in the most highly affected areas, as judged by the relative amounts of secondary deposits.

Many of these same aggregate particles displayed marked zones or rims along their periphery adjacent to the cement paste. These zones were accentuated by their color, which varied from that of the host rock. A description of thin-section examinations of these zones is included in the accompanying report (12). In contrast to the aggregate particles with marked rim zones were those which were completely unaltered at their borders and still others which displayed less salient rim zones. These three aggregate "types," based on visible appearance of rims, were sampled and analyzed. Each sample contained at least 50 gms of carbonate rock from the unaffected, central portions of the aggregate type designated. No portion of the rim zone was included and no more than one gram was taken from a given aggregate particle. The results of these analyses are shown in Table 3. The aggregate which develops rims is consistently higher in insoluble residue and magnesium content than that which does not.

The rim zones were then sampled by tedious chipping and filing. Any cement paste which adhered to the outer margin of the rims was carefully filed away. The inner margin, however, was less abrupt (the unaffected aggregate-rim boundary) and portions

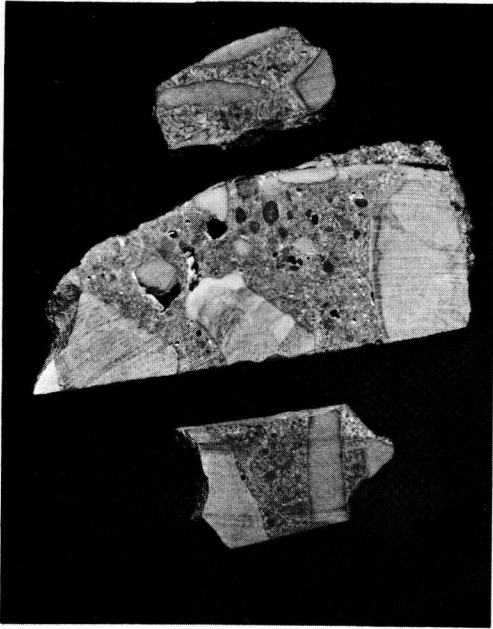


Figure 7. Section of a core taken from a distressed highway constructed with Glory aggregate. Note rims.

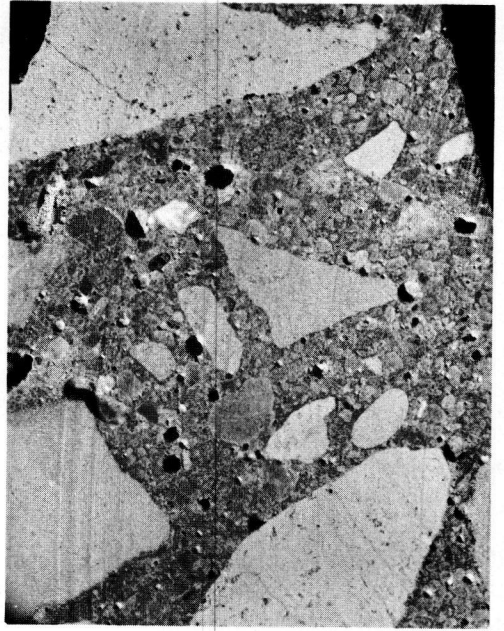


Figure 8. Section of a core taken from a sound highway. Compare with Figure 7.

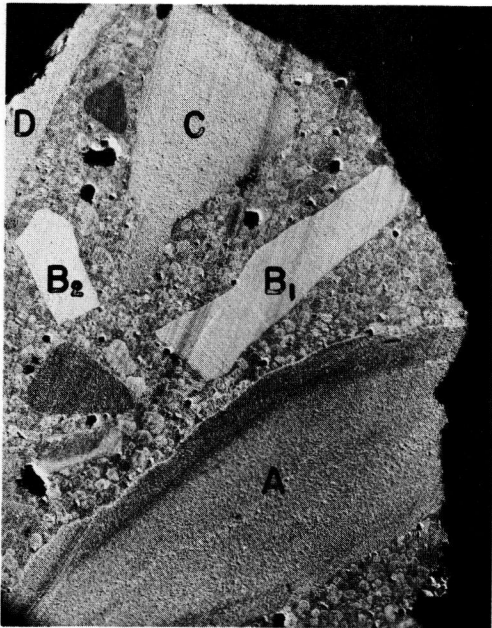


Figure 9. Surface of a piece of affected concrete. A, aggregate particle with rim. B<sub>1</sub> and B<sub>2</sub>, lithographic limestone. C and D non-lithographic carbonate rocks with no rims.



Figure 10. Acid etching readily attacks the pure limestones (B<sub>1</sub> and B<sub>2</sub> in Figure 9). Note that the aggregate-cement paste boundary of these particles is sharp.

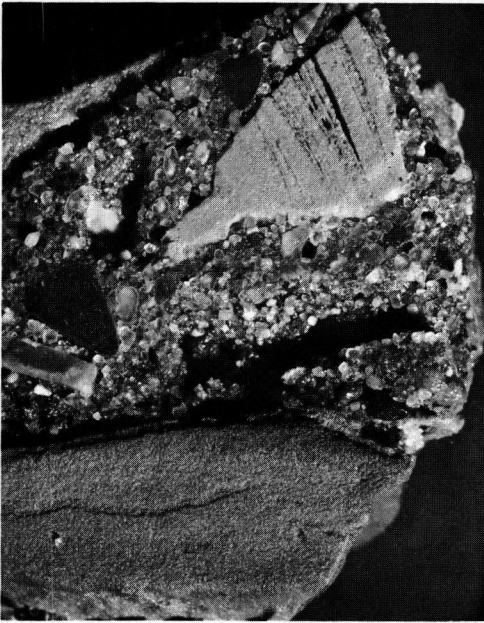


Figure 11. Further leaching has removed the lithographic particles. The boundary zone of particle A (Fig. 9) and the cement paste has already been attacked quite severely.



Figure 12. Advanced leaching has deeply entrenched the boundary zone of particle A and the cement paste while the rim stands in marked relief (see also Fig. 13).

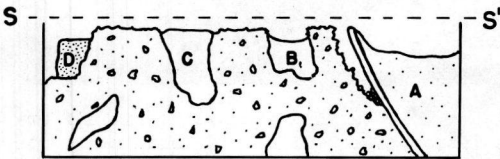
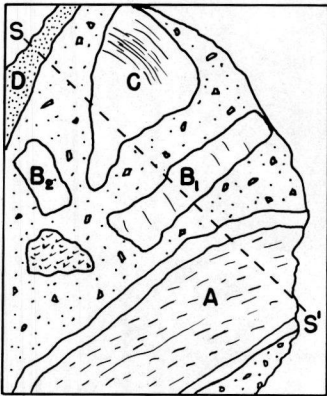


Figure 13. Sketch of cross-section through leached sample to demonstrate relative rates of solubility.

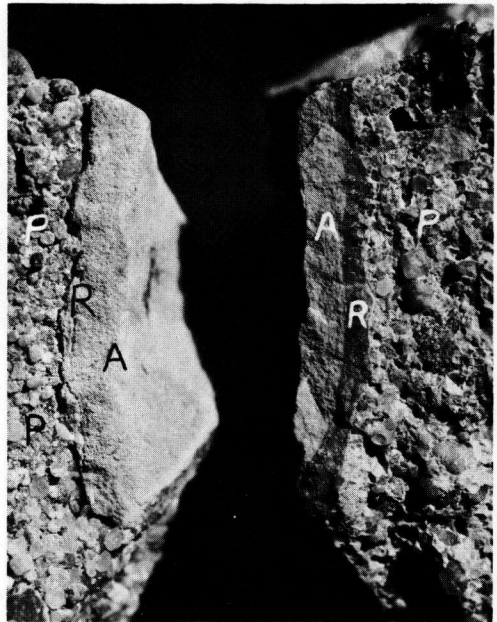


Figure 14. Two pieces of the same rimmed aggregate particle and adjacent cement paste. Before acid etching, right, and after slight etching, left. Note the readily attacked zone at the aggregate-paste boundary. A, unaffected aggregate; R, rim; P, cement paste.

of unaffected aggregate were not entirely removed in many instances. The analyses of two representative samples of rim material, 10 gms from at least 50 different pieces of aggregate A, and 5 gms from at least 30 different pieces of aggregate B, are included in Table 4. The rim zone shows a marked increase in insoluble residue and a decrease in magnesium content. The increase in insoluble residue was assumed to be due to an increase in  $\text{SiO}_2$  content since the rim zones could be accentuated in relief by etching the affected aggregate with  $\text{HCl}$ . A piece of rim material placed in hydrochloric acid, along with a piece of the unaffected host rock, usually dissolved much more slowly; and if agitation was prevented, a "spongy" skeletal structure retained its identity. In many cases these rim particles were buoyed to the top of the solution by entrapped bubbles.

The observed decrease in magnesium content has not yet been thoroughly substantiated as being consistent.

The differential solution of rim zones and host rock is quite striking, and is illustrated in Figures 9 to 12 and an accompanying sketch, Figure 13. Figures 9 to 12 are a sequence of photographs taken at intervals during the progressive hydrochloric acid leaching of a piece of affected concrete taken from a distressed highway containing Glory aggregate. Rock A is an impure, argillaceous stone typical of the Rapid member of the Glory Quarry which usually develop rims in affected concrete. Rocks  $B_1$  and  $B_2$  are light-colored, ultra-fine grained lithographic limestones; that is, high  $\text{CaCO}_3$  content, low  $\text{MgCO}_3$  and insoluble residue content. Their lithographic character is evidenced by their very rapid solution in hydrochloric acid (see Figs. 10 and 11). Rocks C and D are not lithographic in character, nor do they have the "dirty," argillaceous appearance, or characteristic, of Rock A and other rocks (see Fig. 7) which develop rims. The cross-section in Figure 13 was sketched to show the approximate relationships of the rate of solution of the different zones in the sample, and to demonstrate the fact that the cement paste adjacent to the rimmed aggregate is more readily attacked by the hydrochloric acid than is the paste adjacent to the unrimmed particles.

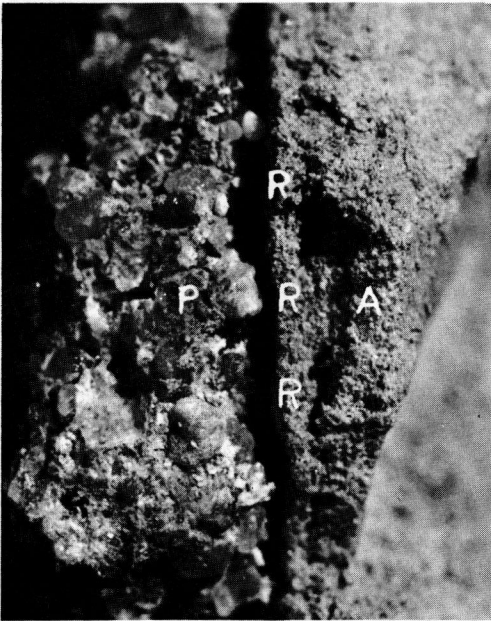


Figure 15. Close-up of a third piece of the same rimmed particle shown in Figure 14 after further acid leaching. A, unaffected aggregate; R, rim; P, cement paste. Note the marked differentiation of the rim zone.



Figure 16. Another example of rim differentiation after mild acid leaching. Note that in this case a more soluble zone occurs on the inner side of the rim. A, unaffected aggregate; R, rim; P, cement paste.

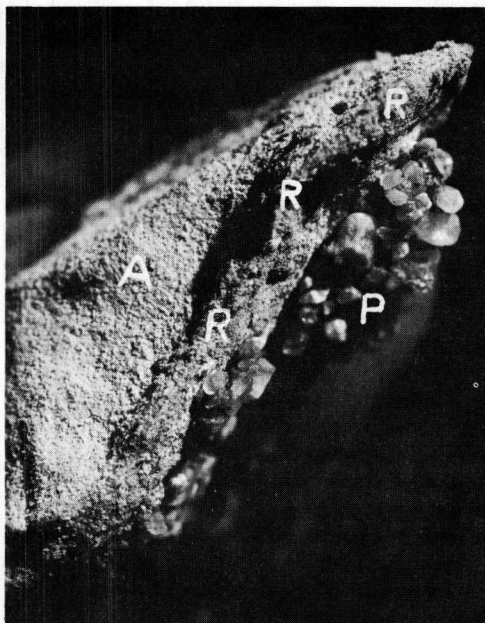


Figure 17. Rim zone accentuated by advanced leaching. A, unaffected aggregate; R, rim; P, cement paste.

In this instance a zone of increased solubility has formed on either side of the rim zone.

Advanced acid leaching of still another sample (Fig. 17) has left the rim zone standing high in relief, while the host aggregate and the cement paste have disintegrated at a much more rapid rate.

The pictures referred to in the preceding paragraphs show but a few examples of many such leachings which have been effected. The marked differences in the acid resistance of these zones leads the authors to the inescapable conclusion that chemical activity and accompanying transfer of material have occurred.

A concurrent study of the effective porosity and pore size distribution of potential aggregate rock is being conducted by Lemish et al. (12) of this laboratory. The device being used is a mercury capillary pressure apparatus manufactured by the Ruska Instrument Corporation, of Houston, Texas. The average effective porosity (that is,  $\frac{\text{volume of mercury injected}}{\text{bulk volume}} \times 100$ ) of the aggregate from the Rapid member in the Glory Quarry was 6.2 percent, while the average effective porosity of the rim zone material taken from aggregate of this type in affected concrete was only 0.2 percent.

TABLE 5  
ANALYSIS OF INSOLUBLE RESIDUES FOR  $\text{SiO}_2$

Insoluble Residue of Aggregate (%)	Insoluble Residue of Rim Material (%)	$\text{SiO}_2$ Content of Insoluble Residue (Aggregate) (%)	$\text{SiO}_2$ Content of Insoluble Residue (Rims) (%)
12.61	16.23	87.0	86.3
11.24	15.12	90.6	89.8
13.88	17.64	89.5	89.2

This same general relationship was readily apparent in a majority of the samples of affected concrete which were leached. It can be seen that while the lithographic limestone particles dissolve quite readily, the paste adjacent to them is relatively unaffected by the same degree of acid treatment. Likewise, the cement paste adjacent to particles "c" and "d," which have no rims, is less affected than the paste adjacent to the rimmed aggregate A.

Figure 14, which pictures two portions of the same rimmed aggregate particle, one of which has been leached with dilute hydrochloric acid and the other unleached, clearly shows the marked increase in acid attack at the aggregate-paste boundary. Figure 15 shows the result of continued leaching of a third portion of the same aggregate particle and the adjacent cement paste. The resistance of the rim zone to leaching is very apparent, and the increased susceptibility to acid attack of the zone at the aggregate-paste boundary is quite distinct.

In Figure 16, the acid leaching of another rimmed aggregate particle again demonstrates that the rim zone is distinct.

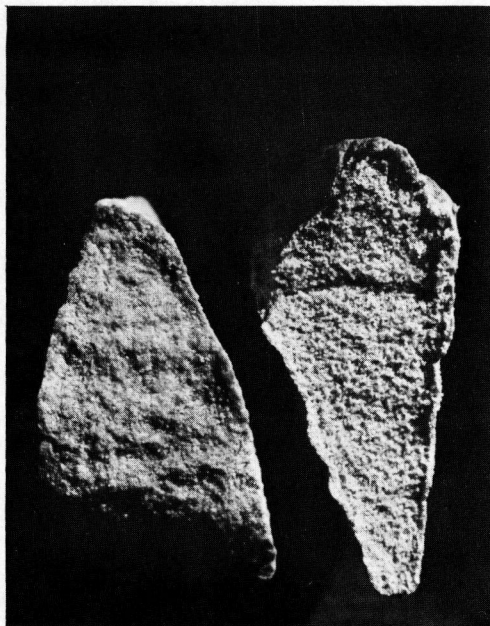


Figure 18. Two halves of a piece of Glory stone (Sample 4, Table 6) after 20 days in a 0.5 percent  $\text{SiO}_2$  solution at pH 12. The half on the right has been acid leached. Length of particle, 1 cm.

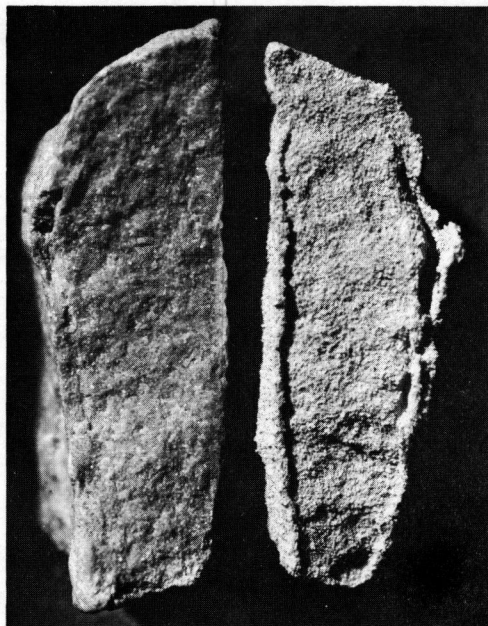


Figure 19. Two halves of a piece of Glory aggregate (Sample 3, Table 6) after 20 days in a 0.5 percent  $\text{SiO}_2$  solution at pH 12. The half on the right has been acid leached. Length of particle, 1.5 cm.

The rim material used in this determination was filed free of all host aggregate and cement paste. It was felt that filing the rim particles might affect the results of effective porosity measurements. A sample of limestone, reduced to comparable-sized chips, and filed to smoothness, was subjected to mercury injection and the results compared with those determined on the natural rock. It was found that the change in effective porosity due to filing was negligible.

When the first draft of this report was submitted to the Committee on Durability of Concrete—Chemical Aspects, at the Annual Meeting of the Highway Research Board (1958), the results of analyses shown in Table 4 were questioned, for two reasons: (a) representability of sampling; and (b) analyses of the insoluble residues for  $\text{SiO}_2$  were not reported.

Since that time, analyses of additional samples have been performed and the increase in insoluble residue content was found to have been accompanied by an increase in  $\text{SiO}_2$  content (Table 5). The  $\text{SiO}_2$  was determined by fusing the insoluble residues with sodium carbonate and utilizing the standard hydrochloric acid double dehydration procedure. Determination of calcium and magnesium in the rim zone was impossible in this case because the rim zone was separated from the affected cement paste by leaching with dilute hydrochloric acid. This, of course, resulted in the loss of carbonates from the rim zone. The siliceous, skeletal structure of the zone remained intact, however, and permitted a physical separation. It is true that some silica may have been leached from the rim zone by the dilute acid.

To further investigate the type of activity indicated by the foregoing observations, an entirely different approach was taken. This approach was based on the assumption that if certain carbonate rocks have a tendency to "react" with some form of soluble silica in a high pH environment, this tendency might be demonstrated in the laboratory.

TABLE 6  
ANALYSES OF GLORY STONES USED IN RIM EXPERIMENTS

Sample No.	CaCO <sub>3</sub> (%)	MgCO <sub>3</sub> (%)	Insoluble Residue (%)	FeO (%)	Al <sub>2</sub> O <sub>3</sub> (%)
3	66.8	19.6	10.6	0.28	0.48
4	62.3	21.7	13.4	0.46	0.38
5	63.3	19.8	14.2	0.33	0.44
6	61.7	22.6	13.1	0.34	0.17

It was observed that solutions of silica<sup>2</sup> in reaching equilibrium with carbonate rocks of the Rapid-type lithology became yellow-colored and the color increased with time. Duplicate samples of the same rock in sodium hydroxide solution at pH 12 gave no discoloration whatsoever in the same period of time. After two weeks several pieces of rock were removed from the silica solution, broken and examined under a petrographic microscope. Faint lines were observed along the periphery of the broken particles. These lines appeared slightly darker than the host rock, and were not present as a "skin" on the aggregate particles, but actually a few millimeters inside the surface. Samples of the same rock which had been in a sodium hydroxide solution at the same pH, for the same length of time, had not developed these visible lines.

As the rock particles began to dry out, the lines became more difficult to see. Etching with 3N hydrochloric acid resulted in differential solution which dramatically accentuated the narrow zones. See Figures 18 and 19, each of which show two halves of a broken particle. In both figures, the particle half on the right has been acid leached to accentuate the line which is not here visible in the unleached half. Figure 20 is a close-up of the leached surface in Figure 18.

The "ridge" which stands in relief after etching is generally wider than the faint line observed before etching. A thin layer of host rock is etched away from the outer boundary of the "ridge," making it appear as though the more insoluble zone extends to the very outer edge of the particle. When slow etching is observed under the microscope, however, it can be seen that a very thin "outer shell" has dissolved away. It has been suggested that this zone corresponds to the highly acid-soluble zone at the aggregate-cement paste boundary in affected concrete samples (see Fig. 13). It should be pointed out, however, that during acid leaching of affected concrete samples, this thin zone dissolves much more readily than the corresponding host aggregate particle.

Samples of several lithologic units from the Rapid member in the Glory Quarry (Table 6) were placed in both sodium silicate and sodium hydroxide solutions for a week. In each case, the solution containing silica became yellowed and the hydroxide solution remained perfectly clear. Since both solutions were at pH 12 throughout the experiment, and both contained sodium ion, it might be concluded that the silica in solution is responsible for the observed "activity" and the development of "rims" in the system.

The results obtained in two additional attempts to experimentally substantiate this postulation are worthy of mention.

<sup>2</sup>The silica solutions used in these investigations were prepared by dissolving 23.70 gms of sodium meta silicate, Na<sub>2</sub>SiO<sub>3</sub> · 9H<sub>2</sub>O, in one liter of distilled water. Such a solution contains 0.50 percent SiO<sub>2</sub> (by weight), or 0.50 gms SiO<sub>2</sub> in 100 ml, and is buffered at pH 12.

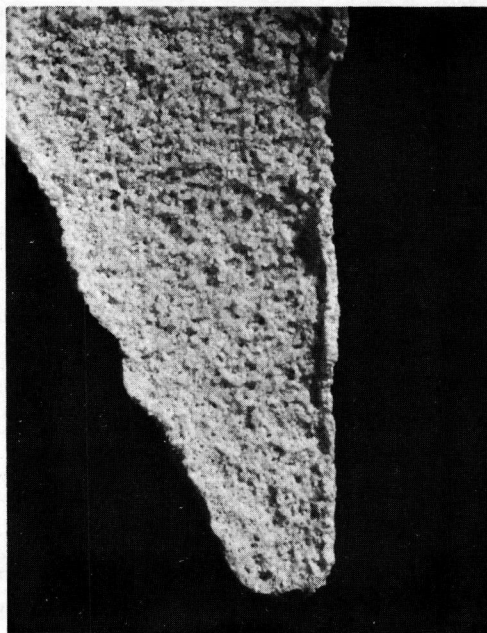


Figure 20. Close-up of leached particle shown in Figure 18.

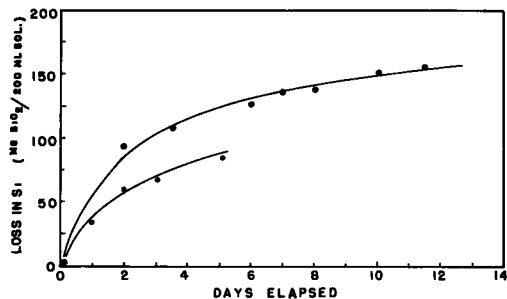


Figure 21. Decrease in  $\text{SiO}_2$  content of a silica solution (pH 12) in equilibrium with certain carbonate rocks. Glory No. 6, 7 points determined and Glory No. 5, 4 points determined. See Table 6.

equilibrium with the impure carbonate rock was definitely depleted, quite rapidly at first and then gradually slower (Fig. 21). Analyses of the solutions in the three blanks showed no appreciable decrease in silica nor did any of the solutions become discolored. The procedure was repeated using sample 5 (Fig. 21).

2. The development of a yellow color was considered quite interesting since the solubility of iron would be negligible at pH 12. It was observed that during the evaporation of acidified aliquots taken from the carbonate rock-silica solution systems, a brown flocculent precipitate formed before the silica began to separate. Some of the brown precipitate was collected on a filter paper and subjected to spectrographic analysis. It contained iron and aluminum with a trace of calcium, magnesium, and manganese. The introduction of iron and aluminum into the solution while silica is being depleted might lead one to suspect that clay is involved. The rock samples involved did contain illite.

Attempts to develop the color of the 1, 10-phenanthroline complex of ferrous iron (after reduction) in the silica solutions were unsuccessful, probably due to the formation of a silicate-iron complex in solution. To establish whether the amount of iron "entering" the silica solution is a function of the silica concentration, a series of samples was prepared as follows.

Exactly 30 gms of carbonate rock (Glory No. 3, passing No. 10 sieve retained on a No. 32 sieve) were placed in each of six volumetric flasks. Two solutions, one of sodium hydroxide, pH 12, and the other a silica solution, pH 12, were mixed in varying proportions to yield solutions of differing silica concentrations, sample 1 containing only sodium hydroxide, and sample 6 containing only silica solution. After two days, the yellow color was quite pronounced in all but sample 1, and increased in intensity with higher silica concentration. After three days, aliquots were taken from each solution, the silica removed by precipitation and dehydration, and the filtrates analyzed for iron via the standard thiocyanate colorimetric method. The amount of iron detected is plotted vs the amount of silica in solution (silica as percent by weight  $\text{SiO}_2$ ) in Figure 22. An identical series gave similar results after 7 days (B in Fig. 22). At the time of

1. Two hundred gms of Glory stone (sample 3, Table 6) of uniform size, passing a standard No. 6 sieve and retained on a No. 10 sieve, were placed in each of a series of seven bottles. Exactly 200 ml of silica solution was added to each sample. Two blanks were prepared by placing a quantity of pure, crushed calcite rhombs and pure, crushed dolomite rhombs in equilibrium with the same silica solution. A third blank was prepared to check the stability of the silica solution.

The silica concentration was determined at intervals by removing a 50 ml aliquot from a different bottle each time and analyzing for  $\text{SiO}_2$  gravimetrically.

The silica concentration in the solutions in

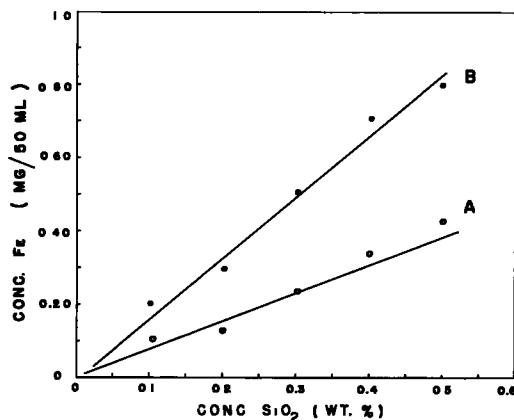


Figure 22. Increase in Fe concentration of solutions in equilibrium with carbonate rock (Glory No. 3) plotted vs the  $\text{SiO}_2$  concentration of the solution after 3 days, A, and after 7 days, B.



this report, similar determinations of the aluminum in solution have not been made. The results to date, however, definitely indicate that certain carbonate rocks are involved in "activity" with silica in a high pH environment. The pH of portland cement paste in equilibrium with distilled water is 12.

For an excellent review of the chemistry of the compounds in cement paste, the reader is referred to the review by H. H. Steinour (24), and the references contained therein. At the time of the first presentation of this report, the authors were criticized for suggesting that silica may be "mobilized" in a cement paste environment and finally, after migration, reside preferentially in aggregate particles. It should be stressed that the discussion in Mr. Steinour's review deals with the  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  system as such. In this case, the mobility of the silica is markedly decreased by any increase in lime concentration (24). The presence of alkali in cement paste, however, may function to free more silica. The solubility of  $\text{CaO} \cdot \text{SiO}_2 \cdot \text{aq}$  and similar compounds is not completely understood (24) and the many equilibria which are involved in a consideration of the chemical "activity" of cement paste render the situation more complicated. The fact that silica can be extracted from cement paste with water was demonstrated as follows.

Bars of hydrated portland cement paste supplied by Bert Myers, of the Iowa State Highway Commission, were reduced to chips by hammering. Three hundred grams of a given size fraction (passing No. 10 sieve, retained on No. 32 sieve) were placed in six polyethylene bottles, 50 gms in each and distilled water added. After several hours, the pH of the resulting solutions was 12. The bottles were stoppered and agitated for 12 hours. The agitation caused considerable abrasion and finer particles were formed. The solids were then separated by filtration and the filtrates combined for evaporation and analysis. The combined filtrates yielded 0.026 gms of  $\text{SiO}_2$ .

The authors feel that it is not impossible for silica originally contained in the cement paste to assume some migratable form enabling it to seek a site of greater stability. Furthermore, the results of the preliminary experiments reported herein are taken to indicate that certain types of carbonate rock, when present as aggregate in concrete, may afford such a site of greater stability.

Further quantitative studies of the observed phenomena are being continued, and more data will be presented in the future.

#### SUMMARY OF OBSERVATIONS

1. When present in the affected concrete samples which were examined, those carbonate rocks which contained clay, a high percentage of insoluble residue, and high magnesium content were characterized by marked reaction rims.
2. The reaction rims are not merely staining phenomena but are definitely the result of chemical activity and accompanying transfer of material.
3. Pure limestones (that is, carbonate rocks with low percentage of insoluble residue and high calcium content) do not develop reaction rims and appear to be relatively inert.
4. The fact that certain impure carbonate rocks in silica solution at pH 12 develop definite zones or rims of more insoluble material while silica is removed from solution and other ions introduced into the solution, may be taken to indicate that the rims in affected concrete are developed via a similar transfer.
5. The nature of the chemical activity postulated in the foregoing would imply that the physical characteristics of the aggregate, such as effective porosity and pore-size distribution, are critical and must be considered in an ultimate evaluation of potential aggregate.

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