FINAL REPORT

PROJECT HR-15 OF THE IOWA HIGHWAY RESEARCH BOARD
IOWA STATE HIGHWAY COMMISSION

BEHAVIOR OF CARBONATE ROCKS AS CONCRETE AGGREGATES

by

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Iowa State University
Ames, Iowa

June 1962

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CHAPTER I

INTRODUCTION

Research project HR-15, sponsored by the Iowa Highway Research Board through the Industrial Research Institute of Iowa State University, was undertaken to find out why certain carbonate aggregates caused distress in highway concrete. The two main objectives of the project were: 1) to understand how certain carbonate aggregates contribute to distress in concrete; and, 2) establish criteria for recognizing and classifying aggregates with potentially poor service records. The project has essentially been a study of the behavior of carbonate rocks as concrete aggregates.

The project has been under the direction of Dr. John Lemish and was conducted at the laboratories of the Geology Department at Iowa State University. The work was accomplished through the efforts of the following research assistants: Francis E. Rush; Ramon E. Bisque; Carl L. Hiltrop; Robert J. Harwood; Michael A. Werner; Frank E. Diebold; William J. Moore; and, Charles M. Wallace.

The generous cooperation of the Materials Department of the Iowa State Highway Commission is acknowledged, and the following men in particular: Alfred F. Faul; Thomas E. McElherne; Stephen E. Roberts; James W. Johnson; Art Myhre; John E. Boring; John Roland; LaVerne Huckstead; and, Max I. Sheeler. Mr. Mark Morris and the late Bert Myers provided important background data as well as encouragement and cooperation. Mr. Theodore L. Welp, Senior Geologist for the Materials Department, and the following members of his staff, have been exceedingly cooperative and are thanked for their services throughout the project: Robert D. Michael, Kermit L. Dirks, and James D. Meyers. Mr. Howard Dixon, former Senior Geologist, gave valuable aid during the initial phase of the project. Drs. Harvey Diehl, Charles V. Banks, and Frederick R. Duke, of the Chemistry Department at Iowa State University, gave valuable advice on many occasions. Drs. Richard L. Handy and Donald T. Davidson, of the Engineering Experiment Station Laboratory, cooperated on some technical procedures developed during the course of the project.

History

The correlation of distress in certain highway concretes to the coarse carbonate aggregates was the first recognition of the deleterious behavior of certain aggregates in Iowa. The two aggregates which were so recognized were those from the Maynes Creek member of the Mississippian Hampton formation at the LeGrand Quarry and those from the Rapid member of the Devonian Cedar Valley formation from the Glory Quarry. The first preliminary research on the problem was done in 1949 by Fred Dorheim as part of his thesis research at Iowa State College while he was serving as the Highway Commission geologist. The purpose of his investigation was to find, through consideration of some geologic aspects, new criteria for the selection of limestone aggregates to be used in concrete. From the parallelism between the service record and clay content he suggested that the presence or absence of clay should be used as a criteria in selection of aggregate.

The research was continued with the establishment of a three-year research project, HR-15, from 1951 to 1954, under the direction of Drs. C. J. Roy and L. A. Thomas of the Geology Department at Iowa State University with the assistance of Weissman and Schneider. The Mississippian rocks of poor service record quarried in the vicinity of LeGrand, Iowa, were of special interest and were compared to stone with good service records from the same stratigraphic horizons at Fort Dodge and Alden. Correlation of petrographic characteristics with service record failed to show any explanation for the poor service record. The study of concrete cores taken from satisfactory and distressed pavements indicated that fresh unaltered stone was associated with cores representing good service; whereas, weathered stone was associated with distress. The study indicated the type and amount of clay mineral present, absorption capacity as increased by weathering, and the variation in the ratio of carbonate minerals were factors which could be related to the poor service of LeGrand stone.

In July 1955, the present project was renewed as HR-15 under the direction of Dr. John Lemish for a three-year period, and extended to the terminal date of June 30, 1962. Much of the work was carried out by graduate students who studied various phases of the problem as part of their Masters and PhD thesis research. A list of theses resulting from the project is presented below.

List of Unpublished Theses

(Library, Iowa State University, Ames, Iowa)

1957　　MS　　-　　F. Eugene Rush
　　　　　　　　　　　Petrography and Physical Properties of Some Devonian
　　　　　　　　　　　Limestone of Iowa

　　　　　　　　-　　Ramon E. Bisque
　　　　　　　　　　　Limestone Aggregate as a Possible Source of Chemically
　　　　　　　　　　　Reactive Substances in Concrete

1958　　MS　　-　　Carl L. Hiltrop
　　　　　　　　　　　Relation of Pore-Size Distribution to the Petrography
　　　　　　　　　　　of Some Carbonate Rocks

1959 PhD - Ramon E. Bisque
               Silicification of Argillaceous Carbonate Rocks

1960 MS - Robert J. Harwood
               Compositional Variations Associated with Carbonate
               Aggregate--Cement Paste Reactions

      PhD - Carl L. Hiltrop
               Silica Behavior in Aggregate and Concrete

1961 MS - Frank E. Diebold
               X-ray Methods Applied to Quantitative Study of Carbon-
               ate Rocks

         - Michael A. Werner
               Equilibria in Cement Paste--Carbonate Aggregate Reac-
               tions

1962 MS - Charles M. Wallace
               Relationship of Pore-Size to Texture in Some Carbonate
               Rocks

1963 MS - William J. Moore
               Studies of Carbonate Aggregate Reactions: Expansion
               Behavior; Environmental Effects; Concrete Matrix
               Investigations.

List of Publications

1. Lemish, J., Rush, F. E., and Hiltrop, C. L.   (1958)
         Relationship of physical properties of some Iowa aggregates to
         durability of concrete. HRB Bull. 196, p. 1-16

2. Bisque, R. E. and Lemish, J.   (1958)
         Chemical characteristics of some carbonate aggregates related to
         the durability of concrete. HRB Bull. 196, p. 29-45

3. Hiltrop, C. L. and Lemish, J.   (1959)
         The relationship of pore-size distribution and other rock proper-
         ties to the serviceability of some carbonate rock. HRB Bull. 239,
         p. 1-23

4. Bisque, R. E., and Lemish, J.   (1959)
         Silicification of carbonate aggregates in concrete. HRB Bull.
         239, p. 41-55

5. Lemish, J. and Bisque, R. E.   (1959)
         Autoclave method for determining susceptibility of carbonate
         aggregates to silicification. Proceedings Iowa Acad. of Sci.,
         vol. 66, p. 210-213

6. Hiltrop, C. L. and Lemish, J. (1959)
   Treatment of carbonate rocks with a vaporous mixture of
   $(CH_3)_2SiCl_2$ and CH_3SiCl_3. Proceedings of Iowa Acad. Sci.,
   vol. 66, p. 214-221

7. Bisque, R. E. and Lemish, J. (1959)
   Insoluble residue--magnesium content relationship of carbonate
   rocks from the Devonian Cedar Valley formation. Jour. of Sed.
   Pet., vol. 29, p. 73-76

8. Bisque, R. E. and Lemish, J. (1960)
   Effect of illitic clay on chemical stability of carbonate
   aggregates. HRB Bull. 275, p. 32-38

9. Hiltrop, C. L. and Lemish, J. (1960)
   A method for determining the relative abundance and composition
   of calcite and dolomite on carbonate rocks. Proceedings, Ia.
   Acad. Sci., vol. 67, p. 237-245

10. Lemish, J. (1962)
    Research on carbonate aggregate reactions in concrete.
    AIME Transactions (Mining), vol. 223, p. 195-198

11. Diebold, F. E., Lemish, J., and Hiltrop, C. L. (1963)
    Determination of calcite, dolomite, quartz, and clay content of
    carbonate rocks. Jour. of Sed. Pet., vol. 33, no. 1, p. 124-139

12. Lemish, J., Harwood, R. J., Hiltrop, C. L., and Werner, M. A. (1963)
    Compositional variations associated with carbonate aggregate
    reactions. Highway Research Record, no. 3, p. 1-8 (HRB, NAS-NRC
    pub. 1067)

13. Lemish, J. (1963)
    Carbonate aggregate research. Proceedings of the 14th Annual
    Highway Geology Symposium, A & M College of Texas, College
    Station, Texas, p. 55-64

Prior to the studies undertaken in Iowa, very little had been done in
carbonate aggregate research. Laughlin published one of the first papers on
carbonate aggregates in 1928 and was followed by others, notably H. S. Sweet
(1948); B. Mather, et al (1953); and K. Mather (1953), who emphasized the
petrographic and physical aspects of carbonate aggregates. The recognition
that certain carbonates are reactive in concrete has led to increased partici-
pation in research in the past few years by groups outside of Iowa. Much of
it is due to the research project HR-15. Significant contributions have been
made by Swenson (1957) and Swenson and Gillot (1960) who, working through the
National Research Council of Canada, studied the deleterious behavior of the
Kingston Ontario aggregate from the Black River formation. This aggregate
passed the water freeze-thaw tests but caused distress in concrete through
expansion. Chaiken and Halstead (1960) in their studies on alkali reactivity
of aggregates demonstrated that dedolomitization occurred in some carbonate
aggregates. Hadley (1961) of the Portland Cement Association has studied the
expansion and dedolomitization of various carbonate aggregates in alkaline
solutions. Recently Newton, in Virginia, has begun research on certain expan-

sive carbonate aggregates causing distress in concrete. Through efforts of Bird, Materials Engineer for the Bureau of Public Works in New York State, a research project to investigate the properties of various carbonate aggregates has been sponsored at Renssalaer Polytechnic Institute.

Approach to Problem

The problem of determining the suitability of carbonate rocks as concrete aggregates is extremely complex and calls for more new data than has been available or obtainable from usual methods.

Since 1955 the approach which has served as a primary basis for the project has been to gather as much new information as possible to apply to the problem. New information obtained by new and different techniques provides better understanding. This approach was decided on since, in all prior studies, a standard petrographic and petrologic approach correlated in many instances with standard engineering tests did not provide the answer in Iowa or elsewhere. One can theorize that concrete fails (excluding external causes such as traffic, foundation failure, etc.) because of stresses of internal origin. The stresses can be of a physical nature, such as frost action, or result from chemical activity such as the alkali aggregate reaction. If, as service records show, the aggregate is considered the cause of distress in concrete, it will without doubt be the manner in which an aggregate can create or contribute to stress of internal origin by physical or chemical means. Therefore the main emphasis was placed on studying physical and chemical properties of aggregates as well as the behavior of carbonate rocks in concrete environments. Although standard geologic and engineering methods were also utilized, the approach adopted required considerable effort in devising new techniques and methods.

The approach discussed above was applied to a variety of rocks with good, poor, and indeterminate service records. Because of its poor service record, rocks from the Glory Quarry have been studied more intensively than any other. Glory aggregate therefore has served as a standard of comparison and made it possible to study the properties and behavior of a variety of other aggregates. Although Glory aggregate is no longer used in highway concrete, it has served an exceedingly useful purpose in this study.

Scope of This Report

This report is intended to be a detailed summary of the research performed. Whenever possible, the work accomplished will be summarized and all pertinent data will be included. For further details, reference to the various theses and publications transmitted with this report or at previous times will be made wherever possible.

A chronological review of the project will not be attempted since many phases of the study were made concurrently.

The subject matter is organized and presented according to the following areas:

        a) Carbonate rocks investigated
        b) Petrologic studies
        c) Pore size and textural studies
        d) Concrete studies
        e) Chemical studies
        f) Engineering tests
        g) Research techniques
        h) Summary and conclusions

CHAPTER II

CARBONATE ROCKS INVESTIGATED

In the course of research, a wide variety of carbonate rocks from eastern Iowa were studied. These rocks represent the Mississippian, Devonian, and Silurian systems. The Mississippian rocks studied were taken from the following formations: Gilmore City; Hampton; Chapin; and, Spergen. The Devonian formation sampled were the Cedar Valley and Wapsipinicon. The Silurian rock was taken from the Hopkinton formation.

The quarries were sampled wherever possible, either on a bed-by-bed basis, or selectively when a specific purpose was intended. Initially a few large hand-size specimens were taken as a sample. As the scope of research expanded, larger samples were needed and a typical sample weighing from 50 to 75 pounds ("block stone") was taken from the stratigraphic unit under investigation.

In order to insure maximum effectiveness of this report, a need exists for the Geology staff of the Iowa State Highway Commission to properly identify the rocks used in this investigation in order to correlate them with their stratigraphic sections. It is necessary for them to be able to correlate the various sample number designations of this report with the unit or bed number (stratigraphic location) of the quarry sample. Therefore the main purpose of this section is to provide these data.

When this project began, detailed stratigraphic data for adequate bed-by-bed sampling were for the most part not available. Therefore, in the first year of the project, detailed stratigraphic sections were made of all the quarries sampled. Later on the sections provided by the chief materials geologist of the Highway Commission were used whenever possible and an effort was made by us to use the same unit or bed number to correspond with the sample number.

In order to properly identify the rock units and/or samples discussed in this report the procedure which will be used is presented below. The quarries sampled according to our stratigraphic section and referred to throughout the report on this basis will be presented graphically, giving the sample and unit locations. Wherever the quarries were sampled according to the sections pro-

vided by the Highway Commission, reference will be made to the section by date and geologists who described the section. In cases where Highway Commission sections were used, but our sample numbers do not correspond with the unit numbers, a brief explanatory correlation table will be provided. In the Alden Quarry, sample numbers correspond with the unit numbers of the section made by Roy and Thomas, and presented in the 1954 Masters thesis of Weissman on file with the Highway Commission.

Devonian System

Cedar Valley Formation

The Cedar Valley formation outcrops in a broad belt in eastern Iowa, trending in a southeast-northwest direction. The quarries occurring in this formation are the Glory, Newton, Pints, Burton Avenue, and River Products. The Glory and River Products quarries are referred to throughout the report exclusively according to our sections which are presented in figures 1 and 2. The Newton, Pints, and Burton Avenue quarries were originally sampled according to our section, but these were modified at a later date with the cooperation of Welp in order to correspond with the Commission's sections. In order to prevent ambiguity, and since so much of the initial research is centered on the Cedar Valley formation, complete sections with sample locations are also provided in figures 3, 4, and 5.

Wapsipinicon Formation

Rocks from the Otis Quarry were sampled according to the Highway Commission section of Tripp dated January 24, 1957. The Kenwood member in the Otis Quarry was also sampled and assigned letter designations A to H for the main beds, from bottom to top. Numbers refer to the Otis member of the formation. In the work done by Diebold on rocks from the Otis Quarry, a different sample numbering system was used. These sample numbers, used in his Masters thesis, correspond to the unit number of the Otis Quarry in the following manner:

Diebold Thesis	Unit Number (Tripp Section)
1	8B
2	2
3	6
4	10
5	Kenwood B
6	6 (Brown Calcite)
7	7
8	Kenwood F

(Cont'd.) Diebold Thesis	Unit Number
9	10
10	2
11	Kenwood A
12	8A

Mississippian System

Chapin and Maynes Creek Formation

Rocks from these formations were sampled according to the Commission sections in the Ferguson and LeGrand North quarries for all studies made after the pore size studies of Hiltrop in 1958. The Ferguson section used is the Dixon, Welp, Michael section of July 13, 1956. The LeGrand North Quarry section was made by Tripp on December 14, 1956.

The rocks used by Hiltrop in his pore-size studies (see Hiltrop - MS thesis, and Hiltrop & Lemish, 1958) were taken from the LeGrand South Quarry. Sample one is at the base of the section. Seven samples representing the main units present were taken from the east wall of the quarry.

Gilmore City Formation

Rocks from this formation were sampled in the Alden Quarry and Fort Dodge Mine. The Fort Dodge Mine was sampled according to the Highway Commission section made by Welp and Michael on November 27, 1956. The Alden Quarry was sampled according to the section provided in the Masters thesis of Weissman (1954) on file at the Highway Commission.

Spergen Formation

This formation was sampled in the Douds Mine according to the Highway Commission section made by Dirks and Meyers on November 7, 1957. The sample numbers correspond with unit numbers except in the thesis of Diebold. The sample number designations are as follows:

Diebold Thesis	Unit Number
(Page 16 & 18)	(Dirks & Meyers)
13	8B (Top of unit)
14	14
15	10

(Cont'd.) Diebold Thesis	Unit Number
16	7A (Base of unit)
17	7B (Top of unit)
18	15
19	Composite of 12 and 13

(Page 11)

Diebold Thesis	Unit Number
5	11B
6A	10
12	11A
8	7B
11A	7A
10B	16 (St. Louis?)

Silurian System

Hopkinton Formation

Rocks from this formation were sampled at the Dyersville Quarry. The Highway Commission section prepared by Meyers and Dirks on April 2, 1959, was used.

GLORY QUARRY

NE ¼, Sec 36, T87N, R12W, Black Hawk Co
CEDAR VALLEY FM.
DEVONIAN

SCALE 1" = 10'

UNIT NO.	SAMPLE NO	LITHOLOGY	THK (FEET)
		19. L.S., TAN, LITHO	1.5'
	x24	18. SH.	0.3
	x23	17. L.S. TAN, LITHO, LAM.	2.1
	x22	16. L.S. TAN, LITHO	0.7
	x21	15. L.S. TAN, LITHO	1.5
	x20	14. L.S. BUFF, MED. GRND	1.0
	x18	13. Sh - BRN	0.4
	x17	12. Dol, TAN	4.3
	x16	11. Dol, TAN, CHERT	0.5
	x15	10. Dol, TAN	2.4
	x14	9. Dol, GRAY, CHERT	7.0
	x13	8. Dol, GRAY, CHERT, FOSS	1.5
	x12	7. Dol, CHERT, GRAY	1.2
	x11	6. Dol, GRAY, FOSS, CHERT	2.6
	x10	5. Dol. GRAY	6.5
	x9	4. Dol GRAY, FOSS	3.7
	x8	3. Dol, GRAY, CHERT	1.7
	x7	2. Dol. GRAY, FOSS	1.0
	x6	1. Dol., GRAY	2.6

CORALVILLE
RAPID

FIG. 1.

RIVER PRODUCTS QUARRY
SW¼, NW¼, Sec 23, T80N-R6W-Johnson Co.
Cedar Valley Fm - Devonian
Scale 1" = 10'

UNIT NO.   SAMPLE NO.   LITHOLOGY   THK. IN FEET

TILL

#	Lithology	Thickness
27.	DOL. L.S., GRAY, LITHO	30.0'
26.	L.S, GRAY, LITHO	8.0
25.	L.S. CREAM, LITHO	5.0
24.	L.S. BUFF, CORALS	12.0
23.	L.S., BUFF, CORALS	8.5
22.	L.S., BUFF, CORALS	3.9
21.	DOL, TAN	1.0
20.	DOL. DK. BRN.	4.7
19.	DOL. GRAY	4.3
18.	DOL., YELLOW, FOSS	0.3
17.	DOL. GRAY	3.5
16.	L.S. GRAY	0.8
15.	DOL. L.S. GRAY	3.0
14.	DOL. L.S., GRAY, CORALS	1.5
13.	L.S. GRAY	1.3
12.	SH. GRAY	0.6
11.	L.S. GRAY, CORALS	2.2
10.	SH. BLK	1.5
9.	DOL. L.S. GRAY	3.9
8.	DOL. L.S BUFF	4.6
7.	DOL. L.S. GRAY	0.8
6.	L.S., GRAY	3.0
5.	L.S. GRAY	2.2
4.	L.S. GRAY	0.8
3.	L.S. GRAY	2.6
2.	L.S. GRAY	2.1
1.	L.S. GRAY	

Formations (left margin): CORALVILLE, RAPID, SOLON

Unit numbers (column): 27, 26, 25, 24, 23, 22, 21, 20, 19, 18, 17, 16, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1

Sample numbers: x32, x31, x30, x29, x28, x27, x26, x25, x24, x23, x22, x21, x20, x19, x18, x17, x16, x15, x14, x13-12, x11, x10, x9, x8, x7, x6, x5, x4, x3, x2, x1

FIG. 2.

NEWTON QUARRY

NE¼, NE¼, Sec 13, T89N, R12W, BLACKHAWK CO.
CEDAR VALLEY FM - DEVONIAN
SCALE 1" = 10'

UNIT NO.		SAMPLE NO.	LITHOLOGY	THK (FEET)
19			19 - L.S. YELLOW, WTHD, DOL	10.0'
			18 - L.S. TAN, LITHO, FOSS	2.5
18		x20	17. SH - GRAY	0.3
17			16 - DOL. GRAY	2.8
16		x19	15 - L.S. TAN	0.9
15-11		x18+1	14 - L.S, TAN, LITHO	0.4
			13 - DOL. GRAY - YELL, LITHO	1.5
10		x13	12 - DOL, TAN.	1.0
9		x12	11 - SH - GRAY	0.2
			10 - DOL. GRAY	1.8
8		x11	9 - L.S. BRN, DOL	1.4
		x10	8 - L.S. GRAY-BRN - FOSS	7.2
7		x8	7 - DOL-L.S-YELL	1.0
6		x7, x6	6 - SH	0.4
5		x5	5. DOL., BRN	5.3
		x4	4. DOL, BUFF	4.5
4		x3	3. DOL. GRAY	1.5
3		FLOOR, x2	2. SH. GRAY	0.1
2			1. DOL. GRAY	4.4
1		x1		

RAPID ← → CORALVILLE

FIG. 3

PINTS NEW QUARRY

SW¼ - Sec 36, T89N, R12W, BLACKHAWK CO,
CEDAR VALLEY FM, DEVONIAN
SCALE 1" = 10'

UNIT NO	SAMPLE NO.	LITHOLOGY	THK (FEET)
		TILL	6-10'
19		19. L.S. BRN-GRAY LITHO	4.0'
18	X 15	18. DOL, SUGARY	1.8
17	X 14	17. DOL. BRN	3.5'
16	X 13	16. L.S. BRN	1.2
15	X 12	15. L.S. GRAY, FOSS	2.6
14	X 11	14. L.S. BUFF	1.7
13	X 10	13. DOL. BUFF	3.8
12	X 9	12. DOL, BUFF	1.2
11	X 8	11. DOL. BUFF	1.0
10	X 7	10. L.S. PINK, LITHO	1.5
9	X 6	9. L.S. BRN GRAY. SHALEY	0.5-1.0'
8		8. L.S. PINK, LITHO	1.0
7	X 5	7. DOL. BUFF, WTHD	5.0
6	X 4	6. DOL. BUFF, WTHD, CHERT	2.6
5		5. SH. BUFF WTHD	0.1
4	X 3	4. DOL. BUFF. WTHD, CHERT	2.6
3	X 2	3. DOL. BUFF, WTHD, CHERT.	3.5
2		2. DOL. BRN. SHALEY	0.2
1	X 1	1. DOL. BUFF, WTHD	7.9

CORALVILLE

RAPID

FIG. 4.

BURTON AVENUE QUARRY
NW¼, Sec 14, T89N, R13W, BLACKHAWK CO.
CEDAR VALLEY FM, DEVONIAN
SCALE 1" = 10'

UNIT NO	SAMPLE NO.	LITHOLOGY	THK (FEET)
16		16. DOL. GRAY, ARGILL.	4.0
15		15. CHERT GRAY	0.8
14	X22	14. DOL. GRAY CHERT	6.5
13	X21	13. DOL. GRAY	3.0
12	X20 X19	12. DOL. GRAY	4.5
11	X18	11. DOL. GRAY	2.5
10	X17 X16	10. CHERT GRAY	2.5
9	X15	9. DOL. GRAY	5.0
8		8. DOL. GRAY, GEODES, FOSS	1.2
7	X14	7. DOL. GRAY	±7.0
6	X13 X12	6. L.S., GRAY-BUFF, SHALEY	0.5
5	X11 X10 X9	5. L.S. BRN, TAN, FOSS.	10.0
	X8	4. L.S. BRN-GRAY, CHERT	8.0
4	X7 X6	3. L.S. GRAY, BRN, CORALS	2.0-3.0
	X5	2. L.S. GRAY-BRN	±5.0
3	X4	1. L.S. GRAY-BRN, ARGILL.	6.0
2	X3 X2 X1		
1			

RAPID

SOLON

FIG. 5

CHAPTER III

PETROLOGIC STUDIES

Included in this section are the phases of the study which were petrologic in nature such as thin section data, mineral and chemical compositions, insoluble residue data, and density data. Many of the data were obtained in initial studies undertaken to learn the characteristic or distinguishing features of a known aggregate with a poor service record, the Glory, which was compared to various aggregates on the basis of their service records and freeze-thaw data.

Later studies investigated the insoluble residue relationships, the occurrence of clay, and improved ways of determining the mineral composition of carbonate rocks.

Comparative Study of Glory Aggregate

In order to describe the character of a bad aggregate (other than that of LeGrand studied by Roy and Thomas) the initial phase of the project was a comparative study of rock from the Glory Quarry. Rocks were sampled in the Glory Quarry on a bed-by-bed basis (Fig. 1). For comparative purposes rocks from the Pints, Newton, and Burton Avenue quarries were also sampled and compared on the basis of their various properties, service records, and water-alcohol freeze-thaw data. The details of this study are presented in the Masters thesis of Rush (1957) and the paper of Lemish, Rush, and Hiltrop (1958) published in Bulletin 196 of the Highway Research Board. The thesis of Rush gives a detailed petrographic description of rocks from the Glory and Newton quarries. Highway Research Board Bulletin 196 gives more petrologic data and relationship of the rocks to freeze-thaw resistance. Tables I, II, III, and IV summarize the data accumulated.

Stratigraphic Relationships

The rocks discussed in this section 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. 6). 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 which, in ascending order, are 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 scattered 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 feet.

IOWA
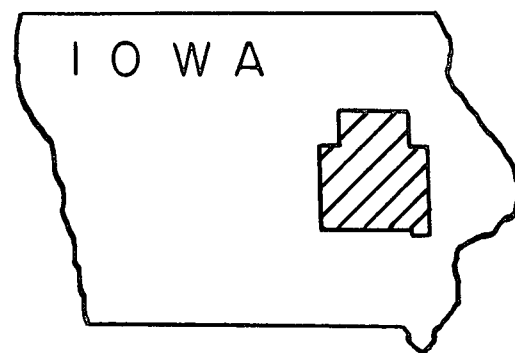
QUARRIES

1   BURTON AVE.
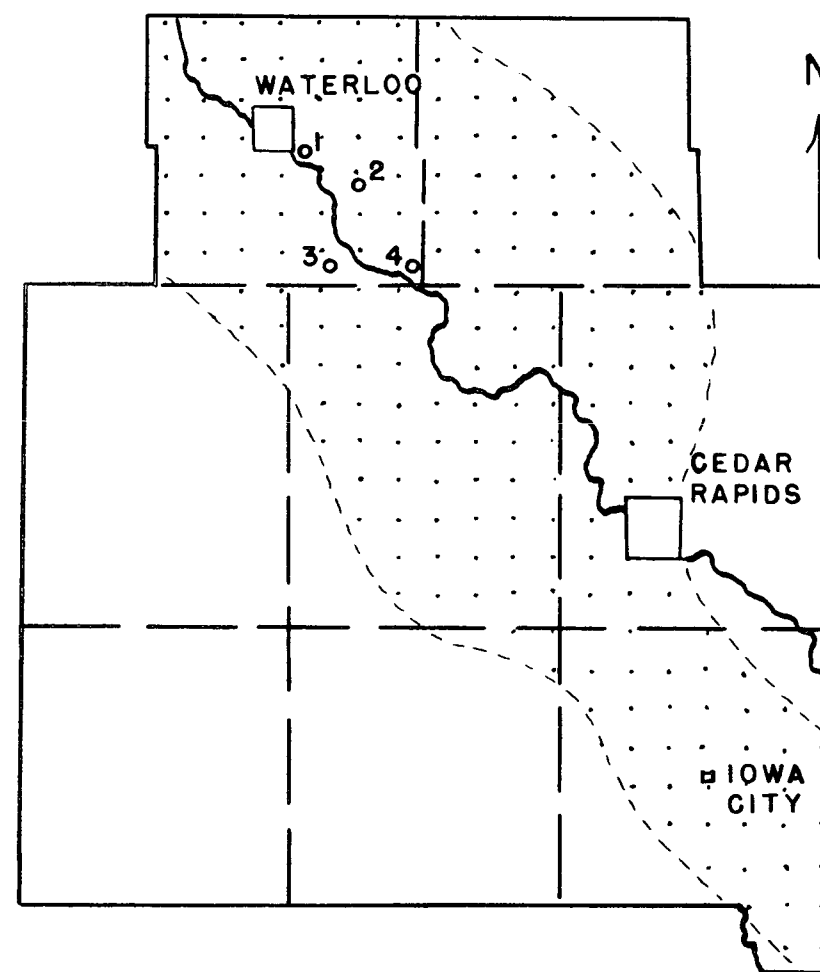
2   PINTS

3   NEWTON

4   OLD GLORY

CEDAR VALLEY FM.

WATERLOO

CEDAR
RAPIDS

IOWA
CITY

N

Fig. 6- Index map showing distribution of the Cedar
Valley formation and the location of the
quarries.

GLORY Q.   NEWTON Q.   PINT Q.   BURTON AVE. Q.

CEDAR VALLEY FORMATION

CORALVILLE

RAPID

SOLON

EXPLANATION

☐ STRATIGRAPHIC RANGE OF ROCKS

▨ LEDGES PRODUCING ACCEPTABLE CONCRETE AGGREGATE

⋮☐ POTENTIAL LEDGES OF ACCEPTABLE CONCRETE AGGREGATE

⊠ FORMERLY USED AS CONCRETE AGGREGATE
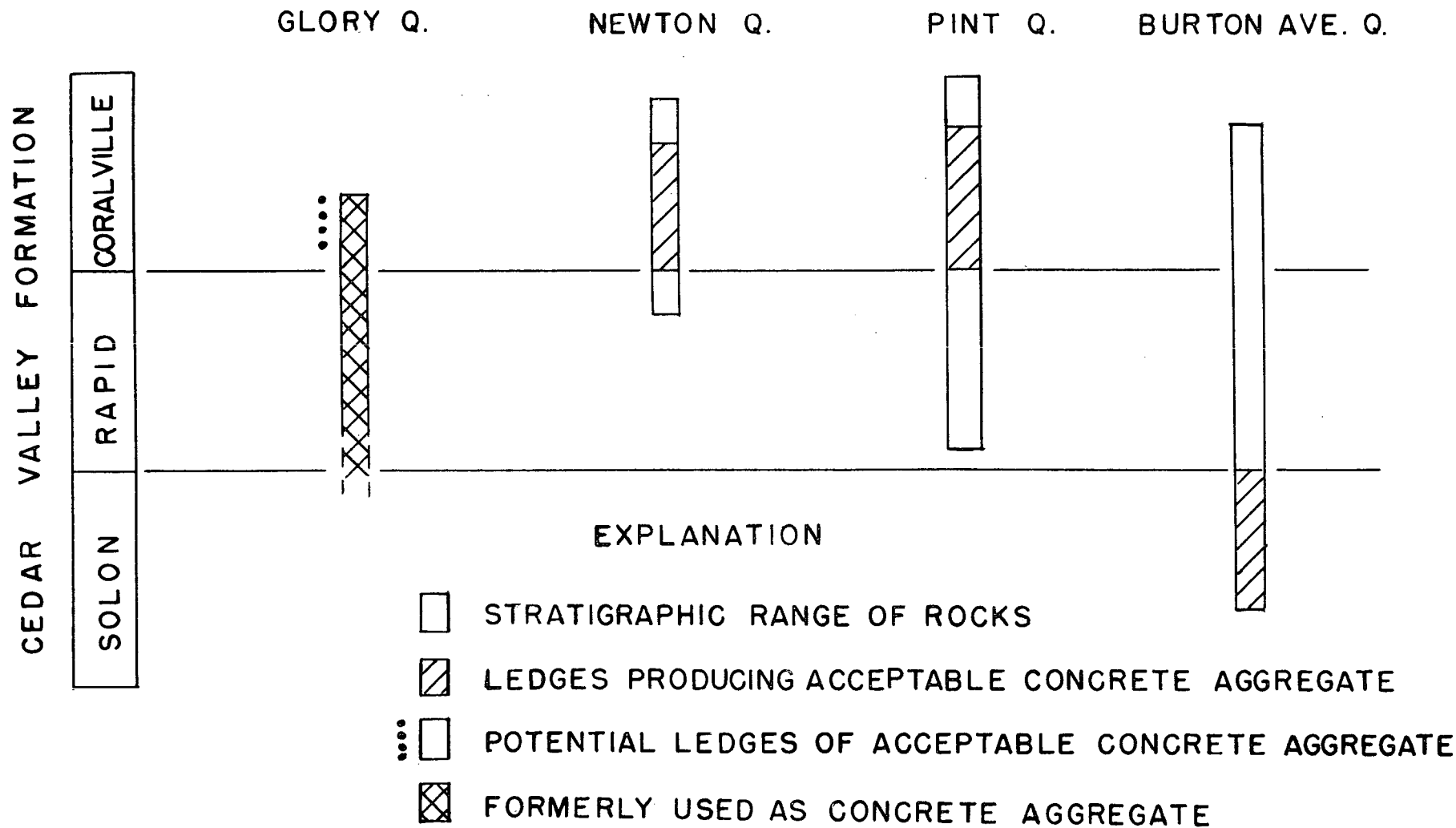
Fig. 7- Stratigraphic range of the rocks exposed in the
quarries and the position of the concrete aggre-
gate ledges.

Figure 7 shows the stratigraphic range of rocks exposed in the various quarries in relation to a standard column for the Cedar Valley formation 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 economically mined. The Coralville is produced at the Pints and Newton quarries. A small portion of the Coralville present at the Glory Quarry will also pass acceptance tests but was mined in combination with underlying Rapid.

The Rapid member is found in all the quarries and generally does not pass present test limits for concrete aggregate. Most of the face exposed in the Glory Quarry is Rapid. Aggregate from this ledge was used extensively throughout eastern Iowa. It is now unacceptable by present standards. The Rapid in these quarries is generally an argillaceous and cherty dolomite with well-defined bedding and primary structures; it is considered a good example of a diagenetic dolomite.

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 Masters thesis of F. E. Rush (1957). Each of the three members of the Cedar Valley formation -- the Solon, Rapid, and Coralville -- have definitive lithologic characteristics.

The Rapid member as exposed in all four quarries, where fresh, is characterized by its gray color and fine-grained texture. Shaley seams or partings separate the beds into units ranging from 3 inches to 3 feet thick. Within these units bedding is generally well-defined by 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 .01 to .03 mm in diameter occurring in a finer-grained (.001 mm) calcite paste or a recrystallized matrix averaging .01 mm. Chert and chalcedonic (fibrous) quartz 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 Pints Quarry, the overall 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 upper 18 feet of the Solon at the Burton Avenue Quarry is used as the concrete aggregate ledge. It is a massive-bedded, buff-gray rock with few fossils. It is characterized by a dense appearance and a 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 .03 to .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 argillaceous dolomite. At the Pints Quarry the lower portion of the Coralville is the concrete aggregate ledge, and occurs as a tan to brown limestone and calcitic dolomite, containing fine- to medium-grained units of variable thickness. In thin section it shows the same variations. The lithographic beds are made up of a dense calcite paste with individual grains averaging less than .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 Pints quarries is composed essentially of rocks with fewer inclusions than the Rapid member. The limestone portions are generally very fine-grained but the dolomitic zones are coarser and consist of grains which average .06 to .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. A small amount of pyrite is present in nearly every residue (as a rule silica in some form constitutes better than 95% of its composition), and 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 I, II, III, and IV. High residue contents ranging from 17% to 27% is characteristic of the rock from the Rapid member in all the quarries. In contrast to this are the low residue values averaging from 2.3% to 6.5% for those beds of the Solon and Coralville members used for production.

A correlation exists between the residue content and the freeze-thaw data. (The freeze-thaw values represent the percentage of material lost after 16 cycles of freezing and thawing in a water-alcohol solution: a maximum of 6% material loss is allowed for concrete aggregate.) 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 (Bisque, Masters thesis, 1957; Rush, Masters thesis, 1957). Previous methods of analyzing clays from insoluble residues proved unsatisfactory because of the damage to the clays by acid treatment. This was true of rocks

TABLE I — CARBONATE ROCK PROPERTIES, GLORY QUARRY

Strati-graphic Unit	Sample No	Lithology	Unit Thickness (feet)	Insoluble Residue	Average Residue	Clay Mineral Present	Powder Density	Bulk Density	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Misc.
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	" "	.7	8.0	8%	-	2.70	2.64	2.2	0.9	10.0	
	20	" "	1.5	2.0		-	2.70	2.66	1.5	.3	5.4	
	19	Dolomitic limestone	1.0	12.0		illite	2.80	2.66	5.0	1.1	20.0	Weathered
RAPID	18	Shaly dolomite	0.4	50.0		illite	2.76	2.41	12.8	-	-	
	17	Calcitic dolomite	4.3	22.0		illite	2.80	2.20	21.4	-	95.0	Badly weathered
	16	" "		16		illite	2.80	2.41	13.9	13.0	68.0	" "
	15	Dolomitic limestone	0.5	6		illite	2.73	2.68	1.8	.1	-	Chert present
	14	Dolomite	2.4	16		illite	2.79	2.45	12.2	10.9	27.0	
	13	Calcitic dolomite	7.0	21		illite	2.80	2.40	14.2	11.5	30.0	
	12	" "		22		illite	2.78	2.45	11.7	-	-	
	11	" "		12	18%	illite	2.79	2.50	10.4	-	42.0	
	10	" "	1.5	10		-	2.76	2.55	7.6	5.8	25.0	
	9	" "	2.6	15		illite	2.80	2.53	9.6	6.4	42.0	
	8	" "	6.5	39		illite	2.68	2.55	4.8	4.6	29.0	
	7	" "		12		illite	2.77	2.56	7.6	2.3	32.0	
	6	" "		19		illite	2.76	2.54	8.0	4.2	33.0	
	5	" "	3.7	15		illite	2.76	2.56	7.3	3.2	36.0	
	4	" "		10		illite	2.68	2.54	5.2	3.4	42.0	
	3	" "	1.7	22		illite	2.70	2.56	5.2	4.2	30.0	
	2	" "	1.0	49		-	2.69	2.48	8.1	4.8	27.0	
	1	" "	2.6	7		-	2.77	2.54	8.3	5.6	11.0	

TABLE II - CARBONATE ROCK PROPERTIES, NEWTON QUARRY

Stratigraphic Unit			Sample No.	Lithology	Unit Thickness (feet)	Insoluble Residue %	Average Residue %	Clay Mineral present	Powder Density	Bulk Density	Total Porosity %	Effective Porosity %	Freeze-Thaw % Loss	Misc.
CORALVILLE			20	Lithographic limestone	2.5	1.		none	2.67	2.57	3.7	-	19.0	
			19	Dolomite	2.8	14		illite	2.75	2.69	2.2	0.9	4.7	
			18	Dolomitic limestone	0.9	6		none	2.69	2.55	5.2	3.0	49.0	
			17	" "	0.4	2		none	2.68	2.65	1.1	-	11.0	
			16	Lithographic dolomite	1.5	10	7%	none	2.79	2.56	8.2	5.0	33.0	
			15	Calcareous dolomite	1.0	2		none	2.73	2.59	6.8	4.4	5.5	
			14	" "	0.2	14		none	2.78	-	-	-	-	
			13	Dolomite	1.8	6		illite	2.79	2.47	11.5		7.5	
	CONCRETE AGGREGATE	LEDGE	12	Calcareous dolomite	1.4	3		none	2.79	2.56	8.3		1.6	
			11	Calcareous dolomite	} 7.2	5		none	2.76	2.44	11.6	10.2	3.2	
			10	" "		2		none	2.73	2.56	6.2	-	1.0	
			9	" "		2		none	2.79	2.49	10.6	10.5	.9	
			8	" "	1.0	4		none	2.72	2.42	11.1	11.0	1.6	
			7	Dolomitic limestone	0.4	5	5%	none	2.69	2.49	7.4	-	-	
			6	" "	} 5.3	3		none	2.73	2.58	5.5	5.4	1.9	
			5	" "		3		none	2.71	2.56	5.5	5.3	1.5	
			4	Calcareous dolomite	} 4.5	2		none	2.76	2.63	4.6	4.1	2.8	
			3	" "		4		none	2.75	2.49	9.5	-	1.2	
			2	" "	1.5	13		illite	2.80	2.58	7.9	1.5	31.0	
RAPID			1	" "	4.4	10	10%	none	2.76	2.59	6.2	4.3	16.0	

TABLE III – CARBONATE ROCK PROPERTIES, PINT QUARRY

Stratigraphic Unit		Sample No.	Lithology	Unit Thickness (feet)	Insoluble Residue %	Average Residue %	Clay Mineral Present	Powder Density	Bulk Density	Total Porosity %	Effective Porosity %	Freeze-Thaw % Loss	Misc.
CORALVILLE	CONCRETE AGGREGATE LEDGE	15	Calcitic dolomite	1.3	1.7		none	2.86	2.58	9.8	8.4	1.7	
		14	Calcitic dolomite	3.5	1.6		Trace – illite	2.88	2.57	10.8	–	3.6	
		13	Calcitic dolomite	1.2	1.7		Trace– illite	2.85	2.56	10.2	8.3	1.0	
		12	Dolomitc limestone	2.6	3.4		none	2.86	2.49	13.0	–	1.9	
		11	Limestone	1.7	2.4	2.3	"	2.83	2.59	8.5	3.8	2.3	
		10	Calcitic dolomite	3.8	2.3		"	2.84	2.56	9.8	6.1	1.7	
		9	Calcitic dolomite	3.2	2.7		"	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	.8		none	2.78	2.68	3.6	–	2.3	
		5	Calcareous dolomite	5.0	18.9		illite	2.78	2.22	20.1	–	–	Extremely weathered. Very soft Rock. Freeze-Thaw losses are Excessive
		4	" "	2.6	16.7	16.6	"	2.87	2.26	21.2	–		
		3	" "	2.6	22.5		"	2.81	2.31	17.8%	–		
		2	" "	3.5	17.5		"	2.80	2.29	18.2	–		
		1	" "	7.9	15.8		"	2.87	2.14	25.4	21.6	58.0	

TABLE IV - CARBONATE ROCK PROPERTIES, BURTON AVENUE QUARRY

Strati-graphic Unit	Sample No.	Lithology	Unit Thick-ness (feet)	Insoluble Residue %	Ave. Residue	Clay Mineral Present	Powder Density	Bulk Density	Total Porosity	Effective Porosity	Freeze-thaw Loss %	Misc.
CORALVILLE	28	Calcitic dolomite	5.0	8.8		Illite Trace	2.86	2.46	14.0	---	---	Weathered
	27	Limestone	2.5	1.6		Illite	2.75	2.55	7.3	1.6		
	26	Dolomitic limestone	0.5	27.5	8.6	Illite	2.86	2.40	16.1			
	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		
RAPID	23	Calcitic dolomite	4.0	12.7		Illite	2.85	2.44	14.4			
	22	" "	6.5	47.6		"	2.81	2.52	10.3			
	21	" "	3.0	17.0		none	2.84	2.24	21.2			
	20	" "	4.5	20.4		Illite	2.82	2.41	14.6			
	19	" "		35.0		"	2.83	2.43	14.1			
	18	" "	2.5	33.	27.0	"	2.83	2.43	14.1			
	17	Dolomitic limestone	0.5	34.		"	2.81	2.42	13.9			Cherty
	16	Calcitic dolomite	5.0	23		"	2.79	2.55	8.6			
	15	Calcitic limestone		23		"	2.88	2.57	10.8		Ave. 16-45%	
	14	Calcitic dolomite	7.0	24		"	2.87	2.52	12.2			
	13	Limestone		16		"	2.80	2.64	5.7			
SOLON — AGGREGATE LEDGE / CONCRETE AGGREGATE	12	Limestone		5.2		none	2.77	2.63	5.1	1.1		
	11	Limestone		7.0		"	2.77	2.63	5.1			
	10	Limestone	10.0	4.0		"	2.80	2.60	7.1	1.3		
	9	Limestone		2.8		"	2.77	2.51	9.4			
	8	Limestone		4.3		"	2.81	2.66	5.4		Ave. 0.8-3.0	
	7	Limestone	8.0	2.9	6.5	"	2.79	2.61	6.5	1.2		
	6	Limestone		12.8		"	2.79	2.52	9.7			
	5	Limestone		2.9		"	2.78	2.62	5.8			
	4	Limestone	2.3	4.5		"	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		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		

from the Glory quarry. In the technique developed for this project, the clays were separated as follows: 50 grams of powdered rock passing 200 mesh 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 was pipetted out and a coated slide prepared for X-ray analysis. The presence of as little as .1% clay in a powdered carbonate rock sample has been separated by this technique, which avoids a harsh acid treatment. Later studies indicated 10 to 20 minutes of settling time was adequate to indicate qualitatively the presence of clay.

The clay mineral data are presented in Tables I through IV. Without exception the only type of clay mineral found in carbonate rocks present in the four quarries was illite. Nearly every bed in the Rapid member contains illite which correlated with the argillaceous appearance so characteristic of this unit. In contrast to the Rapid are the concrete aggregate ledges of 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, Bulk, and Powder Density

The porosity and density of carbonate rocks are other properties investigated. The total porosity has been determined and the effective porosity was measured with the results presented in Tables I through IV.

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%. Powdered rock passing a 200 mesh sieve is used in the determination (Rush, Masters thesis, 1957). 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:

$$\text{Per cent total porosity} = 1 - \frac{\text{Bulk Density}}{\text{Powder Density}}$$

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 and Textural Studies).

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 concrete ledge of 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 rock from the Rapid has been weathered an extreme increase in total and effective porosity is evident in the Pint and Glory quarries. One observation which is evident is that the past history of a rock is very important as a factor in controlling its porosity characteristics.

Summary

A summary of data gathered in the comparative study of Glory aggregate is presented below.

1- The lithologic members of the Cedar Valley formation can be identified fairly well by their petrographic characteristics and other properties. Rock from the Rapid member as found in the Glory Quarry and elsewhere is essentially calcareous dolomite with high insoluble residue and illite is the principle clay mineral present. The rock is argillaceous and has good bedding. This rock has a characteristic mosaic texture under the microscope. Aggregates made from rocks with lithology similar to the Rapid member have poor freeze-thaw resistance and a poor service record. Recent studies on similar rocks in Canada and Virginia have shown that aggregates with poor service record are lithologically similar to the Rapid. They are argillaceous, dolomitic, retain primary structures, have fairly high residues, and characteristically show a "mosaic" texture under the microscope. On the basis of present research and experience elsewhere all rocks with the above lithology should be suspect and not recommended for use as concrete aggregate.

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. Clay minerals are rare or absent in units with good freeze-thaw resistance (present concrete ledges).

4- Porosity data like absorbance data are inconclusive with regard to service and freeze-thaw performance.

Clay and Insoluble Residue Studies

Because of the strong relationship of clay and insoluble residue to poor service and high freeze-thaw values, additional research was carried out in these areas. The data are considered petrologic in nature and are reported in this section although much of it was done as part of the chemical investigation by Bisque (PhD thesis, 1959), supplemented in part by the work of Hiltrop (PhD thesis, 1960).

Insoluble Residue--Magnesium Content Relationship

An interesting relationship was observed and described in a paper by Bisque and Lemish (1959) in which the insoluble residue content of Cedar Valley formation sampled in the Glory, Pint, Newton, Burton Avenue, and River Products quarries was compared to the amount of magnesium in the rocks. The data demonstrated that the relationship of increasing Mg content to increasing impurities is well distributed through a fairly widespread range of rock types (Fig. 29). The soluble iron (FeO) content has a similar relationship and it was interesting to note that a high soluble iron content occurs with an accompanying high magnesium content.

It was noted in megascopic observation of the samples tested that in all cases where a high residue and dolomite occurred, the samples had the characteristic argillaceous lithology which characterizes the Rapid member. Because of the abundant primary features of such rocks, Dunbar and Rogers (1957) call such dolomitic rocks the "S" or syngenetic dolomites. Such dolomites are considered diagenetic in origin.

Several Coralville specimens gave a high magnesium content associated with low residue values. Megascopically such specimens are different from the typical Rapid lithology. They represent beds of porous, medium- to coarse-grained dolomite in which nearly all primary features have been destroyed. These dolomitic zones, many of which commonly are found in the stratigraphic horizons suitable for concrete aggregate (concrete ledges), have contacts which transgress bedding planes. Such dolomites are clearly secondary in origin and form long after diagenesis. Dunbar and Rogers call such rocks "T" or tectonic dolomites. Many of our Silurian and Ordovician dolomite horizons producing suitable aggregate fit this megascopic description and behave well in service.

Clay Studies

Many of the problems in studying clay in carbonate rocks has been due to the difficulty of separating clay from the limestone with acid treatment. This often, as it does in the case of Glory aggregates, destroys much of the clay. With the development of a flotation separation technique (Rush, 1957; Bisque, 1957), it was possible to study the occurrence of clay in concrete rocks more effectively and obtain a better insight on its potential role in aggregates.

X-ray diffraction patterns of the clay-size flotation fraction from 75 different lithologic units of the Cedar Valley formation in five quarries were similar and identified as a 10° Angestrom clay-illite (Fig. 9). Glycolation and heating to 550° C caused no changes eliminating the presence of montmorillonite and vermiculite. Kaolinite was detected in several specimens but in each case it was shown that its presence was due to contamination of the samples by soil at the quarry. When pieces of bulk rock were washed thoroughly before treating to concentrate the clay fraction, kaolinite was not detected. This experience should be heeded by others in sampling the quarries.

Studies of the clay separation techniques to see if they could be made semi-quantitative gave variable results. Bisque's studies indicated that when the technique was standardized and the intensity of the 10 angstrom reflection
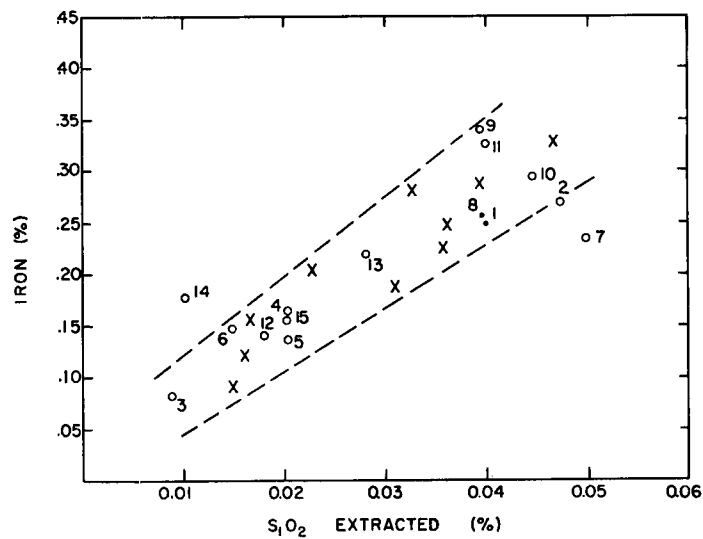
Fig. 8. Relationship of the per cent of soluble iron
(phase 1) to the quantity of silica extracted
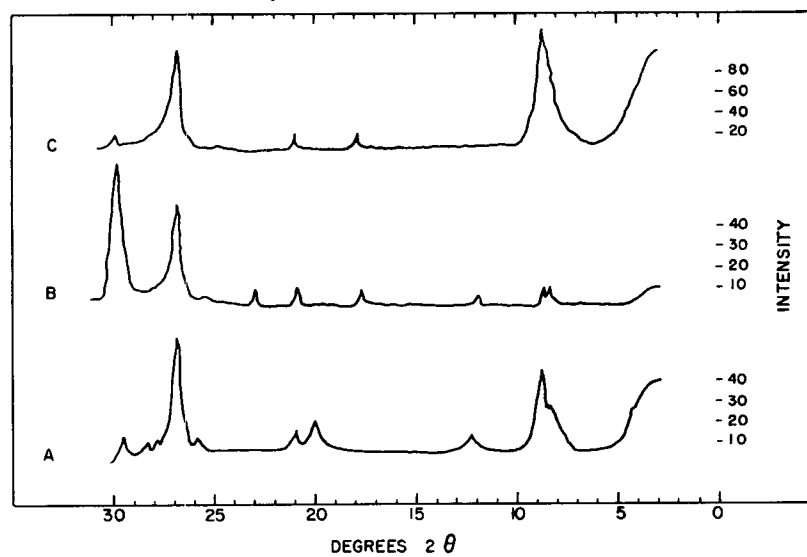(phase 2)

Fig. 9. Relative intensity of major reflections of A,
Fithian illite; B, Fithian illite-calcium
carbonate mixture; and C, illite separated from a
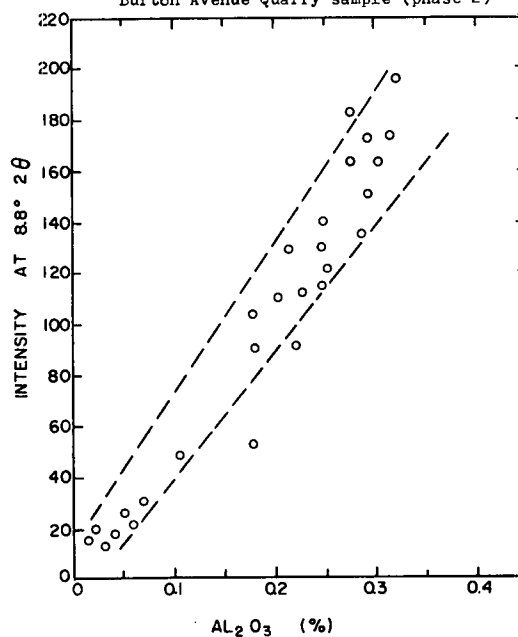Burton Avenue Quarry sample (phase 2)

Fig. 10. 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)

given by the clay fraction after separation was plotted against the amount of aluminum dissolved by hydrochloric acid during a chemical analysis (Fig. 10), a correlation exists. It was decided that a standardized flotation technique may be suitable for a rough approximation. Further work on the flotation technique by Diebold (MS thesis, 1961) gave erratic results, and it was concluded that the flotation technique should be considered mostly a qualitative method.

The amount of clay in a rock could also be indicated by the aluminum content, especially when the flotation technique is used to identify the type of clay which is present. There is no basis to assume that the amount of aluminum soluble in hydrochloric acid is proportional to the amount of clay mineral in a rock. Analyses run to determine the relationship between "soluble aluminum" in rocks and the total amount of aluminum determined by fusing the samples show that (Bisque, PhD thesis) fusion gives 3 to 4 times as much aluminum. Since most of the aluminum in a carbonate rock occurs in clay minerals, a combination of the total aluminum content and flotation identification technique could be developed as an index of the amount of clay in a carbonate rock.

Research by Bisque (PhD thesis, 1959) provides evidence on the occurrence of clay in rock of Rapid lithology. Ordinarily the clay particles in the rock are not easily seen in thin section. They are rarely concentrated in large masses. In Rapid lithology rocks with the typical "mosaic" texture, the clay or residue appears as disseminated specks in the calcite matrix. The dolomite rhombs forming the mosaic are quite clear with considerably less residue. Indirect evidence obtained from the flotation studies indicates that the bulk of clay particles are situated along grain boundaries and pore surfaces, and not enclosed within calcite matrix crystals. Fine grinding of the rock liberates most of the clay, allowing it to be separated by flotation. Since rocks tend to fracture preferentially along grain boundaries during grinding, most of the clay would be abraded from the surfaces of rock fragments.

Perhaps the strongest indication that clay is situated at grain boundaries is afforded by formation of a three-dimensional, siliceous, skeletal structure upon silicification by a variety of methods (i.e.- sodium silicate solutions, silicon tetrachloride vapor). Upon analyses these skeletal structures are found to contain aluminum. In order to occur in the skeletal structure, the clay particles must be situated on pore surfaces and they are "tied" or polymerized together into a network when migrating silica is deposited in these sites. Acid leaching of a silicified portion of a mosaic-textured Rapid lithology commonly leaves a silicified matrix which contains perfect casts of dolomite rhombs (see Figs. 47, 48, 49, and 50). This is further evidence that the bulk of the clay is in the calcite matrix and that the rhombs were surrounded by clay particles. The abundance of clay to tie down silica at the border of a dolomite rhomb may be the result of considerable "space" or pore volume at the dolomite-matrix interface.

The loss of clay minerals when dissolving the Glory aggregate in acid but the presence of it in the same rock when a flotation procedure was used was the first indication that poorly ordered clay particles were present. Further work by Bisque in this area provided more confirmation that in rock of the Rapid member much of the clay-sized non-carbonate fraction is amorphous or psuedo-amorphous groupings of silica and alumina. This was done by taking advantage of the fact that the only clay mineral present in the rock is illite

and performing a chemical analysis of the clay fraction. The clay fraction was separated via the flotation technique from several argillaceous units of Rapid lithology from the Burton Avenue and Glory quarries. The resulting slurries were combined, dried, and two one-gram samples were analyzed with the following results:

TABLE V

ANALYSIS OF EXTRACTED CLAYS

	Sample 1	Sample 2
Loss on Ignition	15.7	11.9
% SiO_2	35.0	38.0
% Al_2O_3	26.9	25.1
% MgO	6.6	7.8
% FeO	3.1	3.2
% CaO	11.5	12.7
TOTAL	98.8	98.7

Although these results cannot be compared to analyses of well-ordered illitic clays, certain conclusions can be drawn. It has been established that there is less substitution of aluminum for silicon in the lattice of illitic clays than there is in the well crystallized micas. About one-fourth of the silicon atoms in a mica are replaced by aluminum, whereas the average for illites is closer to one-sixth (Grim, 1953, p. 67). Referring to the analyses above, if it is assumed that all of the silicon was present in an illitic clay there is an excess of approximately 20 per cent alumina in each sample. Since X-ray diffraction patterns reveal no types of crystalline clay other than illite, it must be concluded that a good proportion of the clay-sized non-carbonate material is amorphous. If part of the silicon occurs as quartz, then even a larger excess of alumina exists and there is a strong possibility the alumina is present as any one of a large number of hydrous aluminum oxide minerals.

Summary

A relationship between insoluble residue and magnesium content appears to be typical of Rapid lithology easily recognized megascopically in the field. This is of considerable value to the geologist in predicting the potential nature of a rock at the outcrop.

The data obtained by Bisque in his PhD research gave more insight on the occurrence and nature of clay in certain carbonate rocks which could not be obtained by conventional petrological techniques. Indirect evidence exists that clay particles occur in pore spaces and along grain boundaries; the most

reactive sites possible in a rock. Indications exist also that the presence of disordered or amorphous clay-sized particles may be present.

This information becomes important when one considers that most carbonate rocks contain insoluble residue, a portion of which is always clay-sized, in a variable amount, but not all rocks are reactive or deleterious. The nature of the distribution of the residue in a rock may be a very important property affecting its behavior. It also occurs that, rather than the total amount of residue present, the size, type, and location of the residue may be far more important in understanding the reactive nature and behavior of a carbonate aggregate.

Study of Otis and Doud Aggregate

In the course of the work by Diebold (1961) on a quantitative X-ray diffraction technique for the determination of carbonate minerals the rock from the Otis Quarry and Doud Mine were used as the basis of the study. Some of the data gathered on these rocks are presented below.

The rock from the Doud Mine are of Mississippian age and occur on the Spergen formation. The sample numbers correspond with bed numbers of the Iowa Highway Commission section prepared by Dirks and Meyers November 7, 1957. At present, beds 10 through 15 form the concrete ledge; bed 15 is at the top of the ledge.

TABLE XV

ANALYSES FOR MAJOR CONSTITUENTS - DOUD MINE

Bed	Ca as Wt.% CaCO$_3$	Mg as Wt.% MgCO$_3$	Wt.% Insoluble Residue	Total %
4	92.0	6.9	- - -	- -
6	88.0	6.8	3.05	98.0
7A	58.0	30.3	10.55	98.9
7B	54.5	32.0	12.59	99.1
7C	59.5	32.4	6.33	98.2
8A	56.0	31.2	11.16	98.4
8B	52.5	28.2	16.7	97.4
16	53.6	33.8	10.37	97.8
Concrete Ledge:				
11A	52.5	34.2	8.80	95.5
11B	56.0	37.4	3.90	97.3
12 & 13	67.2	30.8	- - -	- -
14	59.5	36.4	1.7	97.6
15	64.0	29.1	2.0	95.1

TABLE XVI

DOLOMITE MINERAL CONTENT - DOUD MINE

Bed	Wt.% Dolomite (Tennant & Berger Method)
7A	85
7B	90
11A	95
11B	95
16	90

The rock from the Otis Quarry is of Devonian age and occurs in the Wapsi-pinicon formation. The quarry is at present working in the Otis and overlying Kenwood members of this formation. Rock from the Otis member forms the concrete ledge. Rock from the Kenwood member does not pass the Highway Commission tests. The samples from the Otis member correspond with the Highway Commission section prepared by Tripp on January 24, 1957. The Kenwood has a highly variable lithology throughout the quarry. Each major bed within it was sampled and labeled from A through H, going from bottom to top.

TABLE XVII

ANALYSES FOR MAJOR CONSTITUENTS - OTIS QUARRY

Bed	Ca as Wt.% $CaCO_3$	Mg as Wt.% $MgCO_3$	Wt.% Insoluble Residue	Total %
OTIS MEMBER				
2	79.9	15.5	2.77	98.2
3	55.9	36.9	4.77	97.6
4	58.7	36.6	4.22	99.5
6	81.0	12.8	4.95	98.8
7	55.3	40.0	2.24	97.5
8A	61.0	31.7	5.05	97.8
8B	59.1	34.8	2.94	96.8
10	59.7	40.2	2.38	102.3
			Avg.	98.6
KENWOOD MEMBER				
H	55.0	42.2	3.46	100.7
F	81.5	17.2	10.00	103.7
D	50.5	22.7	- - -	- -
C	59.4	26.8	16.63	102.8
B	65.1	17.5	18.50	101.1
A	56.6	28.6	12.13	97.3
			Avg.	101.1

TABLE XVIII

DOLOMITE MINERAL CONTENT - OTIS QUARRY

Bed	Wt.% Dolomite
OTIS MEMBER	
2	34.60
6	17.28
7	92.90
10	94.89
KENWOOD MEMBER	
F	99.00
B	95.49

CHAPTER IV

PORE SIZE AND TEXTURAL STUDIES

Introduction

The study of pore-size distribution in aggregates and its potential relationship to texture and various rock properties was an important phase of research on behavior of aggregates. The size and distribution of pores in carbonate rocks are one of the most important but difficult properties to determine. Texture, consisting of the size, shape, and arrangement of grains, accounts for the physical appearance of any rock and, like pore-size distribution, is a description of internal geometry. Texture, by definition, should therefore have an important relationship to the properties of a rock. To date it has been an exceedingly difficult feature to determine quantitatively.

Knowledge of pore space characteristics is important because of their direct influence on other physical and chemical properties. Pore characteristics determine the flow of moisture into and out of an aggregate, its water retentivity, and the development of pressure during a freeze-thaw cycle. In addition, the interior surface of the pores provide an area on which surface-chemical reactions can proceed between mobile substances and the constituents of the rock.

In situations where rates of diffusion or availability of internal surfaces are deciding factors, pore sizes present and pore-size distribution could be more important than total pore volume. It might be assumed that such a situation does exist when carbonate rocks are utilized as concrete aggregate in highways.

Considerations of this nature have led Blanks (1949), Rhoades and Mielenz (1948), Lewis and Dolch (1955) to state that characteristics of pore size in concrete aggregates are the most important of all aggregate physical properties. Although investigators have stressed the critical nature of pore size, work has not progressed along this promising avenue of research because of experimental difficulty of accurately measuring the size of pores. Blaine, et al (1953) approached the problem indirectly through measurement of internal surface area by means of nitrogen absorption and found a correlation with durability and freeze-thaw resistance. Sweet (1948) believed 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. This statement is generally correct, but the 5 micron size is related to the optical limit of measuring the pores rather than any critically measured size range.

After a survey of the literature, the mercury capillary pressure method was adopted as the most practical approach for measuring the size and distribution of pores in aggregates. A mercury capillary pressure apparatus was acquired for this purpose. This was the first time this instrument was ever used in an aggregate study.

The first data obtained by this instrument are discussed in the paper of Lemish, Rush, and Hiltrop (published in 1958 as HRB Bulletin 196). Hiltrop continued the work on pore-size distribution as part of his Masters thesis research (1959) and extended this to a study of the statistical relationship to other aggregate properties in HRB Bulletin 239 (1960).

Pore-size studies were continued by Wallace (1962) as part of his Masters thesis research. Of particular interest was the attempt to investigate texture quantitatively.

The research on pore-size and texture will be summarized as: 1) a review of Hiltrop's investigation on pore-size distribution; 2) his statistical study on the relationship of pore-size distribution and other rock properties to the serviceability of carbonate aggregates; and, 3) Wallace's work on pore-size and texture.

Pore Size Determinations

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 equation stating this relationship is:

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

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

The derivation of this equation is presented by Hiltrop in HRB Bulletin 239, p. 6-7.

Mercury Capillary Apparatus

Purcell, in 1949, developed equipment for measuring pores of such size that their capillary pressures would range between 20 and 2,000 psi. This mercury capillary pressure apparatus (Fig. 16) is manufactured and distributed by Ruska Instrument Corporation, Houston, Texas, under license of the Shell Development Company.

The apparatus consists of a modified 100 cc volumetric pump with attached sample chamber which is connected to a manifold system with manometer and pressure gauges. The pump has a special scale arrangement for reading volume changes in the sample chamber to an accuracy of 0.01 cc. The chamber has a cylindrical cavity 2 inches long and 1 inch in diameter provided with two windows for observing reference levels. The manifold system is mounted on a bakelite panel and permits evacuating the apparatus with a vacuum pump and building up pressure with bottled nitrogen.

After the apparatus has been evacuated to a pressure of between 10 and 20 microns of mercury, the sample chamber with the chip samples was filled with mercury by advancing the pump plunger until the mercury level reached the ref-
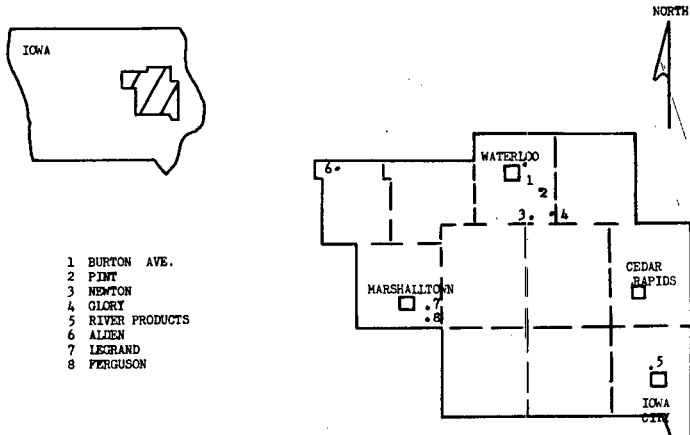
IOWA

1 BURTON AVE.
2 PINT
3 NEWTON
4 GLORY
5 RIVER PRODUCTS
6 ALDEN
7 LEGRAND
8 FERGUSON

NORTH

WATERLOO
1
2
3. 14
MARSHALLTOWN
.7
.8
6•
CEDAR RAPIDS
.5
IOWA CITY

Figure 11 Index map showing the approximate location of the eight quarries sampled.

DEVONIAN CEDAR VALLEY FORMATION

CORALVILLE
RAPID
SOLON

GLORY
NEWTON
PINT
BURTON AVE.
RIVER PRODUCTS

☐ STRATIGRAPHIC RANGE OF ROCKS

▨ LEDGES PRODUCING ACCEPTABLE CONCRETE AGGREGATE

⬚ POTENTIAL LEDGES OF ACCEPTABLE CONCRETE AGGREGATE

⊠ FORMERLY USED AS CONCRETE AGGREGATE

Figure 12 Stratigraphic range of the rocks exposed in five quarries and the position of the concrete aggregate ledges.

MISSISSIPPIAN

GILMORE CITY
HAMPTON FORMATION
IOWA FALLS
EAGLE CITY
MAYNES CREEK
CHAPIN FORMATION

ALDEN
FERGUSON
LEGRAND

▨ LEDGES PRODUCING ACCEPTABLE CONCRETE AGGREGATE

☐ STRATIGRAPHIC RANGE OF ROCKS

⊠ FORMERLY USED AS CONCRETE AGGREGATE

Figure 13 Stratigraphic range of the rocks exposed in three quarries and the position of the concrete aggregate ledges.
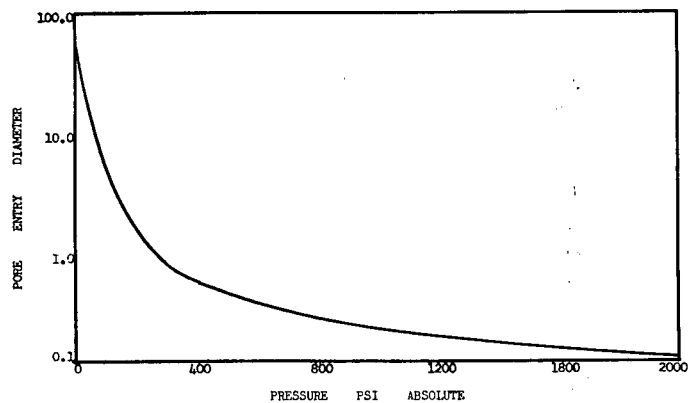
Figure 14 Equilibrium pore diameter in microns vs. absolute pressure in pounds per square inch.

PORE ENTRY DIAMETER

PRESSURE PSI ABSOLUTE

PORE VOLUME OCCUPIED BY HG. CC/GM. (V_o-V)

PRESSURE APPLIED PSIA.

Figure 15 Pressuring curve for sample number 14 from the Rapid member of the Glory Quarry.
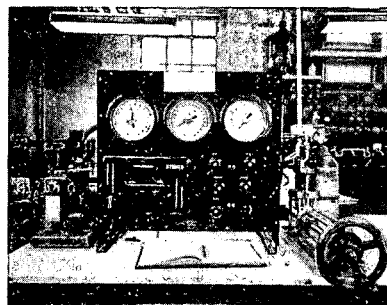
Figure 16 Mercury capillary pressure apparatus manufactured by Ruska Instrument Corporation, Houston, Texas.

erence mark in the upper window. The bulk volume of the sample is read direct-
ly on the scale of the pump. The pressure in the mercury-filled sample chamber
is then increased step-by-step by releasing nitrogen into the system and the
amount of mercury forced into the sample is determined by a reading on the
pump upon returning the mercury level to the reference mark.

Presentation of Data

The data obtained can be treated in a number of ways. The relationship
of pressure to pore entry diameter is semi-logarithmic and is given in fig-
ure 14. This curve shows that the pores ranging in size from 80 to 10 microns
are measured when the first 100 pou nds of pressure are applied. Pores one
micron in diameter are measured at 300 pounds of pressure, but it requires
2,000 lbs. of pressure to measure pores .1 micron in diameter.

A typical pressuring curve plot of a sample is given in figure 15. This
is the method often used to show amount of mercury absorbed at a given pressure.
It is a cumulative curve and slopes, or changes in slope, are considered to be
important by petroleum reservoir engineers interested in relative permeability
measurements.

The method of treating the data used in Hiltrop's studies was through
distribution curves of both the non-normalized and normalized type. A non-
normalized distribution curve represents the frequency of occurrence of one
particular size of pore*. The curves indicate at what size the greatest
number of pores occur. A normalized distribution curve is one in which the
area under the curve has been made equal to one, thus providing a method of
comparing the curves with regard to their shape. The equation for a non-
normalized distribution curve is:

$$D(r) = \frac{P}{r} \frac{d(V_o - V)}{dp}$$

$$
\begin{aligned}
\text{where} \quad D(r) &= \text{distribution function} \\
p &= \text{applied pressure} \\
r &= \text{pore entry radius} \\
(V_o - V) &= \text{volume injected from zero to pressure p} \\
\frac{d(V_o - V)}{dp} &= \text{slope of } V_o - V \text{ versus pressure as presented} \\
&\quad \text{in a pressuring curve}
\end{aligned}
$$

All the terms on the right side of the equation are known or determinable,
and a plot D(r) against r gives the distribution curve.

- - - - - - -

*It should be understood that the term "pore size" is used synonymously
for pore entry radius or diameter

To normalize a typical distribution curve (Fig. 18), the equation to express this relationship is derived by Hiltrop (1960) as:

$$d(r) \ = \ \frac{p}{rVo} \ \frac{d(Vo-V)}{dp}$$

where $d(r)$ is the normalized distribution function

The derivation of all the equations applicable to the study are presented by Hiltrop in his Masters thesis (1959) and HRB Bulletin 239 (1960, p. 6-12).
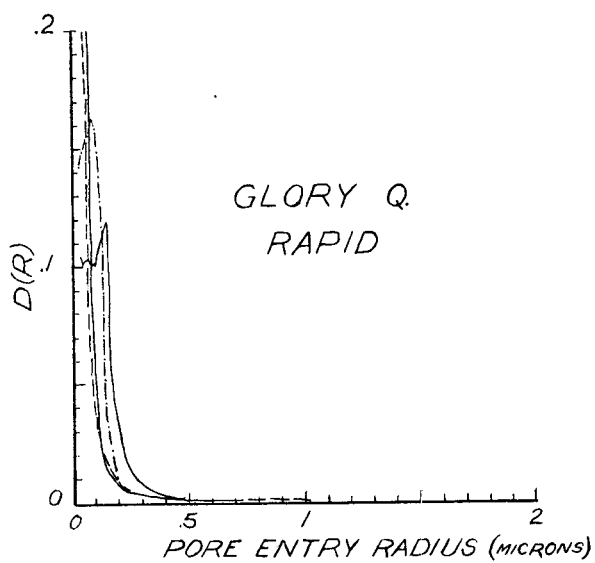
Typical Curves

Examples of some non-normalized distribution curves are presented in figure 17, in which samples representing the Cedar Valley formation were studied. Review of these curves shows that they have a relationship to the distinctive types of lithology found in the different members of the Cedar Valley formation. A discussion of these curves is presented by Lemish in HRB Bulletin 196 (p. 8-11). Observation of these curves demonstrate some interesting features. In all the curves, regardless of rock type, the bulk of the pores have a pore entry radius below .2 of a micron. There are more pores below this size in the rock than any other. These pores do not necessarily account for most of the pore volume, but they do represent the large amount of internal surface available in a given rock. It should be pointed out that visible light waves range from .4 to .8 of a micron in wave length. The bulk of the pores in a rock are therefore invisible because of being smaller than the wave length of light.

In figure 17, the contrast of A to B for Rapid type rock, due to the effects of weathering, is striking. The weathered rocks are characterized by bimodal curves showing a great increase in pore size from .1 of a micron to 1 micron; a ten-fold increase in radius due to the leaching action of the weathering process.

Relationship of Pore-Size and Rock Properties to Aggregate Serviceability

Hiltrop (1960) made an attempt to evaluate statistically the pore-size distribution curves and other rock properties available for a given rock to serviceability. The methods and data of this study are presented in his Masters thesis (1959) and in HRB Bulletin 239 (1960). A summary of this study will be presented in this section.
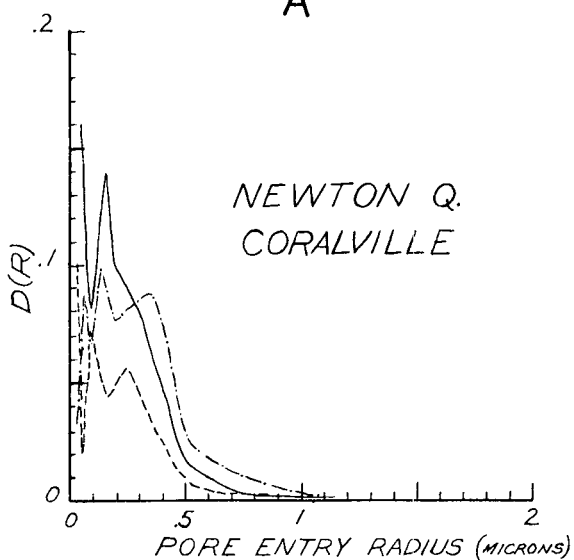
The principle rocks compared were those from the Cedar Valley formation as represented by the Glory, Newton, Pint, Burton Avenue, and River Products quarries (Figs. 1, 2, 3, 4, 5, 11, 12). Rocks of Mississippian age from the Ferguson, LeGrand, and Alden quarries were also studied (Figs. 11, 13).
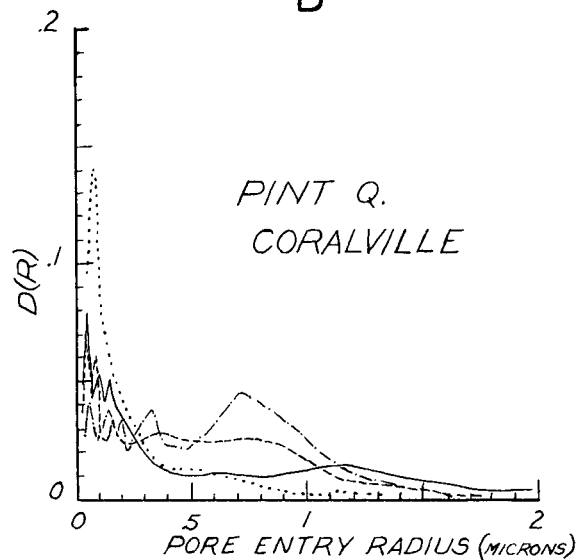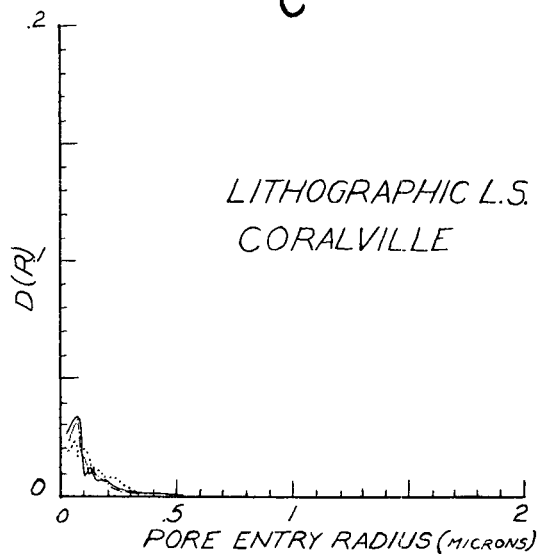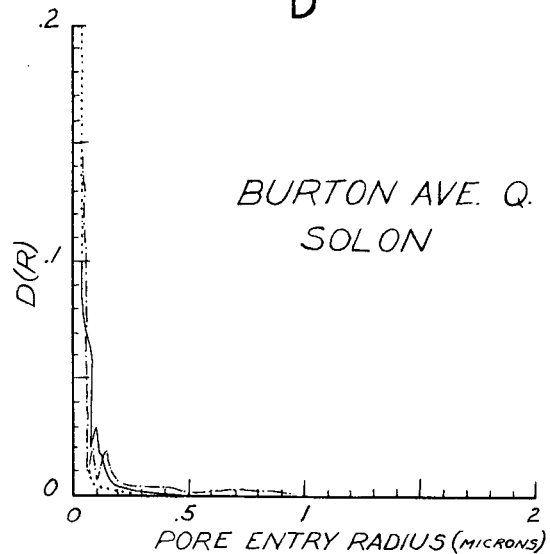
GLORY Q.
RAPID

A

GLORY Q.
WEATHERED RAPID

B

NEWTON Q.
CORALVILLE

C

PINT Q.
CORALVILLE

D

LITHOGRAPHIC L.S.
CORALVILLE

E

BURTON AVE. Q.
SOLON

F
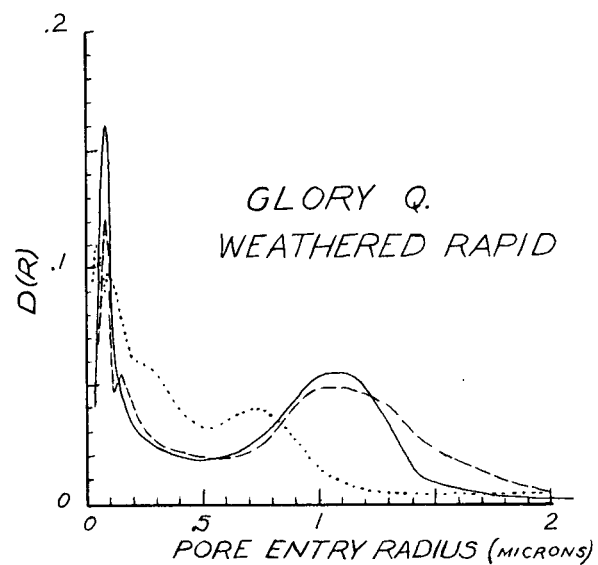
17
Fig. 8— Some representative pore size distribution curves
for carbonate rocks. The plot of the distribu-
tion function (D(R) versus pore entry radius
gives the frequency with which pores of a part-
icular size occur in the rock.

The properties evaluated were insoluble residue, clays present, total porosity, effective porosity, freeze-thaw loss, service record, pore-size distribution, texture, and Ca/Mg ratios. These data obtained on samples from the various quarries mentioned above are tabulated in Tables VI through XIII. These data, exclusive of pore-size distribution, were obtained during earlier studies or specifically determined for this one. A statistical method, based on conditional probability and called frequency of occurrence in this report, was applied to the data in an attempt to determine more closely which properties of a rock are most closely related to serviceability.

Pore-Size Distribution Curve Classification

Pore-size distribution curves were determined for all rocks studied and normalized distribution curves were then established for each sample. The curves were then classified into 8 categories on the basis of the shape of the curves. The typical curve shape for each type of distribution category is given in figure 19. Details for characterizing these curves are presented in HRB Bulletin 239, p. 12.

Insoluble Residue

The insoluble residue was determined by the following method: a 100 gram sample of chip-size material was dissolved in 3N hydrochloric acid; the residue was filtered, dried, and weighed; the per cent of insoluble residue was based on the weight of sample originally taken.

Clay Minerals Present

The clay minerals present in the rock was determined by the flotation method developed by Rush (1957) and Bisque (1957). The only clay mineral observed in any of the samples was illitic in nature, and only the presence or absence of illite was tabulated in the tables presented.

Porosity

Total porosity is a measure of the total void volume in the rock and was determined by measuring the powder and bulk density of the rock. The powder density was determined by the method described by Rush (1957) in his Masters thesis. The bulk density was determined in the mercury capillary apparatus.

$$\text{Total Porosity (\%)} = 100 \left(1 - \frac{b}{p}\right)$$

where b is bulk density and p is powder density

Effective porosity is a measure of the interconnected pores in a rock. It was determined by means of the mercury capillary apparatus. The effective pore volume was the volume of mercury injected into the rock at 2,000 psi. The bulk volume was determined by the amount of mercury displaced by one gram of rock.
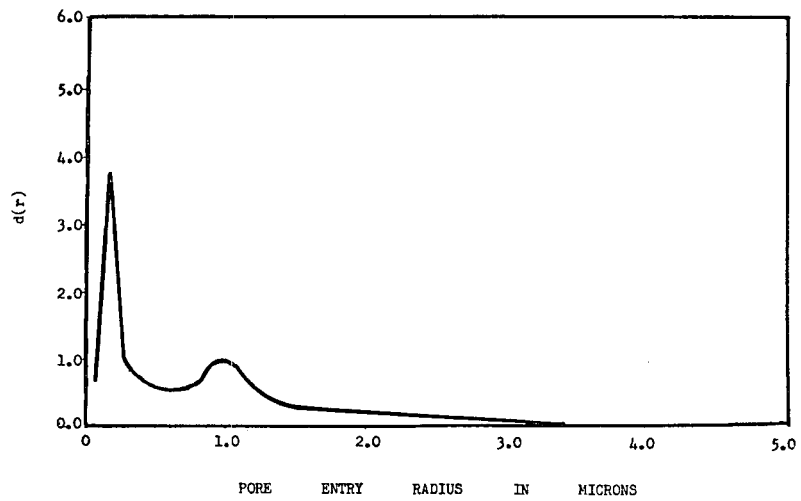
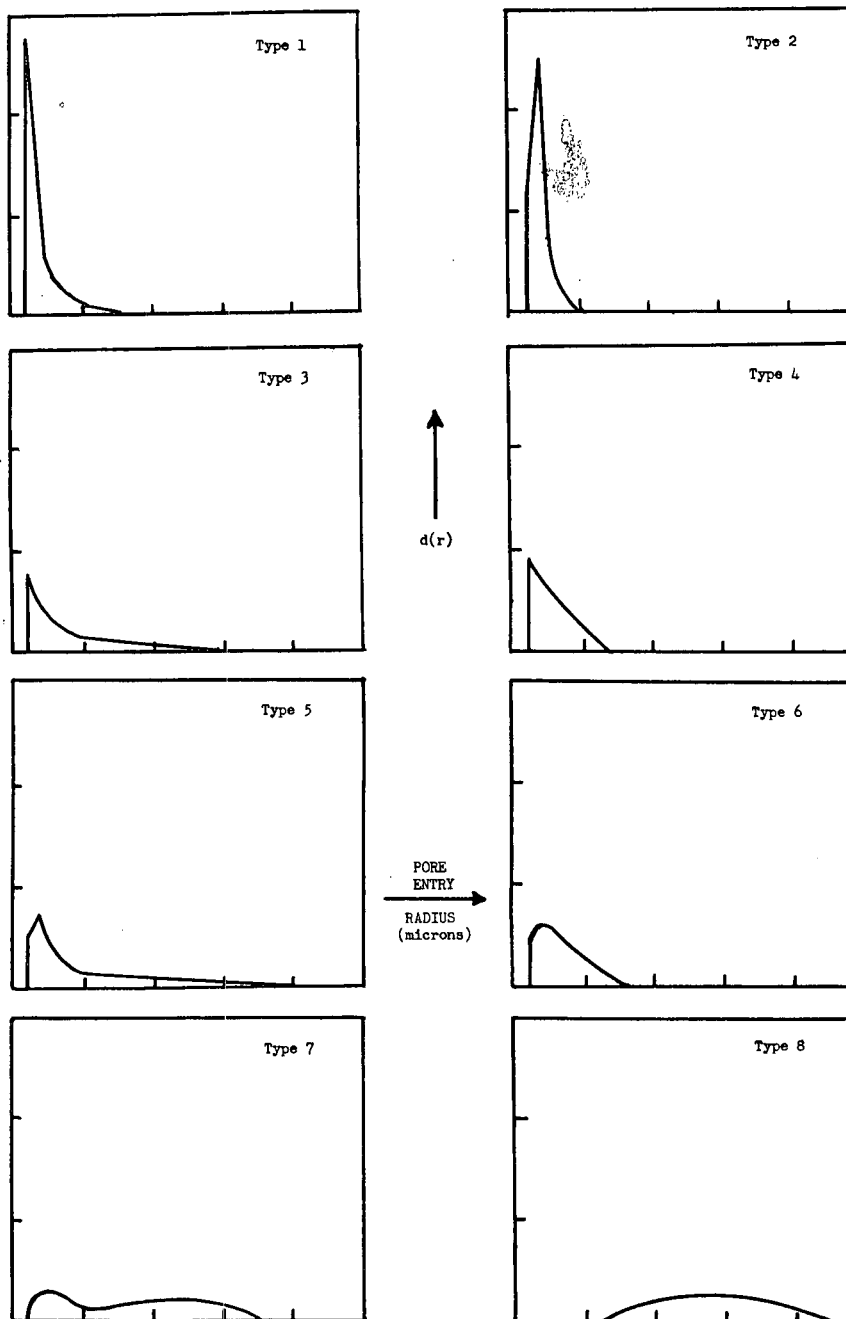Figure 18. Normalized distribution curve. Sample number 14 from the Rapid member of the Glory quarry.

Figure 19. Sketch showing a typical curve of each type distribution.

Freeze-Thaw Results

The freezing and thawing tests were conducted by the Materials Department of the Iowa State Highway Commission on samples provided. The water-alcohol freeze-thaw test was used and is described in the Standard Specifications Manual of the Iowa State Highway Commission.

Service Records

Of the five quarries in rocks of Devonian age, the Glory and River Products quarries have a service record which can be evaluated at this time. Rock from the Glory Quarry was widely used throughout northeastern Iowa as long ago as thirty years. That length of time has been sufficient to prove the unsuitability of Glory stone for concrete highway construction. It is generally agreed to be unacceptable and is used here as an aggregate representative of poor service.

Service records for the aggregate from the other four Devonian quarries are indeterminate, due to the relatively short time these aggregates have been used in highway construction.

Considering the quarries in Mississippian rocks, the Alden has proved itself excellent in service. The "basal" oolitic Chapin at the LeGrand Quarry has had a good service record, but rocks from the overlying Hampton formation are unsatisfactory. The service record of rocks from the Ferguson Quarry is indeterminate, but are satisfactory to date in pavements up to 10 years in age.

Textural Studies

In order that texture could be considered as a parameter in the statistical analysis, each sample was categorized according to the textural characteristics it possessed. All the specimens for which pore-size determinations were made were also studied, both in hand specimen and thin section. This was difficult task, but four textural categories (Fig. 20) were established so that, once a rock was categorized, it could be re-categorized into the same groups (HRB Bulletin 239, p. 14).

Statistical Treatment of Data

The data presented in Tables VI through XIII were studied by the frequency of occurrence method. The frequency of occurrence is a fraction formed by placing in the denominator the total number of rocks with a given set of characteristics; and in the numerator, the number of rocks within the total which meets an additional requirement, or additional requirements. The method is based on conditional probability and the derivation is given in Hiltrop's Masters thesis (1959). This method was employed because of the great number of variables (8 rock properties in this case) which can be considered related to its service in concrete.

The frequency of occurrence is obtained by asking a question concerning possible relationships between certain characteristics in an attempt to see what properties affect the suitability of an aggregate. For example, one would
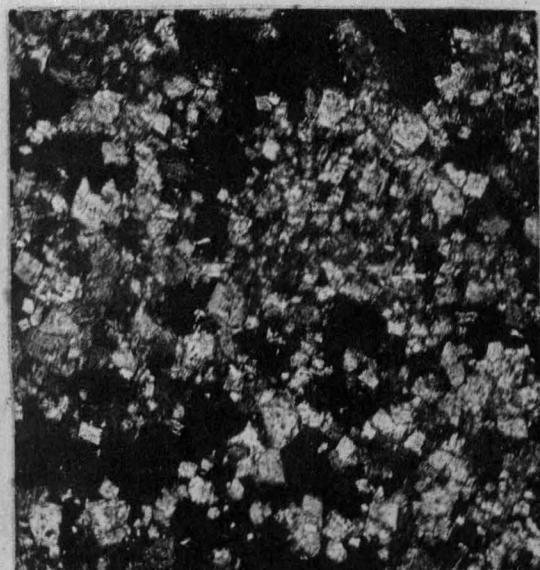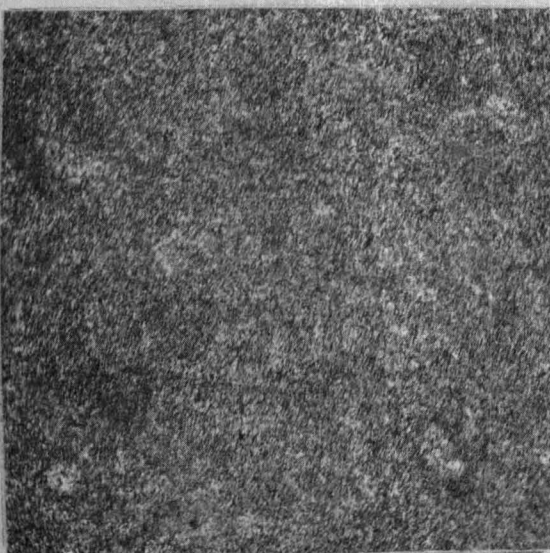
Type 1
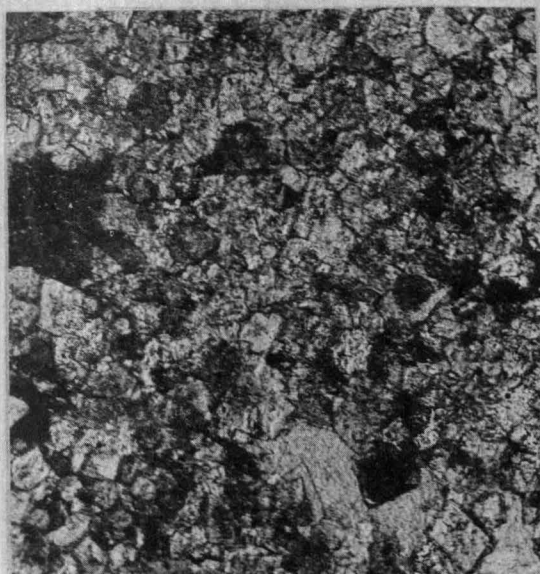
Type 2

Type 3

Type 4

Figure 28. Photomicrographs of typical thin sections representing each of the four categories.

TABLE VI – CARBONATE ROCK PROPERTIES, GLORY QUARRY

Stratigraphic Units		Sample No.	Insoluble Residue	Clay Mineral Present	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Pore-Size Distribution	Texture	Ca/Mg Ratio	Miscellaneous
CEDAR VALLEY FORMATION	CORALVILLE	24	2.0	-	2.5	1.2	6.9	6	-	63.0	
		23	50.0	-	19.0	-	-	6	-	-	
		22	1.0	-	2.2	0.3	1.8	8	-	59.0	
		21	8.0	-	2.2	0.9	10.0	6	1	19.5	
		20	2.0	-	1.5	0.3	5.4	8	4	77.7	
		19	12.0	illite	5.0	1.1	20.0	6	1	8.5	
		18	50.0	illite	12.8	-	-	-	-	-	
	RAPID	17	22.0	illite	21.4	-	95.0	-	-	2.5	Unsatisfactory Service Record
		16	16.0	illite	13.9	13.0	68.0	5	1	2.7	
		15	6.0	illite	1.8	0.1	-	8	1	8.7	
		14	16.0	illite	12.2	10.9	27.0	7	1	2.5	
		13	21.0	illite	14.2	11.5	30.0	7	1	2.4	
		12	22.0	illite	11.7	-	-	-	-	-	
		11	12.0	illite	10.4	-	42.0	-	-	3.4	
		10	10.0	-	7.6	5.8	25.0	2	2	3.3	
		9	15.0	illite	9.6	6.4	42.0	1	2	3.8	
		8	39.0	illite	4.8	4.6	29.0	2	2	-	
		7	12.0	illite	7.6	2.8	32.0	1	2	4.8	
		6	19.0	illite	8.0	4.2	33.0	2	2	3.8	
		5	15.0	illite	7.3	3.2	36.0	1	2	4.5	
		4	10.0	illite	5.2	3.4	42.0	1	2	4.0	
		3	22.0	illite	5.2	4.2	30.0	6	2	4.7	
		2	49.0	-	8.1	4.8	27.0	5	2	5.8	
		1	7.0	-	8.3	5.6	11.0	6	2	8.3	

TABLE VII – CARBONATE ROCK PROPERTIES, NEWTON QUARRY

Stratigraphic Units		Sample No.	Insoluble Residue	Clay Mineral Present	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Pore-Size Distribution	Texture	Ca/Mg Ratio	Miscellaneous
CEDAR VALLEY FORMATION		20	1.0	none	3.7	-	19.0	-	-	1.4	
		19	14.0	illite	2.2	0.9	4.7	6	1	1.7	
		18	6.0	none	5.2	3.0	49.0	2	1	7.1	
		17	2.0	none	1.1	-	11.0	-	-	10.0	
		16	10.0	none	8.2	5.0	38.0	4	4	1.8	
		15	2.0	none	6.8	4.4	5.5	1	1	2.3	
		14	14.0	none	-	-	-	-	-	2.0	
	CORALVILLE	13	6.0	illite	11.5	-	7.5	-	-	1.9	
		12	3.0	none	8.3	-	1.6	-	-	2.3	Concrete Aggregate Ledge / Service Record Indeterminate
		11	5.0	none	11.6	10.2	3.2	4	1	2.6	
		10	2.0	none	6.2	-	1.0	-	-	5.5	
		9	2.0	none	10.6	10.5	0.9	7	-	2.5	
		8	4.0	none	11.1	11.0	1.6	4	-	3.3	
		7	5.0	none	7.4	-	-	-	-	11.1	
		6	3.0	none	5.5	5.4	1.9	4	1	6.0	
		5	3.0	none	5.5	5.3	1.5	3	1	6.5	
		4	2.0	none	4.6	4.1	2.8	6	1	3.4	
		3	4.0	none	9.5	-	1.2	-	-	2.6	
		2	13.0	illite	7.9	1.5	31.0	2	1	2.1	
	RAPID	1	10.0	none	6.2	4.3	16.0	6	1	2.1	

TABLE VIII - CARBONATE ROCK PROPERTIES, PINT QUARRY

Stratigraphic Units		Sample No.	Insoluble Residue	Clay Mineral Present	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Pore-Size Distribution	Texture	Ca/Mg Ratio	Miscellaneous
CEDAR VALLEY FORMATION	CORALVILLE	15	1.7	none	9.8	8.4	1.7	5	3		Concrete Aggregate Ledge / Service Record Indeterminate
		14	1.6	trace	10.8	-	3.6	-	-		
		13	1.7	trace	10.2	8.3	1.0	5	1		
		12	3.4	none	13.0	-	1.9	-	-		
		11	2.4	none	8.5	3.8	2.3	4	1	3.2	
		10	2.3	none	9.8	6.1	1.7	6	1		
		9	2.7	none	10.9	9.1	1.5	7	2		
		8	1.9	trace	4.7	-	3.7	-	-		
	RAPID	7	9.0	trace	6.2	-	-	-	-		
		6	0.8	none	3.6	-	2.3	-	-		
		5	18.9	illite	20.1	-	Weathered High Losses	-	-		
		4	16.7	illite	21.2	-		-	-	2.0	
		3	22.5	illite	17.8	-		-	-		
		2	17.5	illite	18.2	-		-	-		
		1	15.8	illite	25.4	21.6	58.0	7	3		

TABLE IX - CARBONATE ROCK PROPERTIES, BURTON AVENUE QUARRY

Stratigraphic Units		Sample No.	Insoluble Residue	Clay Mineral Present	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Pore-Size Distribution	Texture	Ca/Mg Ratio	Miscellaneous
CEDAR VALLEY FORMATION	CORALVILLE	28	8.8	illite	14.0	9.1	2.8	6	1	2.4	
		27	1.6	trace	7.3	1.6	7.1	4	1	62.7	
		26	27.5	illite	16.1	8.2	-	6	1	3.7	
		25	0.7	none	7.5	1.7	2.8	2	4	4.3	
		24	11.2	illite	12.2	10.4	57.0	6	1	2.6	
	RAPID	23	12.7	illite	14.4	12.1	28.0	7	3	2.8	
		22	47.6	illite	10.3	1.7	17.0	1	3	2.0	
		21	17.0	none	21.2	18.0	32.0	5	3	2.0	
		20	20.4	illite	14.6	9.2	75.0	6	3	2.2	
		19	35.0	illite	14.1	6.4	75.0	2	3	2.0	
		18	33.0	illite	14.1	7.1	81.0	2	3	2.4	
		17	34.0	illite	13.9	4.3	51.0	2	3	8.8	
		16	23.0	illite	8.6	3.4	90.0	1	3	2.4	
		15	23.0	illite	10.8	3.3	56.0	1	3	3.0	
		14	24.0	illite	12.2	4.5	56.0	2	3	2.5	
		13	16.0	illite	5.7	0.7	61.0	4	1	12.5	
	SOLON	12	5.2	none	5.1	1.1	2.5	4	2	20.5	Concrete Aggregate Ledge / Service Record Indeterminate
		11	7.0	none	5.1	0.6	4.2	3	2	22.1	
		10	4.0	none	7.1	1.3	3.0	2	2	30.4	
		9	2.8	none	9.4	1.6	1.9	1	2	39.6	
		8	4.3	none	5.4	0.4	1.8	3	2	23.6	
		7	2.9	none	6.5	1.2	2.9	1	2	41.5	
		6	12.8	none	9.7	3.3	6.7	6	2	27.8	
		5	2.9	none	5.8	1.7		6	2	31.3	
		4	4.5	none	6.5	2.0		2	1	33.0	
		3	5.5	trace	6.1	1.4	3.8	6	1	12.1	
		2	8.0	trace	7.8	0.7		3	1	9.7	
		1	14.4	illite	9.7	1.9		1	1	8.5	

TABLE X - CARBONATE ROCK PROPERTIES, RIVER PRODUCTS QUARRY

Stratigraphic Units		Sample No.	Insoluble Residue	Clay Mineral Present	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Pore-Size Distribution	Texture	Ca/Mg Ratio	Miscellaneous
CEDAR VALLEY FORMATION	CORALVILLE	32	-	none	-	-	-	-	-	-	Concrete Aggregate Ledge Service Record Indeterminate
		31	-	none	-	-	7.9	-	-	-	
		30	1.0	none	4.8	0.7	5.3	5	4	657.0	
		29	1.0	none	8.8	4.0	2.7	6	2	163.0	
		28	3.0	-	6.7	1.8	1.6	5	-	10.4	
		27	1.0	none	6.7	4.4	-	3	-	64.6	
		26	4.0	none	5.4	2.0	-	5	-	212.0	
		25	4.0	none	5.5	2.5	-	3	2	127.0	
		24	2.0	none	7.0	2.0	-	5	1	162.0	
		23	3.0	none	5.5	1.2	4.5	2	2	214.0	
		22	6.0	none	7.5	2.5	4.5	2	-	99.6	
	RAPID	21	5.0	trace	5.5	0.9	53.0	3	2	3.9	
		20	12.0	illite	12.6	6.7	-	6	2	4.1	
		19	11.0	illite	7.0	3.2	31.0	2	2	6.2	
		18	12.0	-	7.5	2.9	42.0	2	2	3.5	
		17	10.0	illite	7.1	4.0	35.0	2	-	4.9	
		16	8.0	trace	3.5	1.1	31.0	7	2	36.3	
		15	5.0	-	4.8	0.8	47.0	5	2	8.4	
		14	13.0	-	5.6	0.9	47.0	5	2	7.4	
		13	8.0	trace	6.4	0.8	47.0	7	2	19.5	
		12	10.0	none	6.0	0.9	-	7	-	13.5	
		11	13.0	illite	5.3	0.8	-	7	2	12.3	
	SOLON	10	12.0	illite	6.0	0.6	68.0	7	2	8.6	
		9	15.0	illite	10.0	0.5	63.0	5	-	7.3	
		8	14.0	illite	7.2	0.5	59.0	5	-	9.0	
		7	10.0	trace	7.0	0.9	50.0	5	2	10.3	
		6	13.0	trace	5.5	0.7	56.0	5	-	15.4	
		5	16.0	trace	6.8	0.4	56.0	7	4	11.1	
		4	12.0	trace	5.0	1.0	46.0	7	2	30.2	
		3	16.0	-	5.5	0.4	61.0	7	4	68.3	
		2	10.0	-	-	-	43.0	-	-	197.0	
		1	15.0	trace	6.0	0.4	3.8	7	-	24.0	

TABLE XI - CARBONATE ROCK PROPERTIES, LEGRAND QUARRY

Stratigraphic Units		Sample No.	Insoluble Residue	Clay Mineral Present	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Pore-Size Distribution	Texture	Ca/Mg Ratio	Miscellaneous
HAMPTON FORMATION		7	1.4	illite	22.8	10.5	5.8	6	2	7.8	Service Record Unsatisfactory
		6	6.1	illite	6.3	5.3	4.0	6	2	18.5	
		5	1.6	illite	6.7	5.5	3.8	3	2	2.9	
		4	1.4	illite	22.5	14.3	1.9	7	2	2.1	
		3	1.1	illite	21.5	9.7	3.0	7	2	3.1	
		2	1.3	illite	13.5	9.2	4.3	6	1	4.5	
		1	2.2	illite	10.0	9.7	3.3	7	2	2.2	
CHAPIN FORMATION		Top.	1.5	none	8.5	5.5	3.5	2	-	∞	Service Record Good
		Mid.	1.2	none	12.5	12.5	3.5	6	-	∞	
		Bot.	1.5	none	10.3	7.3	3.5	4	-	∞	

TABLE XII – CARBONATE ROCK PROPERTIES, FERGUSON QUARRY

Stratigraphic Units	Sample No.	Insoluble Residue	Clay Mineral Present	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Pore-Size Distribution	Texture	Ca/Mg Ratio	Miscellaneous
F O R M A T I O N	1	1.2	illite	10.1	9.4	5.6	5	-	2.0	
	2	1.1	trace	13.3	11.0	3.9	6	-	8.9	
	3	1.5	illite	10.0	15.8	3.5	5	-	7.0	
	4	7.7	illite	3.3	1.6	1.0	5	-	2.1	Concrete Aggregate Ledge Service Record Indeterminate
	5	1.8	illite	6.1	6.5	7.7	3	-	2.3	
	6	0.5	illite	5.3	3.6	1.6	1	-	32.6	
	7	3.3	illite	7.0	2.4	1.1	3	-	1.9	
	8	0.3	none	9.5	7.9	1.5	6	3	81.2	
	9	9.6	trace	4.5	4.4	3.4	5	2	2.8	
	10	4.4	illite	8.5	6.8	2.4	5	2	2.7	
	11	16.9	illite	3.5	2.9	8.5	5	2	2.4	
H A M P T O N	12	1.5	trace	14.5	7.7	4.6	6	2	∞	
	13	2.9	illite	3.4	3.3	3.8	6	1	2.8	
	14	1.9	illite	5.5	3.0	1.0	4	1	5.2	
	15	2.0	illite	10.3	10.2	1.0	5	2	2.8	
	16	1.1	illite	11.5	10.1	2.5	6	-	1.2	
	17	3.1	illite	15.5	14.5	1.3	8	3	1.4	
	18	2.7	illite	18.2	15.3	3.2	7	-	7.9	
	19	1.5	illite	14.5	13.7	1.2	7	-	4.7	
	20	2.3	illite	14.5	14.1	1.2	8	-	1.9	

TABLE XIII – CARBONATE ROCK PROPERTIES, ALDEN QUARRY

Stratigraphic Units	Sample No.	Insoluble Residue	Clay Mineral Present	Total Porosity	Effective Porosity	Freeze-Thaw % Loss	Pore-Size Distribution	Texture	Ca/Mg Ratio	Miscellaneous
F O R M A T I O N	20	0.2	none	2.8	0.8	2.0	5	4	53.7	
	19	0.2	none	6.1	1.2		1	2	42.9	
	18	0.4	trace	8.6	4.3		6	2	26.6	
	17	0.5	trace	11.4	8.2		6	2	49.2	
	16	0.2	none	9.7	6.0		6	2	71.7	
	15	0.3	trace	6.5	2.7		6	2	100.3	
	14	0.1	none	8.6	3.6		6	2	78.4	
	13	0.3	none	11.5	6.9		3	2	64.1	
	12	1.6	trace	12.7	11.4		5	2	87.7	
	11	0.1	none	15.1	12.2		7	2	99.3	
L I T H I C G R O U P	10	1.3	none	17.3	15.3		7	2	99.5	
	9	0.7	trace	17.3	16.1		5	2	88.4	
	8	0.6	none	17.6	15.2		5	2	70.5	
	7	0.4	none	14.8	11.3		7	2	58.5	
	6	0.1	trace	16.6	10.7		7	2	101.7	
	5	0.1	none	15.5	12.9		7	2	102.1	
	4	0.1	none	8.4	7.8	2.0	5	2	100.7	
	3	-	-	-	-	-	-	-	-	
	2	-	-	-	-	-	-	-	-	
	1	-	-	-	-	-	-	-	-	

like to know what the frequency of occurrence is among specimens with pore-size distribution of Type 1 or 2 that have freeze and thaw loss above 6 per cent. 31 specimens in the 8 tables of data have Type 1 or 2 pore-size distribution curves, but only 19 of these exceed 6% freeze and thaw loss. The frequency of occurrence (F of O) therefore is 19/31. It means that for any specimen in the table of pore-size Type 1 and 2, 19 out of 31 times it will exhibit a freeze-thaw loss greater than 6%. In similar manner, a number of questions can be asked of a system containing a large number of variables. For details concerning the questions asked, one is referred to Hiltrop's thesis and HRB Bulletin 239, p. 17-20.

Summary and Conclusions

From the questions asked, in an attempt to find out which property or combination of properties was related to service, several facts emerge.

It must be kept in mind that the probabilities derived here are based only on that population for which data are provided in the tables VI through XIII. Extrapolation of any one of these conclusions to encompass another rock population simply would not be valid at this time. However, it is felt that the techniques described are applicable and the frequency of occurrence do indicate a direction which would be worthy of further investigation.

One conclusion is that, when a rock is dolomitic, has an insoluble residue equal to or greater than 10%, and has a certain texture in addition to possessing a characteristic type of pore distribution, its probability of having poor freeze-thaw characteristics is high. It is this type of statement which may eventually be employed to describe a rock with potentially poor service record.

With regard to whether freeze-thaw can be correlated with poor service, it can be seen that it correlates with poor service only for the Devonian rocks and not the Mississippian rocks. Freeze-thaw data represent freeze-thaw performance and not service. What criteria other than freeze-thaw occur more frequently with poor service? The best answer to date from the data at hand is: the universal presence of illite in rocks with poor service. This is true regarding low Ca/Mg ratios also.

Pore-size distribution alone does not appear to be related closely with either freezing and thawing, or service record, when both Devonian and/or Mississippian rocks are considered. On the other hand, combined with 7 other variables, such as pore-size curves of Types 5, 6 or 7, effective porosity between 0-17%, total porosity between 2-18%, Ca/Mg equal to or greater than 42, residue less than 1.6%, a trace of clay or less, freeze-thaw of 4% or less, and a texture of 2, it is related to good service with a F of O of 13/19. This is a potential description of a "good" aggregate. Considering 9 variables are treated simultaneously, an F of O of 13/19 is interesting. A closer analysis of pore-size distribution could lead to a closer relationship to service record.

Further Pore-Size and Texture Studies

Further work on pore-size was continued by Wallace (1962) as part of his Masters thesis research. The main aim was to follow-up on Hiltrop's studies and investigate further some of the problems which became evident in the earlier study. Part of the study was devoted to a systematic investigation of the mercury capillary technique, to study statistically what variability of results is due to the apparatus and/or sample preparation. The other part of his study concerned the properties of pore size, pore-size distribution, bulk density, pore geometrical factor, and effective porosity -- all of which are obtained with the mercury capillary apparatus -- and attempt to relate these to texture. Ca/Mg ratios, insoluble residue, and optical density were also obtained.

An intensive study was made on a large block of rock from each of five quarries in an attempt to keep lithologic variation to a minimum. A block of rock was taken from the Burton Avenue, Glory, LeGrand, and Ferguson quarries, as well as the Gilmore City formation. As a result, no major correlations were possible although much was learned concerning the optimum size of sample to be used in the instrument and textures which will make future studies more meaningful.

The techniques for measuring pore size and pore-size distribution, insoluble residue, Ca/Mg ratio, bulk density, and effective porosity have already been described in other sections of the report. The pore geometrical factor is a measure of the tortuosity or circuitousness of the connected pores. Optical density was a measure of the amount of light transmitted by a thin section in an attempt to get a measure of the amount of residue and grain boundary a rock might have. The optical density studies were inconclusive.

The problem of texture and the approach used to measure it quantitatively will make up the major part of this section. The review of the variance in data from the apparatus is followed by our conclusions.

Texture

An intensive effort was made to measure textures quantitatively. This has been a major problem since most textures are described on the basis of grain size and subjective terminology. Hiltrop (1959) used this basis in setting up four categories of texture. This was unsatisfactory but it was the only feasible method available at the time. Yet a relationship between pore-size distribution and texture was evident when hand specimens of all the samples Hiltrop studied were placed in eight groups corresponding to his 8 types of pore-size distribution curves. It was then evident that the majority (80-90%) of the rocks in each class were similar in appearance. This was especially true of the Devonian rocks and indicated texture and pore-size data were related.

Texture and the mercury injected into a rock can be considered related to one another if one assumes the porosity of the rocks to be the interstitial type. The injection of mercury measures the porosity resulting from interconnected pores, the bulk of which can be considered interstitial. At maximum injection pressure a model of a given unit of rock would then consist of a large number of irregularly-shaped grains surrounded in part by an intercon-

nected mercury network. The numerical mercury data are therefore a potential measure of pore geometry and the voids in turn are also an expression of the size, shape, and arrangement of grains they surround. Size, shape, and arrangement of grains is also the definition of texture. Since numerical data are available to express void geometry, a correlation between mercury injection and texture could also be expressed in numerical terms providing a truly definitive numerical way could be found to describe texture.

Following a discussion of this problem with Dr. Felix Chayes, of the Geophysical Laboratory in Washington, D.C., a statistical method for measuring the volume'surface ratio was suggested. This method has been developed as part of the thesis research.

The volume/surface ratio was determined on the samples studied. This ratio is in effect a description of internal geometry of the mineral grain configuration in a rock. It was determined by a statistical method developed by Chalkey and Cornfield which gave an expression:

$$\frac{rh}{4c} = \frac{volume}{surface}$$

where r = length of the "dropped" or projected line
h = number of hits
c = number of cuts

The method was originally devised for measuring the volume/surface ratio of cancer cells. In the original study, 2000 needles of a definite length were randomly dropped on slices of a model which contained regular geometric figures of known surface and volume. Hits are defined as the number of times an end of a line falls within a grain. A cut is recorded whenever a line crosses one or more boundaries. By dropping enough "needles" one is able to define the geometry of the figures.

The Chalkey method was applied to the problem of studying rock textures with some modifications. Instead of dropping needles, 10 random lines were drawn in each of twenty 4" x 4" squares on acetate sheet, giving a total of 200 random lines. The squares were then placed on 4" x 4" tracing of the grain boundaries copied from a photomicrograph of a carbonate rock thin section, and the "hits" and "cuts" were determined. For our study we modified the definition of hits so that one hit is recorded when both ends of the line fall within a single crystal, and two cuts when a line crosses one or more boundaries. 400 lines were projected onto each sample tracing and the volume-to-surface was calculated for the samples tested. The ratios range from .00691 to .02437. If these values are converted to the more familiar specific surface or surface/volume ratio, they range from 145 to 41. Three volume-to-surface ratios were determined in each block of rock and, for the most part, they gave fairly good agreement (Wallace thesis, Figs. 5, 6).

To insure the validity of the data obtained in our carbonate rocks, the Chalkey method is being tested thoroughly on a series of 4" x 4" x 6" blocks containing beads, cubes, pipe cylinders, and mixtures of these embedded in Portland cement paste. The volume-to-surface is known for each model. The same random lines are being used. Preliminary data show a surprisingly close relationship of our experimental value with the known volume-to-surface ratio.

A brief summary of the preliminary data obtained to date are as follows:

TABLE XIV

SURFACE/VOLUME DATA

Model Type	X Experimentally Determined Surface/Volume	Y Known Surface/Volume	(X-Y)
Marbles	3.898	3.809	+.089
Beads	10.020	10.078	-.058
Marbles and beads	6.752	6.615	+.137
Brass pipe cylinders	18.420	19.114	-.694
Cubes	10.119	10.129	-.010

These values are surprisingly close and greatly strengthen the method as a powerful tool in future studies of rock properties.

Mercury Capillary Apparatus Data

A careful statistical study was made on the optimum size of chips used in the mercury capillary apparatus. Other properties obtained in this process, such as effective porosity and bulk volume, were also studied. It was found that a definite relationship exists between effective porosity determination and the chip-size used in the mercury capillary apparatus. The most consistent results will be obtained when uniformly graded small chips passing a .185-inch sieve and retained on a .093-inch sieve are used.

It was found that the shape and surface configuration of the chips appear to be an important factor, particularly with bulk density and effective porosity determinations. The bulk density is a function of the surface area of the chips which in turn is a function of the shape of the chips. Since the shape and surface configuration of chips cannot be controlled, it might prove beneficial to run shaped samples, such as cores, in the mercury capillary apparatus.

Summary

The data from this study are presented in the thesis of Wallace (1962) as a set of tables in figures 5 and 6. They are not reproduced here, in that the

number of samples studied was limited. The great value of this study was the location of sources of error in mercury capillary technique, and application and testing of a method for measuring texture in terms of surface area to volume ratio. This promises to be an excellent way of getting numerical data on rocks which will be of extreme value in categorizing them.

Conclusions

The pore size and textural studies reported in this section probably represent the only detailed study of this type ever attempted. It has been a thoroughly experimental endeavor throughout. The data gained are unique, and their greatest value has been the insight they provide in understanding the problems of aggregate. Pore size as of yet cannot be directly related to poor service, but a strong trend does exist. With better data on texture now possible through a measure of their surface/volume ratio, it will be possible to solve this problem in the future.

CHAPTER V

CONCRETE STUDIES

Introduction

Studies on concrete with good and poor service records were made in an attempt to learn more concerning aggregate behavior. The major part of the chemical studies reported in the next section are the outgrowth of the concrete investigations. The initial concrete studies began when, through the efforts of Mr. Art Myhre, the places were located where the broken pieces of concrete were discarded when Highway 218 between Cedar Rapids and Waterloo was replaced. Study of these broken slabs led to a limited coring program of a few highways of good and poor service records. Later a periodic inspection of the condition of certain key highways in eastern Iowa was made in the spring over a three- to four-year period. The results of these investigations are presented in this section.

Concrete Investigations

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. 21). Samples and cores of these highways were obtained, and photographs of the distressed concrete are shown in figures 22, 23, and 24. 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 distinctive Rapid lithology (Figs. 22, 23, and 24) 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 type lithology.

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 reacted aggregates.

2- The dark inner rims show a distinct zonal arrangement which resembles diffusion banding commonly observed in altered or weathered rocks (Figs. 23, and 24). 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 soft and disintegrates quite easily.

4- Some of the coarse carbonate fragments in cores of distressed concrete are fractured.
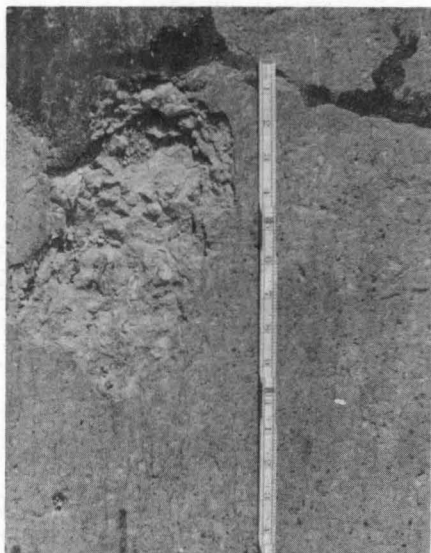
Fig. 21- Distressed concrete from
Highway 151, 2 miles west of
Anamosa, showing hair-line
cracks.
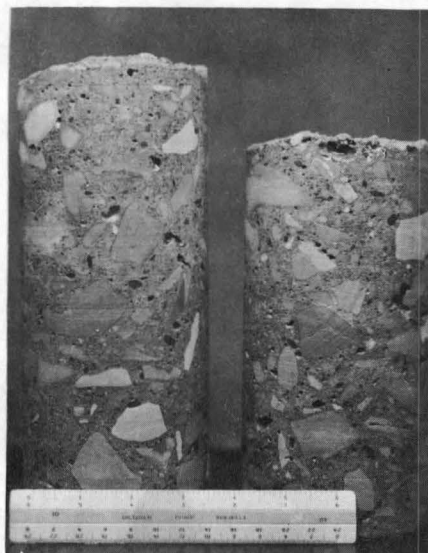
Fig. 22- Cores of distressed conc-
rete showing the reaction
rims. Taken at the same loc-
ation of Highway 151 as in
figure 21.
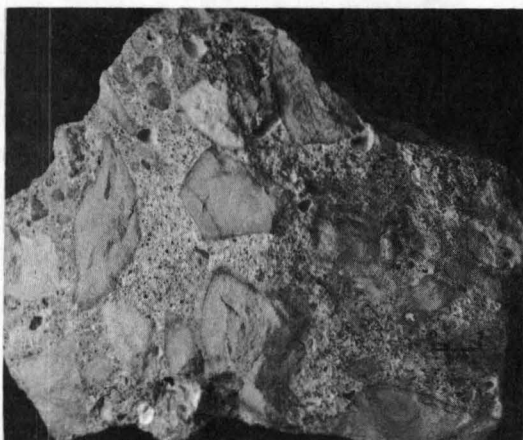
Fig. 23- A piece of distressed conc-
rete with reaction rims taken
from a salvage pile along
Highway 218 south of Waterloo.
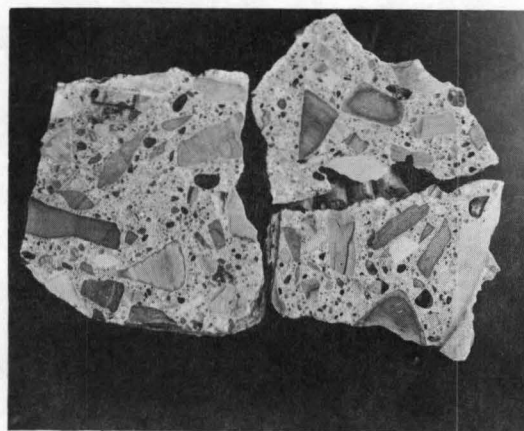
Fig. 24- Sections of distressed conc-
rete showing inner and outer rims
about coarse Rapid-type aggregate.

25
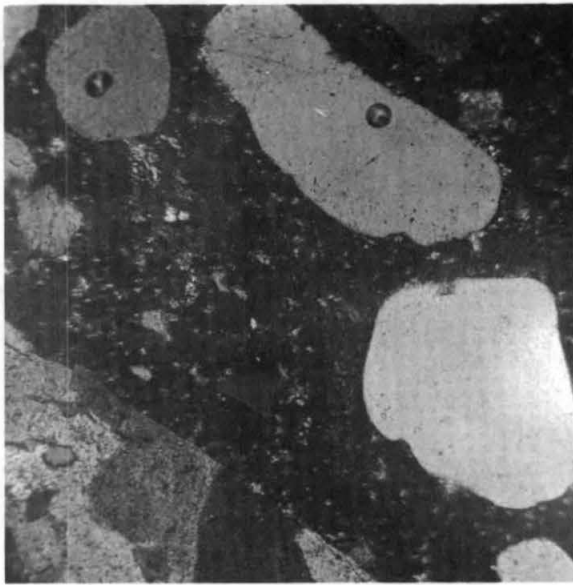
Fig.**-** Photomicrograph of a typical
specimen of distressed concrete
showing abundant birefringent
material in the matrix.(Crossed-
nicols - 75X Mag.)

26
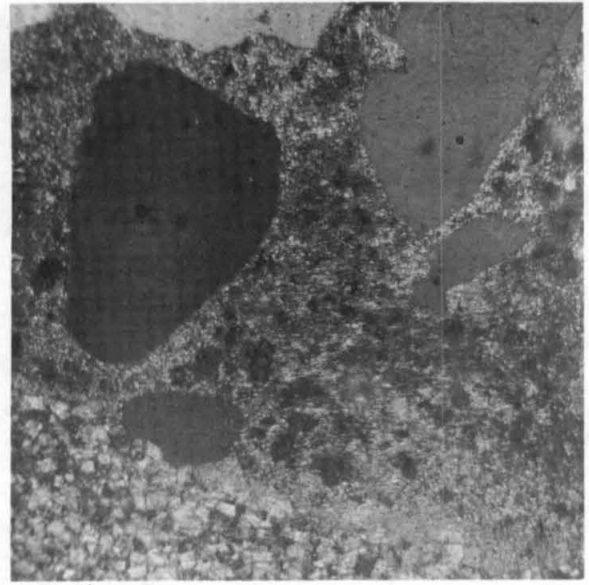
Fig.**-** Photomicrograph of a specimen
of good concrete from Highway 20
showing a darker and more uniform-
ly isotropic matrix.(Crossed-nic-
ols, 75X Mag.)

27
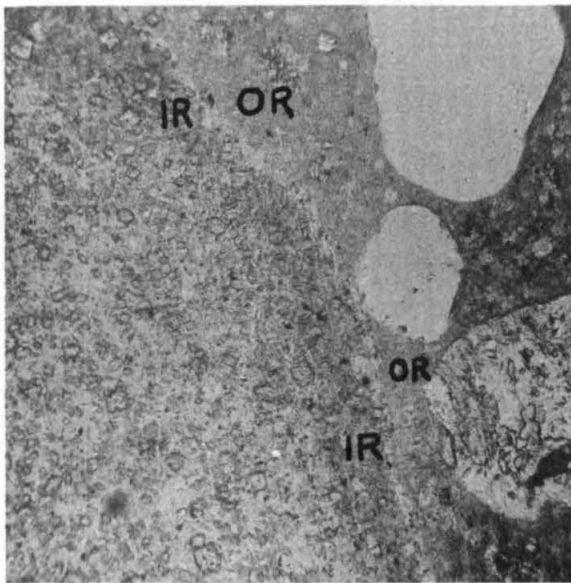
Fig.**-** Photomicrograph showing a typical
inner rim(IR) and outer rim(OR) seen
in distressed concrete around coarse
aggregate of the Rapid-type.(Plane
polarized - 75X Mag.)

28   *27*
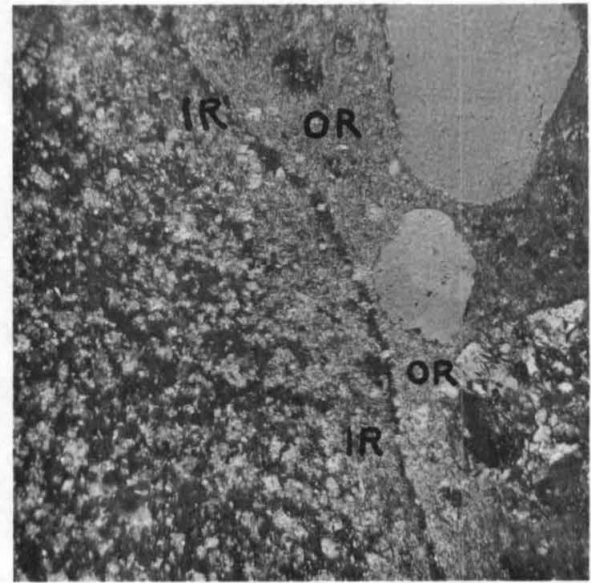
Fig.**-** Same as figure **.(Crossed-nicols-
75X Mag.)

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 poured.

6- The inner reaction rims are characteristically related to the Rapid type aggregate which may be either fresh or weathered.

7- Pieces of lithographic limestone from theupper part of the Glory Quarry show no inner reaction rims.

8- The outer rims are distinctive in many cases and form a zone from one-sixteenth of an inch to one-eighth inch wide in places. This type of outer rim is not to be confused with the thin film of $Ca(OH)_2$ known to form as a coating around any object placed on concrete or cement paste. Such $Ca(OH)_2$ films are much narrower than the typical outer rim and are not selective.

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

a) A general aspect of thin sections of distressed concrete is the over all appearance of the matrix which has been carbonated. It is characterized by a fair amount of birefringent material, identified as calcite, disseminated throughout as small clusters or larger aggregates (Fig. 25). Some calcium sulfaluminate occurs as a lining in larger vugs.

b) 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 (Figs. 27, 28). In refelcted 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.

c) The opaque material preferentially occupies the calcite matrix of the aggregate.

d) The dolomite rhombs which make up the typical mosaic texture of the affected Rapid type aggregate stand out in sharp relief in the area of the inner rim.

e) 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 compound.

f) The outer thin film is evident in thin section and consists of aggregates of low to moderate (.012 - .020) birefringent material with poor crystal form. The index of refraction is about 1.55 to 1.57. This material is considered to be $CaOH_2$. The contact between the aggregate and outer film may either be sharp or gradational. Occasionally a faint crack is evident along the border.(Figs. 27, 28)

g) In most areas with well developed inner rims, an outer rim of fine-grained calcite forms a somewhat irregular border which has the appearance of flooding the concrete matrix with calcite. The fine-grained calcite diminishes gradually away from the interface.

h) The fine aggregate shows little or no evidence of any reaction with the matrix. Overgrowths on quartz sand grains are very common.

From the evidence and observations made, it is evident a reaction probably involving an exchange of materials between the concrete matrix and aggregate has 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 $Ca(OH)_2$ has developed.

The characteristic feature of these sections of good concrete is the generally dark isotropic character of the matrix material (Fig. 26) which is in contrast to the matrix of distressed concrete sections.

Field Studies

Periodically in the spring over a three-year period beginning in 1957, and again in the fall of 1960, an inspection of some highways in eastern Iowa were taken to observe their condition to see if any changes had occurred. It was a rewarding study in that, in some instances of highways made of Otis stone, the deterioration could be followed.

Some of the observations of these studies indicate that distress occurs as general spalling and cracking away from joints. Blue-line cracking characterizes the damaged area. Surface zones of discoloration in form of color variations appear to be the first indication prior to cracking occurring. The spalling extends progressively from the top, downward and outward from breaks such as joints.

In the case of some highways the first signs of discoloration commenced in the 20th year, and distress through cracking and spalling followed -- becoming more evident each year the same area was visited. This observation led the late Bert Myers to call these roads a "20-year concrete". Otis stone was used in these highways.

Mr. Gunnar Idorn, an engineer from Denmark who has had considerable experience with alkali aggregate reaction resulting from chert gravels, made an inspection trip in Iowa during the fall of 1960 for the specific purpose of observing in the field distressed concrete related to carbonate aggregate behavior. It was his considered opinion that deterioration observed in Iowa highways associated with the use of Glory aggregate was not the same as that induced by alkali aggregate reaction.

Conclusions

The most important conclusion of the concrete studies is the observation that distressed concrete has undergone considerable chemical and physical change. It has in effect been severely "weathered" or altered. The subsequent conversion of the calcium silicate hydrates forming the bulk of portland cement into a carbonated matrix is a chemical change. Loss of silica is involved. The recognition of reaction between aggregates of a certain type of lithology (the Rapid type with its concrete environment) was another observation of major importance in this study.

Little is known of the progressive steps that occur during the "weathering" of a concrete. This is an area of major concern if a better understanding of aggregate evaluation is to be realized.

CHAPTER VI

CHEMICAL STUDIES

Introduction

Chemical studies form a major phase of the investigation in which a considerable amount of new data were obtained. These data have provided an insight into the nature of carbonate aggregate behavior in concrete; the principal one is the recognization that aggregates are not inert -- they all tend to react to some degree with their concrete environment.

The initial research in this area began with a series of leaching studies for potential deleterious constituents in aggregates of poor service. With the recognition of reaction rims on Glory aggregate in distressed concrete as evidence of chemical reaction between the aggregate and its concrete environment, the research on chemical behavior accelerated. Reaction rims were studied chemically in distressed concrete and then successfully grown on aggregates in silicate solutions and concrete bars. The ability to induce carbonate aggregate in the laboratory made it possible to pursue this avenue of research in greater detail. The nature of rim growth on various aggregates in concrete environments was found to be a selective type of reaction related to rocks of the Rapid lithology. It was found that the reaction was essentially a silicification process and that the source of some of the silica was in the concrete environment. Quantitative studies of the reaction indicated the reaction was essentially the result of an aggregate attempting to come into equilibrium with the alkaline concrete environment. Expansion studies of various aggregates in alkaline solutions were also undertaken.

This phase of research will be presented in the following order: a) the initial leaching studies; b) rim growth studies; c) compositional variations associated with rim growth; d) equilibria studies on silica behavior; and e) expansion studies.

Extraction Studies

In the initial phases of the project the first approach to the problem of aggregate behavior was to investigate the rock for the presence of potentially reactive constituents. Substances such as chalcedonic chert, opal, sulfates, and chlorides have been shown to be deleterious or are considered potentially so through the chemical reactivity of noncarbonate rocks containing them. For this reason it was the first investigation in the chemical studies undertaken.

The work was accomplished by Bisque as part of his Masters thesis research (1957), and was reported in a paper by Bisque and Lemish (1958) in HRB Bulletin 196. A two-phase approach was used consisting of: 1) determining the major constituents present in the rocks studied; and, 2) determining the type and quantity of potentially "available" deleterious constituents in the rocks by extraction methods.

The rocks studied were the bed-by-bed samples taken from the Devonian Cedar Valley formation in the Glory, Newton, Burton Avenue, River Products, and Pints quarries (Figs. 1 through 5).

Major Constituents Present

The major constituents making up the rock were determined to provide a chemical description of the samples prior to extraction studies. The samples were combined into composites by mixing powdered portions of each sample in proportion to the relative thickness in the formation member.

The analyses were made by dissolving powdered samples in 3N acid at 80° C for 30 minutes. The insoluble portion was separated by filtration via sintered glass filtering crucibles. The filtrate was analyzed for calcium, magnesium, and iron by means of the EDTA (ethylene-diamine-tetra acetic acid) technique. The results of the analyses are presented below in Table XIX.

TABLE XIX

ANALYSES FOR MAJOR CONSTITUENTS

Members and approximate thickness in feet	% Calcium (as $CaCO_3$)	% Magnesium (as $MgCo_3$)	% Insoluble Residue	% Fe
OLD 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 AVENUE 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[a] (24)	71.0	26.5	1.60	0.17

[a]weathered

A plot of the insoluble residue content versus the magnesium content (Fig. 29) shows the relationship of these two constituents previously discussed. The Rapid type lithology is characterized by the high insoluble residue content.

Extraction Studies for Potentially Deleterious Constituents

The same composite samples of powdered rock were used in the extraction studies. Fifty grams of sample were agitated with 450 ml of a dilute solution (0.008M, pH 11.4) of sodium hydroxide for 12 hours in polyethylene bottles. The mixture was 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 Ca^{++}, SO_4^{--}, SiO_4^{---}, Mg^{++}, and traces of Cl^-. Figure 31 demonstrates that 12 hours was adequate time to effect a thorough extraction.

The data obtained are presented in Table XX, as follows:

TABLE XX

CONSTITUENTS EXTRACTED

Members and approximate thickness in feet	% Base Reacted	SiO_2 extracted (mg/100 gms)	% Gypsum extracted
OLD 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 AVENUE 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.[a]
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[b] (24)	96	18.3	N.D.

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[a]N.D. None detected

[b]weathered
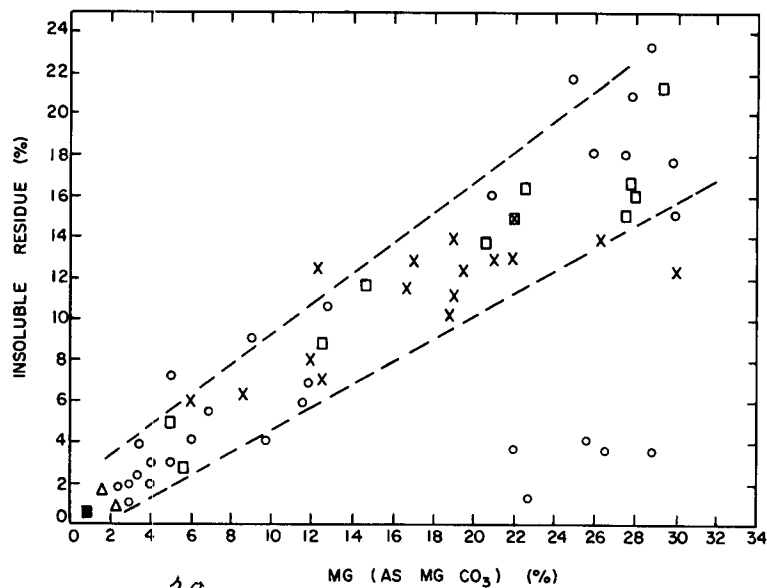
Fig. 29. Relationship of insoluble residue and magnesium content. Data from Bisque (1957) (composite samples of formation members) and results of analyses of lithologic units from four different quarries (phase 1)
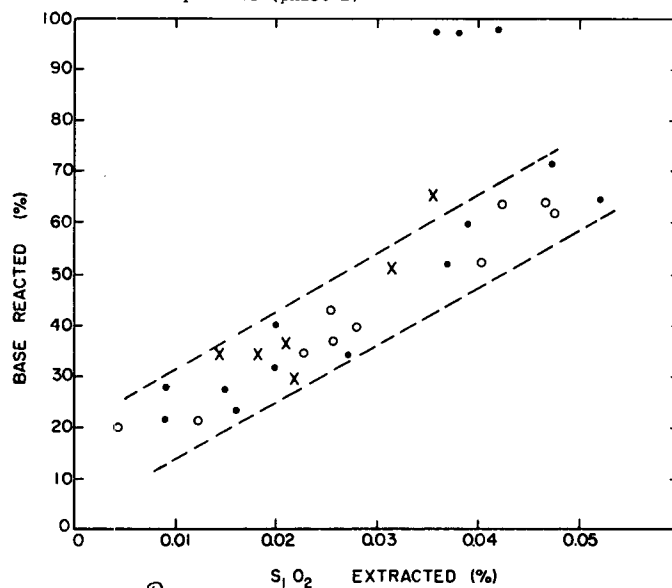
Fig. 30. Relationship of the quantity of silica extracted to the amount of base reacted (phase 2)
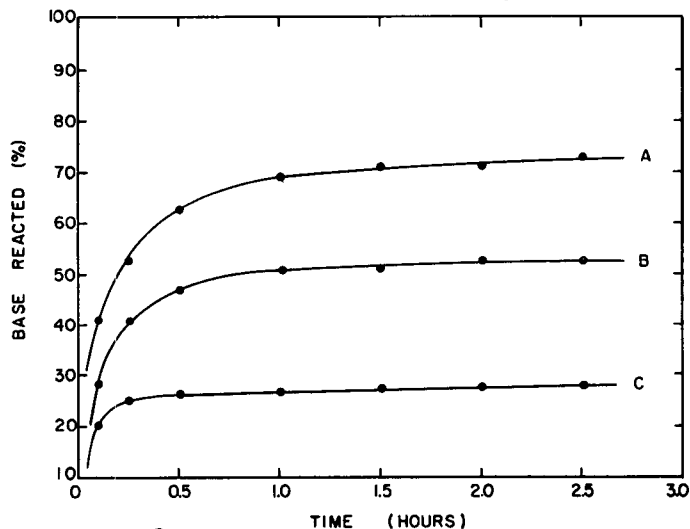
Fig. 31. Rate of base reactivity for three samples from the Glory Quarry. Amount of base reacted after twelve hours; A, 76 per cent; B, 54 per cent; C, 29 per cent

Sulfate was readily extracted from most of the rocks quite readily and determined via the barium precipitation method. The source of sulfate is either disseminated gypsum or sulfate solution in the minute liquid inclusions present in the carbonate minerals. Sulfate is considered to be present in minor amounts in most carbonate rocks. Further studies indicated that the maximum amount extracted never exceeded 0.25 per cent of the total rock (Glory Rapid member).

The silica was extracted and determined by the double dehydration procedure. The amount of silica found correlated with the decrease in basicity (Fig. 30). No doubt some of the decrease in basicity is also caused by reaction of the NaOH with the dolomite (dedolomitization as described by Chaiken and Halstead, 1960). The silica was extracted relatively rapidly (Fig. 31)-- 80 to 90% of the total amount within 30 minutes. The amount of silica extracted from samples of different lithologic units showed no relation to the abundance of chert nodules observed in the respective units. Chert nodules taken from the Rapid member which were powdered and extracted under the same conditions consumed considerably less base and yielded far less soluble silica than the carbonate rock samples.

Summary

The base consumed is a measure of the amount of reaction occurring during extraction. It is consumed mostly by the solution of silica and without doubt some of the carbonate minerals (dolomite mostly).

Although up to 0.25% of sulfate was extracted from the rock, it was assumed that this was not considered critical since careful investigation of the secondary deposits in distressed concrete showed no significant amounts of calcium sulfaluminate. The Bureau of Reclamation restricted the amount of gypsum in coarse aggregate to less than 0.25% (Rhoades and Mielenz, 1948).

The silica extractions indicate that the soluble or "reactive" silica leached from the carbonate rock is in some physical form distinct from that which it exhibits in chert. It is considered to be in some finely-divided amorphous(?) state. It was also interesting to note that a relationship exists between the amount of silica extracted and iron dissolved during analysis for the major constituents (Fig. 8). The source of iron is not pyrite, which is insoluble in hydrochloric acid. It may be related to the occurrence of reactive silica or carbonate minerals in the rock.

The conclusions reached in this phase of the study indicate that soluble sulfate and silica are available for chemical reactivity; but, these may not be potentially deleterious since they occur in relatively small amounts according to the research to date. This aspect should always be kept in mind, since it is possible that some carbonate aggregates may have deleterious constituents in larger amounts. Extraction techniques are relatively simple procedures adaptable for routine tests, should a need for it arise.

Rim Growth Studies

Introduction

This phase of the research was of critical importance because it emphasizes that some carbonate aggregates (generally the Rapid type lithology) are reactive in concrete. Recognition of reaction rims on rock of the Glory Quarry was the first conclusive and direct evidence of carbonate aggregate reaction in concrete even though it had been suspected by the Iowa State Highway Commission on the basis of service records. In investigating this facet of the problem, new techniques and approaches were devised which provided a large amount of new data and a better insight on aggregate behavior.

The initial work in this area was accomplished by Bisque as part of his Masters (1957) and PhD (1959) theses research. Publications regarding this phase are in the Highway Research Board Bulletins: 196; 239; and, 275. Hiltrop also contributed to this phase with his work on vaporous silicon compounds, published in Vol. 66 of the Proceedings of the Iowa Academy of Science (1959). Moore extended this work in current research.

The approach used in this section is essentially chronological because it gives a better understanding of the silica behavior in aggregate reactions. The investigation of rims in distressed concrete will be followed by the growth of rims in silica solution and growth of rims in concrete bars.

Investigation of Rims in Distressed Concrete

The first reaction rims recognized were observed in slabs of distressed concrete found under the Kelly bridge on Highway 218, about 10 miles south of Waterloo. The rims were found to occur only on the coarse aggregate of Rapid lithology from the Glory Quarry (Fig. 24). Coarse aggregate from the Coralville member, easily recognized by its contrasting lithology, did not have rims.

In order to investigate these rims, the distressed concrete was broken into small (1 to 2-inch) pieces. Three aggregate "types", based on the appearance of rims, were sampled and analyzed. Each sample contained at least 50 grams of carbonate rock from 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 given below in Table XXI.

TABLE XXI

ANALYSES OF CENTRAL PART OF AGGREGATES FROM DISTRESSED CONCRETE

Aggregate With No Visible Reaction Rims			Aggregate with less pronounced reaction rims			Aggregate with pronounced reaction rims		
*Insol. res. (%)	$CaCO_3$ (%)	$MgCO_3$ (%)	Insol. res. (%)	$CaCO_3$ (%)	$MgCO_3$ (%)	Insol. res. (%)	$CaCO_3$ (%)	$MgCO_3$ (%)
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

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*Insoluble residue

The aggregate which develops rims is consistently higher in insoluble residue and magnesium content on a weight per cent basis. They represent rock of Rapid lithology. The aggregate which does not grow rims was from the Coralville member.

The rim zones were sampled by tedious chipping and filing. Care was taken not to include any adhering cement paste. The analyses of two representative samples of rim material, 10 grams from at least 50 pieces of aggregate A and 5 grams of at least 30 different pieces of aggregate B (both A and B were Rapid lithology) are presented in Table XXII.

TABLE XXII

ANALYSIS OF REACTION RIM MATERIAL FROM DISTRESSED CONCRETE

	Insoluble Residue (%)	$CaCO_3$ (%)	$MgCO_3$ (%)
A.	19.80	56.12	23.70
B.	17.41	61.00	23.85

Further study of the rim zones was made by checking the SiO_2 content of the insoluble residue contents of the aggregates and rim zones to check if an actual increase in SiO_2 content had occurred. Table XXIII shows that the increase of insoluble residue content of rims was accompanied by an increase of SiO_2 content on a weight per cent basis.

TABLE XXIII

ANALYSIS OF INSOLUBLE RESIDUES FOR SiO_2

Insoluble Residue of Aggregate (%)	Insoluble Residue of Rim Material (%)	SiO_2 Content of Insoluble Residue/Aggregate(%)	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

The change in the effective porosity caused by rim growth in aggregates from distressed concrete was measured with the mercury capillary pressure apparatus. The average effective porosity of a Rapid type lithology from the Glory Quarry was found to be 6.2%. Rim zone material on the same type aggregate was found to be only .02%, indicating that the increase in silica content in the rim zone is essentially a pore-filling process.

In summary, the data obtained from the investigation of rims in distressed concrete show that the rocks of Rapid lithology from the Glory Quarry were selectively "silicified" during rim growth. Rocks of this type may have gained in silica content.

Rim Growth in Silica Solutions

Rims were grown in the laboratory on "reactive" aggregates (Rapid type lithology) to demonstrate that silica in solution from an outside source entered the aggregates. This was the first laboratory attempt to form rims, and it was successful.

It was observed that solutions of silica (23.70 grams of sodium meta-silicate dissolved in one liter of water) at pH 12, in reaching equilibrium with carbonate rocks of the Rapid type lithology, became yellow colored and increasingly so with time. Duplicate samples in sodium hydroxide solution at pH 12 showed no discoloration. After two weeks, several pieces of rock were removed from the silica solution, broken and studied. Faint lines were present as a rim a few milimeters inside the surface. The samples in the sodium hydroxide solution did not develop these lines. Acid etching of the rim zones showed that an outer ridge had formed. The same type of etched ridge forms when rimmed material from distressed concrete was etched. It was concluded that the silica in solution is responsible for the development of the rims.

Further study showed that the yellow color formed in the silica solution was due to the presence of iron. This was interesting, since the solubility of iron at pH 12 was negligible. The iron derived from the carbonate rock formed a silicate-iron complex which accounted for the color. Further tests showed that the iron content of solutions in equilibrium with Glory rock increased linearly with the silica concentration of the solution.

A rate study of depletion of silica from solution by aggregates of contrasting lithology was made. Carbonate fragments from the Rapid and Coralville members in the Glory Quarry were compared by equilibrating 100 grams of each aggregate in polyethylene baths in a 5×10^4M sodium silicate solution at pH 10. Samples of the solution were analyzed at intervals of time, and the data are presented in figure 32. Curve A shows behavior of Coralville aggregate; curve B, the Rapid. The average analyses of each type of aggregate is presented in Table XXIV.

TABLE XXIV

AVERAGE ANALYSES

Member	% $CaCO_3$	% $MgCO_3$	% Insol. Residue
Coralville	90.5	5.5	2.8
Lower Rapid	63.5	20.5	13.7

These data show the impure rocks are more susceptible to reaction. These impure rocks showed the presence of rims after reaction, whereas the low residue Coralville rock did not.

Some additional studies of fluoride reactivity were made to see if the susceptibility of carbonate rock to fluoride replacement might prove to be an index to the "purity" of a carbonate rock. The fluoride ion replaces the carbonate in the lattice of a carbonate rock to form fluorite (CaF_2) and/or sellarite (MgF_2). Data showing the depletion of fluoride concentration caused by two different rocks from the Glory Quarry (OG 7 - Rapid lithology; OG 22 - Coralville lithology) when placed in .01M hydrofluoric acid solution are shown in figure 33. This and other data obtained on a study of fluoride activity of the rocks show that an inverse relationship between silica and fluoride consumption is apparently related to the insoluble residue content of the rock. The same rocks which are differentiated by the presence or absence of reaction rims are also differentiated on the basis of their susceptibility to reaction with silica and/or fluoride in dilute aqueous solutions.

In conclusion, these experiments demonstrated conclusively that rims could be grown experimentally in silica solutions. The growth of rims is a selective process and is related to the insoluble residue content (petrologic character) of the rock.

Rim Growth in Concrete Bars

Since it was learned that the carbonate aggregate-silica reaction occurred in dilute solutions, attempts were made to "grow" reaction rims in concrete bars under laboratory conditions. This was successfully done, and in so doing made it possible to study carbonate aggregate reactions experimentally in a variety of ways.

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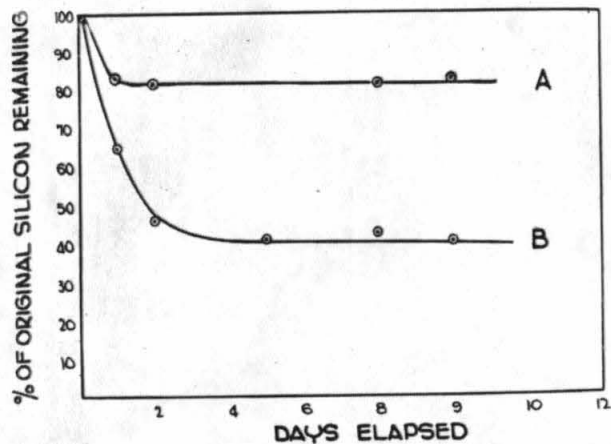
Fig. ●. Depletion of silica concentration caused by two contrasting types of carbonate aggregate.

33
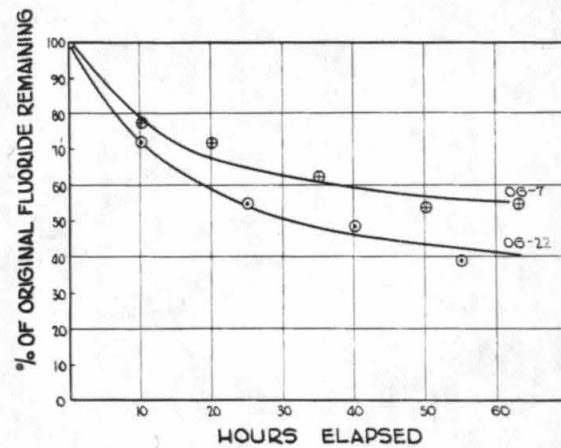
Fig. ●. Depletion of fluoride concentration caused by two different carbonate rocks.

34
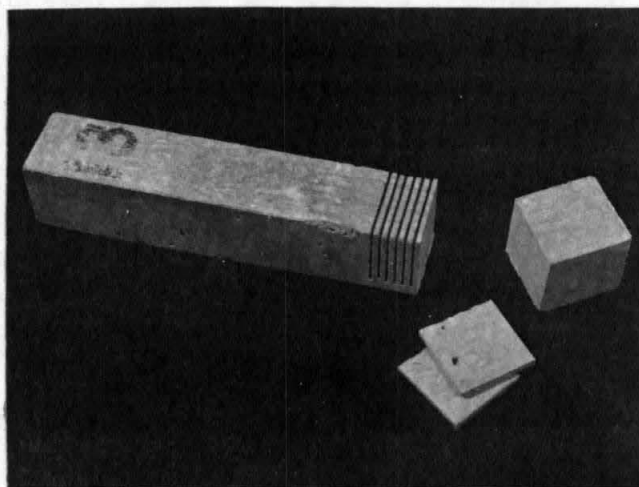
Fig. ●. Test bar and sections cut to expose aggregate.

A series of forty 2 x 2 x 14-inch concrete bars with end-plugs were made at the Highway Commission laboratories, according to the following formula:

Laboratory cement (Penn-Dixie, Type 1)   750 gms

Graded Ottawa Sand   2063 gms

Water   400 cc $\pm$ 50 cc

The coarse aggregate ranged from 1/2 to 3/8-inch in size and represented material considered to be acceptable or unacceptable for service. The "good" aggregate represented bed 1 of the Solon member at the Burton Avenue Quarry (Fig. 5). For "poor" material, coarse aggregate from the Rapid member designated as sample 12 and 14 at the Glory Quarry (Fig. 1) and sample 2 at the Burton Avenue Quarry (Fig. 5) was used.

The bars were cured for two days and removed from the moist room until the rim growth tests and expansion measurements were made a few months later. The water/cement ratio was purposely high, to make the bars as porous as possible, for rim growth experiments.

The bars were subjected to one of three different environments:

A. Room temperature with no added moisture.

B. Immersed in distilled water at 120°-125° F.

C. Alternate soaking and drying (soaked in distilled water at room temperature for 24 hours and dried at 140° F for 24 hours).

After several weeks of treatment, some of the bars were cut into thin wafers to expose the aggregate (Fig. 34). Visible reaction rims had already formed on the unacceptable type in those bars which were kept in environments B or C. These same type rocks developed no rims in environment A. The acceptable aggregate developed no visible rims in either of the three environments. In each case, the presence or absence of the rim was also determined by acid etching of a smooth-cut section of the bar. This was done by immersing the section in several hundred ml of 2 - 3N hydrochloric acid for an appropriate length of time. In many instances the entire carbonate fragments were silicified rather than just a peripheral rim zone.

The above is best illustrated by reference to photographs. Figures 35 through 38 illustrate the appearance of sections of a bar containing acceptable aggregate, before and after being placed in environments A and B. In each case an unetched (left) and an etched (right) surface are shown. Figure 35 shows an unetched section through a bar which was subjected to environment A. Note that each aggregate fragment is bounded by a thin white line. This line is a result of carbonation of a narrow halo of lime $\langle$ Ca(OH)$_2$ $\rangle$ which accumulates at the surface of the aggregate particles before the cement sets. This occurs at the surface of any type of aggregate or other solid object, as can be demonstrated by allowing cement paste to set in a glass container. The lines are more easily seen in figure 39 because of the darker color of the aggregate.
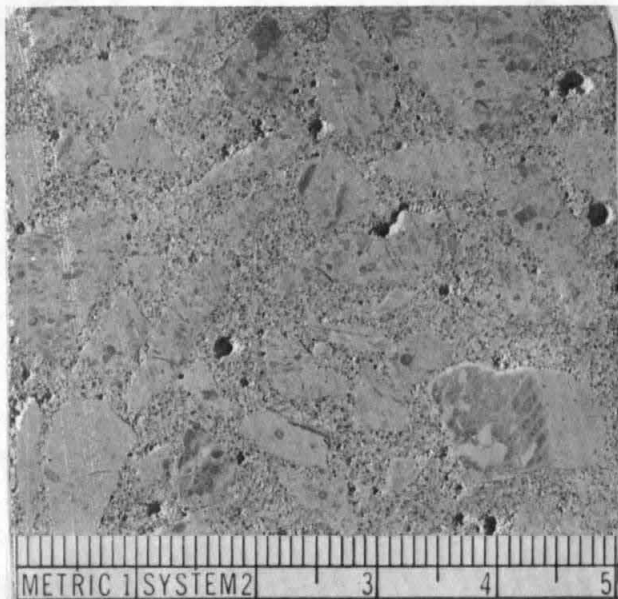
METRIC 1 SYSTEM 2   3   4   5   *35*

Fig. **.**

METRIC 1 SYSTEM 2   3   4   5   *36*

Fig. **.**

METRIC 1 SYSTEM 2   3   4   5   *37*

Fig. **.**

METRIC 1 SYSTEM 2   3   4   5   *38*

Fig. **.**

35, 36, 37, 38

Figs. �. Sections taken from test bars made with acceptable aggregate before (top) and after (bottom) residence in environment B. In each case an unetched (left) and an acid-etched section (right) are shown.
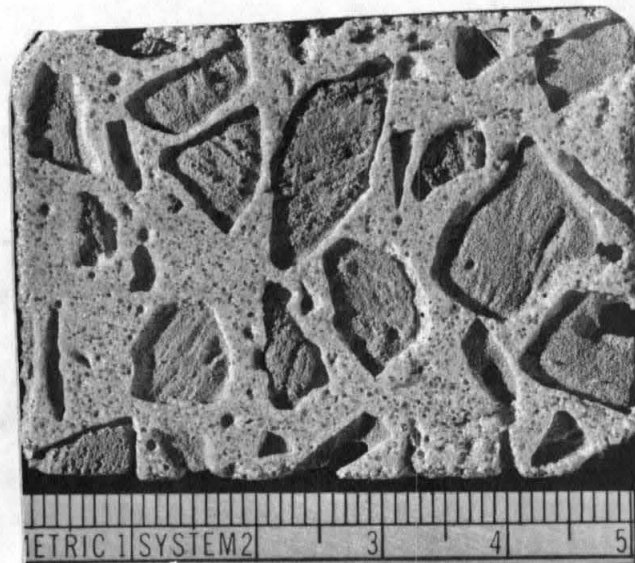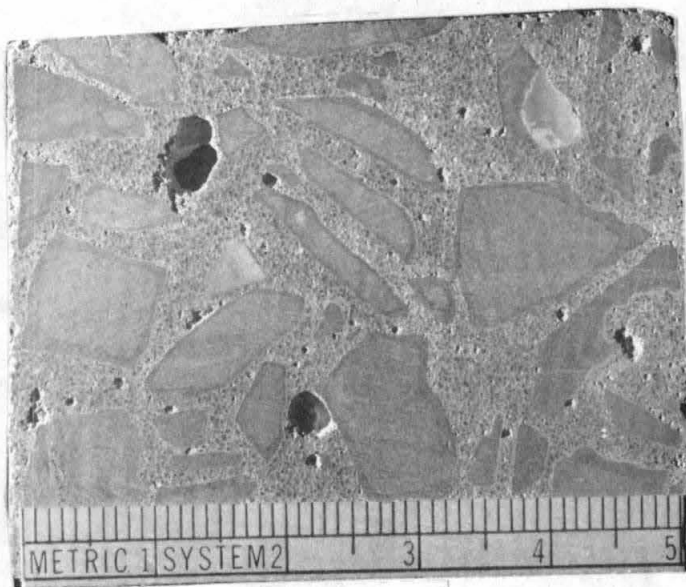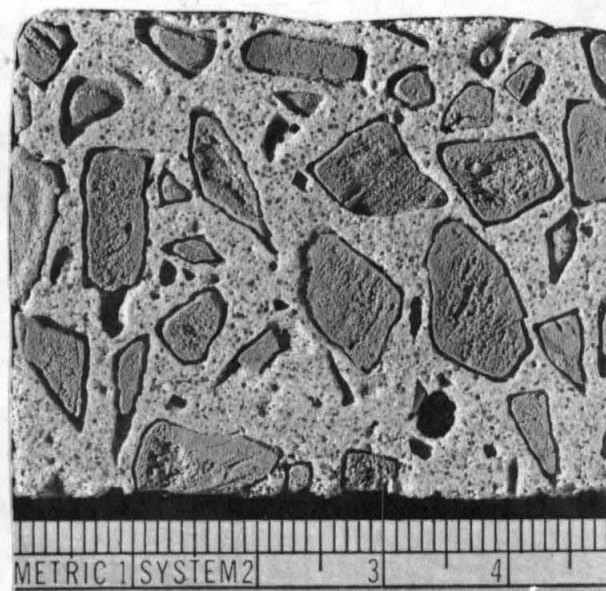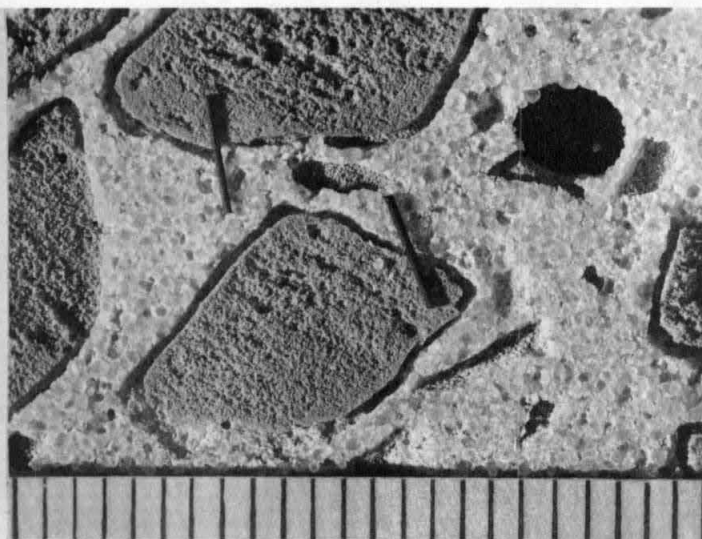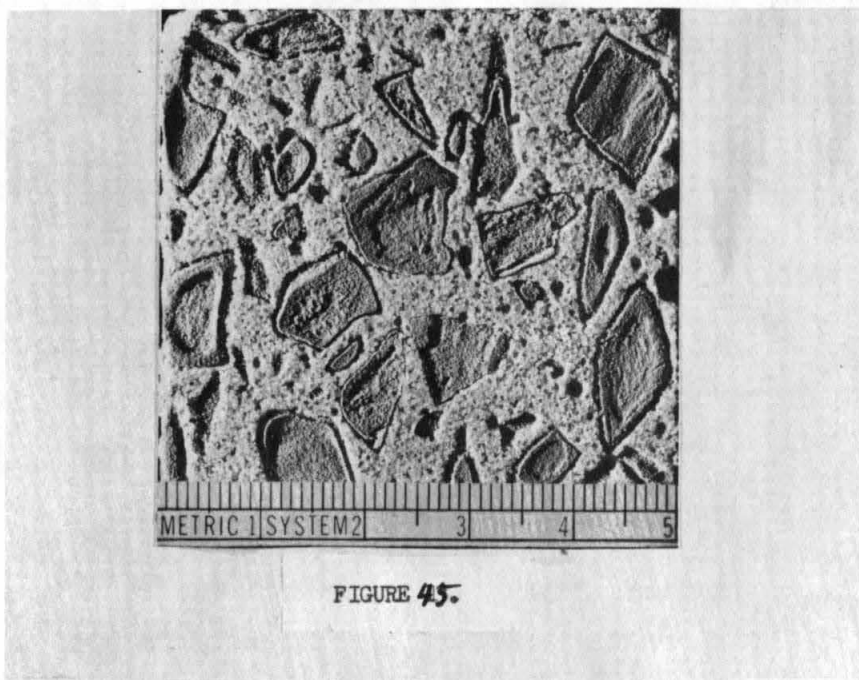
Fig. 8. 39

Fig. 9. 40

Fig. 10. 41

Fig. 11. 42

39, 40, 41, 42

Figs. 8, 9, 10, & 11. Sections taken from test bars made with unacceptable aggregate before (top) and after (bottom) residence in environment B. In each case an unetched (left) and an acid-etched section are shown.

FIGURE 43.

FIGURE 44.

FIGURE 45.

Close-ups of surfaces shown previously in Figures 40 and 42 (top) and an acid etched section of the bar shown in these figures after only 30 days in enviroment B (bottom).

Figure 36 is an acid-etched section from the same bar. The aggregate fragments have been deeply "entrenched" by etching and there is no differentiation of zones at the aggregate-cement paste boundary.

Figures 37 and 38 illustrate the same relationship for a companion bar (i.e.- same aggregate) which was subjected to environment B. Again, there are no visible shells and etching does not differentiate any zones at the particle boundary.

Figures 39 through 42 show the results of identical treatment of sections cut through bars made with unacceptable aggregate. The differences are striking. Although the aggregate in the bar which was kept dry is no different in susceptibility to etching than the acceptable aggregate in the preceeding photo series, a marked difference arises after residence in environment B for 60 days (Fig. 41). In this case, visible shells have formed, and the entire aggregate particle has been rendered less susceptible to acid attack (Fig. 42).

Figures 43 and 44 are close-ups of several of the aggregate particles in Figures 40 and 42, respectively. The black fibers were used to emphasize the relationship of the aggregate to the cement paste in regard to relief. The shadow of the right fiber in figure 43 (illumination from the lower left) shows the depression of the aggregate particle. The fibers in figure 44 are essentially horizontal. Figure 44 also clear y shows the entrenched zone around the larger aggregate fragments.

The surfaces shown in Figures 40 and 42 were etched side-by-side in the same hydrochloric acid solution (3N) for the same length of time. The acid-etched surface of a section taken from the same bar as the section shown in figure 42 after only 30 days of treatment (as opposed to 60 days) shows clearly that the periphery of the particles is silicified before the interior (see Fig. 45).

These photos are not examples of isolated instances. The same decrease in solubility of the unacceptable aggregate fragments occurred in every bar subjected to environments B or C.

Figure 46 is included to demonstrate that an aggregate particle may lack a visible shell zone and still be affected. Two-thirds of the left side of this specimen also illustrates the fact that shell growth may vary in the same rock. This must be due to a variable within the rock structure, since the cement paste is essentially homogeneous. It does not seem likely that this variable is dolomite content since the area of differential shell growth (just below the middle of the left edge of the aggregate block) is replete with dolomite rhombs. It does appear that the most intense shell growth tapers off to the right and corresponds with a slight ridge which can be seen in the etched interior zone.

A closer examination of the etched interior portion of this specimen (the area directly above the numeral 2 on the scale) and of the acid-leached shell zone (upper left edge of the aggregate block) shows an interesting differentiation of dolomite rhombs and "matrix".

A close-up (X50 magnification) of the etched interior portion, Fig. 47, demonstrates that the "matrix" (i.e.- the more calcareous material containing the acid insoluble fraction of the rock) is leached away more readily than the rhombs themselves. This relationship is drastically changed in the shell zone.
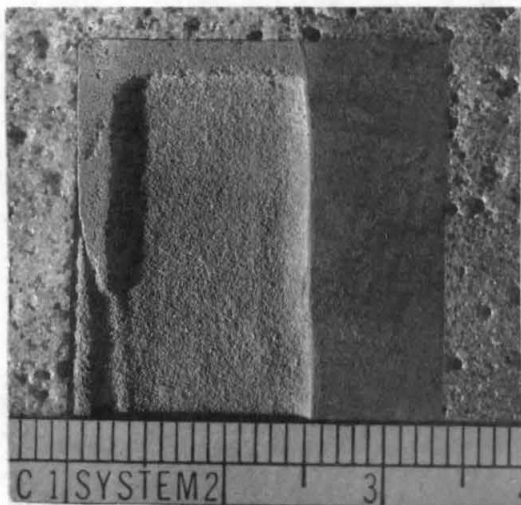
Fig. 29.46 Section of a test bar containing an aggregate block. The left two-thirds has been acid etched to accentuate the shell. Illumination is from the left.
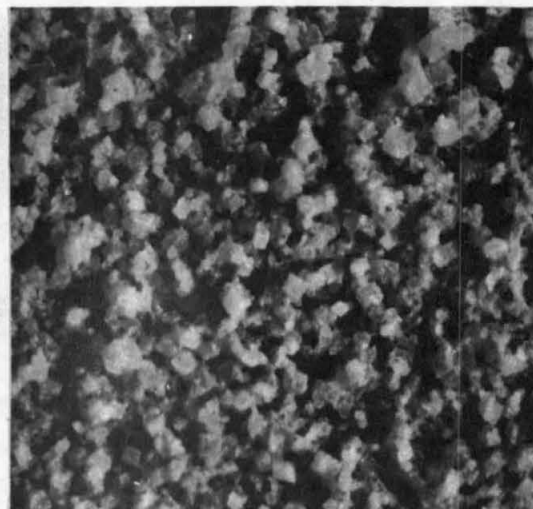

Fig. 29.47 A close-up (x50 magnification) showing the relationship of dolomite rhombs to matrix in the unsilicified interior of the aggregate particle in Fig. 29.46 Compare with Fig. 22.49
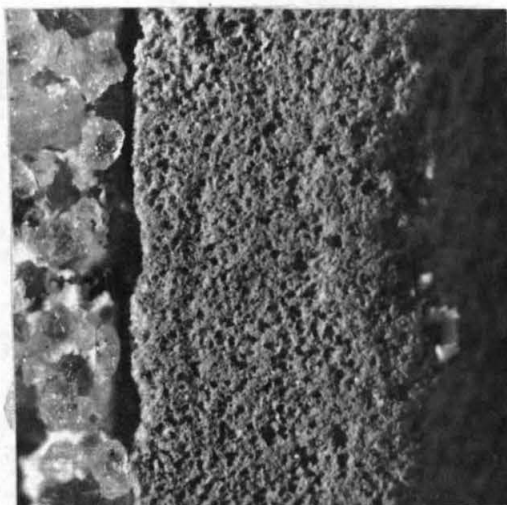

Fig. 29.48 A close-up (x20 magnification) of the acid leached shell zone shown in Fig. 29.46 On the left is leached cement paste.
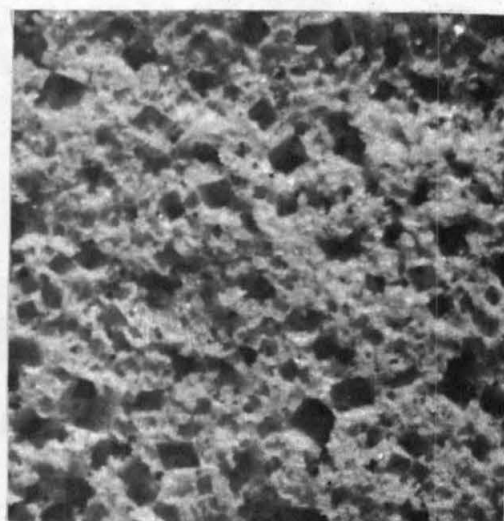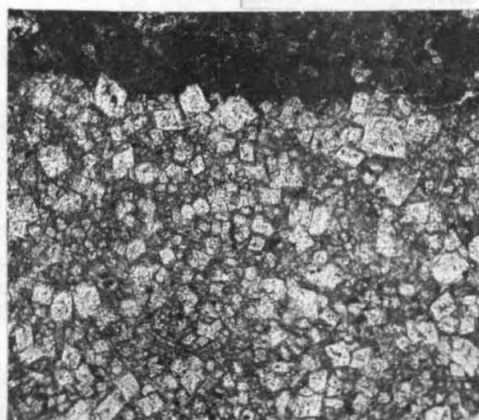

Fig. 29.49 A close-up (x50 magnification) showing the relationship of dolomite rhombs to matrix in the silicified shell of the aggregate particle shown in Fig. 29.46 Compare with Fig. 29.47

Fig. 29.50 A thin-section view (x100 magnification) of dolomite rhombs in a well developed shell taken from a highway sample. No corrosion of the dolomite is apparent. The dark portion at the top is cement paste.

Figure 48 is a close-up (X20 magnification) of the acid-leached shell zone in figure 46. It can be seen that the leached shell is spongy in appearance. A still closer view of the shell (Fig. 49, X50 magnification) shows that the holes are actually casts of dolomite rhombs which have been dissolved out of the silicified matrix. These latter figures illustrate that the material between the rhombs is definitely altered as the shell forms, whereas the dolomite rhombs are unaffected.

Figure 50 is a X100 magnification of a thin section showing dolomite rhombs in a well-developed reaction shell from highway concrete. The dark portion at the top of the photo is cement paste. The lighter field at the bottom is entirely within the shell zone. It is clear that the dolomite rhombs are well defined and not corroded to any marked degree. Hence, this process of silicification is selective. In this case, well organized dolomite rhombs are unaffected, while the calcitic matrix is altered.

The length changes of the experimental bars were also observed. Although distinct rims formed in bars made with unacceptable aggregate, the expansion never exceeded 0.02%, and averaged 0.01%. There is no established value for "excessive expansion". It is generally considered that in an environment of 100° F over water, 0.1% expansion in six months is deleterious.

The rim growth studies in concrete bars clearly demonstrate the selectivity of the reaction for rocks with the Rapid lithology. The technique also provides a potential method for testing aggregate reactivity readily adaptable in any laboratory.

A rapid means of growing rims was developed through the use of an autoclave procedure, and is described in a paper by Lemish and Bisque (1959) in the Proceedings of the Iowa Academy of Science. Concrete bars made according to the same formula as in the above studies with acceptable (Solon) and unacceptable (Rapid) aggregates were treated in an autoclave at a pressure of 295 ($\pm$ 10) pounds, and 420° F in three successive runs, each for three hours. Acid etching demonstrated that well-formed rims occur in bars of unacceptable aggregates within six hours. The bars of acceptable aggregate formed no rims during the entire run. The autoclave technique cuts down the time considerably to demonstrate the reactivity of an aggregate, and has promise as a potential acceptance test for aggregate reactivity.

All of the experimental work on rim growth in bars described up to this point has been essentially descriptive. A quantitative study of the rim zone was essential to determine whether, as in the aqueous solution studies, silica was definitely being introduced from an outside environment. In order to demonstrate the behavior of silica related to the carbonate aggregate reaction quantitatively, a series of experiments were made by Bisque as part of his PhD thesis work (published in HRB Bulletin 239), and concluded by Moore in 1962.

The sampling of shell zones for chemical analysis is tedious. Any practical method of procuring a quantity of a representative sample of these zones and a sample of the adjacent unaffected rock for chemical comparison is open to criticism, since contamination of either portion by the other or by fragments of cement paste and/or fine quartz aggregate would cause serious variations.

The following method was used by Bisque to circumvent sampling difficulties. Chips of a given aggregate, passing a 6-mesh sieve and retained on an 8-mesh sieve, were washed with distilled water and dried to constant weight at 80° C. The chips were then divided into two portions, one of which was set aside for chemical analysis, and the other treated in the manner described below.

Exactly one hundred chips of a known dry weight were placed in "ports" of specially-molded mortar bars (Fig. 51) and the bars placed in environment B. At intervals up to 60 days, the chips were removed with tweezers, counted, rinsed in distilled water, and dried to constant weight at 80° C. Small chips were used so that subsequent shell growth would affect the entire particle, effectively converting each chip to a shell.

The chips of unacceptable aggregate from the Rapid member in Glory and Burton Avenue quarries began to gain weight while samples of purer sublithographic limestones (Coralville member, Glory Quarry) (acceptable aggregate) lost weight. Curves A and B in figure 52 show the weight increase for samples of two different lithologic units during a 60-day period. Samples of these same chips were placed in a basic solution (pH 12) for the same length of time to determine how their weight would be affected. In this case, the chips lost weight as shown by curve C in figure 52. This same curve would serve as an approximate indication of the average weight loss experienced by chips of acceptable aggregate; i.e.- relatively pure limestone. This decrease in weight is due to slow leaching of more soluble components of the rock and probably some mechanical loss of very small fragments due to handling. This weight loss accounts for the slight dip in the early portion of curves A and B. In other words, the aggregate chips are being leached of soluble components and taking on silica at the same time, the latter process dominating.

Chemical analyses of both acceptable and unacceptable type carbonate aggregates (i.e.- acceptability based on actual service records) were made before and after equilibration with concrete in distilled water to determine the variation in silica content, and also to see whether the reaction which causes the formation of shells introduces any soda or potash into the aggregate particles. The results of these analyses are shown in Table XXIV. Soda and potash were determined flame photometrically.

These data show that the unacceptable aggregates gained in silica content; whereas, the acceptable aggregates showed little change. The alkali content of the chips of either type showed no change.

The values for potash were consistently less than ten parts per million in both the original and equilibrated aggregates. These data indicate that the amount of soda and potash in the shell zone does not increase as silicon is introduced. Powers and Steinour (1955) discuss chemical analyses of samples of siliceous gels taken from various concrete structures affected by the alkali-aggregate reaction. These results demonstrate that the gels contain from 6 to 26% soda and potash, soda predominating. The siliceous shell, therefore, is definitely distinct in chemical character from the type of siliceous gel commonly found in concrete which has been weakened by the alkali-aggregate reaction.

TABLE XXIV

CHEMICAL ANALYSES OF AGGREGATE CHIPS BEFORE AND AFTER EQUILIBRIUM WITH CONCRETE

Code[a]	%SiO$_2$	Before %CaCO$_3$	%MgCO$_3$	Na$_2$O (ppm)	K$_2$O* (ppm)	%SiO$_2$	After %CaCO$_3$	%MgCO$_3$	Na$_2$O (ppm)	K$_2$O (ppm)
Acceptable aggregate:										
OG -22	0.10	97.5	2.3	30	10	0.11	97.5	2.3	30	10
OG -24	0.90	96.5	2.1	20	10	9.90	96.4	2.0	25	10
Unacceptable aggregate:										
OG - 1	7.25	74.7	12.9	15	10	13.20	73.1	12.0	15	10
OG - 2	16.25	64.0	15.3	25	10	19.00	62.1	15.1	20	10
OG - 4	15.20	59.2	21.2	20	10	19.10	57.6	20.1	15	10
OG - 5	16.10	57.4	18.1	10	10	20.25	56.1	17.8	10	10
OG - 7	11.30	--	--	10	10	12.85	--	--	10	10
BTN-14	14.30	--	--	30	10	16.10	--	--	20	10
BTN-15	10.75	--	--	10	10	14.50	--	--	5	10

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[a]Code: OG - Glory Quarry
   BTN - Burton Avenue Quarry

*Less than 10 ppm in all cases

Bisque's work clearly indicates that silica was introduced from an outside source. The only possible source of silica in the concrete is either the fine quartz aggregate (Ottawa sand) or the cement paste. In order to check the outside source, Moore repeated Bisque's experiment with a cement paste bar. The main difference was the absence of one of the variables -- quartz sand.

Two ported neat cement paste bars were made at the Iowa Highway Commission from their laboratory Standard Type I cement. Chips of an acceptable aggregate from the Dyersville Quarry, as well as chips of unacceptable aggregate from the Glory Quarry (Rapid member), Otis Quarry (Kenwood member) and
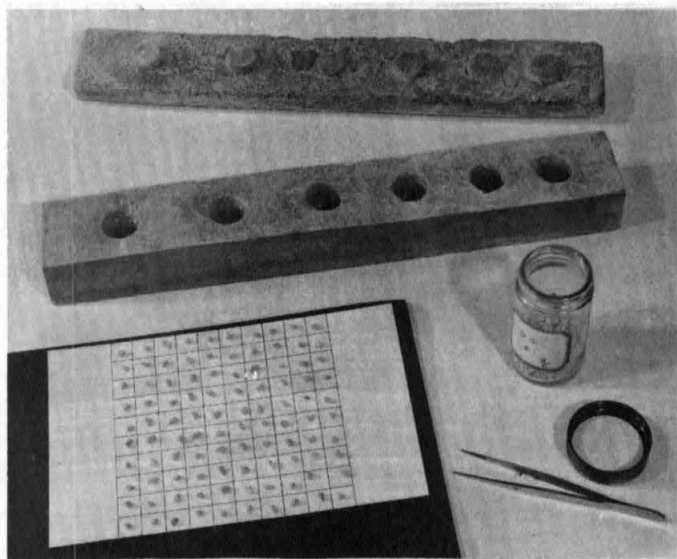
Fig. 51. Specially molded experimental bar containing six "ports" in which aggregate chips were placed.
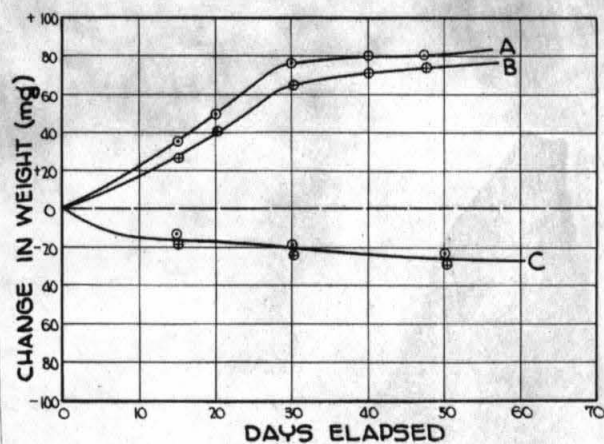
Fig. 52. Change in weight of unacceptable aggregates, curves A and B, and acceptable aggregates, curve C after being stored in the ports of a test bar such as is shown in Fig. 51.
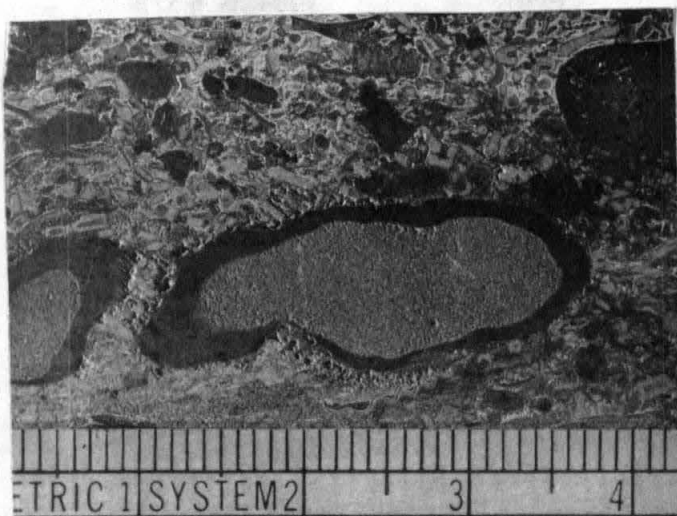
Fig. 53. An example of silicification in nature. A section through a fossiliferous chert nodule, exposing a carbonate fragment. See also Fig. 54.
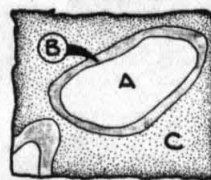
A. HOST ROCK
    $CaCO_3$ - 92.1 %
    $MgCO_3$ - 5.6%
    SiO_2 - 1.4%
           99.1%

B. RIM ZONE
    $CaCO_3$ - 3.5%
    $MgCO_3$ - 0.6 %
    SiO_2 - 94.8%
           98.9%

C. CHERT
    SiO_2 - 98.7%

Fig. 54. Chemical analyses of the section shown in Fig. 53.

Kingston, Ontario, Quarry (Black River formation) were reacted in the same manner as Bisque's experiment for 105 days. The analysis of the chips before and after the experiment are presented in Table XXV. Figure 54A shows the weight changes of the chips during the experiment.

In contrast to Bisque's work, the unacceptable aggregates -- with the exception of a sample from Kingston -- all lost weight and insoluble residue content. The Glory aggregate lost the greatest amount of residue. From past experience, the residue is mostly silica and without doubt a coincident loss in silica content has occurred. Little variation occurred in the alkali content of the samples before or after analyses. The major difference between these data and those of Bisque is that the samples of bad aggregate which had previously gained weight (Glory) now lost weight and residue content in a cement paste environment. It can be postulated on the basis of these data that the outside source of silica migrating into an aggregate during reaction is the fine aggregate in concrete. Cement paste is not considered the source of silica; the aggregate decreases in silica content which appears to have been transferred into the cement paste.

In summary, the experiments with rim growth in concrete bars show that rock of the Rapid lithology are reactive and become "silicified" with silica introduced from its concrete environment. The source of silica in the concrete is considered to be the fine aggregate. Excessive expansion is not related to the reactions in the aggregates tested during these experiments.

TABLE XXV

CHEMICAL ANALYSES OF AGGREGATE CHIPS BEFORE AND AFTER

EQUILIBRATION WITHIN A HYDRATED CEMENT PASTE BAR

Sample	S.G.	Ca as $CaCO_3$ %	Mg as $MgCO_3$ %	% Insoluble Residue	ppm Na	ppm K
BEFORE:-						
Glory 11	2.84	55.0	25.3	16.2	4.0	7.0
Glory 9 (composite)	2.88	46.4	30.4	19.1	4.5	10.0
Otis-Kenwood C	2.83	55.3	19.4	26.0	4.5	8.5
Kingston	2.82	72.4	22.8	3.5	4.2	3.5
Kingston (composite)	2.83	66.3	18.6	12.5	6.0	9.5
Dyersville (concrete ledge)	2.84	51.3	45.7	2.9	4.0	2.0

(Table XXV, cont'd.)

Sample	S.G.	Ca as CaCO$_3$ %	Mg as MgCO$_3$ %	% Insoluble Residue	ppm Na	ppm K
AFTER 105 DAYS:-						
Glory 11	2.80	60.5	25.8	9.5	6.5	7.5
Glory 9 (composite)	2.93	47.8	33.0	14.0	4.9	7.0
Otis- Kenwood C	2.83	55.3	18.0	24.0	3.6	6.0
Kingston	2.81	72.2	19.2	4.0	3.6	3.2
Kingston (composite)	2.80	67.5	18.0	11.0	5.7	7.5
Dyersville (concrete ledge)	2.84	52.5	45.9	0.5	8.5	6.5

Compositional Variations Associated with Rim Growth

Introduction

With the recognition that the silica could be introduced into some aggregates, information was needed on the effects of the reaction on the various components of the aggregate (carbonate minerals, quartz, clay, etc.). In order to gain more information in these areas, a study was undertaken on the compositional variations in aggregate and hydrated cement resulting from aggregate-cement paste reactions*.

The work described in this section was accomplished by Harwood (1960) as part of his Masters thesis research.

Procedure

Cubes of various carbonate aggregate approximately 1 3/4 inches on a side were embedded in 2 x 2 x 14-inch bars of cement paste which were then treated by soaking the bars in distilled water at 55° C for a period of three months. The neat cement paste bars were made from Type I cement with .52% equivalent Na$_2$O content by mixing 2500 grams of cement with 600 ml of water and curing for 48 hours in the moist room. After treatment, the bars were cut in half length-wise and samples were taken by means of a dental drill at 5 millimeter intervals from the cement paste across the interface into the aggregate (Figs. 55 and 56).

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*Hadley of the PCA gave a preliminary report at the 1960 HRB session on the reaction of a specimen of Kingston aggregate and cement paste.
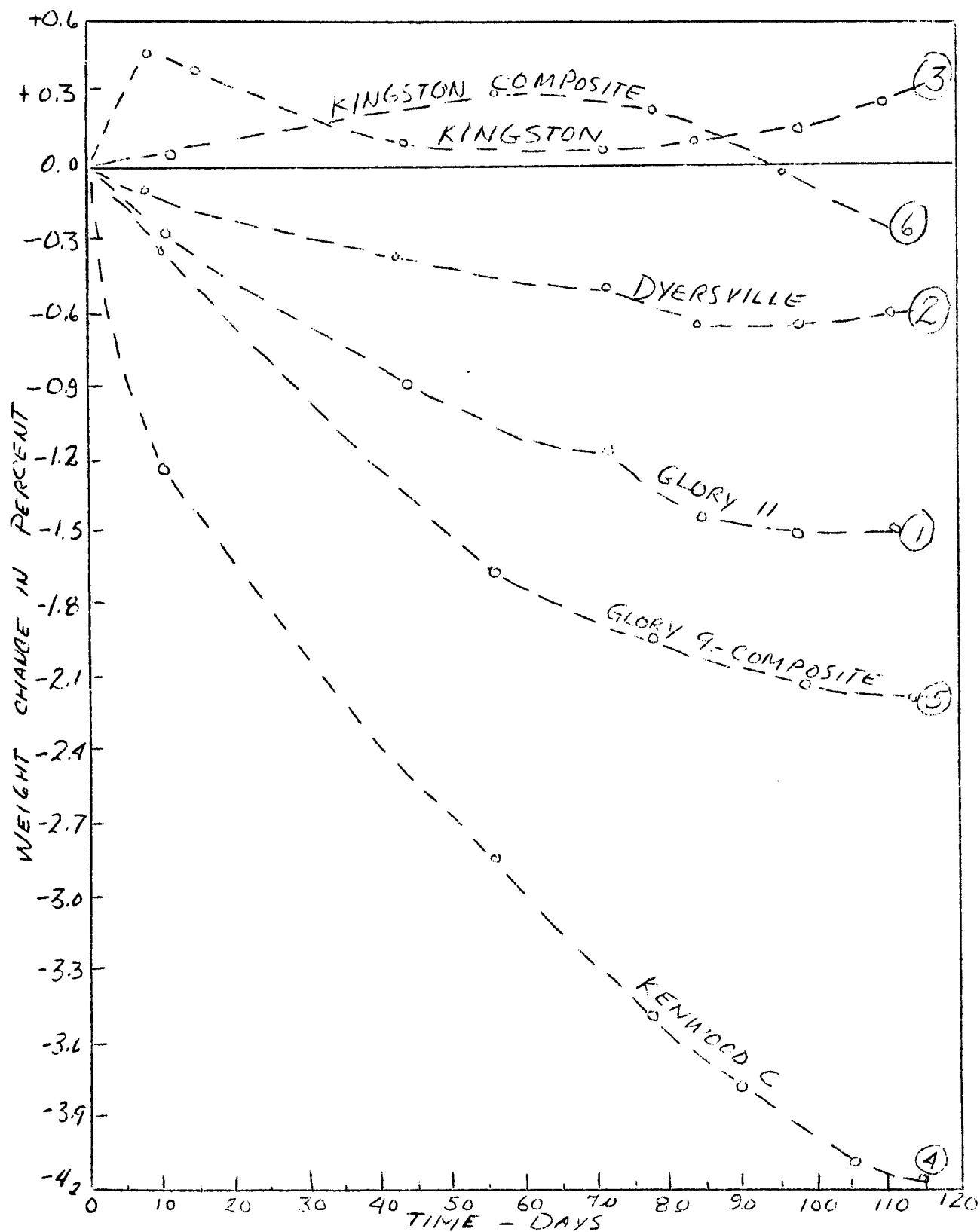
FIG. 54A

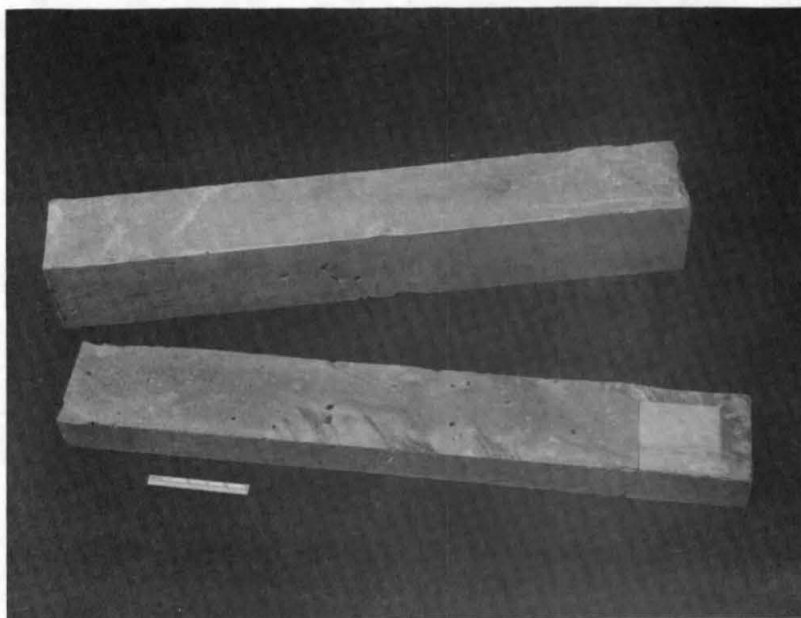WEIGHT CHANGES OF CHIPS IN PORTED CEMENT PASTE BAR.

Fig. 55 Upper bar is a 2 x 2 x 14 inch cement paste bar.
The lower bar has been slit in half lengthwise and
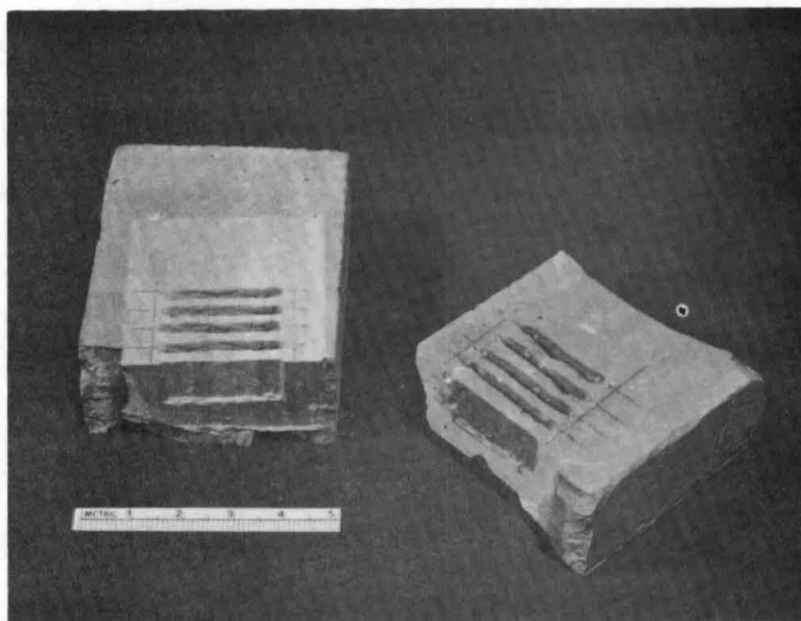shows the embedded carbonate aggregate.

Fig. 56 The left segment shows the spacing of the samples
in the aggregate; the right segment shows spac-
ing of samples in cement paste.

Chemical analyses and X-ray studies were then made on the samples. The CaO, MgO, Al_2O_3, and Fe_2O_3 were determined by Versene titrametric methods. Silica was determined by double dehydration. A semi-quantitative procedure was used to determine the mineral and/or compound content of the aggregate and cement paste, respectively, on the basis of the relative X-ray diffraction peak heights obtained from strip chart recordings of a Norelco X-ray Diffractometer.

To test the effect of the reaction on the constituents of cement, two cubes of the same reactive aggregate were reacted at pH 12 in bars made from the principle silicate compounds of portland cement, alite and belite, under the same conditions as the Type I cement paste bars. They were sampled in the same way.

The aggregates used were argillaceous dolomitic types which had a poor service record or did not pass present acceptance tests of the Iowa State Highway Commission. The Newton 19 and Newton 6A specimens were argillaceous dolomitic limestones from the Coralville member of the Devonian Cedar Valley formation. The Glory 9 and 11 specimens were argillaceous dolomitic limestone from the Rapid member of the Cedar Valley formation. The Kenwood C specimen was an argillaceous calcitic dolomite with a high silica-rich insoluble residue (19%) from the Kenwood member of the Devonian Wapsipinicon formation and was the only specimen in which expansion during treatment occurred to the point of cracking the surrounding cement paste.

Discussion of Data

The data are presented in Table XXVI, and are graphically presented in figures 57, 58, 59, 60, 61, and 62. Although the experimental approach, nature of the sampling, and procedures employed are such that the study is essentially a reconnaissance approach, the results indicate some significant trends regarding aggregate reactions. The data presented, and subsequent interpretations, are based on the following premises:

1. The aggregate and cement are homogeneous in composition before reaction.

2. The central part of the cubes were least affected by the reaction.

3. The system is dynamic and the data represent the extent of reaction to the time when the bars were removed from their reaction environment.

The behavior of silica which can be noted in figures 57, 58, 59, and 60 is summarized in figure 62. In the Newton 19, 6A, and Glory 9 bars (Fig. 62), silica follows a similar pattern in the shell zone interval of 0 to 10 mm from the interface. The silica shows an apparent increase in this zone with the largest amount of silica generally about 5 mm from the interface; whereas, at the interface, no increase or a slight decrease in silica is indicated. In contrast, the Kenwood C shows a general decrease in silica content throughout the shell zone interval. In the hydrated cement paste, the silica shows variable trends with slight increases at the interface for the Newton 19 and

TABLE XXVI -- CHEMICAL ANALYSES OF CEMENT PASTE AND ADJACENT AGGREGATES

Specimen	Distance mm from Interface	Cement Paste					Distance mm from Interface	Carbonate Aggregate				
		%SiO	%CaO	%MgO	%Fe$_2$O$_3$	%Al$_2$O$_3$		%SiO$_2$	%CaO	%MgO	%Fe$_2$O$_3$	%Al$_2$O$_3$
Newton 19	0	20.80	55.2	7.0	1.27	4.32	0-25	8.55	30.2	21.5	1.10	2.16
	5	19.35	48.4	7.0	2.53	3.06	2.5-5	8.60	29.1	17.9	.84	1.95
	10	18.90	47.0	7.6	2.27	3.08	5-7.5	13.50	29.7	18.2	.97	1.84
	15	19.30	47.4	7.7	2.16	3.78	7.5-10	---	28.7	17.8	.78	2.02
	20	19.25	46.8	8.0	2.13	3.88	10-12.5	10.70	28.13	17.9	.72	2.16
	40	20.20	50.5	5.4	2.35	4.00	12.5-15	---	29.8	16.7	1.00	1.88
	60	19.85	50.0	6.5	2.48	3.87	15-17.5	---	24.7	19.8	.35	1.99
							17.5-20	---	28.9	17.8	.77	1.99
							20-22.5	---	28.6	17.8	.76	2.10
Newton 6A	0	9.25	30.5	19.4	--	--	0-2.5	10.40	52.4	3.4	--	--
	5	21.60	50.8	2.9	--	--	2.5-5	12.55	52.6	3.2	--	--
	10	18.45	44.9	7.6	--	--	5-8	9.23	49.0	5.7	--	--
	15	18.35	46.1	3.6	--	--	15	10.80	49.6	5.1	--	--
	20	18.15	48.2	5.7	--	--	20	11.20	49.2	5.8	--	--
	40	19.30	48.2	5.6	--	--						
Kenwood C	0	18.5	53.2	2.10	2.94	4.24	0	15.9	34.6	9.70	.89	1.94
	5	17.6	53.9	2.33	3.00	3.61	5	15.0	36.0	9.60	.95	1.86
	10	18.2	53.4	2.75	3.16	4.23	15	19.0	31.9	11.30	1.30	1.46
	15	18.1	50.8	4.10	2.60	4.26	20	19.7	30.6	11.60	1.10	2.01
	20	18.4	52.1	3.55	2.66	4.58						
Glory 9	0	17.90	57.4	3.37	--	--	0	8.92	38.1	11.80	--	--
	5	18.95	51.6	5.66	--	--	5	11.02	37.1	11.90	--	--
	10	18.70	51.3	6.24	--	--	10	9.84	35.3	12.90	--	--
	20	18.30	52.9	4.90	--	--	20	10.01	36.0	13.30	--	--
Alite and Glory 11	0	21.7	60.3	.43	--	--	0	8.96	39.8	10.4	--	--
	5	20.7	61.0	.76	--	--	5	8.95	38.9	10.1	--	--
	20	20.9	61.0	.81	--	--	20	9.17	39.2	9.3	0.89	1.13
Belite and Glory 11	0	29.2	55.6	1.00	--	--	0	9.5	33.6	12.4	--	--
	5	29.1	56.2	1.00	--	--	5	9.3	33.2	13.1	--	--
	10	29.1	56.7	.98	--	--	10	9.2	32.4	14.1	--	--
	15	29.2	56.8	.95	--	--	15	9.5	32.1	14.5	--	--

CHEMICAL ANALYSES
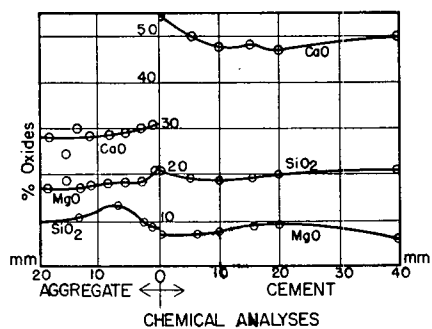
FIG. 52 COMPOSITIONAL VARIATIONS FOR THE NEWTON 19 BAR

CHEMICAL ANALYSES

FIG. 58 COMPOSITIONAL VARIATIONS FOR THE NEWTON 6A BAR

CHEMICAL ANALYSES

X-RAY ANALYSES
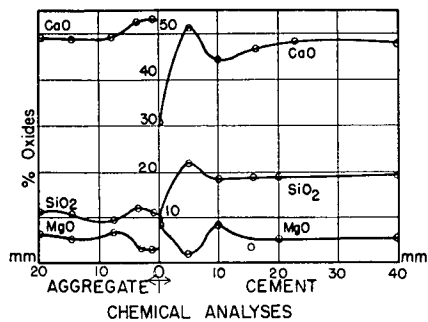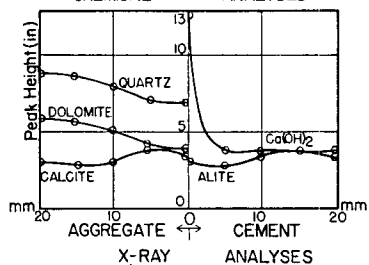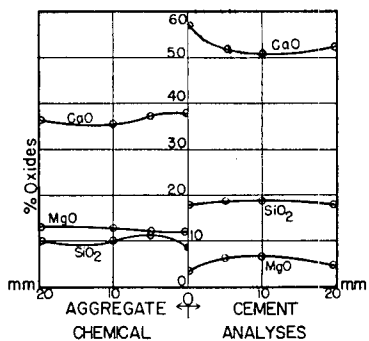
FIG. 59 COMPOSITIONAL VARIATIONS FOR THE GLORY 9 BAR

CHEMICAL ANALYSES

X-RAY ANALYSES
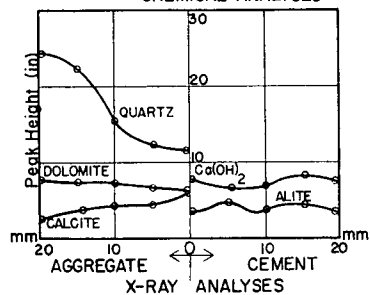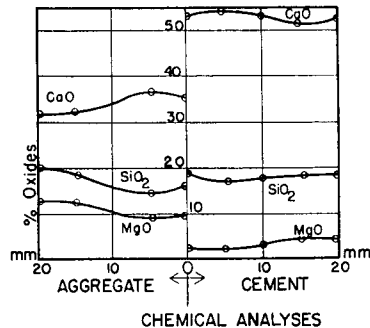
FIG. 60 COMPOSITIONAL VARIATIONS FOR THE KENWOOD C BAR
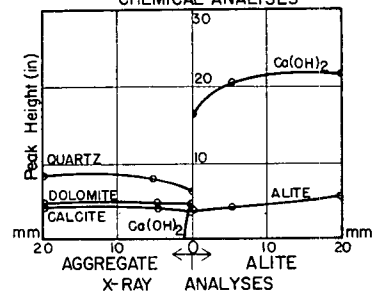

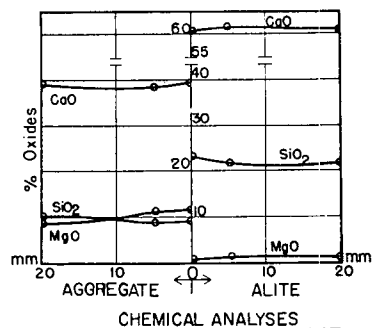CHEMICAL ANALYSES

X-RAY ANALYSES

FIG. 61 COMPOSITIONAL VARIATIONS FOR THE GLORY 11-ALITE BAR
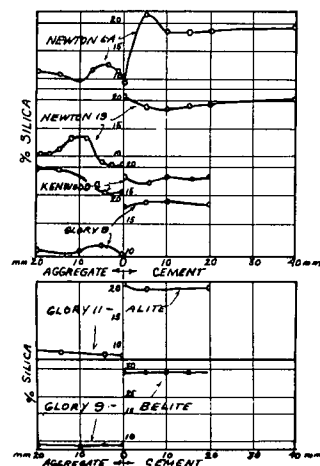

FIG. 62 SUMMARY OF SILICA VARIATIONS

Kenwood C, and decrease in the Newton 6A and Glory 9. The Glory 11 aggregate reacted with the hydrated alite and belite (Fig. 62), shows a slight decrease in silica at the interface, and a corresponding increase on the cement paste side.

CaO shows a general increase in reaction zone interval for all the aggregates and variable behavior in the cement paste. MgO in general decreases in aggregates as the interface is approached. Fe_2O_3 and Al_2O_3, where analyzed, show minor variations and nothing systematic.

The semi-quantitative X-ray data presented graphically in figures 59, 60, and 61 show that the quartz content decreases in the reaction zone of the aggregates. Calcite shows a definite increase in the reaction interval and dolomite a corresponding decrease. The cement compounds are somewhat variable and show evidence of some disorder in the cement paste near the aggregate. $Ca(OH)_2$ was found in the Glory 11 aggregate.

Interpretation of Results

The chemical evidence for CaO and MgO, and X-ray data for the carbonate minerals, show that dolomite appears to be breaking down in the shell zone. This is a concurrent "dedolomitization" reaction. The calcite increase near the interface may be an apparent effect of the relative decrease in dolomite. It may also reflect formation of some new calcite through the combination of calcium, which is released during dedolomitization, or introduced from the cement paste (Fig. 61), with CO_3, made available through dedolomitization.

The chemical and X-ray data regarding silica variation are interesting. Quartz is definitely decreased in the shell zone and must be considered a major source for silica. The quartz is part of the insoluble residue and probably in a finely-divided state. The variable behavior of silica which shows a decrease throughout the reaction zone in the Kenwood C and Glory 11 aggregate, and a slight increase at about 5 mm from the interface of the other three aggregates, indicates that local quartz-derived silica can migrate either OUT OF, or FARTHER INTO a rock. To account for these observations, it was postulated that silica migration is related to the pH environment and moves in a direction to establish equilibrium. A pH gradient is believed to exist and migration direction will depend on the relative amount of locally available silica on either side of the interface, and movement occurs in an attempt to establish equilibrium.

Since hydrated alite and belite appear to be a poor source of silica, and prior research shows that cement paste also appears to be a poor source of silica, one would expect silica to migrate from the rock into the cement. Such is the case with Kenwood C and Glory 11. In the other aggregates however some of the locally-derived silica apparently moves farther into the rock, leaving a narrow somewhat silica-deficient zone immediately adjacent to the interface. Migration in this direction, though in response to local conditions, appears to indicate a difference in the adjustment of some rocks to a hydroxyl-rich environment. The complexities of shell formation indicate more research is needed to account for variations in different shells.

Because of the variable behavior of the silica content of aggregates, the presence of a silicified reaction shell does not mean an increase or decrease

in silica content. It does indicate the presence of amorphous silica, or some silicate compounds. These conclusions are based on the change in the weight per cent silica contents of the before and after conditions of the specimens. Bulk density data of the before and after conditions would be required to calculate the true losses and/or gains caused by the reactions. Unfortunately experimental techniques could not be adapted for bulk density determinations in this experiment. However the reversals in silica contents on a weight per cent basis appear to give a good indication of silica behavior.

From these data it appears that, under conditions of the experiment conducted in cement paste bars, much of the silica in the shell zone comes from breakdown of the quartz in the rock. It is postulated that silica will migrate in the direction required to maintain equilibrium according to the local pH environment. Dedolomitization and possibly an increase in new calcite (calcitization) occurs simultaneously. Alite and belite appear to be quite stable, and are not the source of silica. It is emphasized -- these data apply to a CEMENT PASTE ENVIRONMENT only. Prior research on rim growth in concrete bars indicates the silica would migrate into the bar. More quantitative type studies which would measure the density changes accompanying the chemical changes of the specimens are needed before the true silica behavior could be determined.

Equilibria Studies on Silica Behavior

Introduction

At this stage of research on the chemical behavior of aggregates, it was apparent that a better understanding of the chemistry of silica was essential. It was evident that, when any type of rock is placed in concrete, various reactions {either harmful(?), or beneficial(?)} would be initiated in the attempt of the rock to reach equilibrium with its environment. One of the major components entering into chemical reaction is silica in some "reactive" form. For this reason, as part of his PhD thesis research, Hiltrop (1960) reviewed silicate chemistry, the problem of rim growth, and suggested several approaches for a better knowledge of silica behavior.

The approach demonstrated by Hiltrop, and extended by Werner (1961) in his Masters thesis research, forms the basis of this section of the report. In an attempt to shorten the time for rim growth and circumvent the inherent sampling difficulties in the techniques used by Bisque and Harwood, Hiltrop adapted a refluxing technique to the problem. The refluxing procedure consists of boiling a large number of chips in a flask which has a water jacket condenser installed on the neck of the flask to keep the system from boiling dry. The solution is then analyzed for various ions in solution. The reflux technique provides a better means of measuring what a large number of aggregates contribute to solution more accurately. It also provides a relatively simple means of carrying out the reactions under a variety of conditions.

Hiltrop also develpped a technique to find out what form the "silicate" molecule was in through a modification of the ammonium molybdate blue method of Banks and Carlson (1952) for spectrophotometric determination of silicon. Banks and Carlson showed that treatment of silicon unknowns with hydrofluoric

acid was essential to convert all the soluble silicon to a reactive form, since they suspected the presence of nonreactive forms of silicon composed of some polymers other than the monomeric silicate ion. Since the ammonium molybdate blue complex is formed with monomeric silicate, it was decided to run two samples on each unknown: one with HF treatment; one without HF treatment. The HF-treated sample gave the total silicon, and the sample without HF treatment gave the immediately available species of silicate ion, the monomeric form, which was called molybdate reactive silicon by Hiltrop. It was found the HF treatment always tended to give a higher silicon content indicating that some of the silicate is in a polymeric form.

Preliminary trials with the refluxing technique demonstrated it was suitable for studying equilibria of silica and other ionic migration in aggregate and/or cement systems, providing a silicon-free reflux environment could be found.

Silicon-Free Reflux Environments

A silicon-free container was necessary to allow refluxing of aggregates and other materials in solutions of various silicon concentrations. The migration of silicate (and various other ions) in and out of aggregates could be detected by subsequent analysis of reflux solutions.

An apparatus entirely free of silicon contamination was devised, which consisted of two separate reflux chambers (Fig. 63). An inner chamber formed from an 800 ml high density polyethylene bottle served as the container for the samples to be refluxed. It was placed in a larger outer chamber made from a 1000 ml lipless Berzelius beaker. A large rubber stopper was fitted on the outer chamber, and two Liebig condensers -- one for the outer chamber, and the other for the inner chamber -- were inserted through the stopper. By utilizing a salt solution, the outer chamber was refluxed at 106° C which allowed a boiling temperature to be maintained in the inner chamber.

Experimental Procedure

In order to study the equilibria of various aggregate and cement systems, it was necessary to equilibrate by refluxing aggregates in silica solutions of different initial concentrations and then measure the resulting ionic species in solution after refluxing.

Selected aggregates were crushed and sieved, and the portion of chips retained on a #8 sieve was used. After washing and drying, a 50 gm sample was selected and placed in the inner polyethylene reflux chamber with 300 ml of distilled water. Where necessary the pH was adjusted to the required initial pH with NaOH solution. The silicon environment was controlled by adding a specified amount of sodium silicate solution. The total amount of liquid (i.e.- silicon in solution plus distilled water) was maintained at 300 ml in the reflux chamber. All the samples were refluxed for a period of 48 hours and, after cooling, the liquid was transferred to plasticware containers and analyzed.

The reflux solution was analyzed for silicon spectrophotometrically by the method of Banks and Carlson in which HF was used to insure complete solu-

VAPORS CONDENSE AND RETURN TO SOLUTION

WATER JACKET OUTLET

LIEBIG CONDENSER

WATER JACKET INLET

BERZELIUS FLASK CONTAINING NaCl BOILING SOLUTION

HIGH DENSITY POLYETHYLENE BOTTLE CONTAINING CHIPS OF AGGREGATE AND $Na_2S_2O_3$ or $NaOH$ SOLUTION
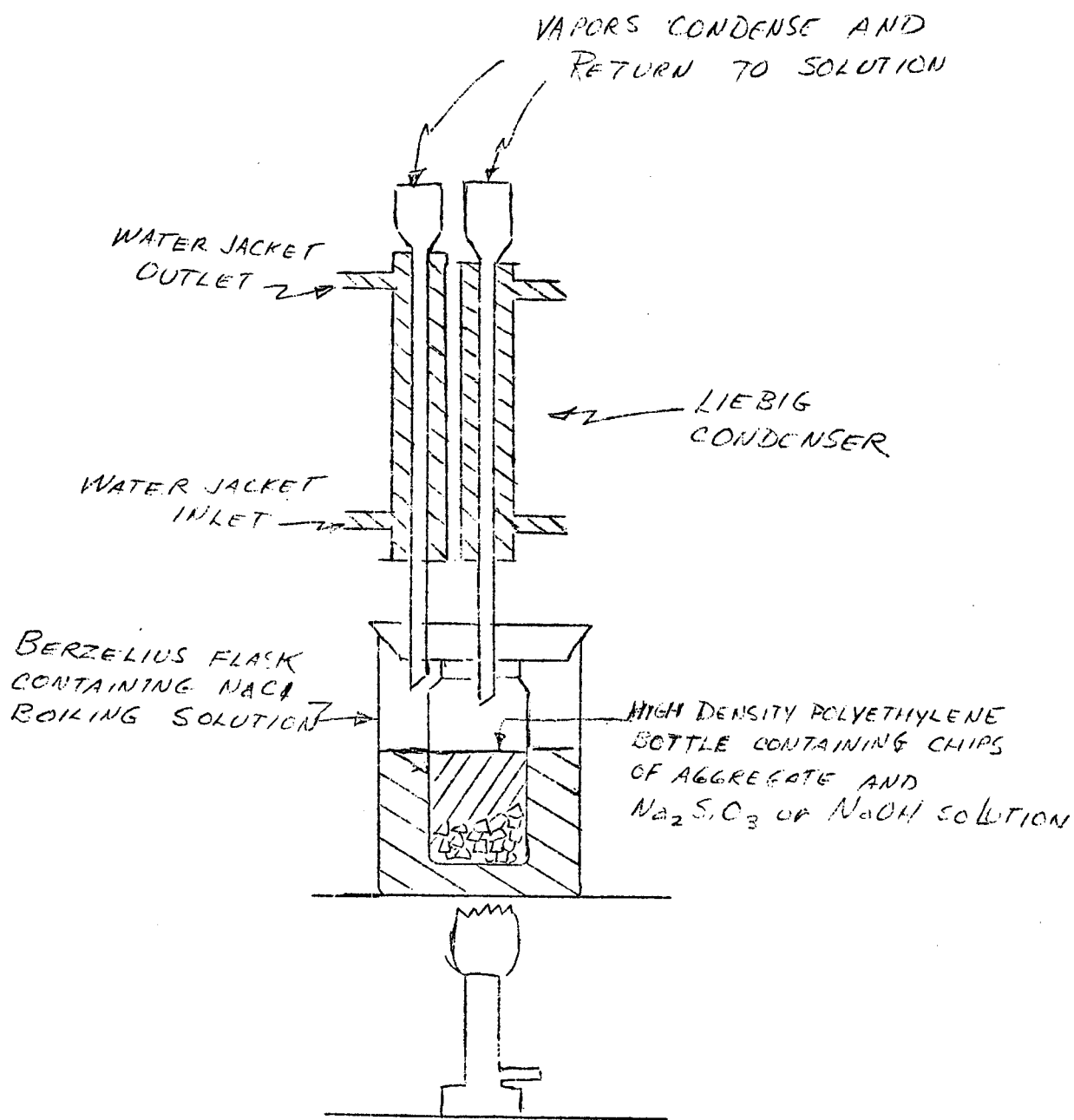
FIG. 63 SILICON FREE REFLUX APPARATUS.

tion of all silicon. The molybdate reactive silicon was determined by the same method, but omitting the HF treatment.

A versene titration method was used for calcium and magnesium as well as for aluminum and iron.

Samples Studied

Refluxing procedures were carried out on carbonate aggregates, Ottawa sand, and hydrated cement paste chips made from standard cements of low (.25%), medium (.60%), and high (1.36%) alkali content. Some hydrated alite and belite was also refluxed.

The carbonate rocks studied were obtained from quarries which have furnished aggregates for Iowa highways, and have produced aggregate of poor service record or do not pass present acceptance tests.

Glory 9 and Kenwood C were described previously in Harwood's compositional variation studies. The Douds 16 specimen represents rock of Mississippian St. Louis formation from bed 16 at the Douds Quarry, and is a light greenish-gray argillaceous dolomitic limestone. LeGrand 9 is a light-yellow crystalline massive magnesian limestone from bed 9 of the LeGrand Quarry and has a poor service record. Table XXVII gives the chemical analysis of the rock samples.

TABLE XXVII

CHEMICAL ANALYSES OF ROCK SAMPLES BEFORE REFLUXING PROCEDURE

Sample	$\%CaCO_3$	$\%MgCO_3$	$\%Al_2O_3$	$\%Fe_2O_3$	$\%SiO_2$	% Insol. Residue
Glory 9	60.48	25.08	--	0.20	15.83	16.00
Kenwood C	56.16	29.92	--	0.30	11.55	14.00
Douds 16	65.30	24.60	0.75	1.00	5.46	8.20
LeGrand 9	81.00	17.00	0.10	0.17	1.80	2.00

Experimental Results

Data for the four rocks on which reflux experiments were made are presented in Table XXVIII and in figures 64, 65, 66, 67, and 68. A series of refluxing operations with initial silicon concentration in solution ranging from 0.000 to 67.92 milligrams per 300 ml were carried out and the final silicon concentration, calcium, magnesium, and per cent reactive silicon were determined for each rock. A similar series of reflux experiments were carried out on hydrated cement paste chips (Table XXVIII; Fig. 68), and on Ottawa

TABLE XXVIII -- REFLUX EXPERIMENT DATA

Sample	Initial Silicon Conc.Mg	Final Silicon Conc.Mg	Milli-moles Calcium	Milli-moles Magnes.	% React. Silicon	pH
Glory 9	0.000	2.27	1.908	0.19	85.0	7.0
	0.000	4.50	0.950	0.22	87.0	8.5
	0.000	7.44	0.000	0.00	84.0	12.0
	0.566	4.17	0.914	0.12	86.0	8.6
	1.132	4.41	0.873	0.12	83.0	8.5
	5.600	4.50	0.780	0.12	84.0	8.6
	9.065	4.41	0.426	0.13	87.0	8.6
	10.19	4.20	0.424	0.05	86.0	8.6
	11.32	4.53	0.420	0.10	86.0	8.4
	22.64	4.56	0.072	0.00	89.0	8.7
	28.30	5.84	0.060	0.00	87.0	9.0
	33.96	6.18	0.030	0.00	88.0	9.3
	39.62	6.48	0.060	0.00	88.0	10.0
	56.60	11.68	0.030	0.00	86.0	10.2
	67.92	13.32	0.000	0.00	89.0	10.8
Kenwood C	0.000	4.50	0.03	0.00	87.0	9.8
	0.000	3.58	1.130	0.09	86.0	8.5
	0.000	1.80	1.401	0.17	89.0	6.5
	0.566	3.66	1.120	0.09	86.5	8.5
	1.132	3.39	0.948	0.09	84.3	8.6
	2.264	3.42	0.960	0.06	86.0	8.5
	5.660	3.52	0.948	0.07	87.2	8.6
	9.056	4.08	6.780	0.05	89.0	8.6
	11.32	3.75	0.519	0.04	88.0	8.8
	22.64	4.96	0.030	0.02	82.5	8.4
	33.96	5.20	0.060	0.00	84.0	8.7
	45.28	5.58	0.000	0.00	90.0	10.3
	56.60	7.38	0.000	0.00	91.0	10.5
	67.92	11.64	0.000	0.00	90.0	10.9
High Alkali Cement	0.000	0.24	0.790	0.00	55	11.5
	1.132	0.27	0.740		56	11.4
	5.660	0.21	0.585		54	11.5
	11.32	0.48	0.400		58	11.5
	16.98	0.84	0.005		57	11.6
	28.30	1.08	0.005		59	11.5
	56.00	1.20	0.00		55	11.6
	73.00	1.30	0.00	0.00	54	11.5

Sample	Initial Silicon Conc.Mg	Final Silicon Conc.Mg	Milli-moles Calcium	Milli-moles Magnes.	% React. Silicon	pH
LeGrand 9	0.000	1.32	0.380	0.00	90	7.6
	0.000	2.83	0.300		92	9.3
	0.000	4.38	0.000		92	10.0
	0.566	2.76	0.280		87	9.3
	1.132	2.80	0.270		89	9.3
	5.660	2.82	0.070		92	9.4
	11.32	4.08	0.000		94	9.5
	16.98	7.02	0.000		96	9.7
	22.64	10.08	0.000		99	9.9
	28.30	14.00	0.000		100	10.2
	33.96	16.32	0.000	0.00	100	10.6
Doud 16	0.000	5.76	0.000	0.00	92.0	10.5
	0.000	2.50	0.320	0.06	90.0	8.5
	1.132	2.52	0.162	0.01	88.0	7.7
	3.396	2.28	0.178	0.00	100.0	8.3
	5.660	2.82	0.113	0.00	95.0	8.3
	11.32	2.43	0.256		95.0	8.4
	16.98	4.62	0.000		94.0	9.4
	19.24	3.66	0.000		96.0	9.6
	22.64	3.51	0.045		93.0	9.7
	28.30	4.92	0.000		92.5	9.8
	33.96	6.84	0.000		65.0	9.9
	45.28	8.48	0.000		95.0	10.0
	60.00	12.30	0.000	0.00	95.0	10.4
Low Alkali Cement	0.000	0.03	0.213	0.018	87	11.5
Medium Alkali Cement	0.000	0.15	—	—	75	11.5
High Alkali Cement	0.000	0.24	0.79	0.00	55	11.5
Alite	0.000	0.05	4.25	0.00	—	—
Belite	0.000	1.44	1.00	0.00	—	—

TABLE XXIX -- CALCIUM-SILICON RATIOS

Sample	Initial Silicon Conc. Mg	Mg Silicon Lost	Milli-moles Silicon Lost	Milli-moles Calcium Lost	$\dfrac{Ca}{Si}$
Glory 9	0.566	0.60	0.021	0.034	1.62
	1.132	1.44	0.051	0.075	1.47
	5.660	5.69	0.204	0.168	0.83
	9.065	9.19	0.328	0.522	1.59
	10.19	10.52	0.376	0.524	1.39
	11.32	11.32	0.404	0.500	1.24
	22.64	22.81	0.804	0.876	1.09
Kenwood C	0.566	0.40	0.014	0.006	0.43
	1.132	1.24	0.044	0.182	4.20
	2.264	2.26	0.085	2.170	2.00
	5.660	5.62	0.200	0.182	0.91
	9.056	8.48	0.304	0.350	1.15
	11.32	11.07	0.396	0.611	1.56
	22.64	21.16	0.751	0.800	1.07
	45.28	43.20	1.540	1.130	0.72
	67.93	56.78	2.130	1.130	0.53
Doud 16	1.132	1.11	0.040	0.058	1.45
	3.396	3.62	0.129	0.142	1.10
	5.660	5.30	0.190	0.207	1.09
	11.32	11.39	0.405	0.260	0.64
	16.98	14.86	0.528	0.320	0.61
LeGrand 9	0.566	0.560	0.020	0.030	1.50
	1.132	1.132	0.040	0.035	0.88
	5.660	5.640	0.200	0.230	1.15
High Alkali Cement	1.132	1.102	0.039	0.050	1.28
	5.660	5.690	0.203	0.204	1.00
	11.32	11.08	0.394	0.390	0.99
	16.98	16.38	0.584	0.785	1.34

TABLE XXX -- EFFECT OF pH ON THE SOLUBILITY OF 25 GRAMS OF OTTAWA SAND

pH	Milligrams of Silicon in Solution	% Reactive Silicon
6.0	1.13	95.5
7.0	1.35	91.0
8.0	2.06	98.0
8.5	2.55	95.0
9.0	2.50	96.5
10.0	3.80	92.0
11.0	5.30	97.0
11.7	6.85	93.0

sand (Table XXX; Fig. 73) over a pH range of 6 through 11.7 to determine its solubility.

Calcium-silicon ratios (Table XXIX; Figs. 69, 70, 71, and 72) were also calculated from the amount of silicon and calcium lost from solution during the refluxing operation. The silicon value is the numerical difference between the initial silicon concentration plus the average value for the rock alone, and the final silicon concentration. The amount of calcium lost from solution is obtained by taking the average value for the rock when refluxed alone and subtracting the value for calcium in solution after refluxing.

It is necessary to assume that 48 hours was sufficient time for equilibrium conditions to develop in the systems studied. This assumption was validated by allowing pilot samples to reflux for longer periods and the subsequent results showed no significant increase in component concentrations in solution.

Discussion of Data

The silica behavior of the aggregate and a high alkali cement are graphically demonstrated in figures 64, 65, 66, 67, and 68; and, in each of these figures, the behavior of the materials refluxed is compared to the theoretical no absorption curve. This curve represents no change in silicon concentration in the refluxing solution before or after the operation.

Examination of figure 64 shows that at zero initial silicon concentration of Glory 9 gives off silicon into solution. But as the initial silicon concentration in solution is increased the rock begins to absorb silicon. The final concentration remains fairly constant as the initial silicon concentration is increased up to about 28.3 milligrams after which it begins to rise. Coinciding with the constant silicon plateau is a constant pH (Table XXVIII). Calcium and magnesium decrease with increasing initial silicon concentration. Consideration of the amount of silicon and calcium lost from solution is graphically presented in figure 69, and indicates that the calcium-silicon ratio approaches the value of one. The depletion of calcium and silicon from solution on a one-to-one molar relationship indicates that a calcium silicate compound is being formed. Comparison of the slopes of the silicon absorption curve (Fig. 64) with the slope of the no-absorption curve indicates that silica is still being absorbed by the rocks after the soluble calcium was depleted. The degree of absorption in the upper range is considerably less and may be expected to eventually parallel the no-absorption curve.

The Kenwood C and Douds 16 aggregates (Table XXVIII; Figs. 65 and 66) are somewhat similar to Glory 9, except that the Kenwood rock absorbs more silicon (has a wider constant silicon plateau).

The LeGrand 9 (Table XXVIII; Fig. 67) gave interesting results and a somewhat different behavior. It is different chemically (low residue, high calcium content) from the other three aggregates. The silicon absorption curve shows only a small constant silicon plateau (limited silica absorption) and the slope of the curve approaches closely that of the no-absorption curve indicating the rock is absorbing only a very small amount of silicon after the calcium is depleted. Calcium-silicon ratios approach one (Fig. 72) until the available calcium is depleted.
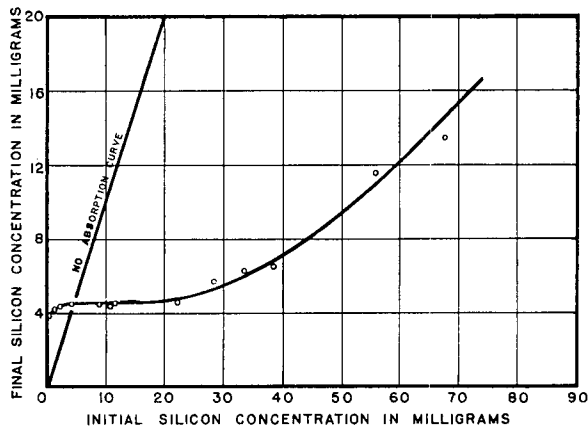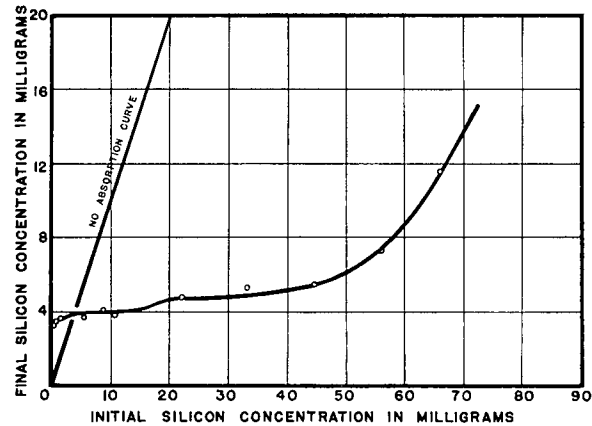
FIGURE 60. SILICON ABSORPTION CURVE FOR GLORY 9

64

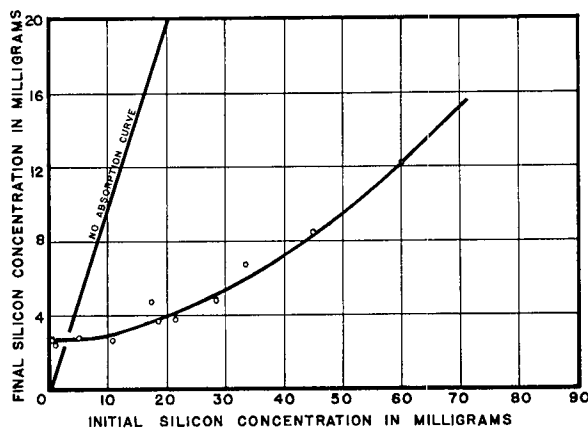FIGURE 61. SILICON ABSORPTION CURVE FOR KENWOOD C

65

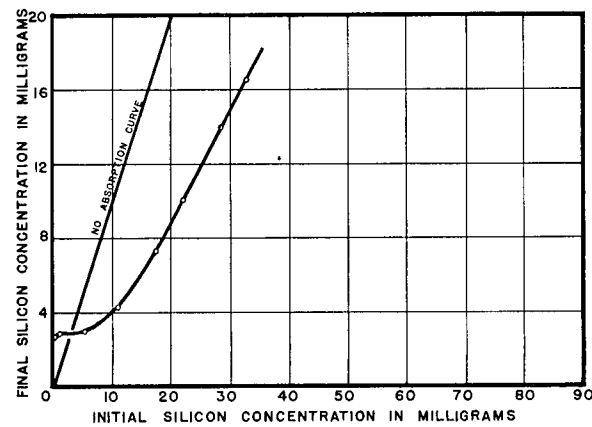FIGURE 62. SILICON ABSORPTION CURVE FOR DOUDS 16

66

FIGURE 63. SILICON ABSORPTION CURVE FOR LEGRAND 9

67

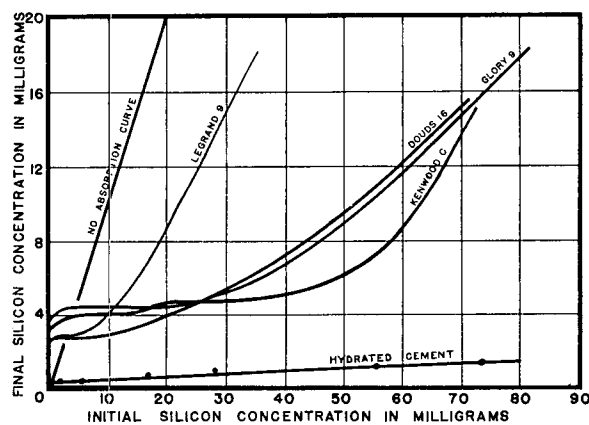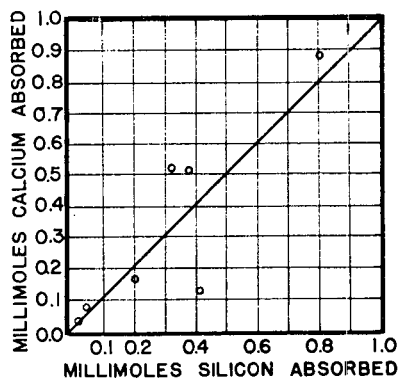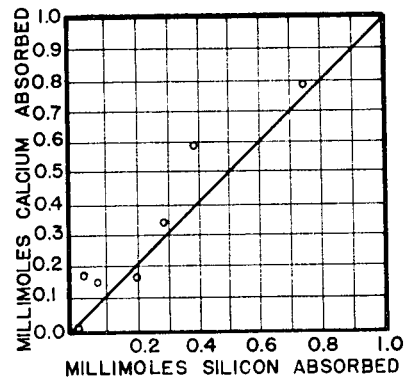
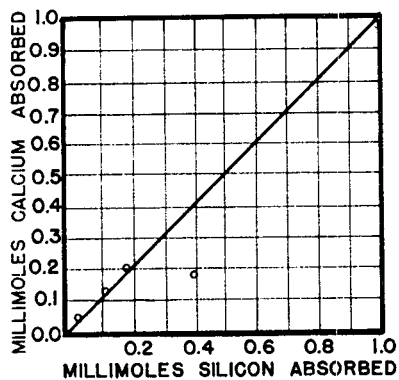
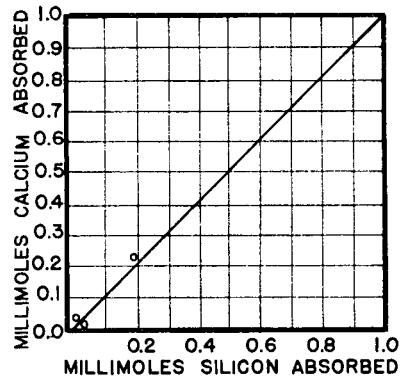FIGURE 64. SUMMARY OF ABSORPTION CURVES

68

69

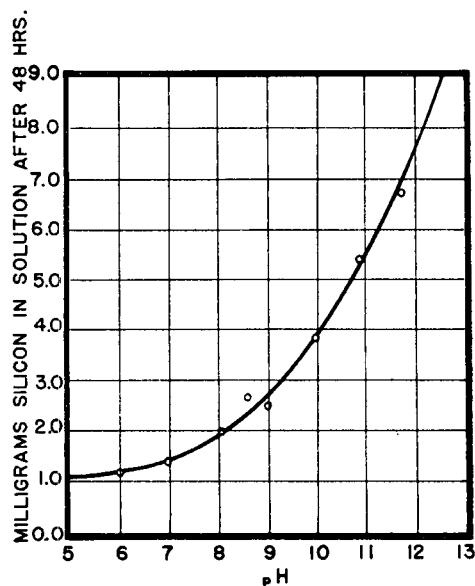FIGURE 69. CALCIUM-SILICON RATIOS FOR GLORY 9

70

FIGURE 70. CALCIUM-SILICON RATIOS FOR KENWOOD C

71

FIGURE 71. CALCIUM-SILICON RATIOS FOR DOUDS 16

72

FIGURE 72. CALCIUM-SILICON RATIOS FOR LEGRAND 9

73

FIGURE 73. QUARTZ SOLUBILITY CURVE

In all the rocks studied, the per cent of reactive silicon present varies from 82.5 to 100 with the average about 85-90. This indicates that some 10-15% of complex or polymerized species of silicate is present in solution.

Three standard cements as well as alite and belite were refluxed in a silicon-free environment. The data in Table XXVIII show that they contribute little silicon to solution and much less than the aggregates studied.

When chips of hydrated high alkali (1.34% equivalent Na_2O) were refluxed over the same range of initial silicon concentration as the aggregates, the data (Table XVIII; Fig. 68) show that the cement has a marked affinity for silicon. The cement does give up some silicon to solution at zero or very low initial silicon concentrations but as the initial silicon concentration is increased it shows a greater ability to absorb silicon than aggregates under comparable conditions (Fig. 68). Calcium is depleted from solution and the calcium-silicon ratios (Table XIX) show that calcium is instrumental in absorption of silicon from solutions of low concentrations up to concentrations of 17 milligrams. The silicon saturation limit appears to be well over 70 milligrams for a 50 gram cement sample. The pH remains at about 11.5 and the cement gives the lowest per cent of reactive silicon. After refluxing the chips of cement in a high silica environment, it was found to have a white powdery coating of material considered to be a calcium silicate compound*.

A silica solubility study at various pH's was made by means of the reflux procedure on some Ottawa sand in order to see if fine aggregate could be a feasible source of silicon in the silicification commonly observed in reaction shells. The data in Table XXX and figure 73 indicate that at the pH environment approaching that of cement, a 25 gram sample of Ottawa sand refluxed for 25 hours gives off 6.85 milligrams of silicon which is over 90% in the reactive monomeric form. At this pH sand gives off 58.4 times as much silicon as high alkali cement and should seriously be considered a source of silica in mortars and concrete.

Summary of Data

Rocks contribute silicon, calcium and in most cases magnesium to solution with relatively low initial silicon concentrations. As soon as silicon is introduced to the solution, the concentration of calcium and magnesium in solution begin to decrease. Silicon was absorbed from solution by all the rocks at essentially a constant rate (constant silicon plateau) until both the calcium and magnesium in the solution are depleted. The calcium and silicon are absorbed at essentially a one-to-one ratio. A constant pH plateau corresponds to the constant silicon plateau and then rises when the calcium is gone from solution. Rocks continue to absorb silicon though at a lesser rate after calcium is depleted and the silicon plateau does not exist.

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*The exact compound has not been determined but powder X-ray films of such white coatings give a weak pattern whose strong lines compare favorably to those typical of some hydrated calcium silicates.

Three standard hydrated cements were refluxed and contributed very little silicon but considerably more calcium to solution. Cements show a high affinity for silicon and, like rocks, the calcium and silicon are taken from solution on a one-to-one basis. Calcium silicate forms on the pores and surfaces of the cement chips.

Ottawa sand, when refluxed at various pH conditions, shows an increasing quartz solubility. At pH 11.7, approximately the pH of cement environment, a 25 gram sample of sand gave 6.85 milligrams of silicon to solution.

Interpretation

The experimental data indicate that silicon may either move into or out of a rock, depending upon the silicon concentration of the surrounding environment. Definite equilibrium pH and silicon concentrations* exist below which silicon moves out of the rock and above which it moves into the rock. Each of the rocks appears to have its own characteristic absorption behavior. In each case the ability of rocks to absorb silica far exceeds their ability to release it.

The magnitude of silicon absorption appears to be influenced by the impurity of the rock. Glory 9, a deleterious aggregate, and Kenwood C, an unacceptable aggregate with expansive characteristics, have high insoluble residues and their silicon absorption is high. Douds 16, a potentially bad aggregate, with an intermediate amount of residue, has an intermediate degree of silicon absorption. LeGrand 9, another aggregate of poor service record, contains the least amount of insoluble residue and showed the least amount of silicon absorption. It might indicate that another mechanism other than silicification and dedolomitization causes the deleterious behavior of the LeGrand rocks. It also appears to account for the lack of well defined rims in distressed concrete containing LeGrand aggregate.

The rocks when refluxed alone contribute calcium and a lesser amount of magnesium to solution. This is to be expected in view of the dedolomitization previously discussed. However, the probable formation of brucite, $Mg(OH)_2$, which is considerably less soluble than calcium hydroxide, accounts for the relatively small amount of magnesium in solution. A strong possibility exists for the formation of magnesium silicate in relatively small amounts although to date none has been observed.

The tendency of calcium and silicon to be absorbed in a one-to-one basis indicates that initial silicon absorption over the range of the silicon plateau probably results in the formation of hydrous calcium silicate compounds within the rock. The continued silicon absorption by the rock after all the calcium was depleted probably is related to the polymerization of silica on clay particles on the rock.

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*Under the conditions of the experiments, the equilibrium silicon concentration ranges from 2.5 to 4.5 mg per 300 ml of solution for the aggregates studied and .25 mg per 300 ml for the cement.

The data presented indicate that cements when refluxed alone are a minor source of silicon but when refluxed in a silicon-rich environment they demonstrate a very large capacity to absorb it. The silicon absorption coincides with calcium depletion on a one-to-one basis and physical evidence of formation of calcium silicate compounds was observed. The behavior was expected in view of the tendency of silica to react with the hydrated lime present in cements. These data indicate that cement is a doubtful source of silicon found in reaction shells in aggregate.

Reflux experiments with Ottawa sand (quartz) indicates that the fine aggregate is a source for abundant reactive silicon.

It should be noted that the refluxing procedure probably liberates all the carbonate released during dedolomitization. The formation of calcium silicate compounds at lower temperatures may be influenced (retarded) if some or all of the available calcium should unite with released carbonate ions and form calcium carbonate (calcite) in the reaction zone. Evidence for this possibility is suggested by the general increase of calcite content in the reaction zone as noted in Harwood's studies.

The direction of silica migration in or out of the rock is well established by the reflux experiment. The ambiguity associated with the reaction in concrete or cement paste environments caused by lack of density data to coincide with chemical data is obviated. This method deals with solutions only and demonstrated that silica migrates to establish local equilibrium.

In conclusion, it should be stressed that the observations and interpretations made above are related to the experimental results obtained by refluxing. They are not the conditions found in nature and more research would be needed to see if they can be extrapolated. These data however have provided a better insight on the reactions which can occur between aggregates and their environment in concrete. The refluxing technique provides a means of studying aggregate reactions more quantitatively than formerly possible and with a great deal more flexibility. It may one day form an excellent acceptance test for predicting the behavior of an aggregate.

Expansion Studies

The expansion of carbonate aggregates in response to their alkaline concrete environment has received considerable attention in the past. Although excessive expansion of aggregates has not been a problem in Iowa, distress in concrete has been related to the expansion of carbonate aggregate and its resulting concrete in Canada and Virginia. Swenson and Gillott (1960) describe the expansive characteristics of the Kingston, Ontario, aggregate. Newlon (personal communication) has described an expansive carbonate aggregate in Virginia. The only highly expansive rock encountered in Iowa prior to our expansion studies was rock from the Kenwood member at the Otis Quarry.

Recently, Hadley (1961) of the Portland Cement Association, has described a simple method for measuring the expansion of carbonate aggregate prisms. The conically-tapered prisms are immersed in individual polyethylene bottles con-

taining a solution of 1.0 N NaOH and are measured at weekly intervals on a
specially-adapted micrometer gauge.

Procedure

Hadley's method was adapted with modification and applied to single-bed
samples from the LeGrand and Glory quarries by Moore, as part of his Masters
thesis research. Instead of using tapered prisms, 1/2" x 2" cylinders were
cored on a drill-press adapted with a special diamond bit. The core is cut
in about two minutes. The cylinders are rapidly and accurately tapered
conically at a 45° angle by placing them in a half-inch chuck mounted on the
horizontal shaft of an electric motor. The rotating chuck is then placed at
a 45° angle against the edge of a rotating emery wheel and the necessary
taper is easily obtained.

The tapered cylinders were immersed in polyethylene bottles containing
the following environments: distilled water; 1N NaOH solution; 1N sodium
silicate solution at pH 12. The cylinders were removed each week, washed with
distilled water, and measured on a special gauge.

Results

The samples from beds 8, 9, 10, 11, 12, and 13 of the North LeGrand
Quarry (Tripp section, 1956) showed no expansion after 75 days in any of the
environments (water, sodium hydroxide, and sodium silicate solutions). These
data confirm the experience on concrete beam studies carried out by the
Materials Department of the Iowa State Highway Commission.

After five days the samples from the Glory Quarry showed detectable
expansion of almost identical amount in both the sodium silicate and sodium
hydroxide solutions. Data relating to these expansive rocks are presented
below in Table XXXI.

TABLE XXXI

EXPANSION AND CHEMICAL DATA ON GLORY AGGREGATE

Bed	% Expansion after 75 days	Ca as % $CaCO_3$	Mg as % $MgCO_3$	% Insoluble Residue	Wt. % Silica	Wt.% R_2O_3 (residue)
2	0.64	66.50	24.76	7.24	5.19	28.3
3	1.60	65.19	23.40	10.12	6.82	32.6
4	0.29	60.94	26.13	10.91	7.53	31.0
5	0.88	61.92	23.92	12.09	8.57	29.1
6	0.50	62.88	22.05	12.79	9.20	28.0
8	0.15	68.44	20.66	9.05	6.93	23.4

The per cent expansion in 75 days was plotted against the insoluble resi-
due and per cent of R_2O_3 in the residue (Fig. 74). These graphs suggest

FIG. 74

PER CENT FIG. 74 RESIDUE

FIG. 75

WEIGHT % R₂O₃ IN RESIDUE

Mg AS WEIGHT % MgCO₃

FIG. 75
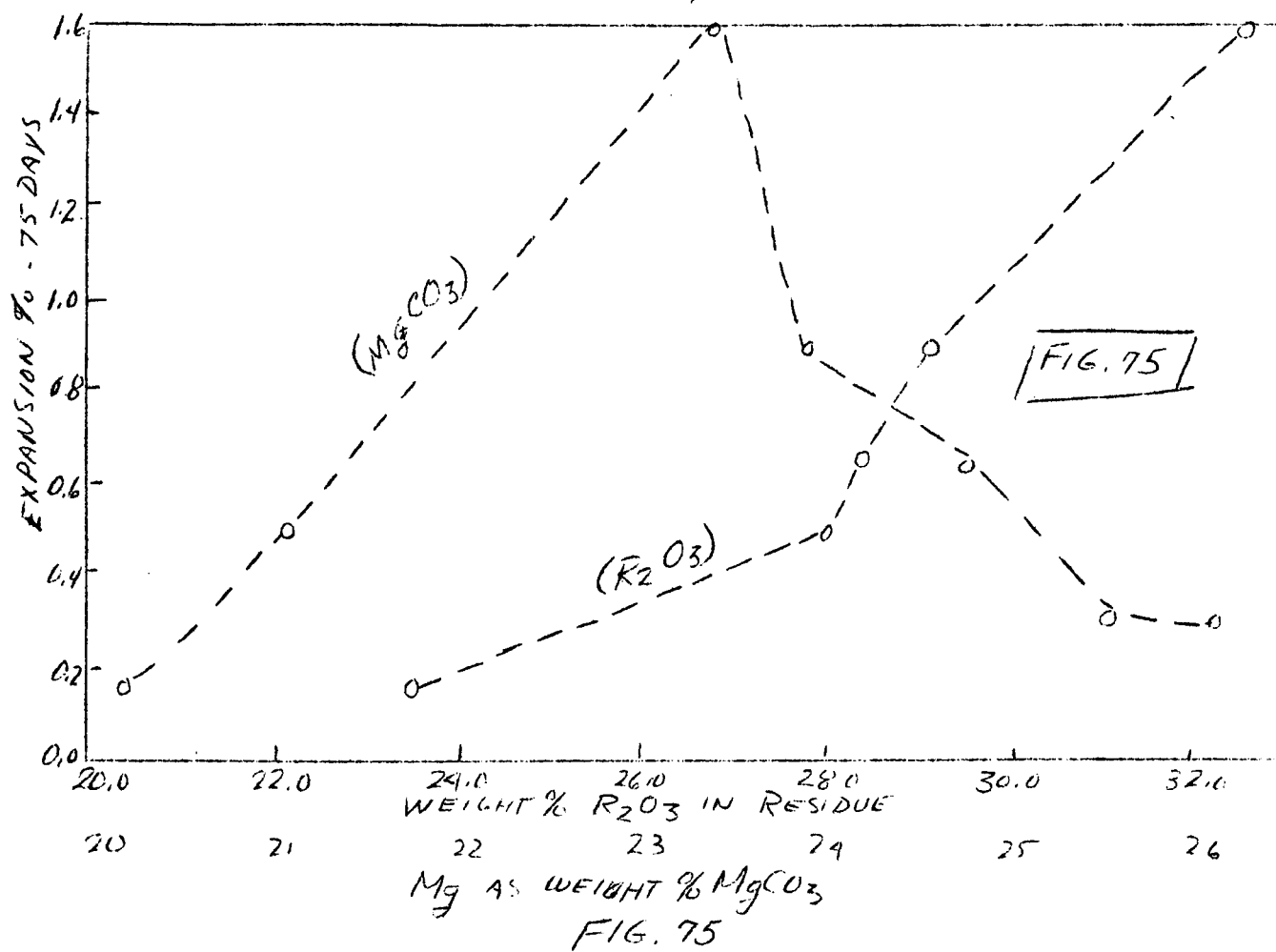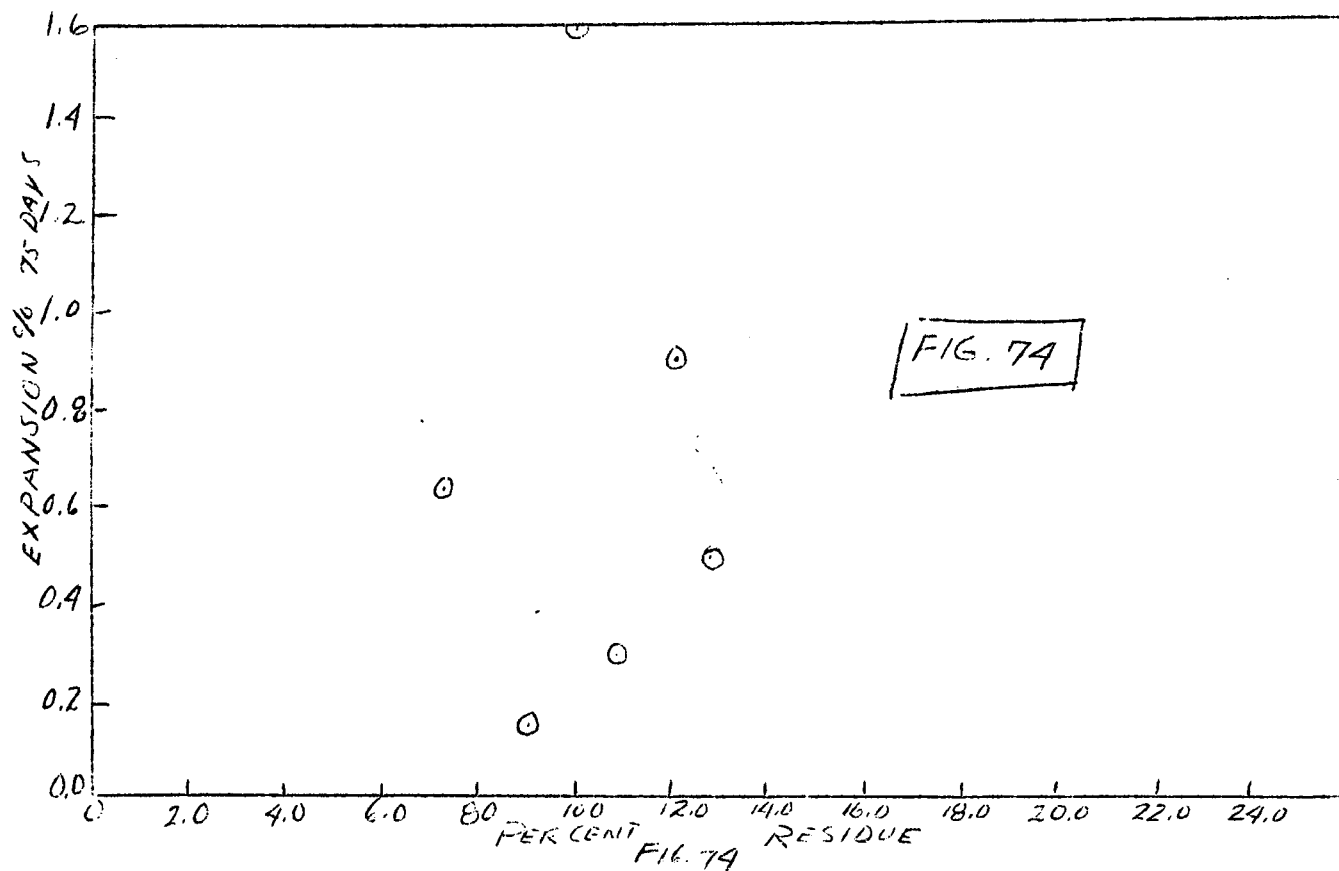
qualitatively that the expansion of Glory aggregate is a function of the clay content if R_2O_3 is considered a valid estimate of the clay.

These data suggest the feasibility of more work in this area. Although excessive expansions are not experienced in past research by the Iowa Highway Commission, some correlation may yet exist between slight expansion and other characteristics. The procedure is simple and could easily be adapted to a standard test, should the need arise.

Conclusions

Detailed summary of the chemical studies will not be made here, but some of the pertinent conclusions will be mentioned. The research to date has shown that distressed concrete made from Glory aggregate provides evidence that Glory aggregate of Rapid lithology has reacted. This reaction in concrete was a silicification process characterized by an increase in silica content on a weight per cent basis of the rim zone. Rims were experimentally grown in silica solutions. Rims were also experimentally grown in concrete bars within 30 days by soaking the bars in water at 130° F or in 8 hours in an autoclave at a higher temperature. These studies show that the carbonate aggregate reaction is selective and the reactive aggregates are argillaceous dolomitic rocks characterized by relatively high insoluble residues.

The compositional variations associated with aggregate reaction in concrete and the equilibrium studies via the reflux technique indicate that the carbonate aggregate reactions represent an attempt of an aggregate to come into equilibrium with a high pH environment. Calcium silicate compounds form in shell zones and cement during refluxing, but at lower temperatures or more natural conditions there is a possibility that calcium carbonate may be forming in the shell zones of reactive aggregate. Dedolomitization is a concurrent reaction and attention is called to the potential role of released calcium and possibly magnesium. Cement pastes are fairly stable and probably are not the source of silica found in the shell zone. In experiments with cement paste bars, much of the silica in shell zones is locally derived from quartz present in the carbonate aggregate. The fine aggregate in concrete is considered a potential source of silica in rims formed in concrete environments. The occurrence of a reaction shell indicates the presence of amorphous silica or other form of silicate and is not indicative of an increase or decrease in silica content unless something is known about the relative silica concentrations in the system. More quantitative experiments which would measure the density changes associated with chemical changes during a reaction are necessary to establish the true migration directions of the components in concrete systems.

One important result of the work to date is the realization that the problem of carbonate reactions in concrete involves consideration of the coarse aggregate, fine aggregate, and the cement. None of these materials are inert, and their interactions should be considered in future research.

CHAPTER VII

ENGINEERING TESTS

During the investigation, data were needed which could only be obtained by engineering tests according to ASTM methods. Such work was done at the Materials Laboratory of the Iowa State Highway Commission. This work which forms the basis for this section was a cooperative project undertaken in 1958 with the Materials Department to: 1) check the expansion of concrete bars made from Glory and other types of aggregate; and 2) stimulate growth of reaction rims on Glory and other aggregates in concrete test bars. These data were needed to understand the behavior of aggregates in concrete, and also to provide some basis for correlation with other phases of investigation carried out by HR-15. Rocks of good and poor service records were used in the study.

In order to accomplish the objectives, three types of tests were agreed upon:

> TEST   I - Alkali-aggregate reactivity test (ASTM Test C227-52T) which utilized sand-size carbonate aggregate.

> TEST II - Concrete volume change (ASTM Test C151-54T) in order to evaluate any excessive growth in mortar bars which may be due to the increased surface area.

> TEST III - Potential growth of rims.

Tests I and II were carried out by the Materials Department, and Test III was the responsibility of HR-15. All of the bars were made by the Materials laboratory on March 4, 5, 6, and 10 (1958). Information on the method of testing the aggregates in cement and concrete mixtures is presented below.

> TEST   I - Alkali-aggregate reactivity test, ASTM Test C227-52T
>> Size of bar - 1" x 1" x 10"
>> Total number of samples tested - 18
>> Total number of bars (4 per sample) - 72
>> Mortar mixed as per ASTM specifications
>> Grading of crushed aggregate as per ASTM specifications
>> Aggregate is to be saturated, surface dry
>> If possible, excess dust should be removed.

> TEST II - Concrete volume change test, as per ASTM Test C157-54T
>> The ASTM test will serve as a general outline
>> Size of bar - 4" x 4" x 18"
>> Number of samples tested - 8
>> Number of bars (2 per sample) - 16; 1 bar stored in curing room, other bar buried
>> Concrete mixture - Standard No. 2 mix, 1:2:3 approximately corrected for volume
>> Fine aggregate - Ottawa sand (graded)
>> Coarse aggregate - graded from 1", down; saturated, surface dry.

TEST III - Growth of reaction rims

    Size of bar - 2" x 2" x 14"
    Number of samples tested - 4
    Number of bars (10 bars per sample) - 40
    Concrete mixture - 1:2:3 with slightly more water
    Fine aggregate - Ottawa sand (graded)
    Coarse aggegate grading - 100% passing 1/2"
                        40% passing 3/8"
                        0% passing #4
    Coarse aggregate is to be saturated, surface dry
    Curing time - 2 days
    End plugs should be fixed in the bars

NOTE:- Type of cement in all three tests is to be TYPE I cement.

In Table XXXII the sample information for the three types of tests are given.

TABLE XXXII

SAMPLE INFORMATION FOR TESTING AGGREGATES IN CEMENT AND CONCRETE MIXTURES

Sample Number	Quarry	Quarry Sample Number	Stratigraphic Unit	*Test I	**Test II	***Test III
1	Burton Ave.	10	Solon	x	x	x
2	Burton Ave.	14	Rapid	x		x
3	Burton Ave.	18	Rapid	x	x	
4	Burton Ave.	22	Rapid	x		
5	Newton	5	Coralville	x	x	
6	Newton	11	Coralville	x		
7	Newton	16	Coralville	x		
8	Newton	18	Coralville	x	x	
9	Pints	1	Rapid	x	x	
10	Pints	9	Coralville	x	x	
11	Pints	11	Coralville	x		
12	Glory	6	Rapid	x		x
13	Glory	9	Rapid	x	x	
14	Glory	13	Rapid	x		x
15	Glory	22	Coralville	x	x	
16	Platte River class V				x	
17	LeGrand		Maynes Creek		x	
18	LeGrand	Eagle City			x	

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  * TEST I   - Standard ASTM alkali-reactivity test (mortar bar)
 ** TEST II - Concrete volume change test, using 4" x 4" x 18" bars
*** TEST III - Rim growth tests, using 2" x 2" x 14" bars

0

Results

Test I

Three additional aggregates, the Platte River Class V gravel, LeGrand-Maynes Creek, and LeGrand-Eagle City were added to the original 15 samples agreed upon to be tested. This was done by the Materials Department because space in the test cans was available. The tests were completed in 1961 under the direction of John Boring. The data supplied by the Materials Department are presented below in Table XXXIII.

TABLE XXXIII

HR-15 ALKALI-AGGREGATE REACTIVITY TEST
ASTM DESIG. C227-52T

Sample Number	Aggregate	-----Percent Growth at Various Ages-----					
		1 Mo.	2 Mo.	3 Mo.	6 Mo.	9 Mo.	12 Mo.
10	Burton Ave., Solon	0.02	0.02	0.01	0.02	0.02	0.03
14	Burton Ave., Rapid	.01	.01	.01	.02	.03	.04
18	Burton Ave., Rapid	.00	.00	.01	.01	.01	.02
22	Burton Ave., Rapid	.00	.01	.01	.01	.02	.03
5	Newton Coralville	.01	.02	.02	.02	.02	.03
11	Newton Coralville	.01	.01	.01	.02	.02	.03
16	Newton Coralville	.02	.02	.01	.02	.02	.02
18	Newton Coralville	.01	.01	.01	.02	.01	.02
1	Pints Rapid	.01	.01	.01	.03	.03	.04
9	Pints Coralville	.02	.02	.02	.03	.02	.03
11	Pints Coralville	.02	.02	.02	.03	.02	.03
6	Glory Rapid	.01	.01	.01	.02	.02	.03
9	Glory Rapid	.01	.01	.01	.02	.02	.03
13	Glory Rapid	.01	.01	.01	.02	.02	.03
22	Glory Coralville	.01	.01	.01	.01	.01	.03
	Platte River Class V	.02	.02	.02	.03	.04	.06
	LeGrand-Maynes Creek	.01	.01	.01	.01	.01	.02
	LeGrand-Eagle City	.02	.01	.01	.02	.02	.02

None of the expansions in the alkali reactivity test are excessive. The highest was found in the Platte River gravel which was expected. The relatively low expansion in concrete bars containing reactive or non-reactive aggregates has been a common experience in the past as well.

Test II

Data on this test are still being gathered. The 4 x 4 x 10-inch beams have been buried vertically in the ground, and readings were taken at 1½ years and 3½ years.

Test III

The details on rim growth concerning Test III were discussed in Chapter VI, under "Rim Growth in Concrete". Reaction rims were successfully grown on bars made from Rapid member aggregates. No excessive expansions accompanied the rim growth experiments. The highest expansion of a 2 x 2 x 14-inch bar was 0.02%, and the average for all bars was .01%. These data tend to repeat the results of Test I.

As part of the rim growth experiment, compression tests were run on some of the bars used in the alternate wetting and drying method (environment C) of growing rims. Six bars subjected to this treatment were selected; four developed reaction rims; two did not. For comparative purposes, a companion bar made with the same aggregates but left in a room environment was selected for each of the bars soaked. The bars were cut into 2 x 2 x 4-inch pieces and capped according to ASTM designation C192-57 and the compressive strength measurements were made in accordance with an ASTM procedure (ASTM designation C116-49). The results are shown in Table XXXIV. For explanation purposes: environment A is room environment; environment C is the alternate soaking and drying (soaked in distilled water at room temperature for 24 hours and dried at 140° F for 24 hours). Review of the table indicates that the bars made from the reactive Rapid aggregate did not gain much strength after soaking and drying. Reaction rims were present in these bars. The bars made from acceptable aggregate did gain considerable strength (.50% increase), probably as the result of a curing associated with the soaking.

It was concluded that an increase in strength which normally should occur during curing (soaking) was inhibited by the carbonate aggregate reactions which occurred. This was the first evidence obtained on the effect of carbonate aggregate reactions on the performance of concrete.

Further Studies

A follow-up experiment to see what affect carbonate aggregate reaction would have on the performance of concrete bars was initiated. A wide variety of aggregates was used in the experiment. The bars were made in a similar manner as in Test III, but with these differences:

> All the bars were cured in the moist room for 28 days after being made. The bars were reacted for 90 days by continual soaking at 130° F in a water bath. Portland cement supplied by the Portland Cement Association of low, medium, and high alkali types were used.

The experiment has not been completed. Preliminary results indicate that regardless of the type of aggregate used, the expansion (though minimal) increases with the alkali content of the cements used. The compression strength data obtained to date show little difference, due to the presence of reactive or non-reactive aggregates. A complete evaluation of the data will be made when the tests are completed, but a preliminary evaluation indicates the manner of inducing rim growth (i.e.- continual soaking versus alternate soaking

TABLE XXXIV

COMPRESSIVE STRENGTH OF CONCRETE MADE WITH
ACCEPTABLE AND UNACCEPTABLE AGGREGATE

	SET 1 After residence in Environment A - 4 months		SET 2 After residence in Environment C - 4 months		Effect of Environment C

Acceptable aggregate (non-argillaceous)

-Burton Solon-   -Burton Solon-

Bar No. 17	4400 psi		Bar No. 20	6200 psi	
	4100			6500	
	4400			6400	
14	3500		11	6300	
	3500			5700	
	4100			6300	
	-----			-----	
Average	4000 psi		Average	6200 psi	+2200 psi

Unacceptable aggregate (argillaceous)

-Burton Rapid-   -Burton Rapid-

Bar No. 9*	4200 psi		Bar No. 1	4300 psi	
	3800			3600	
	4100			4000	
7	4400		5	4400	
	4100			4600	
	3900			4200	
	-----			-----	
Average	4100 psi		Average	4200 psi	+100 psi

-Glory Rapid-   -Glory Rapid-

Bar No. 27*	4600 psi		Bar No. 30	5400 psi	
	4400			4900	
	5000			4800	
33	5100		21	5400	
	5000			4800	
	5100			5200	
	-----			-----	
Average	4900 psi		Average	5100 psi	+200 psi

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*Length changes for Bars No. 9 and 27 are not included in Table III. Their expansion did not exceed 0.02%.

and drying) may be of critical importance in explaining the difference in the results of the two series of tests.

CHAPTER VIII

RESEARCH TECHNIQUES

The data obtained in this research have come about largely through the development and/or adaptation of new research techniques to the problem of aggregate behavior in concrete. Considerable effort has been expended in developing the techniques. The noteworthy techniques which required this effort will be briefly discussed in this section and reference will be made to the thesis and/or published papers which contain a detailed description of the method. The techniques will be presented essentially in the chronologic order in which they were developed.

These techniques are a valuable and important contribution of HR-15 in that many of them can provide a basis for a future acceptance test. They also will prove of great use in future research.

Clay Separation Technique

An original clay separation technique which allows one to determine the type of clay(s) present in a carbonate aggregate without dissolving the rock in acid was developed by Rush (1957) and Bisque (1957) as part of their Masters thesis research. A flotation separation method was used, and is described in their theses. Bisque carried out further research on the method and found that 10 to 20 minutes of settling time was adequate to get a representative sample of clay in the settling column.

Diebold investigated the method further and it was decided its best use would be in the qualitative determination of clays. It is widely applicable to a variety of petrologic studies.

EDTA Method for Aluminum Determination

The determination of aluminum with the same EDTA (Versene) solutions used to determine calcium, magnesium, and iron in carbonate rock and portland cement, is a major contribution. The method is described in detail in the PhD thesis of Bisque (1959), who developed it with the advice of Dr. Charles V. Banks of the Iowa State University Chemistry Department. It has been of use to the chemistry section of the Materials Department of the Iowa State Highway Commission.

The method has a great possibility of being developed as an index to the amount of clay in a rock.

A complete description for using EDTA in analysis of carbonate rocks has been published by Bisque in the Journal of Sedimentary Petrology, vol. 31, p. 113-122 (1961).

Rim Growth in Concrete Bars

The techniques of growing rims on reactive aggregates has been described in the section on chemical studies. This technique has great value in any experimental study of carbonate aggregate reactions.

Autoclave Method of Growing Rims

A rapid method of growing rims in concrete bars was described by Lemish and Bisque in an article in the Proceedings of the Iowa Academy of Science, vol. 66, p. 210-213 (1959). The method is a potential laboratory test for aggregate reactivity.

Mercury Capillary Pressure Apparatus and Pore-Size Distribution Determinations

The application of the mercury capillary apparatus provided the FIRST measurements of pore size and pore-size distribution in aggregate studies. It is a valuable tool in describing the physical properties of a rock. Prior to adaptation to the aggregate problem, it was used mainly in petroleum reservoir research. Description on the operation of the instrument and derivation of the equations for determining pore size and pore-size distribution curves are given in the Masters thesis of Hiltrop (1958). More details concerning the optimum way of using the instrument are embodied in the Masters thesis of Wallace (1962).

Statistical Treatment of Rock Properties

A potentially useful statistical technique for analyzing a large number of variables for correlation purposes is described by Hiltrop in his Masters thesis. Conditional probability (frequency of occurrence) was applied in an attempt to determine which rock properties were related to serviceability of an aggregate. This method will become more valuable as more information on aggregate properties are accumulated.

Molybdate "Reactive" Silica

Hiltrop derived a method applied for the first time in aggregate studies for determining the relative amount of monomeric silica to higher silica polymers present in solution. He modified the ammonium molybdate blue method for silicon determination to accomplish this. It was described in his PhD thesis (1960). The method has great use in silica migration and other silicification studies where the species or form of the silica molecule is important.

Refluxing Technique in Silicon-Free Environment

The refluxing technique was adapted to the carbonate problem by Hiltrop in his PhD (1960) research. Refluxing in a silicon-free environment was developed by Werner in his Masters thesis research (1961). This technique is a powerful tool in equilibria studies, and may become an excellent way of characterizing carbonate rocks as to their potential reactivity. Its great advantage is in the ease with which the solution environment during refluxing can be varied to measure the performance of an aggregate. Adaptation of this technique into an autoclave method is possible, which would allow it to be used on a large scale.

Aggregate Treatment With Vaporous Silanes and $SiCl_4$

This method was developed by Hiltrop, and is described in a paper published in the Proceedings of the Iowa Academy of Science, vol. 66, p. 214-221 (1959). Silicification of argillaceous carbonate rocks is possible with these varporous compounds. The silica deposits on any reactive site and polymerizes the fine residue (clay, etc.) into a network which becomes acid insoluble. The technique has a wide variety of applications in petrologic studies. It is capable of making rocks water-repellant, and might be a potential method of beneficiating aggregates.

Quantitative X-Ray Determination of Calcite, Dolomite, Quartz, and Clay

This technique was developed by Diebold, as part of his Masters thesis research (1961). It has great value in future research by making it possible to quantitatively determine the major minerals present in the typical carbonate aggregate. Calcite, dolomite, and quartz are determined by an internal standard method. Clay is determined by difference.

The development of this technique required considerable effort. A complete review of various techniques applied to quantitative mineral determination will be presented in a paper by Diebold, _et al,_ to be published in the

Journal of Sedimentary Petrology, vol. 62 (1962). It is highly applicable as a routine rock analyses.

Quantitative Textural Determination in Terms of Surface/Volume Ratio

This method represents one of the first attempts ever made to determine rock textures quantitatively. It is accomplished through a statistical method of counting the number of times a line cuts the border or falls within a mineral grain. Current model studies indicate the method is feasible, and has great promise of describing the internal geometry of the mineral grain arrangement inside a rock. The ability to do this would make it possible to correlate texture to a wide variety of measurable rock properties. The technique is described in the Masters thesis of Wallace (1962).

CHAPTER IX

SUMMARY AND CONCLUSIONS

The research is briefly summarized below with regard to the most perti-
nent knowledge acquired.

Study of distressed concrete in the laboratory and field indicates that
it is characterized by general spalling and cracking away from joints. Blue-
line cracking and surface discoloration is evident. The concrete is soft and
in a weakened condition. The concrete matrix is highly carbonated and dark
borders or reaction rims outline argillaceous carbonate aggregates. Consider-
able physical and chemical change has occurred in distressed concrete.

Petrologic study of unacceptable and acceptable aggregates show that the
deleterious (Glory) aggregate is best described as an argillaceous dolomitic
limestone or calcareous dolomite. The abundant clay is illite and evidence
exists that the clay fraction may be in a poorly ordered state. The insoluble
residue content is high. 12-15% is average, and several are over 20%. Rock
with good service records are essentially a pure limestone or dolomite with a
low insoluble residue content. Such rocks are usually dense, compact in
appearance, with the exception of certain oolitic beds.

Pore-size determination studies in both good and bad aggregates are small
and average from .1 to .2 microns which permits them to retain fluids tena-
ciously. The pore-size distribution characteristics of a rock show a general
relationship to freeze-thaw performance and to its megascopic textural appear-
ance. A statistical analysis shows that pore-size distribution alone is not
indicative of aggregate performance, but that the presence of clay and the
Ca/Mg ratio of a rock were closely related to serviceability.

The recognition of reaction rims on unacceptable (Glory) aggregates indi-
cated that the aggregate had reacted chemically with its concrete environment.
Analyses of reaction rims on aggregates from distressed concrete showed they
were silicified and contained relatively higher silica contents on a weight
per cent basis than the interior of the aggregate. Rims were grown in the
laboratory on argillaceous dolomitic aggregates by immersing them in silica
solutions at pH 12, demonstrating that these rocks would react chemically in
equivalent concrete environments.

Reaction rims were also selectively grown on impure dolomitic aggregates
in concrete or cement paste bars by soaking them in water at 125° F or by
alternate wetting and drying; by leaving them in a moist room at 70° F for
longer periods of time; or, in an autoclave in a matter of 3 to 9 hours.
Quantitative study of rim growth on chips of acceptable and non-acceptable
aggregates in concrete bars indicated that rim growth on reactive aggregate
gained in weight and in silica content on a weight per cent basis. A similar
experiment with both types of chips in a cement paste bar showed that the un-
acceptable aggregate lost weight and silica. Sodium and potassium were not
introduced in rims.

Study of compositional variations on a weight per cent basis across the
aggregate rim zone into the cement paste showed that silica tends to migrate

out of the rim zone, either into the paste, or farther back into the rock. In all cases, dedolomitization occurs. X-ray data show that quartz and dolomite decrease in the shell zone; calcite increases; and some $Ca(OH)_2$ is introduced in some aggregates from the paste. Silicification of the rim zone indicates the presence of amorphous silica and not necessarily an increase or decrease in silica content.

Refluxing investigations indicated that unacceptable rocks have a greater capacity to absorb silica than to give it off. Each rock can be characterized by its own equilibrium concentration, below which silica moves into the rock, and above which it moves out of the rock. Argillaceous types have a greater affinity for silica. Rocks with less residue content, such as the LeGrand, absorb less silica. Cement pastes, because of their high lime content, have a much greater capacity to absorb silica than the argillaceous aggregates. They give off little, if any, silica. Sand gives off eight times more silica than cement paste or aggregates. The silica absorbed in an aggregate is probably in the form of a monocalcium silicate hydrate.

LeGrand rocks show little expansion in concrete bars and cylinders of the rock show none in alkali or sodium silicate solutions. Glory aggregate shows little expansion when used in concrete bars, but it can expand up to 1% when cylinders of it are soaked in alkaline or sodium silicate solutions.

Concrete bars in which rims were grown on unacceptable aggregates do not show excessive expansion and do not appear to gain strength during the alternate soaking and drying operation. Bars from acceptable aggregates grow in strength (50% increase) when similarly treated. Continued tests on bars representing a wider variety of aggregates showed variable results.

Several conclusions can be drawn from the data obtained in the research. The reactive type of aggregate can be defined by its distinctive dolomitic and argillaceous lithology. Such rocks react in response to the hydroxyl-rich alkaline environment of concrete. Several reactions (silicification, dedolomitization, calcitization) occur concurrently to form a silicified dedolomitized shell. Rim growth is by a diffusion phenomena and the reactions represent the attempt of the rock to come into equilibrium with its alkaline environment. All the components of the aggregate react. Reaction of unacceptable aggregates proceed farther because they contain greater amounts of reactive substances -- finely divided quartz, clay, dolomite. Acceptable aggregates react also, but because they have less reactive substances, they are relatively stable. Expansion effects of the reaction in concrete bars are slight.

Data were also obtained during the research which provide an insight on certain aspects of the entire system of concrete. Cement paste is not a source of silica. Its important role is to provide a source of calcium and the high alkaline environment. Indications from the chip experiments in cement paste and concrete bars, as well as the refluxing data, point to the conclusion that the fine aggregate (sand) cannot be considered an inert substance. It is a potential source of silica and evidently reacts with the alkaline environment to some degree, however slight, whenever concrete or mortar is made.

In reviewing the research data with regard to conclusions drawn, in the light of the objectives of the project, considerable progress was achieved in

attaining them. The exact mechanism of how the carbonate aggregate reaction contributes to failure cannot be answered, although some laboratory evidence exists that it does. Considerable progress has been made regarding the recognition and classification of potentially deleterious aggregates to the point where argillaceous dolomitic aggregates with high residue should be suspect and not recommended for use in concrete.

Perhaps the major contribution of HR-15 has been in the area of defining the problem of behavior of carbonate aggregates in concrete. A much better definition exists now than when the research commenced because of our increased knowledge concerning the properties of aggregates and their chemical behavior brought about through the development of several new approaches and techniques.

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