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A GEOLOGIC STUDY OF THE SOUNDNESS OF LIMESTONE
FOR USE AS CONCRETE AGGREGATE

By

Irvin Verne Kuehner

A THESIS

Submitted to the School of Graduate Studies of Michigan
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ABSTRACT

Concrete aggregates are usually selected and appraised by the application of various performance tests which measure certain of their physical properties. The significance of the inherent characteristics and response of the minerals comprising concrete aggregates lack quantitative definition. This geological analysis has been conducted to statistically and petrographically relate the quantitative significance of the various constituents of limestone; clay, chert, sand, dolomite, total silica and total clastics, to the measures of their soundness and absorption as determined by the Michigan State Highway Department Research Laboratory, It was found that the Bayport limestone contained excessive concentrations of montmorillonite clay which is positively related to the lack of soundness. The chert and other contaminants have also contributed to the failure of the material but their effect is masked by the predominance of the clay. Due to the presence of the excessive concentration of swelling clay the Bayport limestone aggregate should not be recommended for use under moist weathering conditions. The quantitative information from this investigation should be related to other measures of performance of the aggregates. This type of quantitative analysis comprehending all varieties and types of aggregate materials would be of inestimable value to concrete technology in the selection and evaluation of concrete aggregates.

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INTRODUCTION

A small but important field of investigation almost entirely neglected by the geological profession until recent years is the organized search and critical examination of those products of geology, minerals and rocks, suitable for use as aggregates for concrete construction. In view of the complexity and extent of modern engineering endeavors in this post-war construction boom ever increasing demands are being made on our rapidly decreasing supplies of accessible sound aggregate materials. The geologist will more and more be called upon to play an increasingly active and important role in the joint venture with engineers to not only find new sources of satisfactory construction materials but also to establish new criteria and methods for judging the suitability of such materials to meet the exacting demands of future architectural and engineering uses. This study is a beginning step in the critical geological examination of one of the most common aggregate materials and the quantitative significance of its constituents to one of the very important but not entirely understood criteria of acceptance.

Previous Geologic Study of Aggregates for Concrete.

The geologic literature is practically devoid of published reports devoted to the detailed study of aggregate materials and their relation to engineering problems. The investigator has to turn instead to the various engineering periodicals to find determinate accounts of geological studies conducted by large federal agencies, such as the U. S. Bureau of Reclamation or the U. S. Corps of engineers, and occasional state organizations. Their responsibility for gigantic concrete structures such as dams, dikes, locks, and canals, and for many miles of concrete highways and numerous bridges necessitates the utilization of the finest of construction materials available. A thorough understanding of the constituents of those materials and their relation to the strength, durability, and soundness of the final concrete product is essential.

A perusal of the literature pertaining to this geological - engineering problem reveals two general categories into which a majority of the articles can normally be classified. The first category includes those articles of a very general nature dealing with the broad aspects of the petrographic and mineralogic characteristics of aggregates (Rhoades and Mielenz, 1948) and (Rhoades, 1950), the value of petrography in the selection and study of aggregate materials (Mielenz, 1946), (Blanks, 1950) and (Mielenz, 1946), and the methods and procedures of petrographic examination (Mather and Mather, 1950). The second category is more specific and includes several articles on the cement-aggregate reaction between high alkali cements and certain deleterious minor mineral constituents, namely opal, chalcedony and tridymite. A recent review and reappraisal of this problem has been made by the U. S. Bureau of Reclamation and is included in the noteworthy Geological Society of America "Berkey Memorial Volume" on engineering geology (McConnell etal, 1950).

Outstanding among the investigations of the problems of aggregates is the thorough and exhaustive study of chert and its quantitative significance to concrete which has been conducted by Purdue University and the State Highway Commission of Indiana. (Sweet and Woods, 1942). It is this type of quantitative research directed toward the determination of the specific properties of specific rocks and minerals that is urgently needed by concrete technology.

Reasons for Quantitative Study of Limestone Aggregate

Concrete aggregates constitute the preponderant bulk of concrete ranging from 80 - 85 percent by weight (Mielenz, p. 309). Crushed limestone comprises approximately one fifth of the coarse aggregate used in the manufacture of concrete (Rhoades, p. 437), in general, and in many areas accounts for a much greater proportion of suitable aggregate material. Limestone, therefore, has a marked effect upon the strength, elasticity, soundness, durability, thermal properties and unit weight of a substantial portion of concrete.

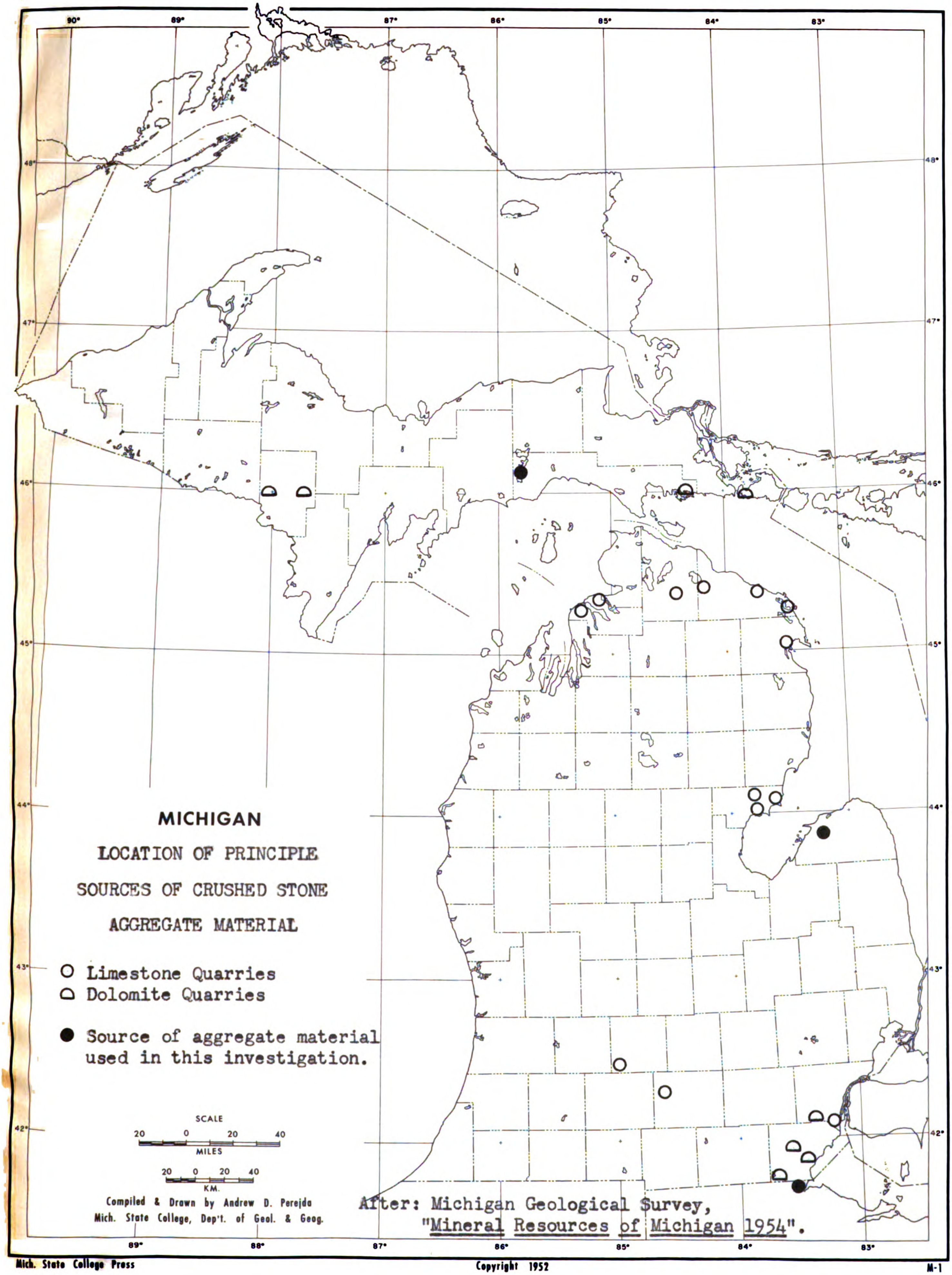
Concrete aggregates have been appraised and selected by engineering laboratories in the past primarily through application of a series of standardized empirical tests to determine their strength, specific gravity, absorption, abrasive resistance, soundness under freezing and thawing or with the accelerated sodium or magnesium sulphate tests. Such tests have been correlated with field service over many years and on the basis of this long experience serve as guides for establishing specifications for the approval or rejection of proposed aggregate materials (Rhoades, p. 458). These empirical tests, however useful they may be for practical purposes in measuring certain physical properties of aggregates, fail to provide any clue to the fundamental substance which defines the quality of a particular rock material and its individual reaction to internal and external forces encountered by concrete (Rhoades, p. 458).

An intimate knowledge of the inherent character of the variety of minerals comprising concrete aggregate materials, "each with its own physical and chemical characteristics and with its own unique response to enviromental condition" (Rhoades p. 438), is lacking by concrete technology. Many properties of aggregates are understood in some imperfect way, "they are recognized as important; their effect on concrete can be gaged qualitatively; but their significance lacks and badly needs quantitative definition" (Rhoades, p. 458). It is this quantitative analysis which must be contributed chiefly by geologists and petrographers, with their special knowledge of rocks and minerals, if the geologist is to take his proper place in the appraisal and selection of concrete aggregate by supplementing the limited engineering information furnished by standard acceptance tests.

Availability of Satisfactory Aggregate in Central Michigan

The central area of Michigan's lower peninsula is fortunate in having many gravel laden glacial eskers which have supplied the needs for concrete aggregate for many years. However, as the choicest portions of these gravel deposits become depleted by this current construction pace, together with ever higher and more exacting concrete specifications, the concern for available sources of concrete aggregate will become more acute year by year. Although the Pliestocene glaciers blessed this area with abundant gravel deposits they at the same time masked quarryable rock with a thick mantle of overburden. The chief sources of available quarried limestone to be found occur around the outer edge of the state; namely the northern-most five counties of the lower peninsula, the Saginaw Bay area and the two extreme southeastern counties, where suitable paleozoic limestones extend out of the Michigan Basin and occur near enough to the surface to be economically worked.

Crushed stone from Huron County has recently been used as a substitute for gravel aggregates on one important Highway Department project in Lansing. Another such project used crushed limestone from Mackinac County, in the upper peninsula, which had to be rehandled several times before reaching its destination. Crushed dolomite from Drummond Island is also shipped by boat for use as aggregate throughout the state. Quarries in Charlevoix, Cheboygan, Presque Isle,



MICHIGAN

LOCATION OF PRINCIPLE
SOURCES OF CRUSHED STONE
AGGREGATE MATERIAL

○ Limestone Quarries
◒ Dolomite Quarries

● Source of aggregate material used in this investigation.

Compiled & Drawn by Andrew D. Perejda
Mich. State College, Dep't. of Geol. & Geog.

After: Michigan Geological Survey, "Mineral Resources of Michigan 1954".

Mich. State College Press

Alpena, Arenac, Wayne and Monroe counties Michigan and Lucas county, Ohio, supply local aggregate requirements but most of these quarries are operated primarily for other purposes, notably to provide raw materials for cement and for blast furnace flux. The only limestone quarries producing concrete aggregate in the central Michigan area are near Bellevue in extreme southwestern Eaton County and a small operation in western Jackson County.

One of the primary considerations of concrete as a construction material is its relatively low cost. The possible rejection of cheap local material in favor of beneficiation or the costly importation of aggregate from more distant sources depends on the standards of acceptance and judgement of the engineers and geologists who must unequivocally assure that the advantages to be gained are commensurate with the added expense (Rhoades, p. 438).

It is of interest to note that commercial application of beneficiation using a heavy media separation unit to upgrade gravel materials has been inaugerated in Michigan. The process removes objectionable chert and shale in order to meet Michigan State Highway Department specifications. At the present time three gravel beneficiation plants are in operation in the state.

PURPOSE

Late in 1950 the Michigan State Highway Department completed a large highway bridge in Lansing which carries a four lane divided high-

way across the Grand River, a railroad spur line and a four lane interstate highway. Crushed limestone shipped in from Huron County was used exclusively as the coarse aggregate in the construction of the superstructure of this bridge.

Approximately one year after the project was completed excessive scaling, crazing and cracking was noted on the curbs, divider strip, sidewalks and deck. In addition to the above failures a large number of pits and pop-outs were developing.

In view of the above premature deterioration and excessive failure the Michigan State Highway Department Research Laboratory, Testing and Research Division, East Lansing, Michigan, conducted a thorough investigation of the bridge itself and the materials used in its construction. Several cores were cut and removed from the divider strip, curbs, deck and sidewalks for testing and study. Believing the failure to be predominantly due to the coarse aggregate used, an investigation of the Bayport limestone was conducted at the same time. This part of the study was carried on not only to help fix the responsibility for the failures of the concrete but also to judge the advisability of further use of Bayport limestone for future Highway Department construction projects.

Lacking trained petrographers on their staff the Research Laboratory, Testing and Research Division, made the samples and test data available for geologic study. The solution to the problem, at first hand, seemed to be simply a thorough petrographic examination of the samples. It soon became apparent that such an examination could not begin to explain the wide diversity of results obtained by the standard acceptance tests except in very general terms. It was obvious that the several constituents of the multifarious samples must be reduced to measureable terms in order to relate the quantitative effect of each constituent to the physical properties of each sample. Lacking precedent in this kind of quantitative correlation, and not knowing precisely which component was responsible for producing the greatest effect on the inherent physical properties of the samples, it was necessary to isolate each and every integral fraction of the sample in order to relate their individual effects on the total physical characteristics of each specimen.

The chief objection to the standard acceptance tests and strength tests made by all engineering laboratories is the expense and especially the time involved to obtain satisfactory and conclusive results. The sulphate soundness tests take at least five days; the freezing and thawing in water test requires twenty-five days; various compression and strength tests involve seven to thirty days. Each of these tests must be carried on in a laboratory with special equipment and trained personnel. No satisfactory field tests have as yet been devised to measure the essential properties of concrete aggregates. It was the hope of the author, and the idea pervaded throughout this investigation, to not only unmistakably relate the effects of the fundamental constituents of limestone to its soundness and absorption, but to do so simply and directly without employing complicated equipment or lengthy procedure.

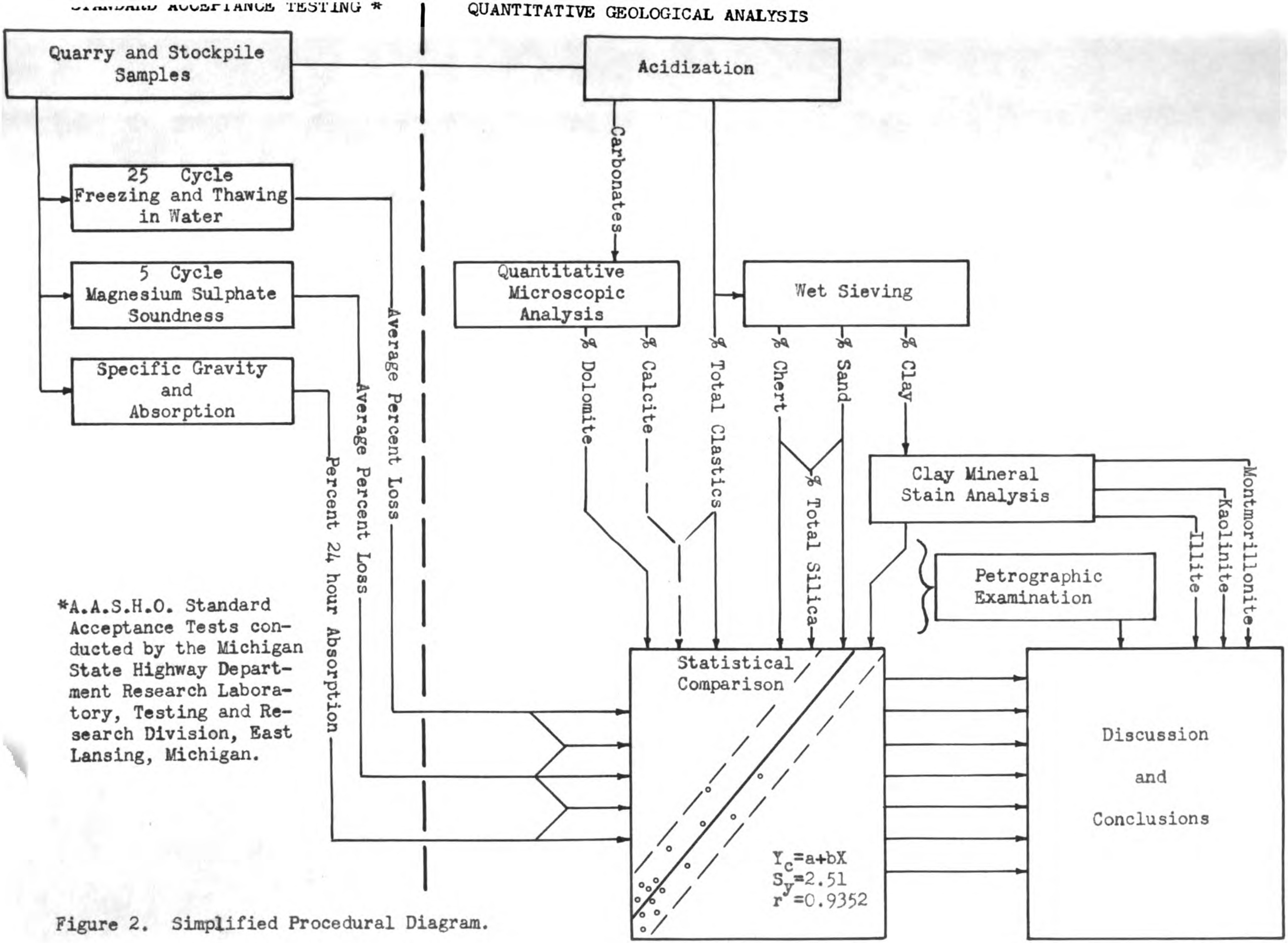
Reference or evidence of this goal will crop up many times throughout this report. In other words, it is hoped that the results of this study will point the way towards a satisfactory and acceptable field evaluation of concrete aggregates which can be used to evaluate developed deposits and also in the exploration for new sources.

PROCEDURE

The first part of this investigation, the collection of the samples and the physical testing of their specific gravity, absorption and response to freezing and thawing and to magnesium sulphate soundness tests, was performed by the Michigan State Highway Department Research Laboratory, Testing and Research Division, East Lansing, Michigan. Additional strength tests and measurements of thermal expansion were not performed on the individual Bayport samples so that correlation with these special factors could not be accomplished.

Collection of Quarry and Stockpile Samples.

The quarry and stockpile samples used in this study were collected by Highway Department personnel in the latter part of 1951. The Bayport limestone samples from Huron County were collected from three locations on the exposed quarry face in order to include each prominent ledge of the Bayport (Mississippian) Formation from this area. Representative sampling from top to bottom of each ledge, to simulate channel sampling as much as possible, was undertaken to insure complete representation of each ledge.



*A.A.S.H.O. Standard Acceptance Tests conducted by the Michigan State Highway Department Research Laboratory, Testing and Research Division, East Lansing, Michigan.

Figure 2. Simplified Procedural Diagram.

The two quarry samples of the Delaware (Devonian) limestone from Silica, Lucas County, Ohio, were taken from near the top and bottom of the current quarry face as representative of the formation from that location.

The remainder of the samples used in this study are "composite" samples of Bayport limestone, Delaware limestone and also Burnt Bluff (Silurian) limestone from Mackinac County, Michigan. The samples were taken from graded crushed stone stockpiles either at the quarry site or on-the-job locations.

Although this investigation was orginally and predominately concerned with the Bayport limestone these latter samples were included primarily for comparison. In addition they also serve to increase the size of the statistical sample. Comparatively, the crushed Burnt Bluff limestone from Mackinac County is considered to be superior concrete aggregate by the State Highway Department. In order to determine the cause of failure of a relatively poor aggregate it was advisable to include an acceptable aggregate for comparative purposes.

Engineering Standard Acceptance Testing

The soundness or durability of concrete aggregates refers to their ability to resist disintegration as a result of weathering, variations in temperature, changes in moisture content and certain chemical reactions. Aggregates which disintegrate under such conditions are detrimental to concrete and should be avoided. Soundness tests are especially applicable to aggregate materials from new sources which may be of doubtful quality. The results of soundness tests are regarded as indicative rather than conclusive (Bateman, p. 65).

The principle of the freezing and thawing test is relatively simple, depending on the breakdown resulting from one or more of the following reasons; (1) development of excessive hydrostatic pressure within materials of low permeability during progressive freezing, (Blanks, pp. 420-1), (2) differential thermal expansion or contraction of dissimilar materials, and (3) the expansive force of freezing water or the formation of void filling ice crystals.

The freezing and thawing test has been almost entirely replaced by the more rapid magnesium or sodium sulphate soundness tests. The American Society for Testing Materials has withdrawn the freezing and thawing test from their specification standards. However, many organizations have retained the freezing and thawing test to the extent that any aggregate failing the more rigorous sulphate soundness test may be approved if it successfully passes a suitable freezing and thawing test. Time, more equipment, and difficulty in standardizing the freezing and thawing test have contributed to its abandonment.

The mechanism of the sulphate soundness tests differs in some respects from the processes by which freezing and thawing of water cause breakdown. During the drying period precipitated crystals of Na_2SO_4or $MgSO_4$ fill the pores of the aggregate material. Upon reimmersing the aggregate the precipitated crystals hydrate to $Na_2SO_4\cdot$

$10H_2O$ or $MgSO_4 \cdot 7H_2O$. The resultant expansion of the crystals create stresses which rupture the walls of the pores and cause breakdown of unsound materials (Mielenz, p. 313). The result of the freezing and thawing test and sulphate soundness tests do not parallel each other. The sulphate soundness tests are much more harsh than the longer freezing and thawing in water test.

Specific gravity and absorption are sometimes used as preliminary indications of unsoundness but extreme care should be taken to avoid final appraisal of an aggregate on the basis of these tests alone. For example, chert usually has a very low degree of absorption but is very unsatisfactory as a constituent of concrete. Also a high gravity rock may be very unsound due to deleterious impurities.

25 Cycle Freezing and Thawing in Water

(A.A.S.H.O. Method T 103-42).

The freezing and thawing test and the following two tests are defined completely and in exacting detail in the American Association of State Highway Officials "Standard Specifications for Highway Materials and Methods of Sampling and Testing, "Part II, 1942; and/or the American Society for Testing Materials "1955 Book of Standards", Part 3, 1956. Only a brief resumé of the procedures will be attempted here.

In the freezing and thawing test the crushed limestone was washed, dried and separated into appropriate sizes by screening. In order to reduce the tedious time-consuming procedure involved in handling too many sieve fractions the Testing and Research Division made certain innovations in the standard sieve sizes specified for the test and the amount of aggregate used in each size fraction. Only that material smaller than 1 inch and larger than the openings in the # 4 sieve seperated into proportions which were retained on the ½ inch, 3/4 inch, and 1 inch screens was used in the test. In general, approximately 400 to 700 grams of material was retained in each size with the smaller sizes being proportionately smaller then the next larger sieve fraction. After weighing, each separate size of each sample was placed in a shallow metal tray specified as 2½ inches x 18 inches x 2½ inches in depth. The samples were immersed in water for 24 hours. The water in excess of that necessary to cover the aggregate by ¼ inch was poured off. Then the trays were nested in a metal container 3 7/8 inches x 18¼ inches x 20 inches and placed in a suitable freezing chamber. The temperature was maintained between -10° and -20° F. After freezing for six hours the trays were submerged in a thawing tank at 80° F. Upon thawing for 18 hours the excess water was again removed and the cycle repeated until 25 cycles had been completed.

When the final cycle had been completed the samples were oven dried and sieved over each original sieve on which the material was retained at the beginning of the test. The loss in weight of each sieve fraction was calculated as the percentage loss of the fraction. A weighted average loss based on the grading of the material was computed. This weighted "average percent loss" is recorded in column 4 of table 2 and is used in the statistical comparison. Michigan State Highway Department specifications do not designate the average percent loss allowed for sound aggregate material on completion of 25 cycles of freezing and thawing in water. However, the 12 percent loss allowed with 5 cycles of immersion in magnesium sulphate may be used as a guide.

5 Cycle Magnesium Sulphate Soundness

(A.S.T.M. Designation: C88-39T; also A.A.S.H.O., Method T - 104-46).

The same quantities and methods of preparation are used in this test as were outlined for the freezing and thawing test above. The Michigan State Highway Department Research Laboratory uses magnesium sulphate exclusively because of its superior temperature stability over sodium sulphate. Magnesium sulphate is also preferred because of its greater solubility and its reliability in producing more consistent results.

The saturated solution of magnesium sulphate was prepared by dissolving sufficient salt in water at 77° to 86° F. The solution was then cooled to 70° F. and maintained at that temperature for 48 hours before use.

The aggregate was placed in wire baskets for ease in draining and immersed in the solution of magnesium sulphate for 16 to 18 hours at 70° F. The samples were then drained and dried to a constant weight in an oven with the temperature at from 221° to 230° F. When thoroughly dried the aggregate was cooled for 2 hours at room temperature and then reimmersed in the solution for the beginning of the next cycle. This process was repeated until 5 cycles had been completed. Upon completion of the final cycle the samples were washed free of magnesium sulphate and the weighted average percent loss determined in the same way as described under the freezing and thawing soundness test. Any aggregate having more than 12 percent loss after 5 cycles of the magnesium sulphate soundness test is classified as unsound for all major highway uses by Michigan State Highway Department specifications (Mich. State Highway Dept., Table 2, p. 444). The average percent loss resulting from the magnesium sulphate soundness test are compiled in Column 3, Table 2, pages 28 and 29.

Specific Gravity and Absorption

(A.S.T.M. Designation: C 127-39; also A.A.S.H.O. Method T-85-35.)

Specific gravity and absorption are always measured simultaneously in the same test procedure. Approximately 500 grams of the crushed stone was washed, immersed and allowed to absorb water for 24 hours. The samples were then rolled in a cloth to remove all visible films of water from the particles. The weight of the material in this saturated surface dry condition was obtained. The aggregate was then placed in a wire basket suspended in water to determine its weight in water. Finally, the sample was oven dried to constant weight, cooled to room temperature and weighed.

Using these weights the following values were computed;

$$\text{Bulk Specific Gravity} = \frac{\text{Weight of saturated surface-dry sample in air}}{\text{Weight of saturated surface-dry sample in air} - \text{Weight of saturated surface-dry sample in water}}$$

$$\text{Percent Absorption} = \frac{\text{Weight of saturated surface-dry sample in air} - \text{Weight of oven-dry sample in air}}{\text{Weight of oven-dry sample in air}} \times 100$$

The results for specific gravity and absorption can be found in Columns 1 and 2, Table 2, pages 28 and 29.

Geologic Examination and Investigation

The geologic procedure followed in this investigation is simple and direct, being nothing more than an enlargement on the usual methods employed in various insoluble residue studies combined with ordinary petrographic examination and the practices of sedimentary petrography. Only the usual equipment found in a geologic laboratory was used in this part of the investigation so no complicated description of apparatus and equipment will be necessary.

Petrographic Examination

The samples used had been previously crushed by the Michigan State Highway Department Research Laboratory for the purposes of their investigation. Therefore, a general megascopic description of the ledges was not practical. Several of the larger fragments of each sample, the polished sections prepared for the quantitative microscopic analysis and the chert, sand and clay fractions of the clastic residues were examined with the aid of a stereomicrescope. These descriptions

COMPOSITE SAMPLE DESCRIPTION

Sample Number	Source*	Sample Description	Acidized Chert Residue	Sand	Minor Minerals
Bayport Limestone, Huron County, Michigan. Collected 10-10-51.					
1	Southwest face Ledge A Thickness 18"	Gray v. finely crystalline - dense sli. sandy agrillaceous limestone. Fine-med. dolo. & siliceous foss. fragments.	Tan porous amorphous fragments. White fossiliferous.	Fine grained, fairly sorted, rounded and polished.	White siliceous oolites. Glauconitic. Quartz crystals.
2	North face Ledge A'	Same.	Same plus; gray concretionary. White bryozoa and coral fragments.	Same; guartz grains darkly iron stained	Quartz crystals.
3	Southwest face Ledge B Thickness 12"	Gray finely crystalline, sli. porous, sli. sandy, very cherty fossiliferous argillaceous limestone.	White fossiliferous, gray concretionary and buff amorphous. Abd. coral remains.	Fine grained, sub angular to rounded, polished	Siliceous oolites. Quartz crystalls. Trace pyrite.
4	Southwest face Ledge C Thickness 42"	Gray very finely crystalline sandy, very cherty, fossiliferous agrillaceous limestone.	White fossiliferous, gray concretionary and tan amorphous.	Fine to medium grained, rounded, fairly sorted.	Glauconitic. Trace pyrite.
5	Southwest face Ledge D Thickness 6"	Gray finely crystalline, sli. porous, very argillaceous limestone. Buff obscure dolo fossil frags. Streaked.	White amorphous and buff concretionary to fossiliferous.	Fine to medium grained, rounded, polished.	Clustered oolites. Quartz crystals. Glauconitic. Trace pyrite.
6	West face Ledge D'	Same.	Same plus abundant coral fragments.	Fine grained, rounded, polished.	Clustered oolites. Glauconitic. Quartz crystalls. Trace pyrite.
7	Southwest face Ledge E Thickness 36"	Gray v. finely crystalline - dense, sandy, slightly argillaceous limestone. Streaked. Fine dolomitic fossil frags.	Buff amorphous, fossiliferous and concretionary.	Fine to medium grained, rounded, polished.	Clustered oolites. Trace pyrite.
8	Southwest face Ledge F Thickness 54"	Gray v. finely crystalline, sli. fossiliferous, very sandy agrillaceous limestone. Distinctly streaked.	Buff very porous amorphous. Gray concretionary and	Fine to medium grained, rounded, polished.	Clustered oolites. Trace pyrite.
9	Southwest face Ledge G Thickness 12"	Gray v. finely crystalline - dense, sli. fossiliferous, sli. sandy limestone. Siliceous and dolo. fossil frags.	Trace of buff to white fossiliferous.	Fine to medium grained, rounded, polished.	Chert pseudo-rhombs. Trace pyrite.

Table 1. (continued)

COMPOSITE SAMPLE DESCRIPTION (continued)

Sample Number	Source*	Sample Description	Acidized Chert Residue	Sand	Minor Minerals
Bayport Limestone, Huron County, Michigan. Collected 10-10-51.					
10	North face Ledge G'	Gray finely crystalline to dense slightly sandy limestone.	Trace of white to buff amorphous and fossiliferous.	Fine to medium grained, rounded to sub angular.	Abundand pyrite
11	Stockpile 6B Grading Sample K	Composite of above ten samples.			
Burnt Bluff Limestone, Mackinac County, Michigan. Collected 1951.					
12	Stockpile 6B Grading Sample 1	Tan very dense limestone. Abundant obscure fossil fragments. Scattered voids.	Slight trace of white amorphous fragments.	None.	Trace of crystalline quartz.
Delaware Limestone, Lucas County, Ohio. Collected 1951.					
13	Stockpile 4A Grading Sample 3	Tan finely crystalline to dense very porous dolomitic limestone.	None.	Very large grained, well sorted, frosted.	None.
14	Bottom new cut 10'below surf. Sample 4	Tan fine to medium crystalline, fairly porous dolomitic limestone. Slightly stylolitic. Scattered voids.	Gray angular amorphous chert frags. cemented with white silica.	Slight trace fine grained.	None.
15	Top new cut 2-3'below surf. Sample 5	Tan fine to coarse crystalline dolomitic limestone.	White amorphous and concretionary. Trace fossiliferous.	Very well rounded, very fine grained, frosted.	Trace pyrite.

*Quarry position and stockpile source. Number and letter designation in this column assigned by the Michigan State Highway Department Research Laboratory, East Lansing, Michigan, for various research projects.

Table 1. Petrographic description of crushed aggregate fragments, polished sections, acidized chert remains and sand residue.

are compiled in Table 1, pages 25 and 26, and need no further explanation at this time. Their special significance will be touched upon in the conclusion of this report.

Removal of Acid Soluble Carbonates.

Approximately 600 grams of each sample was washed to remove all dust, clay and foreign matter, thoroughly dried, and crushed as finely as possible with a steel mortar and pestle to help speed the complete digestion by acid. The relatively large sample was used in order to reduce the proportion of experimental error and to obviate the necessity of performing the minor details of the procedure with several smaller portions of the samples and then averaging the results. The samples were carefully weighed and each placed in the bottom of a very large beaker (4000 ml.) in preparation for acidizing. The finely crushed limestone reacted very violently when treated with dilute hydrochloric acid so the extra large container was necessary to prevent minor losses of clay and other fine material contained in the voluminous rising froth and bubbles.

The samples were first wet with water and then the 10 percent solution of hydrochloric acid was slowly added. The treatment with hydrochloric acid was continued, gradually increasing the concentration of the acid, until complete digestion of all the soluble carbonates was assured.

Wet Sieving to Separate Clastics - Chert, Sand and Clay.

In the usual insoluble residue study the clastic residue would be

COMPOSITE DATA SHEET

Sample Number	Source*	STANDARD ACCEPTANCE TESTING				GEOLOGICAL ANALYSIS						
		Bulk Specific Gravity	Percent 24 hr. Absorption	Soundness		Percent Total Clastics (Insoluble Residue)					% Soluble Carbonate	
				Average Percent Loss 5 Cycle Magnesium Sulphate Soundness	Average Percent Loss 25 Cycle Freezing and Thawing in Water		Percent Total Silica			Percent Clay		Percent Dolomite $CaMgCO_3$ (Unstained)
								Percent Chert	Percent Sand			
Column Number		1	2	3	4	5	6	7	8	9	10	11
Bayport Limestone, Huron County, Michigan. Collected 10-10-51.												
1	Southwest face Ledge A Thickness 18"	2.61	3.1	46.80	21.4	14.3	2.8	0.9	1.9	11.5	85.7	3.2
2	North face Ledge A'	2.61	2.5	63.41	27.1	13.4	5.1	1.1	4.0	8.3	86.6	17.9
3	Southwest face Ledge B Thickness 12"	2.58	3.3	66.50	54.3	31.8	20.5	16.9	3.6	11.3	68.2	26.8
4	Southwest face Ledge C Thickness 42"	2.64	1.2	21.91	13.9	19.6	12.6	6.2	6.4	7.0	80.4	22.5
5	Southwest face Ledge D Thickness 6"	2.62	1.9	73.10	28.9	16.8	1.5	0.6	0.9	15.3	83.2	3.4
6	West face Ledge D'	2.60	2.0	70.38	27.8	16.8	2.1	0.6	1.5	14.7	83.2	1.8
7	Southwest face Ledge E Thickness 36"	2.65	1.3	12.35	18.5	8.2	5.0	0.3	4.7	3.2	91.8	2.9
8	Southwest face Ledge F Thickness 54"	2.63	1.4	14.89	11.5	19.9	15.5	1.2	14.3	4.4	80.1	16.1
9	Southwest face Ledge G Thickness 12"	2.66	0.9	33.51	8.4	6.3	3.1	1.0	2.1	3.2	93.7	5.5
10	North face Ledge G'	2.68	0.5	11.27	5.3	4.2	2.1	1.0	1.1	2.1	95.8	0.2
11	Stockpile 6B Grading Sample K	2.67	1.27	11.60	13.1	14.6	8.4	0.5	7.9	6.2	85.4	9.8

Table 2. (continued)

COMPOSITE DATA SHEET (continued)

Sample Number	Source*	STANDARD ACCEPTANCE TESTING				GEOLOGICAL ANALYSIS						
		Bulk Specific Gravity	Percent 24 hr. Absorption	Soundness		Percent Total Clastics (Insoluble Residue)					% Soluble Carbonate	
				Average Percent Loss 5 Cycle Magnesium Sulphate Soundness	Average Percent Loss 25 Cycle Freezing & Thawing in Water		Percent Total Silica			Percent Clay		Percent Dolomite $CaMgCO_3$ (Unstained)
								Percent Chert	Percent Sand			
Column Number		1	2	3	4	5	6	7	8	9	10	11
Burnt Bluff Limestone, Mackinac County, Michigan. Collected 1951.												
12	Stockpile 6B Grading Sample 1	2.67	0.58	0.57	13.8	2.0	0.02	0.02	none	1.2	98.8	-
Delaware Limestone, Lucas County, Ohio. Collected 1951.												
13	Stockpile 4A Grading Sample 3	-	-	11.30	2.0	1.7	0.8	none	0.8	0.9	98.3	-
14	Bottom new cut 10' below surf Sample 4	2.54	3.84	3.58	3.2	5.1	3.4	3.4	trace	1.7	94.9	-
15	Top new cut 2-3'below surf Sample 5	2.53	3.52	7.73	4.7	3.4	2.6	0.3	2.3	0.8	96.6	-

*Quarry position and stockpile source. Number and letter designations in this column assigned by the Michigan State Highway Department Research Laboratory, East Lansing, Michigan, for various research projects.

Table 2. A compilation of the results from standard acceptance testing and geological analysis on limestone aggregates.

removed at this stage, dried, separated and weighed. Because of the very large percentage of clay present in some of the samples difficulty in separating the clay and coarser clastic fractions by screening after the residue had been dried was anticipated. Wet screening seemed to be the best method of effecting complete separation of the chert, sand and clay so it was expedient to do so while the residue was still wet and thus eliminate extra and unnecessary steps.

After complete acidization of the samples the residue was allowed to settle in the bottom of the beaker and the excess acid solution was decanted with a siphon. More water was added to the remaining solute and residue, at the same time washing down the clay clinging to the sides of the beaker, then the settling and siphoning process was repeated. This cycle was duplicated several times until the solution no longer gave evidence of being acidic when tested with litmus paper. This neutralization of the acid was necessary to prevent damage to the delicate copper wire screen of the 200 mesh sieve used to separate the clay from the coarser clastics.

The No. 200 and No. 35 (U.S.Sieve Series) size sieves were used to separate the three clastic fractions. The two 6 inch diameter sieves were nested together and placed over an appropriate size (2000 ml.) beaker. The residue was carefully and thoroughly washed through the sieves with light water pressure being careful to remove all clay from the sand and chert. The No. 35 sieve served not only to separate the sand from the clay but also prevented the sharp harsh chert from coming in contact with and damaging the delicate 200 mesh screen.

All that material passing the 200 mesh sieve was considered to be clay for the purposes of this study. All that residue passing through the No. 35 sieve but retained on the No. 200 sieve was considered sand, and all that material larger than the openings in the No. 35 mesh sieve was chert. The No. 35 sieve was selected by trial and error as the sieve size which allowed nearly all the quartz sand grains to pass through but successfully retained the majority of the small angular chert fragments.

The chert and sand fractions were oven-dried, weighed and put aside for further examination. The amount of chert and sand were computed as percent of total sample individually, Columns 7 and 8, and combined as total percent silica, Column 6, Table 2, pages 28 and 29.

The clay passing the No. 200 sieve was allowed to settle thoroughly and the excess water decanted. Due to the large amount of clay and its extremely low permeability it was found that the ordinary laboratory glass funnels with filter paper would not be satisfactory for removing all the excess water from the clay fraction. Removing the water with this equipment would have taken an interminable amount of time. A No. 4 Büchner funnel, placed in the top of a suction flash with a rubber stopper, and connected to a continous vacuum, worked very well for this stage of the separation. As the flask was evacuated enough pressure was created to drive the water through the impermeable clay where it then collected in the bottom of the flask. It was found that if the vacuum was left in operation after all the excess water was removed that the flow of air through the clay tended to dry it out sufficiently so that the thick clay residue shrank away from the sides of the funnel for easy removal and was solidly compacted for ease in handling.

The clay "billets" thus produced were dried, weighed and their percentage of total sample computed. The results are found in Column 9, Table 2, page 28. The amounts of each of the clastic fractions, chert, sand, and clay were added together and deducted from the original weight of each sample, the remainder being the percentage of total soluble carbonates. The total percent carbonates is tabulated in Column 10, Table 2.

Separating the water from the clay would probably have been quicker and easier by evaporating in an oven. However, alteration of the clay by inadvertent burning or baking would have been detrimental to further investigation of the clay fraction. The more tedious mechanical separation procedure was selected in order to avoid any adverse effects on the clay minerals.

Quantitative Microscopic Determination of Calcium Magnesium Carbonate

Exacting separation and determination of the proportion of calcium magnesium carbonate (dolomite) in combination with calcium carbonate (calcite, or limestone) is a difficult quantitative chemical procedure involving considerable skill, equipment and time. It was not felt that such a quantitative chemical analysis was in keeping with the scope of this study. However, it was desireable to determine the extent of dolomitization, or percent dolomite, inasmuch as porosity is probably one of the major factors in the response of a limestone aggregate to the various soundness tests. It is becoming a generally accepted fact that increased dolomitization is a direct cause of increased porosity in limestones.

The following method using ordinary mineralogic staining techniques and a mechanical integrating stage in conjunction with a polarizing microscope was suggested as a substitute for determining the degree of dolomitization of the samples.

Calcite and dolomite are closely allied minerals which are difficult to tell apart even under the microscope. A number of methods employing various stains have been recommended for use in differentiating between the two minerals. Some stains are considered to be better than others by each investigator but all seem to depend on the greater solubility of calcite as the distinguishing feature.

In preparation for the quantitative microscopic analysis three to five fragments of each sample were either cut-off with a diamond saw or ground off flat on one side and polished smooth with a horizontal lap using emery and aluminum oxide abrasives. These polished sections, if the opposite side was left uneven, were mounted on glass slides with a small amount of modelling clay.

Before mounting the polished sections on the glass slides they were first stained using the Fairbank's Method, a refinement of the long used Lemberg's solution. The staining solution was prepared by bringing to boil:

0.24	grams haematoxylin (logwood)
1.6	grams aluminum chloride
24	cc. water

The solution was allowed to cool and a small amount of hydrogen peroxide added to completely oxidize the haematoxylin to hematein to insure uniform results (Fairbanks, pp. 126-127). The prepared polished sections were marked for identification, immersed in the Fairbanks solution and then boiled for approximately 5 minutes. This boiling is not a previously recommended practice but was necessary to insure distinct staining of the calcite to aid in the planimetric measurement which was to follow.

Several other staining methods were attempted including the Copper Nitrate Method, the Silver Chromate Method, the Potassium Ferricyanide Method and the old Lemberg Method (See: L.W. LeRoy, "Stain Analysis", Subsurface Geologic Methods, 2nd Ed., Colorado School of Mines, Golden Colorado, 1950, pp. 195-196, for a complete resumé of calcite-dolomite staining methods). With practice it was found that the Fairbank's Method produced the most consistent and most distinct results.

The stained polished sections mounted on glass slides were then placed in the E. Leitz Integrating Stage under a polarizing microscope. The integrating stage is a precision mechanical device for measuring microscopic planimetric distances on thin or polished sections. The apparatus has six independent measuring spindles for measuring proportional amounts in one direction, plus one spindle on the side for offsetting the line of measurement to return on a new traverse. In this way a planimetric determination of the proportion of unstained dolomite and stained calcite was accomplished.

To reduce the proportion of possible error in measurement, the total length measured should exceed at least 1000 times the average size of the individual crystals. The unstained dolomite crystals averaged 0.5 mm. so the total planimetric measurement exceeded 500 mm. for each polished section. The percent of dolomite in the total sample was computed from the total carbonate fraction by first calculating the average percent of dolomite from the total distances measured on each of the three to five polished sections for each sample. This total percent dolomite (unstained) is recorded in Column 11, Table 2, pages 28 and 29.

Although this planimetric method of determining the percentage of dolomite in a sample of limestone may need qualitative chemical confirmation to become generally accepted, the range of percentages determined by this method do approximate and include the percent of magnesium carbonate in a composite sample of the Bayport limestone determined by chemical analysis by the Michigan State Highway Department Research Laboratory.

Chemical Analysis

	Bayport Composite	Burnt Bluff Composite
SiO_2	15.54%	0.83%
R_2O_3*	1.44%	0.75%
$CaCO_3$	75.83%	88.28%
$MgCO_3$	7.19%	10.14%

The Burnt Bluff samples from Mackinac County and the Delaware samples from Silica, Ohio were not included in this quantitative microscopic analysis. Even though the Burnt Bluff limestone is almost

---

* Tri valent iron and aluminum oxides.

10 percent magnesium carbonate by chemical analysis, the samples were so dense that none of the staining methods attempted were successful in penetrating the calcite. The Delaware samples, because of their unusually high absorption, reacted just the opposite. The whole sample became darkly stained even without boiling so no differentiation between dolomite and calcite could be discerned. Fragments of the Delaware samples reacted comparatively slowly when treated with dilute hydrochloric acid and are probably highly dolomitic.

Clay Mineral Stain Analysis

Clay minerals of the montmorillonite and illite groups expand and contract significantly with wetting and drying (Blanks, p. 409). The expansion and volume change resulting from the hydration of montmorillonite type clays is accompanied by potential pressures of several thousand pounds per square inch which may greatly exceed the tensile strength of concrete (Rhoades and Mielenz 1948, p. 35). The expansion of a stratified limestone may differ in different directions and can expand more than 0.1 percent in length upon wetting (Rhoades and Mielenz 1948, p. 35). Even though some limestones may be considered sound according to standard acceptance tests they can still cause deterioration of concrete when their interstitial clay swells as it absorbs water from the concrete (Blanks, p. 409).

Identification of the various clay mineral groups and especially each species within the groups is extremely difficult due to their minute size. Optical methods are very unsatisfactory and uncertain. Chemical, X-ray, electron-diffraction and differential thermal-dehydration methods are required for precise and reliable identification.

Several stain tests have been employed to aid in the determination of the various clay groups. Caution should be used in the application and interpretation of these tests because impurities and complex clay-mineral associations may lead to inconsistent and erroneous results. (LeRoy 1950, p. 197).

In order to determine if the excessive clay present in the Bayport limestone, occuring both interstitially and in concentrated clay streaks, was of the swelling (montmorillonite) type the following clay mineral stain tests were employed. Inasmuch as the clay residue had already been thoroughly acidized, washed, sieved and dehydrated, the malachite-green and crystal-violet tests were used. By using both tests the results were mutually confirmed and should be more reliable.

Both the malachite-green and crystal-violet tests make use of the same technique, the only difference being the organic dye employed. Both dyes were prepared by dissolving 0.1 gram of crystal-violet or 0.1 gram of malachite-green respectively in 25 cc. of nitrobenzene. Approximately one milligram of the acidized clay fraction placed in a watch glass and treated with a few drops of either dye solution reacted by assuming characteristic colors as given in Table 3 below.

SUMMARY OF CLAY-STAIN RESULTS*

Mineral Group	Malachite-green	Crystal-violet
Kaolinite	Green	Violet
Montmorillonite	Yellow to greenish-Yellow	Yellow, greenish-yellow or orange yellow
Illite	Yellow	Dark Green

*after L. W. LeRoy, 1950, Table 7, p. 199.

Table 3. Summary of clay-mineral-group stain results using acidized samples.

The stained clays were observed with a stereomicroscope in reflected light using fairly high magnification. The results of the clay mineral stain tests on the aggregate samples are tabulated in Table 4, pages 39 and 40.

Statistical Comparison of Physical Testing and Geologic Analysis

Upon completion of all the tests and analysis just described we find that we have a mass of random data. From the three engineering tests we have arrived at various percentage measures of soundness; from the geological analysis we have isolated six percentage measures of the basic constituents of the samples which we hope to relate to the measures of soundness. These together times the 15 samples used for the study give us roughly 135 individual quantitative measurements of the variables on which the concrete making properties of the samples depend.

Individually these percentage figures have only a very limited value and then only in a general sense. It is essential that we group

RESULTS OF CLAY MINERAL STAIN TESTS

Sample Number	Source*	Crystal Violet Clay-Stain Results	Predominant Clay Mineral	Malachite Green Clay-Stain Results	Predominant Clay Mineral
Bayport Limestone, Huron County, Michigan. Collected 10-10-51.					
1	Southwest face Ledge A Thickness 18"	Dark yellow to greenish with finest material violet.	Montmorillonite, with trace of kaolinite.	Yellow, with trace of greenish.	Montmorillonite, with trace of kaolinite.
2	North face Ledge A'	Yellow, greenish yellow and dark green with trace of violet.	Montmorillonite and illite with tr. of kaolinite.	Yellow and green.	Montmorillonite and illite.
3	Southwest face Ledge B Thickness 12"	Dark yellow to greenish with finest material violet.	Montmorillonite, with trace of kaolinite.	Dark yellow and green.	Montmorillonite and kaolinite.
4	Southwest face Ledge C Thickness 42"	Yellow and violet.	Montmorillonite and kaolinite.	Yellow and green.	Montmorillonite and kaolinite.
5	Southwest face Ledge D Thickness 6"	Dark yellow to greenish with finest material violet.	Montmorillonite, with trace of kaolinite.	Yellow and green.	Montmorillonite and kaolinite.
6	West face Ledge D'	Dark greenish yellow, green and trace of violet.	Montmorillonite, illite with trace kaolinite.	Brownish yellow.	Montmorillonite.
7	Southwest face Ledge E Thickness 36"	Yellow and greenish yellow.	Montmorillonite.	Yellow to greenish yellow.	Montmorillonite.
8	Southwest face Ledge F Thickness 54"	Yellow and violet.	Montmorillonite.	Yellow to greenish yellow.	Montmorillonite.
9	Southwest face Ledge G Thickness 12"	Dark yellow to greenish with trace of violet.	Montmorillonite, with trace of kaolinite.	Brownish yellow.	Montmorillonite.
10	North face Ledge G'	Greenish yellow with trace of violet.	Montmorillonite, with trace of kaolinite.	Brownish yellow.	Montmorillonite.
11	Stockpile 6B Grading stone Sample K	Greenish yellow with trace of violet.	Montmorillonite, with trace of kaolinite.	Brownish yellow and green.	Montmorillonite and kaolinite.

Table 4. (continued)

RESULTS OF CLAY MINERAL STAIN TESTS (continued)

Sample Number	Source*	Crystal Violet Clay-Stain Results	Predominant Clay Mineral	Malachite Green Clay-Stain Results	Predominant Clay Mineral
Burnt Bluff Limestone, Mackinac County, Michigan. Collected 1951.					
12	Stockpile 6B Grading Sample 1	Violet with trace of orange yellow.	Kaolinite, with trace of montmorillonite.	Green, with trace of yellow.	Kaolinite, with trace of montmorillonite.
Delaware Limestone, Lucas County, Ohio. Collected 1951.					
13	Stockpile 4A Grading Sample 3	Violet.	Kaolinite.	Green.	Kaolinite.
14	Bottom new cut 10' below surf. Sample 4	Violet.	Kaolinite.	Green and dark yellow.	Kaolinite, with trace of montmorillonite.
15	Top new cut 2-3' below surf. Sample 5	Violet with trace of greenish yellow.	Kaolinite, with trace of montmorillonite.	Green.	Kaolinite.

*Quarry position and stockpile source. Number and letter designations in this column assigned by the Michigan State Highway Department Research Laboratory, East Lansing, Michigan, for various research projects.

Table 4. Clay-Mineral analysis results from malachite green and crystal violet tests using thoroughly acidized limestone residues from quarry ledge samples and aggregate stockpile samples.

these figures in some logical way so that they may become significant and useful.

Just by arranging all these results together in one place, as has been done in Table 4, we can begin to see a relationship developing between the physical testing and the geological analysis results. Such obvious relationships as the increase in clay to the increase in percent loss with the freezing and thawing soundness test are readily apparent. But, which of the other constituents, chert, sand, dolomite et cetera, produce the greatest influence on the durability of the samples? In order to study the relative effect of each of the basic components of the aggregates we much employ some mathematical means.

Various statistical techniques could be used to aid in understanding the problem. However, when the relationship consists of random quantitative data, the appropiate statistical tool for discovering and measuring the relationship is known as "simple correlation". Simple correlation is a useful and indispensable tool for the research worker in the social and natural sciences.

Only a brief discussion of the various statistical measures relating to simple correlation will be included here. The statistical methods used in this report follow those techniques outlined by Croxton and Cowden, "Applied General Statistics", Chapter XXII, with minor variations.

The Line of Regression - $Y_c = a + bX$

If the relationship between two variables - e.g., percent clay vs. percent loss on freezing and thawing in water - is plotted on a coordinate system, the resulting chart is known as a scatter diagram. Each dot represents the observations for one sample (e.g.,see Fig. 3). The relationship between the two variables seems to be linear, the straight line obviously being as good a fit as a more complicated curve. The equation of the line is

$$Y_c = a + b\,X$$

or substituting the correct values calculated from the collected data

$$Y_c = 4.2 + 2.08\,X$$

This straight line has been so fitted that the sum of the squares of the Y deviations of the points from the line are less than those from any other straight line. From this equation we can estimate the percent loss from freezing and thawing in water by substituting a hypothetical value (10 percent) of clay for X in the equation

$$Y_c = 4.2 + (2.08)\ (10.0) = 25.0 \text{ percent loss}$$

or the estimate could be read directly from the regression line on the chart.

In the estimating equation 'b' tells us the amount by which the dependent variable changes with a change of one unit of the independent variable. In other words, referring to the example above again, a one percent increase in clay results in a 2.08 percent increase in expected percent loss. Thus, a comparison of the relative value of 'b' for each of the statistical relationships, (the value of 'b' has been underlined for emphasis in each of the diagrams), or a visual cognizance of the steepness of the angle of the line of regression from the horizontal, is a direct indication of the relative degree of importance of the effect of the independent variable. In this case it is an indication of the relative importance of each of the analyzed constituents of the aggregates to the measured degree of soundness. In discussing the slope of the regression line it shall be referred to as the "degree of correlation".

In this study of the relationships of the various constituents of limestone aggregate to their soundness, all of the measures of the various constituents have been purposefully reduced to percentages of the total sample. Also, an equalized scale (the scale of the X axis is equal to the scale of the Y axis) was used throughout in presenting the statistical relationships. This has been done so that it would only be necessary to visually scan the slope of the regression line, or degree of correlation, in order to immediately see which constituent was responsible for producing the most critical effect on the soundness of the samples.

Another factor needs brief mention. This is the value of 'a' in the estimating equation. Statistically 'a' gives that point on the Y axis at which the line of regression begins; or 'a' gives the value of Y when X is equal to zero. A high value of the point of origination of the line of regression is partially described by the standard deviation. Perhaps an understanding of this factor 'a' will help in understanding the meaning of the standard deviation. We should recall that we are comparing one isolated constituent of the samples, e.g., percent clay, with the soundness of the total sample which is a measure of the total effect of all the constituents of the sample to freezing and thawing. Therefore, this value 'a' is an unexplained representation of the effect of the other constituents which contributed to the measure of soundness. If it were possible to isolate and measure the contribution of percent clay alone to the measure of soundness then our line of regression would begin at the zero point on the Y axis.

Standard Deviation - S_y

The variation of the observations from the line of regression are not explained by the estimating equation but are probably due to influences of other factors in each sample as just discussed. When dealing with natural phenomena it is not possible to isolate and study each individual factor involved. If a situation existed where, "all other things being equal", then all the observed points would follow the estimating line.

We should not expect that all limestone samples having 10.0 percent clay should lose 25.0 percent after 25 cycles of freezing and thawing in water. Rather, the 25.0 percent should be thought of as an estimate of the average loss expected.

The standard deviation is computed in terms of the difference between the observed average percent losses and the percent losses estimated from the line of regression. The standard deviation is also known as the scatter, or standard error of estimate and is denoted by S_y. It yields an estimate of the range above and below the estimating line within which 68.27 percent of the items can be expected to fall.

About 95 percent of the items will be included in two standard deviations, and practically all within three standard deviations.

Two standard deviations, ± 2 S_y's, have been plotted on the accompanying scatter diagrams along with the line of regression. Two standard deviations was selected as a compromise which gave the best visual comparison of the degree of scatter while including almost all the observed values within its bounds. The numerical value of the standard deviation, line of regression and coefficient of correlation are also shown on each diagram.

Coefficient of Correlation - r.

The correlation coefficient is a measure of the degree of relationships between two variables. The correlation coefficient is stated independent of units or the terms in which the data was orginally expressed. This is done so that one coefficient can be compared with another regardless of the subject matter or units in which the various correlations are stated. The correlation coefficient is a number varying from +1, through zero, to -1. The sign indicates whether the slope of the relationship is positive or negative and always agrees with the sign of 'b' in the estimating equation. The magnitude of the coefficient indicates the degree of association.

The calculations for the correlation coefficient are usually carried out to four places beyond the decimal point. By mentally moving the decimal point two places to the right the coefficient may be thought of as the percent of reliability of the statistical relationship. In other words, if $r = 0.9102$, then we may consider the relationship 91.02 percent reliable for comparative purposes.

CONCLUSION

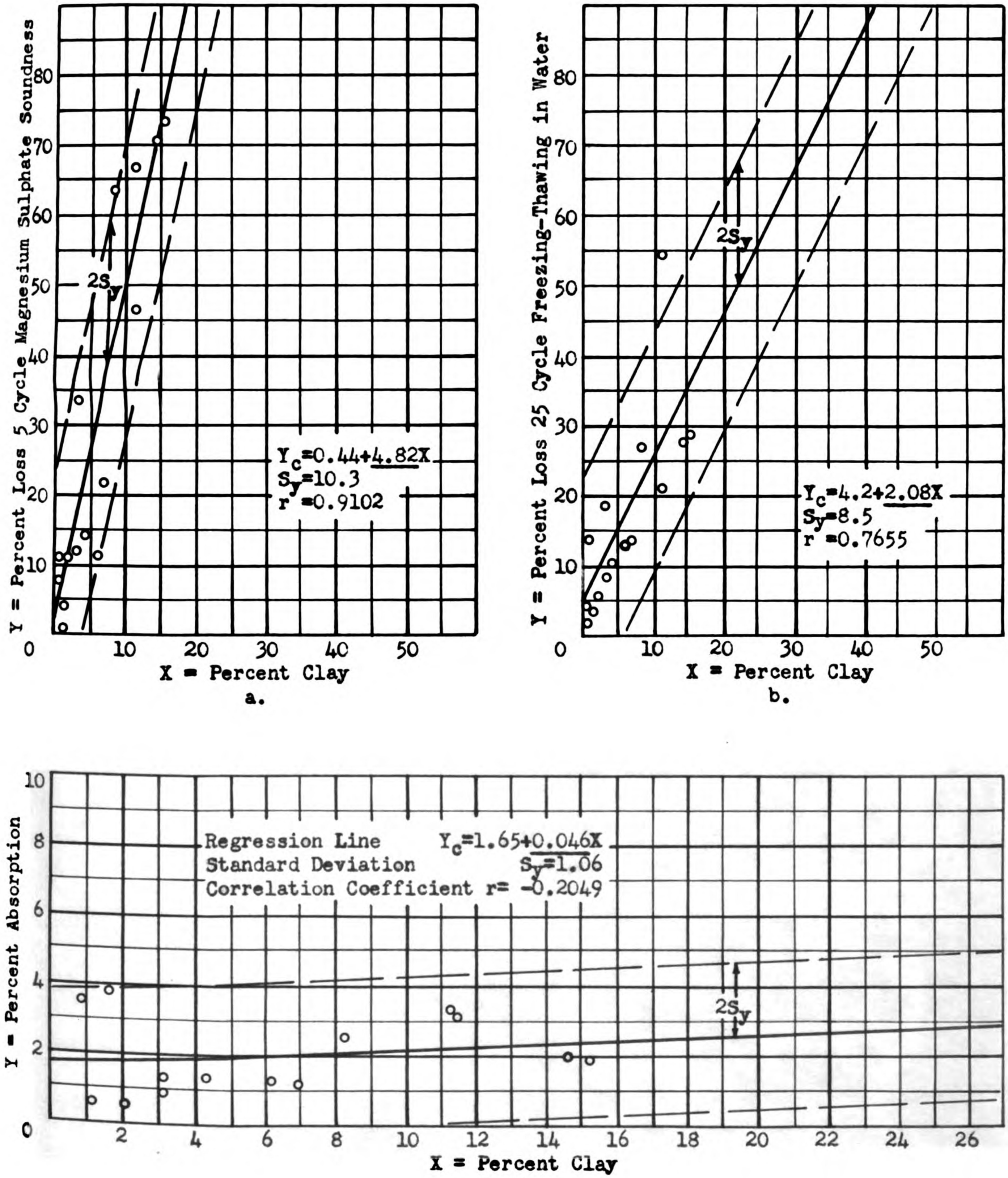
The Relationship of the Integral Constituents of Limestone to Soundness.

The various integral constituents of the limestone samples have been separated, examined, and compared statistically, alone and in various combinations with several engineering measures of their soundness. Now let us interpret the effect of these constituents on the soundness and thus the concrete making possibilities of the samples.

The Influence of Clay on Soundness.

The results of this study indicate conclusively that clay is the major factor contributing to the unsoundness of the samples analysed. This may be somewhat of a surprise to many who have had an interest in this problem and were of the opinion that the chert was largely responsible for the failure of the Bayport limestone from Huron County. Chert, of course, also contributed to the lack of soundness of the aggregates but its effect is of secondary importance. The superiority of the relation of clay to soundness is outstanding even with only a cursory comparison of the statistical relations of the various constituents to the soundness of the samples (Fig's. 3 to 9).

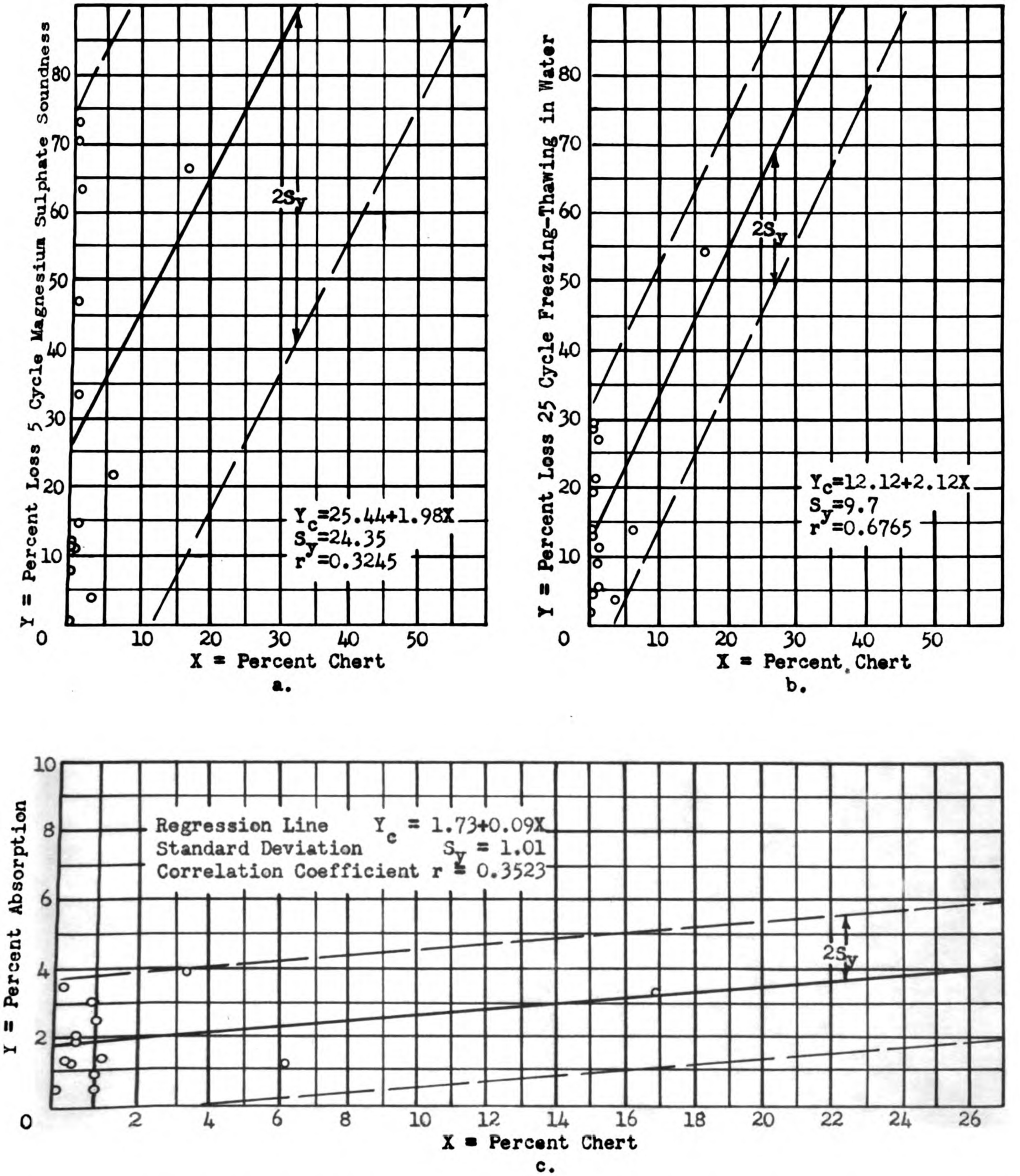
There are several factors illustrated by the statistical relationship between clay and soundness (Fig's. 3a and b) which support this conclusion. Outstandingly noticeable are; (1.) How well the points are apread out along the line of regression which produces a



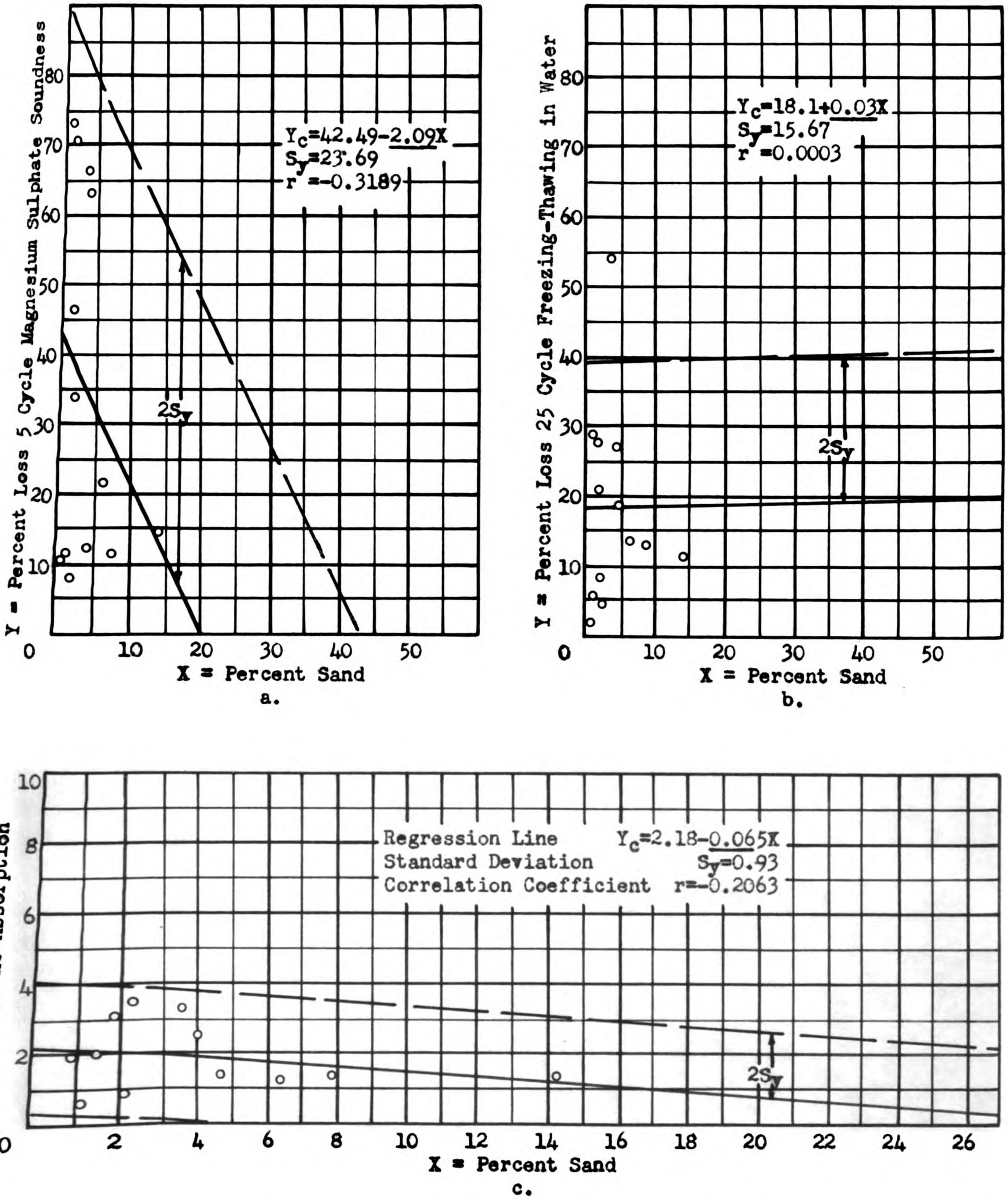
a. b.

c.

Figure 3. Comparative relation of total clay to magnesium sulphate soundness, freezing-thawing soundness and absorption.



igure 4. Comparative relation of total chert to magnesium sulphate soundness, freezing nd thawing soundness and absorption.



igure 5. Comparative relation of total sand to magnesium sulphate soundness, freezing nd thawing soundness and absorption.

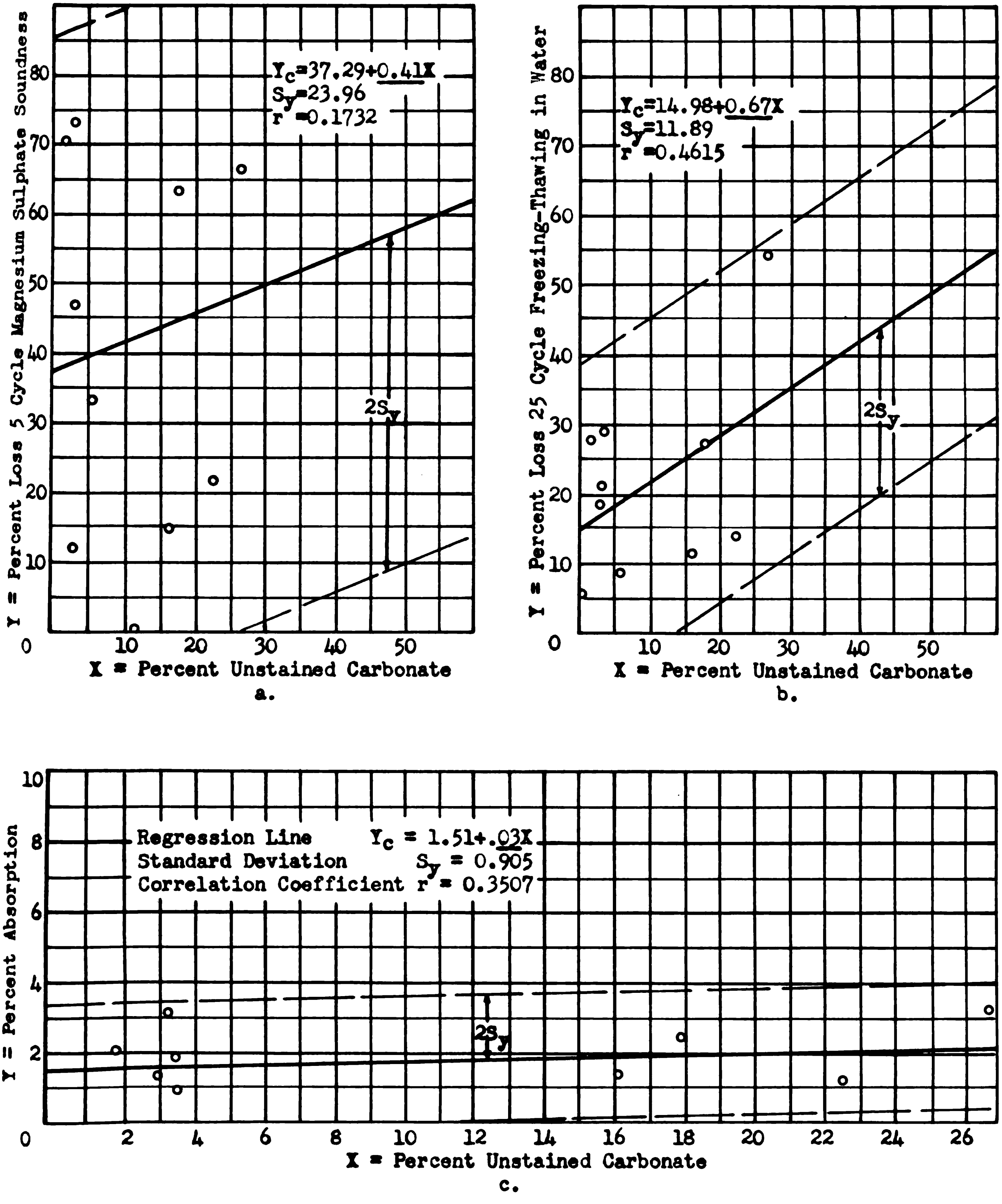
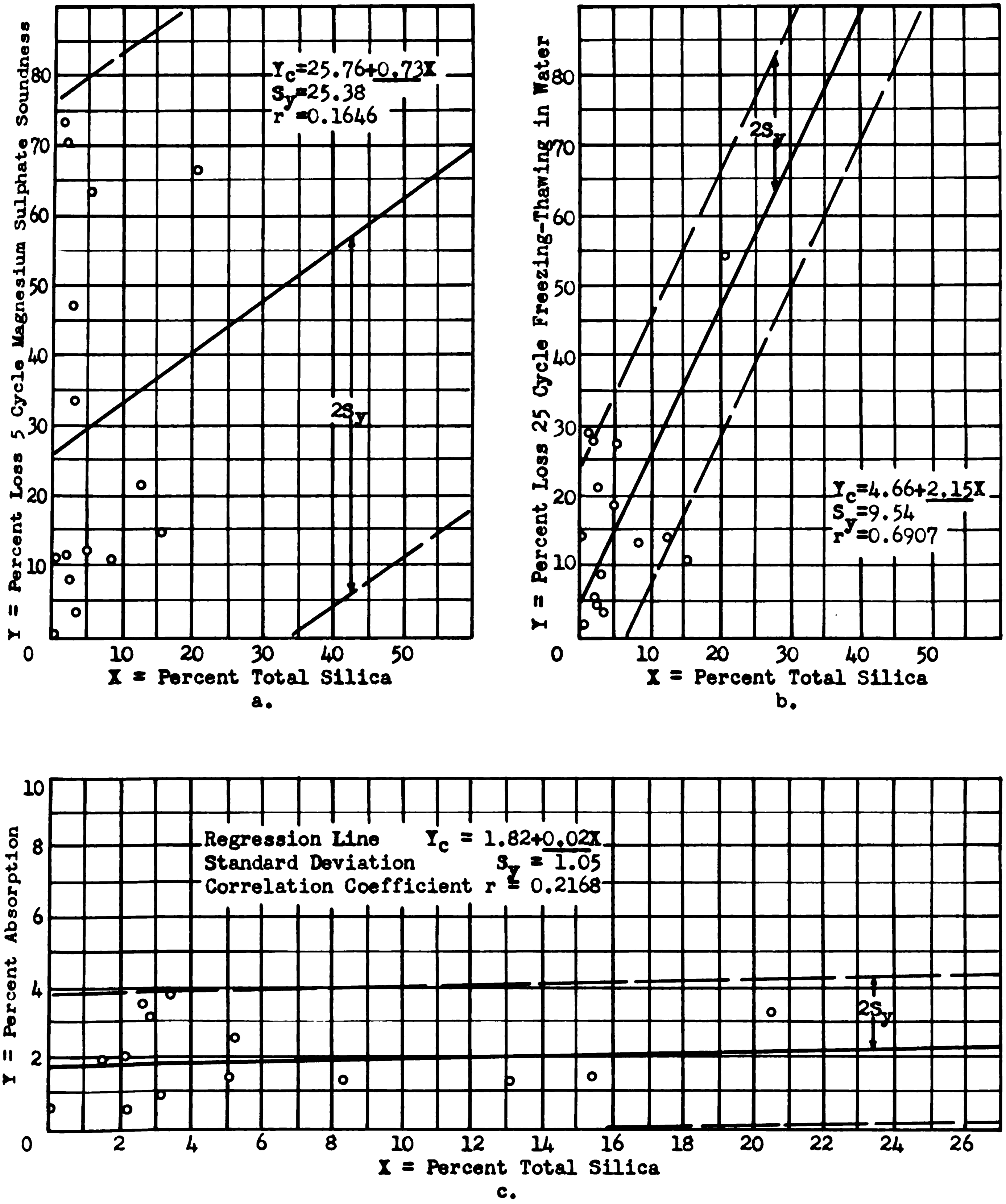


Figure 6. Comparative relation of total unstained carbonate (dolomite) to magnesium sulphate soundness, freezing and thawing soundness and absorption.



a.

b.

c.

Figure 7. Comparative relation of total silica (sand and chert) to magnesium sulphate soundness, freezing and thawing soundness and absorption.

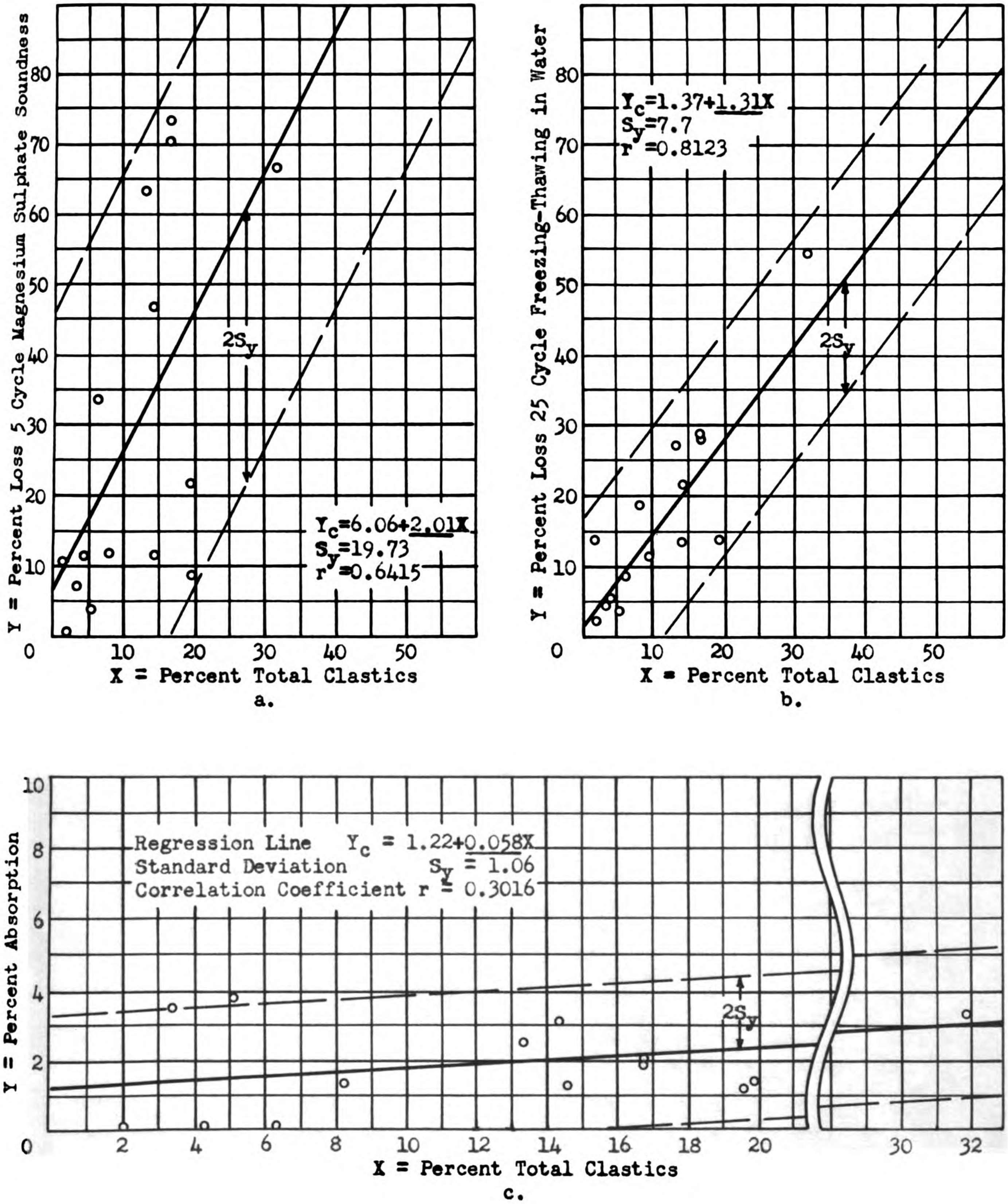
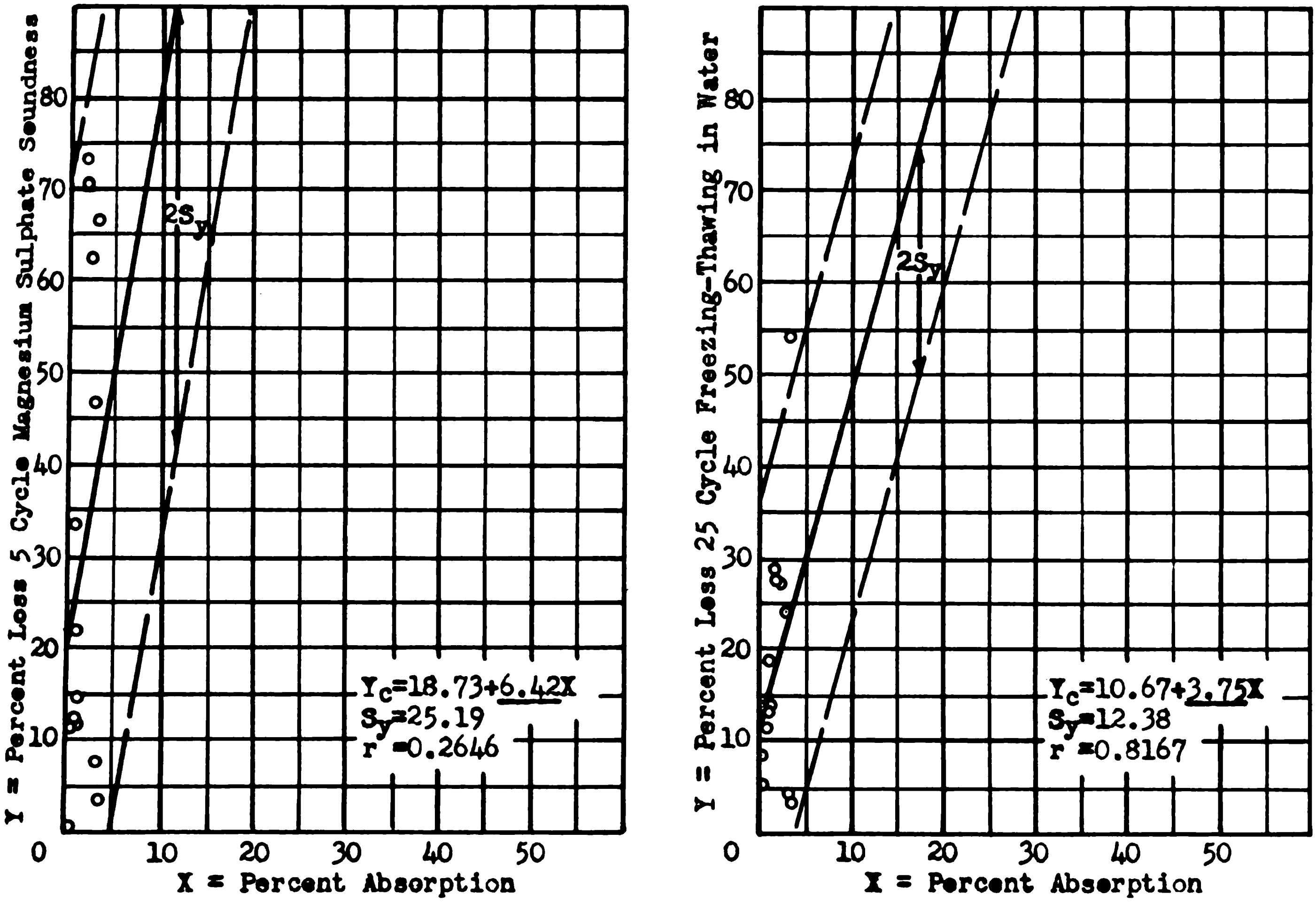


Figure 8. Comparative relation of total clastics (chert, sand and clay) to magnesium sulphate soundness, freezing and thawing soundness and absorption.



a.

b.

Y_c = Regression Line
S_y = Standard Deviation
r = Correlation Coefficient

Figure 9. Comparative relation of percent absorption to magnesium sulphate soundness and freezing and thawing soundness.

very high coefficient of correlation; 0.9102 for magnesium sulphate soundness, and 0.7655 for freezing and thawing soundness. These are considerably higher than the correlation coefficients of the other constituents of the samples to soundness. (2) How well the points fit the line of regression which produces a very narrow band encompassed by two standard deviations. (3) The high degree of dependence of soundness to clay which is illustrated by the factor 'b' in the estimating equation and visually noticeable by the steepness of the line of regression, which almost approaches vertical for magnesium sulphate soundness. In other words, for each one percent increase in clay we can expect almost 5 percent (actually 4.85%) increase in average loss on 5 cycles of magnesium sulphate soundness, and a 2.08 percent increase after 25 cycles of freezing and thawing in water. (4) The closeness of the point of origin of the line of regression to the zero point is a definite indication that only 0.44 percent of the loss from 5 cycles of magnesium sulphate soundness is due to reasons other than clay, and all but 4.2 percent of the loss on 25 cycles of freezing and thawing is due to clay.

Attention should be called to how well the points line up just below and parallel to the regression line in Fig. 3b. A few stray data draw the line away from the row of points but their remarkable alignment attests to the closeness of correlation between clay and freezing and thawing soundness. Such a close alignment is more than we could reasonably expect from such a small statistical sample but is so close that we could almost accept the factor 2.08 as the mathematical coefficient defining the effect of clay on the freezing and thawing of limestone aggregate. Such a "clay coefficient" firmly established by the study of many more samples would be invaluable in estimating the soundness of concrete aggregates.

It should be noted that those samples drawing the regression line away from the concentrated row of points possess a high percentage of chert or are heavily streaked.

Two special characteristics of the clay probably aided in its predominating influence on soundness. The high percentage of clay in the Bayport samples was prevalently of the swelling types, montmorillonite and illite (Table 4). The Burnt Bluff and Delaware samples had only traces of montmorillonite. Most of the clay in the Bayport limestone was concentrated in thin scattered shale streaks (Fig. 10b). The individual undulating streaks do not persist more than a few inches but are concentrated in certain ledges in the quarry forming heavily streaked lenticular zones which may continue for several feet.

When the rock is crushed into fragments less than 1 inch in size these shale streaks produce zones of weakness transecting the individual fragments. Water entering these porous shaly zones by capillarity is probably the major cause of disruption of the samples. The progressive entrance of water and the pressures produced by the swelling clay is in itself force enough to cause failure. Add to this the expansive force of freezing water and there is little doubt that the Bayport limestone is inclined to be unsound. Such lightly streaked to heavily streaked argillaceous limestone comprises from 30 to 60 percent of the Bayport limestone section in Huron County.

The Influence of Chert on Soundness

Chert has often been blamed for being the major cause of the disruption of concrete which has been subjected to freezing. This may be true when chert is actually encased in cement but the results of this investigation show a relatively low correlation between chert and soundness.

At first glance (Fig. 4a and b) there appears to be a reasonably fair correlation especially between freezing and thawing and percent chert. However, a closer observation shows that almost all the points are concentrated on the lower end of the chert scale. This illustrates the fact that we do not have a very representative sample for studying the effects of chert to soundness. With ninety percent of the samples having less than 3.5 percent chert we cannot rely on the statistical measures which we have computed.

The effect of chert on the soundness of the samples has been almost entirely masked by the predominance of the effect of clay. This is shown by the high value of 'a' in the estimating equation. There is 25.44 percent loss with magnesium sulphate soundness and 12.12 percent loss from freezing and thawing due to other reasons, probably predominately clay.

A much higher correlation between chert and soundness would be expected from an examination of the chert residue. The chert fraction

Figure 10a. Photomicrograph of aphanitic fossiliferous chert and amorphous chert fragments extracted from sample No. 3 using dilute hydrochloric acid. Magnified approximately 5 times.

Figure 10b. Photomicrograph of finely crystalline argillaceous limestone showing the undulating concentrated clay streaks. Polished section using reflected light. Magnified approx. 5 times.

A.

B.

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119 E. Grand River
Williamston, Mich. Ph. 273 or 546M

consists largely of non crystalline silicified fossil remains, mostly corals and bryozoa, whose acidized remains are liberally penetrated with voids (Fig. 10a). Of course these voids are all filled with calcite in the natural state and when the limestone is used as concrete aggregate. But such an impure intimate combination of calcite filled voids in chert with their differential thermal expansions should be very conducive to unsoundness when subjected to freezing, and thawing. Freezing of a calcite filled coral fragment similiar to the one shown in Figure 10a should open up countless expansion cracks which would make way for further penetration of water and progressive disruption.

The failure to achieve a dependable correlation between chert and freezing and thawing soundness in this investigation should not discourage further attempts along this line. The closeness of the points to the regression line (Fig. 4b), even though they are all concentrated at one end, is indicative of what might be accomplished using a good representative set of samples with a wider range of percentages of chert and without the detracting influence of clay.

The inferiority of the results obtained with magnesium sulphate soundness compared to freezing and thawing soundness is of considerable interest. It suggests that the pores and cracks in the chert, or produced by the chert, may be so minute that the magnesium sulphate solution was not able to penetrate as easily as water alone. It also suggests that at least part of the failure caused by 25 cycles of freezing and thawing may be due to differential thermal expansion.

The Influence of Sand on Soundness

Although there was considerable sand in some of the samples it has produced little or negative effect on the soundness of the aggregates. There is only a minutely positive correlation between the percentage of sand and freezing and thawing in water (Fig. 5b). This correlation is of little consequence because of the widely scattered array of the points around the lower end of the line of regression. The influence of sand to 5 cycles of magnesium sulphate soundness produced a very negative correlation (Fig. 5a) which is of doubtful value.

The sand occuring in the Bayport limestone is thoroughly disseminated throughout the rock. If it were concentrated in thin streaks then it might possibly be a source of trouble. The sand extracted from the Bayport limestone consists of poorly sorted, fine to coarse grained sub angular to sub rounded quartz. The sand from the Delaware samples was both very fine and very coarse grained well sorted well rounded frosted quartz. Probably any cracks or weaknesses in the quartz grains were opened up long ago while the grains were in the process of erosion, weathering and transportation to their present state and environment.

The Influence of Dolomite on Soundness

The degree of dolomitization as determined by the staining and quantitative microscopic analysis apparently has had little effect on the soundness of the samples. However, this lack of close correlation between dolomite and soundness may be due partially to the method employed in determing the percentage of dolomite but is primarily due to the overwhelming masking influence of the clay. There is a fair correlative relationship between percent unstained carbonate and freezing and thawing in water (Fig. 6b). The range of the percent dolomite is amply representative but the amount of deviation, low degree of correlation and high point of origin of the line of regression cast doubt upon the reliability of the relationship.

The failure of the method employed to produce a good correlation does not necessarily condemn the technique. The relation of percentage dolomitization to soundness should be firmly established by quantitative chemical analysis. If there is a close relationship between these two factors then staining and quantitative microscopic analysis can certainly be recommended as a rapid technique for determining the percent of dolomite. The small statistical sample does not give the technique an adequately fair trail.

The Influence of Total Silica on Soundness

The percent sand and percent chert have been statistically analysed together as total silica to see if their combined effect produced a closer correlation than either of the two separately. This was done primarily to find out if the extra separation of sand from chert was necessary to achieve conclusive results.

The resulting statistical relation of total percent silica (Fig. 7) nearly parallels the relation of percent chert to soundness (Fig. 4) but gives a slightly poorer correlation. This is what should have been expected. When combining the low or negative influence of the sand to the high positive effect of chert the two together would average out somewhere in between. The small degree of improvement in the relation of chert alone over total silica when correlated with the more reliable freezing and thawing test would not warrant separating the sand from the chert in evaluating a concrete aggregate.

The Influence of Total Clastics on Soundness

The total percent of insoluble residue, chert, sand and clay, have also been combined for statistical correlation for the reasons mentioned above. The resulting statistical comparison (Fig. 8) is as good or better than relationships achieved with either chert, sand or total silica alone when correlated with soundness. This is especially true when correlating with the accelerated magnesium sulphate soundness test. This improvement is due to the dominating influence of the high percentage of clay when it is added to the silica.

The total insoluble residue would be satisfactory for a preliminary estimation of the expected soundness of an aggregate but the clay and silica or chert fractions should be isolated and their individual influence analysed for a thorough evaluation of the concrete making properties of an aggregate material.

The Influence of the Constituents of Limestone on Absorption

Each of the constituents of the limestone samples have been correlated with the percent absorption. (Figs. 3c to 8c). If the percent absorption is a reliable indication of the expected results from soundness tests then that constituent possessing the highest degree of correlation with soundness will also have a high rate of correlation with absorption. Unfortunately, this was not found to be significantly evident.

In relating the various constituents of the aggregates, alone and in combination, with the percent absorption, the six resulting correlations were so remarkably similar in almost all respects that discussing the relationships individually would be very repetitious. The reason for this lack of character in correlating with absorption is the very narrow range of percentages of absorption for the samples analysed.

This duplicity of the statistical relations of the constituents to their absorption would indicate that the individual constituents have no important effect on the absorption of the limestone. The negative relation between sand and absorption (Fig. 5c) would add to this supposition as we can be reasonably certain that the quartz sand grains have no porosity. This leads us to a very interesting conclusion. Evidently the porosity of limestone is not due to the porosity of its integral mineral constituents but is produced by other factors, probably erosion, leaching and the negative space relationship produced by mineral alteration.

The Influence of Absorption on Soundness

The unexpected lack of a positive relationship between any of the constituents of limestone and absorption prompts an investigation of the relation ob absorption to soundness. The comparative relations of percent absorption to average percent loss magnesium sulphate soundness and freezing and thawing soundness is shown in Figures 9a and b.

A close and very high degree of correlation is found between absorption and the two measures of soundness. However, the narrow range of the data concentrated below 4 percent absorption does not produce a fair estimation of the relationship between the two variables. Here again, the high percentage failure of most of the samples is primarily due to the excessive amount of montmorillonite concentrated in zones of weakness. The effect of porosity on unsoundness has been obscured by this excessive clay. This fact is further emphasized by the high point of origin of the line of regression. The two statistical relations indicate that from 10.67 percent to 18.73 percent of the failure is due to reasons other than absorption for sulphate soundness and freezing and thawing soundness respectively. In addition, the Delaware samples, which had very low percentages of non swelling clay but rather a high rate of absorption, proved to be very sound aggregate material.

A Summary of the Influence of the Impurities in the Bayport Limestone on Its Soundness

In summary, all of the impurities found in the Bayport limestone, the clay, chert, dolomite and sand have contributed to its unsoundness in the order named. The clay, its type and mode of occurance is the major cause in the failure of the aggregate to resist the simulated forces of weathering. The chert and dolomite probably exert a greater influence on the durability of limestone than was determined by this investigation but their effect was obscured by the preponderant influence of the clay. The sand had little or no effect on the soundness. A few minor mineral constituents, namely pyrite, crystalline quarts and glauconite were present in small amounts in a few of the samples but their isolated occurence was too insignificant to warrant analysis.

One constituent, calcite, has been supposedly ommitted from the previous statistical analysis and discussion. If each of the analysed impurities contribute to the lack of soundness of the limestone, then it follows that the more pure the limestone the more sound it should be. This relation of calcite to soundness may be seen if we examine Figure 8 and mentally add a percentage calcite scale along the horizontal axis in reverse (from right to left) to the total insoluble residue scale. Thus, we have a negative correlation with essentially the same values as for total insoluble residue for the estimating equation, standard deviation and coefficient of correlation only the sign of the factors 'b' and 'r' will be negative.

The porosity (percent absorption) of the Bayport limestone is secondary to clay as a cause of failure.

The lack of a representative number of samples from the Burnt Bluff and Delaware formations prevent us from making any definite conclusive statements about these particular aggregate materials. However, the samples from these two sources are very free of impurities so they should make sound concrete aggregate.

The Suitability of the Bayport Limestone For Use as Concrete Aggregate.

Before this geologic analysis was begun it was already known that only one of the ten Bayport ledge samples successfully passed the magnesium sulphate soundness test and only one additional sample could pass specifications after the freezing and thawing in water tests. The unsound samples comprise 94 percent of the section tested. In addition, the thin black brittle carbonaceous shale stringer, commonly under 1 inch thick, which persistently underlies the limestone and forms the base of the quarry has not been included in this geologic analysis. Its clay was, however, also found to be montmorillonite. Any of this shale material inadvertently picked up and added to the limestone will noticeably detract from the soundness of the aggregate.

Inasmuch as the main cause of failure was found to be excessive montmorillonitic clay any condition in which the Bayport limestone aggregate might be used should avoid exorbitant moisture and water. Such conditions multiplied by repeated freezing and thawing should be exceedingly conducive to failure. Avoiding these moist conditions would nearly cancel the use of Bayport limestone for almost all Portland Cement concrete uses. However, if the dry aggregate fragments were thoroughly encased in asphalt cement the Bayport limestone should be satisfactory for asphalt base, binder and leveling courses in bituminous concrete paving.

The Value of Quantitative Geologic Analysis of Limestone Aggregates

Using the 12 percent specification allowable for percentage failing the soundness tests we can now compute the maximum allowable percentage of clay this geologic study and statistical analysis has determined to be within the limits of sound aggregate material. Reading directly from the regression line (Figs. 3a and b) or substituting 12 percent in the estimating equations we find that there should be less than 2.4 percent clay present in the samples in order for the material to successfully pass the sulphate soundness specifications. Freezing and thawing soundness allows almost one percent more clay, or 3.3 percent. This can also be done for chert.

To be able to furnish reliable information of this nature would be of inestimable value in predicting the quality of an aggregate and in providing an explanation of the results obtained from performance and soundness tests. Of course, the above factors are based on the results obtained from only fifteen samples. They are therefore of very limited value. This same type of analysis performed on many more aggregate samples with a full range of the variables involved would provide us with a means of predicting the performance of limestone containing all possible percentages and combinations of impurities.

Recommendations for Further Study

As a result of this investigation many problems which need further study are suggested. One has already been discussed immediately above.

This same type of analysis, in fact the data obtained from this geological analysis, should be correlated with various strength tests or performance tests to determine what effect the various impurities have on the strength factors of the aggregates and concrete. The large variety of percentages of montmorillonitic clay in the Bayport samples would provide an interesting study of the relation of swelling clay on the coefficient of expansion of the aggregate.

To determine the true relation of the montmorillonitic clay in the Bayport samples to the forces of moist weathering conditions, the samples should be subjected to a test similar to the magnesium sulphate soundness test using water alone. Several cycles of soaking in water and subsequent drying should indicate whether the expansive pressures of montmorillonite were sufficient to cause disruption of the limestone aggregate.

The influence of differential thermal expansion on a cherty limestone should be defined. If the dried samples were subjected to repeated cycles of arid freezing and thawing conditions, the relation of the differential thermal expansion of chert to limestone could be determined.

Sources of Error

In further quantitative geologic investigations of this type certain practices should be avoided.

Closer correlations probably could have been obtained if the same identical samples used in the soundness testing had also been used in geologic analysis. Care was exercised in selecting representative portions of the field sample for both parts of the study but the use of two separate samples introduce minor experimental error in exacting quantitative laboratory analysis which could be easily avoided. In evaluating an aggregate for possible use in concrete it is necessary to secure a representative sample of a whole ledge or quarry face. However, for purely laboratory investigations of the influences and properties of an aggregate material the sample should be confined to a single uniform sample of rock. Instead of trying to include a representation of a whole ledge or quarry face, thereby compounding the variables involved, one uniform piece of rock would be preferable for laboratory use.

In preparing the limestone for acidization in this investigation the samples were crushed with a mortar and pestle. This practice should be avoided. A few of the fine chert fragments produced in crushing contaminated the sand fraction and are difficult, if not almost impossible, to remove conveniently.

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1956

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BIBLIOGRAPHY

American Association of State Highway Officials, "Standard Specifications for Highway Materials and Methods of Sampling and Testing," Part II, Published by the Association, 1942.

American Society for Testing Materials, "1955 Book of Standards," Part 3, Cement, Ceramics, Thermal Insulation, Road Materials, Waterproofing, Soils; Published by the Society, 1956.

John H. Bateman, "Materials of Construction, Putman Publishing Corp., New York, 1950.

R. F. Blanks, "Modern Concepts Applied to Concrete Aggregate", Trans. Amer. Soc. Civil Eng., vol. 115, 1950, pp. 403-431.

Frederick E. Croxton and Dudley J. Cowden, "Applied General Statistics," Prentice - Hall, Inc., New York, 1939.

Ernest E. Fairbanks, "A Modification of Lemberg's Staining Method," Amer. Mineralogist, vol. 10, pp. 126-127, 1925.

L. W. LeRoy, "Stain Analysis," Subsurface Geologic Methods, Ed. by L. W. LeRoy, 2nd Ed., Colorado School of Mines, Golden, Colorado, 1950.

Katharine Mather and Bryant Mather, "Method of Petrographic Examination of Aggregates for Concrete," Amer. Soc. for Testing Materials, Proceedings, Vol. 50, 1950, pp. 1288-1312.

Duncan McConnell, Richard C. Mielenz, William Y. Holland, and Kenneth T. Greene, "Petrology of Concrete Affected by Cement - Aggregate Reaction, "Application of Geology to Engineering Practice," Berkey Volume. Sidney Paige, Chairman; The Geol. Soc. of Amer., 1950, pp. 225-250.

Richard C. Mielenz, "Petrographic Examination of Concrete Aggregates", Bull. Geol. Soc. Amer., vol. 57, April 1946, pp. 309-318.

Michigan Geological Survey, "Mineral Resources of Michigan, 1954". State of Michigan, Department of Conservation, Geological Survey Division.

Michigan State Highway Department, "Standard Specifications for Roads and Bridges, 1950." Published by the Department, 1950.

Roger Rhoades, "Influence of Sedimentation on Concrete Aggregates," Applied Sedimentation, edited by Parker D. Trask, John Wiley and Sons, Inc., 1950, pp. 437-463.

Roger Rhoades and Richard C. Mielenz, "Petrographic and Mineralogic Characteristics of Aggregates, "*Symposium on Mineral Aggregates 1948*," Amer. Assoc. for Testing Materials, Spec. Tech. Publ. No. 83, pp. 20-48.

Harold S. Sweet and K. B. Woods, "A Study of Chert as a Deleterious Constituent in Aggregates", Highway Research Bull. No. 9, Purdue Univ. 1942.

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