Highway Materials Research Laboratory
132 Graham Avenue, Lexington 29, Ky.
March 24, 1947

File: A-1-6
Res. Proj. C-22

Memo. to Dean D. V. Terrell
Director of Research

Attached is our first written report of progress on Research Project C-22, "A Study of The Properties of Coarse Aggregates", prepared by James L. Young, Materials Engineer. This study was approved at the meeting of the Research Board on February 25, 1946 (see page 3 of the minutes of that meeting), and a preliminary oral report or discussion was given by Mr. Young during the laboratory inspection last November 25. You will recall a large wall display with photographs, small samples, and diagrams used to illustrate the project.

Initial portions of the work have been directed toward limestones, and a large part of that originally planned has been completed insofar as techniques and comprehensive mineralogical properties are concerned. In this category there remains, however, detailed analyses for clay minerals which are thought to be determining factors in aggregate performance. Several other incidental measurements have also been planned as set forth in that part of the report headed "Future Work". Finally, the last of four quarries originally selected must be sampled and treated as have the others.

The important point at this stage is the fact that practically all of the primary development work on techniques and means for analyses has been done, and we are now at a point where detailed physical tests on the different materials themselves can be started, and also stone whose intrinsic properties are known can be placed in concrete and bituminous mixes to give us the performance data we are seeking. From that point on, development of new physical tests and correlative specifications (if possible) will be our objectives.

Because of the complexity of this report and the fact that its contents are strange to engineering literature, I have asked Mr. Young to give a brief summary of his work at the Research Board Meeting today.

L. E. Gregg
Associate Research Engineer

LG:k

cc: Research Board Members:
Commissioner Watkins
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Commonwealth of Kentucky
Department of Highways

Progress Report No. 1

on

Research Project C-22

A STUDY OF THE PROPERTIES OF COARSE AGGREGATES

by
James L. Young, Jr.
Materials Engineer

Highway Materials Research Laboratory

Lexington

March, 1947

OUTLINE

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Research Project C-22 is an investigation of the geologic aspects of limestone aggregate that might cause failure if used in highway construction. This represents work being carried on at the Highway Materials Research Laboratory in Lexington. The end point of this work is to determine the cause or causes of failure and provide a test that will delete faulty materials from construction work.

In order to evaluate the engineering aspect of the author's work, a study of the physical tests of these same aggregates is to be made. A correlation between Laboratory Analysis and Performance Surveys of these same aggregates in roads should be sufficient to make pertinent observations.

Limestone varies in any and all proportions of its basic constituents, with the introduction of some new minerals from time to time. As defined, limestone should be composed of calcium carbonate plus some small amount of impurities. The variation in amount and types of impurity give a limestone its characteristics and this variation is so unique that very rarely will two limestones be identical. The variation in minerals is complex, inasmuch as two different minerals having the same elements, may have entirely different reactions to any influence brought upon them. As to the limits set on the name "limestone", the presence of 50% carbonate material should assign a rock as limestone. A chemical analysis, although helpful, will not be a positive criterion as the analysis tells only the compounds present and not the way in which they are combined.

It seems a reasonable hypothesis that the impurities present are the dominant agents in any failure of limestone aggregate and a careful comparative study of these impurities should show whether the premise is well founded. This, then, is the main objective of the study.

The impurities present could be roughly classified as follows:

1. Elements*
2. Sulfides and Sulfo Salts
3. Halides
4. Oxides
5. Nitrates, carbonates, etc.
6. Sulfates, Chromates, Tungstates
7. Borates, Aluminates, etc.
8. Phosphates, Vanadates, Arsenates
9. Silicates, Titanates, etc.
10. Organic Compounds

As the myriad possibilities could occupy three or four hundred typewritten pages, an effort to simplify and concentrate on the more obvious and common things present has been made. Listed below are the most common minerals which are expected to be of consequence in variable reactions of limestone as a coarse aggregate.

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* Example: Diamond which is native carbon.

1. Elements - negligible

2. Sufides and Sulfo Salts - Pyrite $Fe S_2$
   Galena $Pb S$
   Sphalerite $(Fe,Zn)S$
   Marcasite $Fe S_2$
   Pyrrhotite FeS

3. Halides - Fluorite $Ca F_2$

4. Oxides - Water H_2O
   Hematite Fe_2O_3
   Rutile TiO_2
   Pyrolusite $Mn O_2$
   Bauxite $Al_2O_3 \cdot n H_2O$
   Limonite $Fe_2O_3 \cdot H_2O$
   Zinkite ZnO

5. Nitrates, Carbonates and Manganites -
   Dolomite $Ca (Mg, Fe, Mn)(C_2O_6)$
   Magnesite $MgCO_3$
   Siderite $Fe CO_3$
   Rhodochrosite $Mn CO_3$
   Aragonite $CaCO_3$**
   Smithsonite $Zn CO_3$
   Strontianite $Sr CO_3$
   Witherite $Ba CO_3$
   Cerussite $Pb CO_3$

6. Sulfates, Chromates, Tungstates, Molybdates
   Barite $Ba SO_4$
   Anhydrite $Ca SO_4$
   Celestite $Sr SO_4$
   Anglesite $Pb SO_4$
   Gypsum $Ca SO_4 \cdot 2 H_2O$

7. Borates, Aluminates, and Ferrites - Magnetite $(Fe, Mn, Zn) Fe_2O_4$

8. Phosphates, Vanadates, Arsenates, Columbates -
   Apatite $Ca_5F (PO_4)_3$

9. Silicates, Titanates (Most formulas are too long to be reported here)

   Orthosilicates - Garnets $[(Mg,Fe,Mn)_3Al_2Si_3O_{12}$
   through $Ca_3(Al,Fe,Cr)_2 (Si_3O_{12})]$

** Calcite also is written $CaCO_3$ but occupies different crystalline habit.

Metadisilicates - Micas - - - - - - - -
Metasilicates (Rings) Pyroxines - - - -
Metasilicates (Chains) Amphiboles - - -
Hydrous - Zeolites - - - - - - - - - - -
Special Metadisilicates - Clay Minerals - - -
Dioxide type - Quartz Si Si O_4
(all varities)
Feldspars - - - - - - - - - - - - - - - - - -

10. Organic Compounds - Nothing is known of these as yet.

In order that the scope of the problem be simplified, the number of operations has been limited to a few elementary steps. Any results will serve to direct work into more detailed investigation along significant paths.

The operations have been designed to determine the amount, kind, and arrangement of impurity. Thus preliminary work on this project as reported herein was concentrated on procedures applicable to these determinations.

TECHNIQUE

Sampling

Four quarries were selected for study, three of which have been sampled. The tool used was a geologic hammer. The operator selected some vertical face which was accessible, marked off levels with a hand level, and was then ready to sample.

Specimens were collected from every foot of the quarry and marked according to their elevation above the quarry "floor". The ideal size was 3" x 3" x 2" in each case enough material being present to insure sufficient quantity for every test. Two specimens were collected every foot, one oriented with an arrow for the purpose of making thin sections, and the other unoriented for the purpose of determining the amount and type of insoluble residue. When it was determined what part of the quarry was "stripped" that part was omitted with notations made thereof. Care was taken to insure the "freshness" of each sample. No shale was taken. (See page 55 for Possibility of Error and Conclusion).

Separation

The samples were carefully arranged on a laboratory desk in preparation for study. They were segregated into zones by two methods. (1) Visual with optical assistance, and (2) specific gravity determinations. These zones were arbitrary and were included in this study for correlation purposes with Quarry Logs that have been prepared in the past.

In the visual examination, the samples were examined in order to write a brief description of the rock. In difficult determinations the use of a hand lens (Coddington) or binocular microscope was the quickest method. Any description of this nature would not be final as a more detailed description was made later.

The method of bulk specific gravity(1) was used in checking samples. Its relation to mineral constituents of aggregate is not direct, but because this determination has been fundamental to prior logging and classification, it was retained for check purposes. (See page 55 for Possibility of Error and Conclusion).

Crushing

The sample intended for use in the insoluble residue test was crushed to a material finer than 3/8 inch in order to facilitate the action of acid in the insoluble residue process. The crusher used was a jaw type Universal Crusher, Size 1 M. (See page 55 for Possibility of Error and Conclusion).

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(1) Bulk S. G. - $\frac{\text{Weight of sample in air}}{\text{Loss of weight in water}}$ (no drying precautions)

About three drops of Canada Balsam were slowly heated on the frosted side of a clinical glass slide, to the point where a drop of the balsam on a needle point snapped when pressed against a solid surface. The square slice of rock was simultaneously heated to the same temperature as the balsam. At the completion of "cooking" the balsam, the rock slice was lowered onto the heated balsam and pressed down firmly with a slight rotation to force out excess balsam and air bubbles. If bubbles were present, it was necessary to remount the specimen.

When cool, the slide was used as a hand hold in order to grind the specimen to a required transparency. Coarse Carborundum grain was used to remove the largest part of the specimen and the final abrading was done with 3F powder. This final grinding was exceedingly delicate and much care was exercised to avoid complete loss of sample due to excess grinding. Final thickness was approximately 0.1 mm.

When the specimen was at its required transparency, a cover slip was covered with Canada Balsam and slowly heated. Only partial "cooking" was required at this time. The heated balsam was poured on the warm specimen with a gentle rotation. When all air bubbles and excess balsam had been removed, the slide was allowed to cool. The overflow balsam was cleaned off with xylol or white gasoline and the slide was properly labeled. It was then ready for study. (See page 56 for Possibility of Error and Conclusion).

Insoluble Residue Process

The crushed material was weighed out on a beam balance. Twenty grams of material was put in a 800 ml. beaker and 20 grams of material was put in sample bottles as an assurance of having enough material in case of loss of one sample in the process of insoluble residue determination. The material in the beaker was partly dissolved in about 50 ml. of 6N-HCl at room temperature. Acid was added slowly to insure that violence of the reaction was not sufficient to cause loss through overflow of the beaker or through effervescence. As soon as all reaction had ceased another 50 ml. of 6N-HCl was added. This was kept up until complete digestion of the sample occurred.

At this point distilled water was added and the sample deflocculated. After being allowed to settle for eight or more hours, the supernatant liquid was filtered off with an Olmstead, Middleton, Alexander pressure filter apparatus(1) (See Fig. 2). Six separate filtrations were carried on; at the conclusion of each, the sample was deflocculated with 150 ml. of distilled water. At the conclusion of each deflocculation, the sample was allowed to settle for eight hours. After six filtrations, the sample was dried on a water bath, the beaker was carefully cleaned on the outside, and the beaker and its contents were then weighed.

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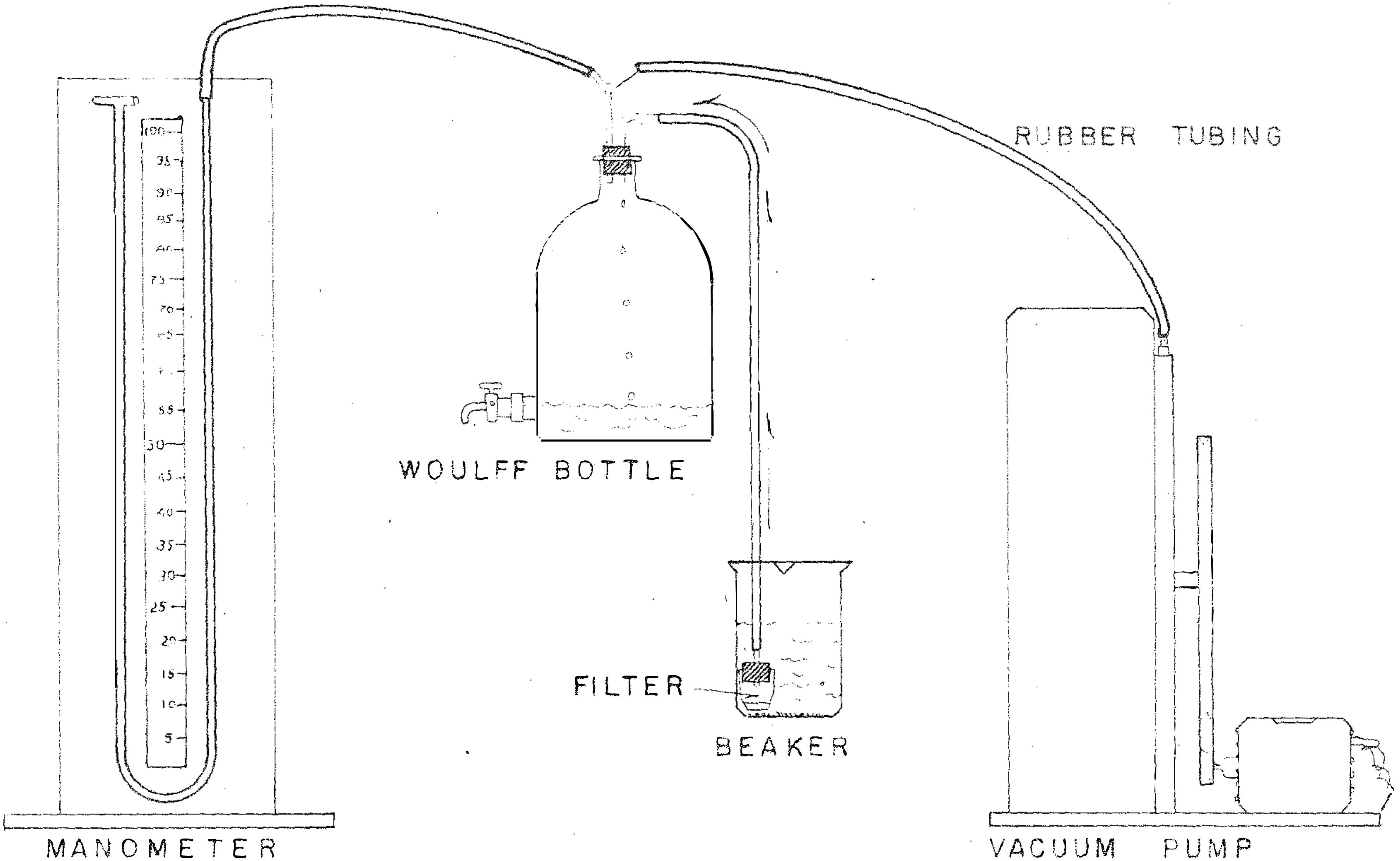
(1) Krumbein, Pettijohn - "Sedimentary Petrography", p. 67, McGraw, Hill.



OLMSTEAD, ALEXANDER, MIDDLETON PRESSURE FILTER APP.

The insoluble residue was scraped out and placed in labeled sample bottles which were filed for study. The beakers were washed, dried and reweighed, the difference in weight being the amount of insoluble residue. The recovery of the residue was not one hundred percent but only approximately so. The percentage was known and a representative fraction retained.

At the conclusion of these operations, the amount and arrangement of impurities in the rock were known. Subsequent study will reveal something of the geologic history of the rock. In order to find out the nature of the material present in the residue, special methods were used.

These methods represent work that has been approached, but not completed. The identification of clay minerals is but one of the endeavors in the determination of the materials present in insoluble residue. For other pertinent methods, see the discussion headed "Future Methods".

The presence of one of the expanding lattice type clay minerals could be the most active source of decomposition. This type of mineral has the highest affinity for water, the largest volume increase on wetting and has a high affinity for base exchange together with several other extreme properties which could make the presence of this mineral very deleterious. The method of insoluble residue determination which was first used was impractical for clay mineral determination and so a special method was used:

Clay Mineral Recovery (1)

Samples left after the thin sectioning process were ground to pass a twenty mesh sieve and placed in a glass vessel containing two liters of distilled water. Chemically pure HCl was added a few drops at a time until the limestone was dissolved. The solution and insoluble residue was then stirred vigorously and allowed to stand for five hours or longer when the suspended material was siphoned off. The material which settled was discarded as it was believed, on the basis of previous experience (2), that the suspended material would provide a representative sample of the clay mineral content.

Enough Ammonium Hydroxide was added to the suspension to neutralize any hydrochloric acid present, and produce an alkaline condition. After standing overnight, the suspended material

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(1) The Clay Minerals in Illinois Ls & Dolo. - Grim, LaMar, Bradley, Journal of Geology, Vol. 45, pp. 829-843, 1937.

(2) Attempts to analyze an ordinary insoluble residue by X-ray analysis were balked because quartz obscured the clay pattern.

had usually flocculated and settled so that the supernatant liquid could be removed by siphoning. The solid material was recovered on a filter paper, thoroughly washed and dried. Hydrated iron oxide in quantities sufficient to mask X-ray diffraction patterns was eliminated by boiling the solid sample in HCl until the iron oxide dissolved and the clay minerals were recovered by filtration. The solid recovery was kept in a 2 ml. sample bottle in preparation for X-ray analysis. (See page 56 for Possibility of Error and Conclusion).

X-Ray Diffraction

After the sample was obtained, it was ground in a mullite mortar to pass a 350 mesh sieve. The sample was then mixed with collodion and ether and coated uniformly on a cotton thread several times. When the thread had uniform strength, about one inch of it was trimmed off. This thread was mounted on the movable collet of a small Debye camera with movable motor driven chuck. Film was loaded in the camera and clamped, filters were inserted and the camera sealed. A NiO filter was used with Cu radiation.

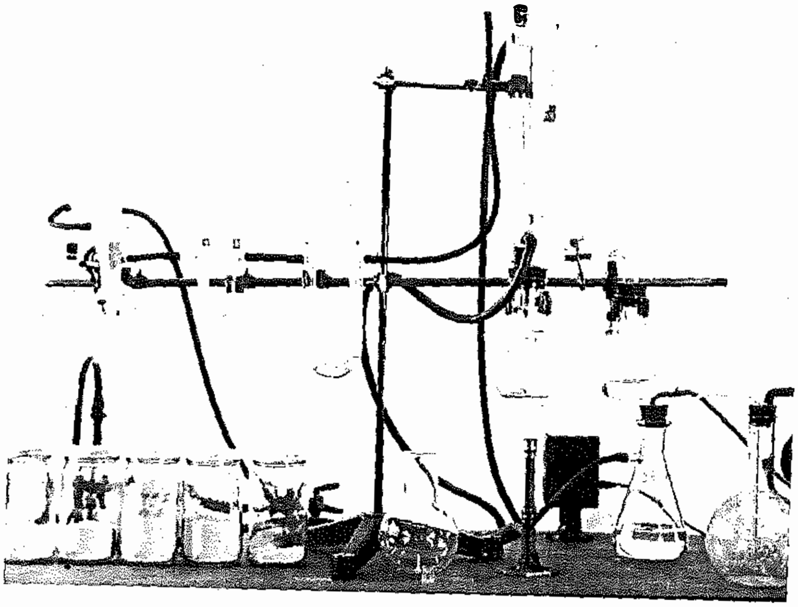
A second method which might be followed is to use an oscillating center loaded powder wedge specimen holder which permits the use of organic polyoxides in difficult expanding lattice type determinations. The small Debye Camera is used with a specially adapted type eccentric. This equipment, however, is not available at present.

In the process that was followed, the X-ray tube was evacuated to the point where only a few molecules of air were retained to carry the electronic charges across the intervening area from anode to cathode. The cooling system was started prior to this and kept the tube sufficiently cool. Now slowly a charge was built up to the point where an intensity of 10 mm. amps was observed and the "hardening" process started. When a voltage of 60,000 volts and an intensity of 10 mm. amps was obtained, a NiO filter was used to test the intensity of X-rays by removing a lead shield from a "window".

When this was observed to be sufficiently intense, the "hardening" process was finished and the tube was spoken of as "hardened". The small Debye Camera was now lined up so the X-rays struck the sample and the motor that revolves the sample was started. The sample was exposed a minimum of two hours and the negative was then developed. A series of lines were present on the film, the pattern of these lines indicated minerals present in the material tested. (See page 57 for Possibility of Error and Conclusion).

Chemical Analyses

Another endeavor to ascertain the type of impurity and perhaps the most obvious one is Quantitative Chemical Analysis. Much of this is still in the stage of speculation, but a few preliminary tests of a general nature have been completed. These



The Apparatus Used for Carbon Dioxide Determination were largely routine determinations, the efficacy of which is still to be determined. Possibly the methods of differentiating specimens for analysis are more important than the analytical techniques themselves, and it is with regard to those possibilities that the following comments are given.

There is no standard chemical procedure which can be outlined as being applicable to all situations. Of all the possible determinations which can be made, certain ones can be considered insignificant and irrevelant depending upon the purpose of the analysis and the conclusions which are expected to be withdrawn from the information gained by the analysis.

The first general rule in almost any analytical work is the understanding of the necessity of duplicate analyses of all samples. This precaution serves to add proof to results and also verifies to a great extent the procedure from beginning to end. Once a method has been adopted, it should be strictly enforced until the study has been completed because many conclusions are drawn from the comparative study of results.

As an introduction to the study of limestone, it is necessary to understand that limestone is composed essentially of calcium carbonate and almost an innumerable variety of other minerals, all of which may appear in variable proportions.

It would be desirable to know the exact nature of all the minerals present; however, due to the complexity of the mineralogical and geological formations, a separate study of this kind is beyond the scope of ordinary chemical analysis. This is mentioned as a point of interest to show the scope of an ordinary chemical analysis. To illustrate this point further: a determination of Calcium Carbonate does not show whether it exists inside or outside of chert particles. A separate analysis of the chert particles would be necessary to prove the difference. The existence of phosphorous in the insoluble residue requires the separate analysis of the insoluble residue.

In view of this complexity, it is a customary procedure to analyze a sample as a whole, reporting the result of each determination as the total percentage of the material present. It is not intended to discredit the advantages of an analysis on this basis, but it is merely intended to show that where more exact information is desired, it is necessary to isolate the material in question so that it may be separately analyzed. (See page 60 for Possibility of Error and Conclusion).

(For detailed technique, see Appendix 2
on page 58)

RESULTS

Four quarries were selected tentatively representing four distinct classifications: Excellent, Good, Fair, and Poor. This differentiation was based entirely upon performance records applicable to pavements in which aggregate from the different sources were used. Naturally, the rating at best must be general in view of the fact that no distinction with regard to different strata or zones in the quarries could be made. However, the source rated "poor" has proven to be of pronounced low quality insofar as pavement service is concerned; likewise, tests on concrete poured on the Louisville-Cincinnati road - Project SN-FA 194 E(3), F(3), L(2) - definitely indicate that aggregate from this source was of superior quality. Otherwise, the rating is largely a matter of interpretation based on visual ratings of pavements that could be influenced by many variables. The quarries, together with geologic ages and ratings, are as follows:

Quarry No. One - Ordovician - Lexington - Fair
Quarry No. Two - Mississippian - Mt. Vernon - Good
Quarry No. Three - Mississippian - Olive Hill - Poor
Quarry No. Four - Silurian (Avoca / Prospect) - Excellent

The first study of these quarries is not final but is shown in as much detail as is thought necessary for a beginning. Future tests intended on these quarries will be discussed later.

Quarry No. One
Source No. F1-1L-Q

Quarry No. One, sampled on April 18, 1946, is an open pit type of limestone quarry, used for construction and agricultural purposes. It has been abandoned in favor of a better source and all but about five feet of the lower geologic formation is covered by water now. Lately, the quarry has been reopened after seven inactive years. This source may be roughly classified as "Fair" for highway construction.

The quarry is composed of the uppermost six feet of the Jessamine limestone, and the lowermost forty feet of the Benson limestone, both members of the Lexington limestone series. By lithology one formation is undifferentiated from the other, but by paleontology the division may be made. A zone of residual chert may be found in the weathered Benson, conspicuous at three levels.

The lithology may be roughly classified as follows: Massive, weathering lenticular, dark gray weathering buff, medium grained, irregular fracture, finely crystalline, bedding faintly irregular and derived from shale streaks. The bedding is horizontal, non-rhythmic thickness. There are no discernible concretions but a geode is rarely found. The contact is conformable and no deformation is indicated. The porosity is evidently primary, as no especial recrystallization or jointing features were encountered. All changes are interpreted as having occurred post depositional and prior to lithification. The limestone is argillaceous in the usual sense of the word with varying amounts of silicious matter present in the form of quartz and chert, the chert rarely replacing fossils. The faunal content has a distinct tendency to be horizontal in arrangement and evidence of its being contemporaneous with bedding phenomena is positive. This again is taken to be primary.

The quarry was sampled from water level to the point at which the stripping operation commenced, a total of thirty-one feet occurring here. All shale was omitted and care taken to get a "fresh" sample in every case.

Table No. One

Bulk Specific Gravity and Percentage Insoluble Residue of Individual Samples From Quarry One

Geologic Formation	Zone Number	Elevation	Bulk Specific Gravity	Insoluble Residue	Zone Average
Benson	5	30 Ft.	2.67	6.0%	I.R. 6.5% S.G. 2.68
		29 "	2.69	3.5%	
		28 "	2.70	6.5%	
		27 "	2.70	6.5%	
		26 "	2.70	5.5%	
		25 "	2.65	8.5%	
Benson	4	24 "	2.68	2.5%	I.R. 3.9% S.G. 2.68
		23 "	2.69	4.5%	
		22 "	2.69	6.5%	
		21 "	2.67	2.5%	
		20 "	2.70	2.5%	
		19 "	2.65	5.0%	
Benson	3	18 "	2.68	6.0%	I.R. 4.2% S.G. 2.69
		17 "	2.69	6.5%	
		16 "	2.71	4.0%	
		15 "	2.69	3.5%	
		14 "	2.69	4.5%	
		13 "	2.69	2.0%	
		12 "	2.69	2.5%	
		11 "	2.72	5.0%	
Benson	2	10 "	2.70	4.0%	I.R. 2.83% S.G. 2.70
		9 "	2.67	3.0%	
		8 "	2.67	1.0%	
		7 "	2.74	1.0%	
		6 "	2.71	3.0%	
Jessamine	1	5 "	2.71	8.0%	I.R. 9.0% S.G. 2.68
		4 "	2.67	10.0%	
		3 "	2.67	10.0%	
		2 "	2.66	6.5%	
		1 "	2.66	8.5%	
		0 "	2.69	10.5%	

Quarry Average - Insoluble Residue 5.145%
Specific Gravity 2.687

Lab. No. 14

Dept. of Highways Div. of Tests

QUARRY NO. 1

County **FAYETTE** Prop. Owner CENTRAL ROCK CO. Operator SAME

Location AT LEXINGTON CITY LIMITS, ON SOUTH SIDE OF OLD FRANKFORT PIKE.

Sampled by STOKLEY AND YOUNG

Date Sampled 2-13-39
Date Received 2-14-39
Date Reported 4-14-39

PHYSICAL TESTS					PASSED FOR		LAB. NO.	LEDGE		QUARRY LOG
Specific Gravity	Soundness	% LA Wear	Deval	Absorption %				No.	Thickness	
					Stripping				12'	Brown soil and bouldery limestone.
2.70	9.3	34.7			All Uses	Not exposed in present operation	64066	1A	2½'	Fine grain powdery blue gray limestone.
2.68	5.3	26.8	3.4		" "		64067	1B	6'	Fine to medium grain brown flakey limestone, containing much included shale. Irregularly bedded.
2.71	7.2	30.3	6.8		" "		64068	2	2½'	Coarse grain crystallineto flakey dark gray limestone. 3 Beds with 2" shale seams between.
2.65	6.0	43.5	8.0		Failed for all uses		64069	3	3½'	Coarse grain crystalline yellow brown limestone. Thin beds with thin shale seams between beds.
2.70	7.2	29.9	5.6		All Uses		64070	4	5'	Medium to coarse grain black crystalline limestone Thin even beds with thin shale seams between.
2.66	8.0	31.9	4.5		" "	Zone 5	64071	5	7'	Coarse grain flakey dark blue gray limestone. Beds 6" to 1' with 1" to 3" shale seams between beds.
2.70	2.4	35.0	5.7		" "	Zone 4 Zone 3 Zone 2	64072	6	18'	Coarse grain flakey blue gray to brown gray fossiliferous ls. Massive bed. Contains small amounts of included shale.
2.71	9.6	29.1	5.4		" "	Zone 1	64073	7	4½'	Coarse grain flakey fossiliferous brown to brownish gray limestone. Contains some included shale.

Water Level

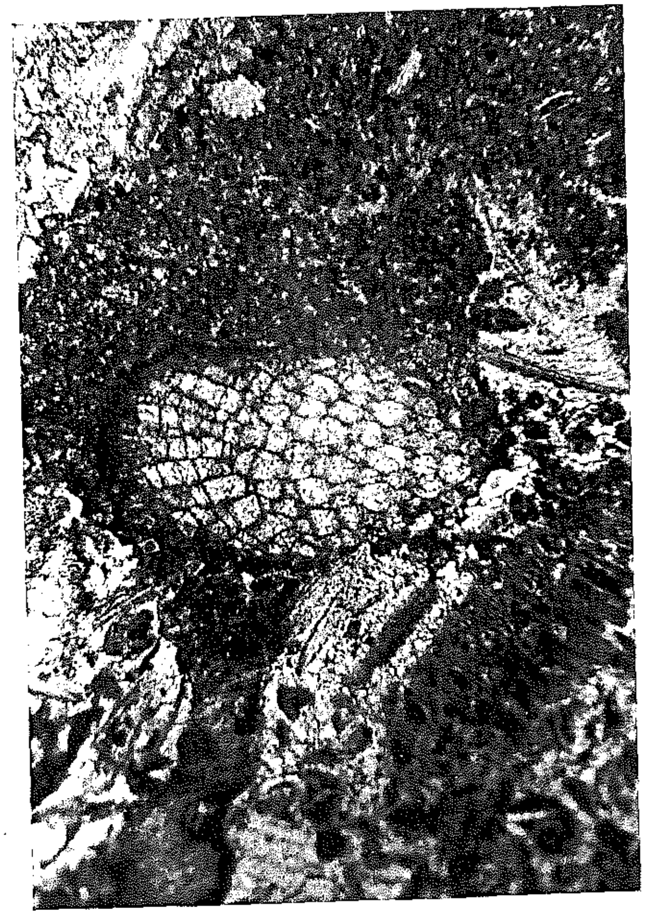
Copy to: CANTRILL

Remarks: Stone from this quarry should be checked ~~very~~ closely for shale content.

Zone I - This zone comprises six feet of the top of the Jessamine limestone. It averages 9% insoluble residue, the highest average reached in this quarry, and is quite impure in appearance. It averages 2.68 Specific Gravity. At the very top of the Jessamine, the appearance of a black glassy mineral is peculiar. It is thought to be obsidian.

Zone II - This zone is deliniated from Zone I by a faunal break which distinguishes the Jessamine from the Benson formation. The zone averages 2.83% insoluble residue and 2.70 Specific Gravity. It is a fairly impermeable zone showing gypsum constantly throughout. This is the lowermost Benson limestone of the Lexington series.

Zone III - This zone is marked by an increase in the size of crystals, whereas, there is an increase in the size of calcite crystals and a marked tendency for shale to appear more often. Gypsum, although not a good criterion, is more abundant and the whole indicates a higher initial porosity than its neighboring zones. The zone averages 4.2% insoluble residue and 2.69 Specific Gravity. A photomicrograph is here submitted as being fairly typical of the whole quarry.



This is a photograph of a thin section X 30. In the center of the field, you will see a bryzoa or fossil. The lines traversing it are old walls for the individual animals' living chambers. Surrounding this fossil you will see a concentrated ring of organic matter outside of which is impure limestone. Veins of crystalline calcite, another fossil and some small individual calcite crystals are also visible.

Zone IV - This zone, assigned arbitrarily by a slight change in size of crystallization, proved to be highly silicious and high in $MgCO_3$. With reference to the Al_2O_3, it should contain the largest amount of clay minerals. It includes six feet at the top of the eighteen foot ledge in basal Benson. Insoluble Residue average is 3.9% and Specific Gravity is 2.68.

Zone V - This zone includes six feet of the seven foot ledge directly overlying the eighteen foot ledge. Over this ledge the stripping operations begin in the present operation and the top one foot was omitted due to any weathering effects that might occur. At this point a drop in Specific Gravity was encountered indicating higher permeability. This followed in several divisions, and so indicated a change in sedimentation conditions, possibly the completion of a periodic cycle. The zone averages 6.5% insoluble residue and 2.68 Specific Gravity.

TABLE II

REPORT OF CHEMICAL ANALYSIS OF SAMPLES FROM QUARRY NO. 1

Zone No.		1	2	3	4	5
Elevations (ft)		0-5	6-11	12-18	19-24	25-30
Geologic Formation		Jessamine	Benson	Benson	Benson	Benson
Constituent Compounds (Pctg. by Weight)	SiO_2	3.51	3.78	2.15	3.95	2.26
	Fe_2O_3	.75	.84	.61	.83	.53
	Al_2O_3	1.76	1.69	1.46	2.32	1.53
	$Ca_3(PO_4)_2$	.93	2.55	2.61	2.81	2.93
	$CaCO_3$	86.10	82.60	85.80	82.00	87.40
	$MgCO_3$	6.94	8.51	7.28	8.00	5.29
Totals		99.99	99.97	99.91	99.91	99.94

It will be noted that there is a gradual increase in the percentage of $Ca_3(PO_4)_2$ from zone No. 1 through zone No. 5. Zone No. 1 indicates that the Jessamine limestone may contain considerably less $Ca_3(PO_4)_2$ than the Benson series. Phosphorous in the insoluble residue and soluble phosphorous were determined separately. Both are reported as $Ca_3(PO_4)_2$, but there is a possibility that that held in the residue exists as apatite $(Ca_5F(PO_4)_3)$.

	(1)	(2)	(3)	(4)	(5)
Soluble	.66%	1.87%	2.11%	2.01%	2.48%
Residue	.27%	.68%	.50%	.80%	.45%

Quarry No. Two
Source No. R2-1L-Q

This quarry, sampled May 16, 1946, is an open pit type, composed of the Ste. Genevieve limestone and its members overlain by the Gasper member of the Chester Series, both of Mississippian age. Both of these formations plus the St. Louis and perhaps Golconda are grouped under the general term "Big Lime". The St. Louis which Butts recognized in this quarry was not recognized by the author. The possibility of the Golconda formation's presence was ignored as its occurrence would be out of the area of quarrying. A description of this quarry as given by Charles Butts in his "Mississippian series of Eastern Kentucky" is as follows.

19. Top of hill. Slabs of yellow limestone with "Archimedes". This yellow limestone in the town of Mt. Vernon carries also "Agassizocrinus" and "Pentremites". May be Golconda?

Gasper Oolite:

19. Not exposed - 10 Ft.
18. Limestone, blue, crystalline. Large crinoid stems twenty feet below top. "Composita subquadrata" in bottom. - - - - - - - - - - - - - - - 43 Ft.
17. Limestone, compact, yellow in two layers - - - - 5 Ft.
16. Oolite, blue, "Agassizocrinus","Girtyella", "Composita" - 2 Ft.
15. Oolitte, blue, compact, blended - - - - - - - - - - 2 Ft.
14. Limestone, compact, brittle, blue, weathers yellow - $1\frac{1}{2}$Ft.
13. Limestone, shelly, and shale, green, 6 inches to - 1 Ft.
12. Oolite, coarse, white, "Pentremites pyriformis", "Talarucrinus", equivalent to "Bowling Green" quarry rock - 17 Ft.

$81\frac{1}{2}$ Ft.

Ste. Genevieve Limestone:

Ohara (?) limestone member of Ste. Genevieve Limestone.

11. Limestone, light blue, brittle, Top 2 ft. seamed with calcite veins, appears brecciated, top 6 in. conglomerate in yellow matrix. Hummocky top surface with depressions occupied with green shale - 5 Ft.
10. Limestone, coarse, light gray, slightly oolitic - 5 Ft.
9. Oolite, dark or drab - - - - - - - - - - - - - - - - - 4 Ft.

Total Ohara (?) about - - 14 Ft.

8. Cobbles and shale - - - - - - - - - - - - - - - - - - $\frac{1}{2}$
7. Limestone, compact, brittle, pearl gray - - - - 9
6. Oolite, bluish gray, weathers white - - - - - - - 9-3/4
5. Oolite, coarse, cross bedded, white - - - - - - - $8\frac{1}{2}$
4. Limestone, dark, drabbish gray, thin layered or flaggy - 3-1/3

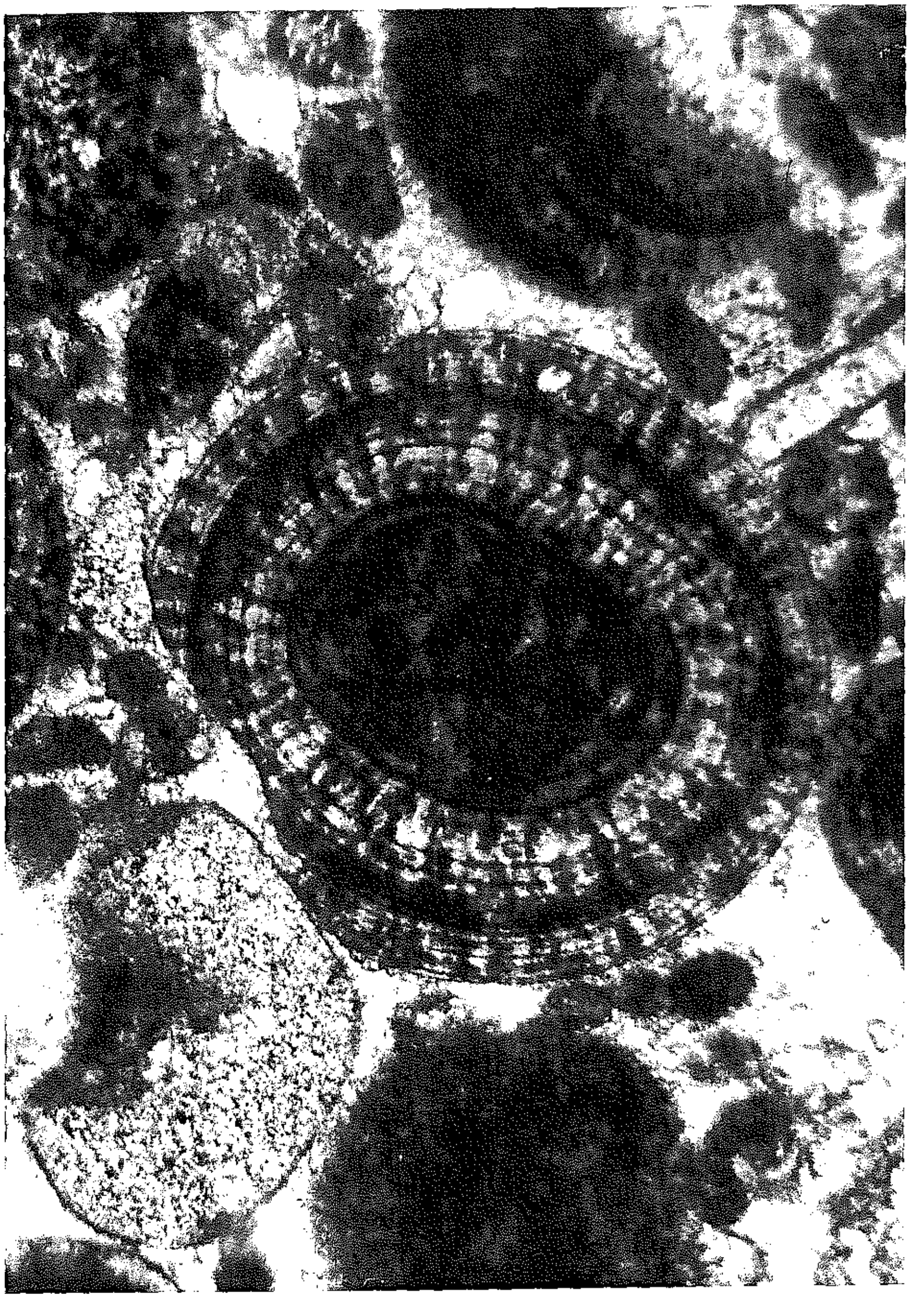
3. Oolite, compact, white, some chalky texture, "Platycrinus penicillus" in this bed at Dick Owens cut, 1 mile farther west	5 Ft.
2. Limestone, compact, brittle, pearl gray, evenly bedded flags	4
Oolite, thick bedded, drab gray	5
Oolite, drab gray with angular fragments of black chert	2½
Total Ste. Genevieve limestone below Ohara (?) member	47-7/12
St. Louis limestone:	
1. Limestone, dark or drab, hummocky, suncracked surface, black chert nodules, exposed	1
Total quarry	144-1/12

It is well to call to mind that the beds herein pinch and swell to a marked degree, so that a description of the rock from year to year will not tally in thickness and some variations in lithology may be observed.

I sampled from the quarry floor to the point at which stripping operations commenced, a total of 135 feet. No general description can be given other than the fact that variations in lithology and faunal content occur every few feet. Detailed descriptions will be given by zones.

An explanation of oolites might be pertinent, however. Oolites are small spherical growths of calcite around a nuclei. The nuclei can range from a small shell to fish eggs or a mineral fragment. Gas bubbles have been suggested. The internal structure of an oolite is concentrically laminated. Oolites are present in the geologic column from Pre-Cambrian to the present. Maximum dimensions may be placed at 2 mm. Particles larger than 2 mm. with the same shape and internal structure are termed pisolites. A photograph is here submitted to show oolitic structure. (See following page for photograph).

The radial structure of these spherical structures will be noted. Cementing material is calcite. Impurities are present both in the oolites and in the cementing material.



Photomicrograph of Oolites

TABLE NO. III

Bulk Specific Gravity and Percentage Insoluble Residue of Individual Samples from Quarry No. Two

Geologic Formation	Zone Number	Elevation	Bulk Sp. Gr.	Insoluble Residue	Zone Ave.
Ste. Genevieve	7	34	Shale parting		I.R. 6.7% Sp.G. 2.69
		33	2.71	17.5	
		32	2.70	3.5	
		31	2.68	2.5	
		30	2.68	3.5	
Ste. Genevieve	6	29	2.70	6.5	I.R. 3.3% Sp.G. 2.64
		28	2.68	2.5	
		27	2.62	4.0	
		26	2.61	3.0	
		25	2.61	1.5	
		24	2.63	3.0	
		23	2.65	3.0	
Ste. Genevieve	5	22	2.69	8.0	I.R. 6.5% Sp.G. 2.68
		21	2.69	4.0	
		20	2.69	6.5	
		19	2.68	7.0	
		18	2.68	8.0	
		17	2.69	6.0	
Ste. Genevieve	4	16	2.54	3.0	I.R. 1.2% Sp.G. 2.53
		15	2.43	1.0	
		14	2.43	1.0	
		13	2.43	1.0	
		12	2.52	0.5	
		11	2.62	1.0	
		10	2.70	1.0	
Ste. Genevieve	3	9	2.70	2.0	I.R. 1.8% Sp.G. 2.70
		8	2.70	0.5	
		7	2.70	2.5	
Ste. Genevieve	2	6	2.70	3.5	I.R. 4.9% Sp.G. 2.69
		5	2.70	4.5	
		4	2.70	7.5	
		3	2.69	5.0	
		2	2.69	4.0	
Ste. Genevieve	1	1 ft.	2.69	1.5	I.R. 1.5% Sp.G. 2.69

TABLE NO. III (Con't)

Geologic Formation	Zone Number	Ele-vation	Bulk Sp.Gr.	Insoluble Residue	Zone Ave.
Gasper	15	86	2.67	10.0	I.R. 9.6% Sp.G. 2.65
		85	2.65	12.0	
		82	2.64	10.5	
		83	2.66	6.0	
Gasper	14	82	2.67	3.0	I.R. 2.3% Sp.G. 2.55
		81	2.62	2.5	
		80	2.61	3.0	
		79	2.31	1.0	
Gasper	13	78	2.56	0.5	I.R. 1.6% Sp.G. 2.48
		77	2.49	1.0	
		76	2.36	2.0	
		75	2.42	1.0	
		74	2.45	2.5	
		73	(covered)	(covered)	
		72	2.59	4.0	
		71	2.58	2.0	
		70	2.57	2.0	
		69	2.58	2.0	
		68	2.58	1.5	
		67	2.59	1.0	
		66	2.59	1.0	
		65	2.58	1.0	
		64	2.66	2.0	
Ohara	12	63	2.68	4.0	I.R. 4.5% Sp.G. 2.65
		62	2.62	8.5	
		61	2.67	1.0	
Ohara	11	60	2.67	5.0	I.R. 4.3% Sp.G. 2.70
		59	2.69	2.5	
		58	2.72	6.5	
		57	2.72	2.5	
		56	2.70	5.0	
		55	2.72	4.5	
Ohara	10	54	2.67	2.5	I.R. 2.70% Sp.G. 2.68
		53	2.68	2.5	
		52	2.67	2.5	
		51	2.72	2.0	
Ohara	9	50	2.72	8.0	I.R. 7.5% Sp.G. 2.70
		49	2.70	7.5	
		48	2.71	5.5	
		47	2.66	10.0	
		46	2.73	6.5	
Ste. Genevieve	8	45	2.70	5.5	I.R. 4.1% Sp.G. 2.70
		44	2.73	3.5	
		43	2.73	5.0	
		42	2.71	3.0	
		41	2.71	3.0	
		40	2.70	2.5	
		39	2.72	3.5	
		38	2.70	3.0	
		37	2.69	4.5	
		36	2.70	5.5	
		35	2.69	6.5	

TABLE NO. III (Con't)

Geologic Formation	Zone Number	Elevation	Bulk Sp. Gr.	Insoluble Residue	Zone Ave.
		Stripping			
Gasper	24	135	2.66	5.5	I.R. 5.5% Sp.G. 2.66
Gasper	23	134	2.69	4.0	I.R. 4.0% Sp.G. 2.69
Gasper	22	133	2.62	7.0	I.R. 4.1% Sp.G. 2.66
		132	(Covered)	(Covered	
		131	2.65	6.0	
		130	2.68	5.5	
		129	2.69	2.0	
		128	2.66	4.0	
		127	2.69	3.0	
		126	2.69	5.0	
		125	2.69	2.5	
		124	2.62	2.5	
Gasper	21	123	2.57	3.0	I.R. 3.2% Sp.G. 2.60
		122	2.48	4.0	
		121	2.65	2.5	
		120	2.65	3.5	
		119	2.69	3.0	
		118	2.64	10.0	
		117	2.61	2.0	
		116	2.57	1.5	
		115	2.68	2.5	
		114	2.55	1.5	
		113	2.55	2.5	
Gasper	20	112	2.68	5.5	I.R. 2.8% Sp.G. 2.69
		111	(Covered)	(Covered	
		110	2.69	3.0	
		109	2.63	1.0	
		108	2.56	2.0	
Gasper	19	107	2.62	1.5	I.R. 2.6% Sp.G. 2.59
		106	2.56	3.5	
		105	2.53	3.5	
		104	2.65	2.0	
Gasper	18	103	2.69	2.5	I.R. 3.4% Sp.G. 2.69
		102	2.69	3.0	
		101	2.69	5.0	
Gasper	17	100	2.69	3.0	I.R. 3.2% Sp.G. 2.66
		99	2.66	3.5	
		98	2.64	3.5	
		97	2.67	3.0	
Gasper	16	96	2.64	8.0	I.R. 5.4% Sp.G. 2.64
		95	2.67	7.0	
		94	2.63	4.5	
		93	2.65	3.5	
		92	2.70	5.0	
		91	2.64	4.5	
		90	2.65	7.0	
		89	2.61	3.5	
		88	2.55	3.0	
		87	2.66	5.5	

Lab. No. 14

Dept. of Highways Div. of Tests Page 1 QUARRY NO. 2 State of Kentucky

County ROCKCASTLE Prop. Owner KY. STONE CO. (MT. VERNON) Operator KY. STONE CO. Date Sampled 3-26-41

Location 1 Mi. from MT. VERNON ON CRAB ORCHARD ROAD Date Received 3-27-41

Sampled by JOHN STOKLEY AND WALKER SHEARER Date Reported 4- 9-41

PHYSICAL TESTS					PASSED FOR	Lab. No.	LEDGE		QUARRY LOG
Specific Gravity	Sound-ness	% LA Wear	Deval	Absorp-tion			No.	Thick-ness	
					← Stripping →		3' to 5'		Red Brown Soil
2.71	2.5	27.4			PASSED FOR ALL USES	76577	1	0' to 14'	Boulders of coarse grain gray white oolitic limestone with mud and soft stone.
						WASTE		1'	Green Shale
2.69	2.0	23.9			" "	76578	2	10'	Coarse grain brownish-gray fossiliferous oolitic limestone. 1 Bed. Weathers rusty white.
						WASTE		8"	Shale and shaly limestone.
2.70	2.9	22.6			" "	76579	3	8'	Coarse grain brownish-gray oolitic limestone. Beds 3.5' and 4.5' thick. Weathers rusty white.
2.61	4.1	29.6			" "	76580	4	5'	Coarse grain gray oolitic limestone. 1 Bed. Weathers light.
2.69	1.2	25.7			" "	76581	5	5.5'	Medium grain grayish brown limestone. Beds 4" to 6" with shale partings.
2.69	3.0	31.0			" "	76582	6	3'	Medium grain brown-gray oolitic limestone. 1 Bed.
2.69	0.8	25.6			" "	76583	7	2'	Fine grain smooth brown limestone. Flecked with calcite crystals.
2.67	1.0	23.3			" "	76584	8	2'	Fine grain gray limestone. Conchoidal fracture. Weathers yellow.
2.69	1.4	20.3			" "	76585	9	4'	Fine to medium grain gray limestone. Weathers yellow.
2.69	0.9	28.3			" "	76586	10	2.5'	Fine grain gray limestone. Weathers yellow-gray.
2.65	3.2	24.4			" "	76587	11	2.5'	Medium grain gray oolitic limestone.
2.55	37.2	49.0			FAILED FOR ALL USES	76588	12	14'	Coarse grain white oolitic limestone, weathers rusty white. One massive 14' bed in most of quarry.
2.66	11.3	36.6			BASE COURSE AND CONCRETE ONLY.	89231	12A		4' coarse grain gray white oolitic limestone. Slightly crystalline. Present only in N.W. Section of quarry.

Lab. No. 14

Dept. of Highways Div. of Tests   Page 2   QUARRY NO. 2   State of Kentucky

County ROCKCASTLE   Prop. Owner KY. STONE CO. (MT. VERNON)   Operator KY. STONE CO.   Date Sampled 3-26-41

Location 1 Mi. from MT. VERNON ON CRAB ORCHARD ROAD   Date Received 3-27-41

Sampled by JOHN STOKLEY AND WALKER SHEARER   Date Reported 4-9-41

PHYSICAL TESTS					PASSED FOR	Lab. No.	LEDGE		QUARRY LOG
Specific Gravity	Soundness	% LA Wear	Deval	Absorption			No.	Thickness	
						WASTE		6"	Shale Seam.
2.70	0.8	22.6			PASSED FOR ALL USES	76589	13	8'	Fine grain smooth limestone. Brown at top and becomes gray toward bottom. Weathers white.
2.69	1.5	26.1			" "	76590	14	14'	Medium to coarse grain dark gray crystalline limestone. Bedding indistinct. Weathers light.
2.69	1.0	26.8			" "	76591	15	4'	Medium grain dark gray limestone. Fine in places. Weathers dark.
2.68	1.9	33.6			" "	76592	16	3'	Fine grain smooth brown limestone.
2.68	1.8	27.6			" "	76593	17	5'	Fine grain light brown limestone. 1" shale seam. - - -
2.69	4.0	31.0			" "	76594	18	5'	Medium grain porous gray oolitic limestone. 1" shale seam. - - -
2.52	21.1	36.4			FAILED FOR ALL USES	76595	19	4' to 5'	Medium grain gray oolitic limestone. Coarser and porous near center of ledge. 1/2" shale seam. - - - -
2.66	6.2	31.6			PASSED FOR ALL USES	76596	20	3'	Fine to medium grain tan-gray limestone. Finer toward top, medium at bottom.
2.71	1.3	36.4			BASE COURSE & CONCRETE ONLY	76597	21	8'	Coarse grain dark gray granular limestone. Has a greenish cast.
						WASTE		3" to 5"	Shaly material sticking to top of ledge.
2.62	24.9	22.2			FAILED FOR ALL USES	76598	22	2.5'	Fine grain dark gray to brown siliceous limestone. Contained much chert & flint.
2.67	8.7	27.0			PASSED FOR ALL USES	76599	23	2.5'	Fine grain tan-gray limestone. Darker at bottom. Straight flat fracture.
						WASTE		2"	Green Shale.
2.68	1.2	27.6			" "	76600	24	2.5'	Medium to coarse grain gray flaky crystalline limestone. Slightly oolitic.
2.60	6.3	41.6			FAILED FOR ALL USES	76601	25	2'	Coarse grain very porous chalky oolitic limestone. Flaky in places.

Remarks: Crushed stone from this quarry must be checked carefully for shale and soft stone.

Zone I - This zone represents a vertical distance of one foot. A well cemented oolite, which fractures across the oolites, occurs here. It averages 2.69 Specific Gravity and 1.5% insoluble residue. It is a very pure looking oolite and its appearance suggests that it should be a good aggregate.

Zone II - This represents a second oolite, much more argillaceous and poorly cemented than that of Zone I. The impurities are mainly quartz ranging up to 85% of the insoluble residue. The zone represents five feet of limestone, from two feet up to the seven foot level. It averages 2.69 Specific Gravity and 4.9% insoluble residue. It is characterized by its chalky appearance and black flint nodules. There seems to be a fine balance between chemical and mechanical deposition. It fractures easily around the oolites.

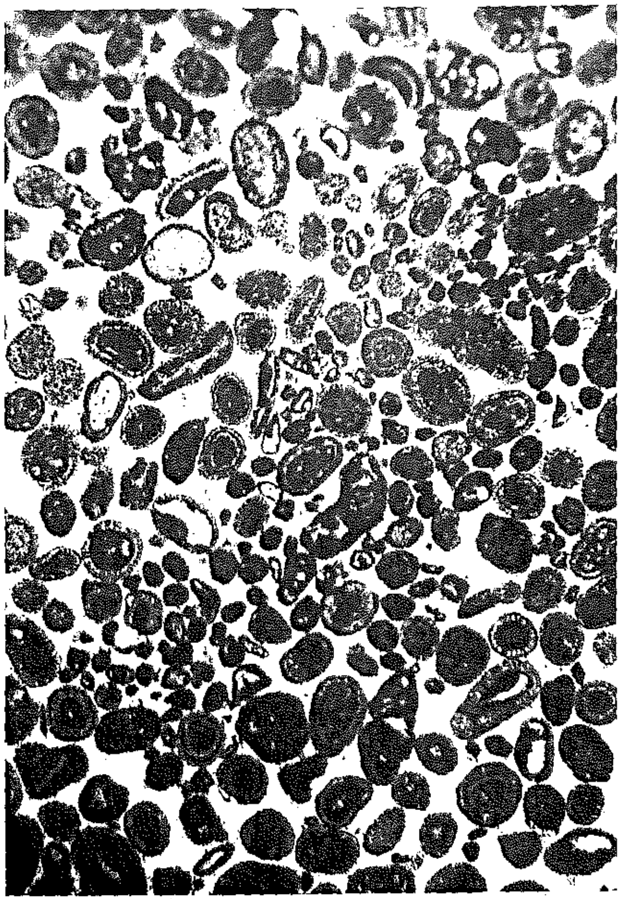
Zone III - This zone is composed of three feet of light greenish gray, fine grained non-fossiliferous limestone, an abrupt change from the oolite. A thin section reveals that the transition was fairly abrupt, the apparent change being one of speeding up of chemical deposition. The zone averages 2.70 Specific Gravity and 1.8% insoluble residue.

Zone IV - This zone marks the return of oolitic limestone, impermeable at first due to compaction during lithification, no doubt; but steadily becoming more permeable. This zone includes seven feet of limestone averaging 2.53 Specific Gravity and 1.2% insoluble residue. The entire zone appears quite porous and friable. A photomicrograph is submitted to show the arrangement of oolites and quartz particles. Some quartz particles are coated and look like oolites. Look for the concentric laminations to establish the identity of an oolite. (See following page for photomicrograph).

Zone V - This zone is made up of impermeable, fine grained well lithified and compacted limestone. It appears to be quite high in clay content, averaging 2.68 Specific Gravity and 6.5% insoluble residue. The fine grained character ranges to a medium grained character as the zone of sedimentation is depleted.

Zone VI - This zone becomes lighter colored, purer and more permeable. In spots, oolites and spherulites appear, gypsum becomes more abundant. Iron stains are found with regularity and a chrome yellow stain is peculiar. A general over-all finer grained appearance is observed. This zone comprises seven feet averaging 2.54 Specific Gravity and 3.3% insoluble residue.

Zone VII - This zone is comprised of four feet of impermeable oolite as opposed to two surrounding non-oolitic limestones, averaging 2.69 Specific Gravity and 6.7% insoluble residue, an unfair average as the last foot has 17.5% insoluble residue. This is the result of a gradual transition of the oolite into shale.

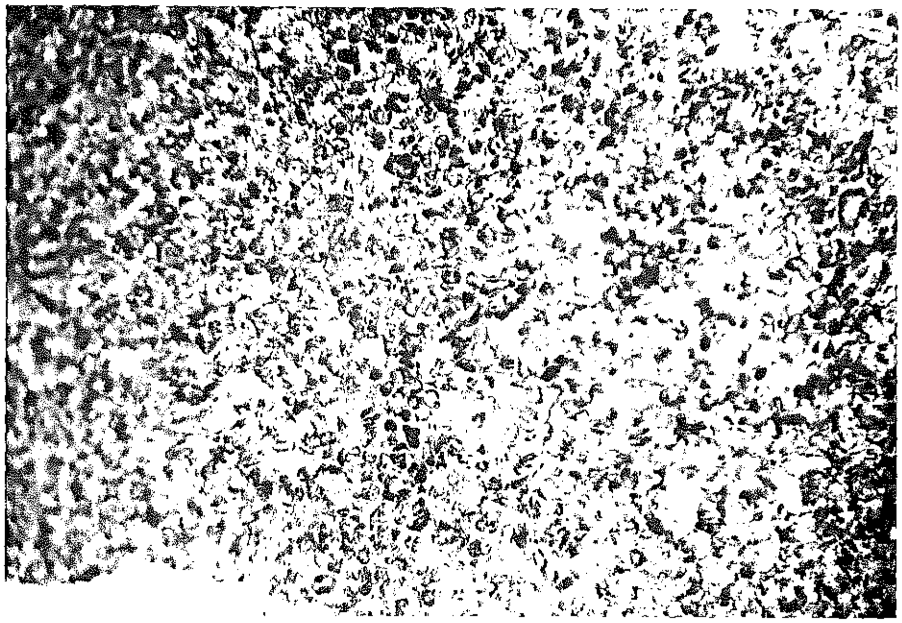


Photomicrograph illustrating Zone IV

Zone VIII - This zone comprises eleven feet of dove gray, fine grained, impermeable non-fossiliferous limestone and ranges in the same general character up to the last five feet where pockets of crystalline calcite occur with a distinctive frequency throughout the rock, such as is observed in a "birds-eye limestone". It averages 4.1% insoluble residue and 2.70 Specific Gravity. A photomicrograph is submitted to show the frequency with which these scattered pockets of calcite occur. This is not an accepted photograph for filing, but is submitted here for illustration.

Zone IX - This zone marks the introduction of the Chara limestone member of the Ste. Genevieve formation. The zone is composed of five feet of impermeable, fine grained, non-fossiliferous, partly oolitic limestone ranging to a good oolitic limestone at the close of the zone. It is very impure looking, highly organic and silicious. Medium fine quartz sand is the predominant impurity. It averages 2.70 Specific Gravity and 7.5% insoluble residue.

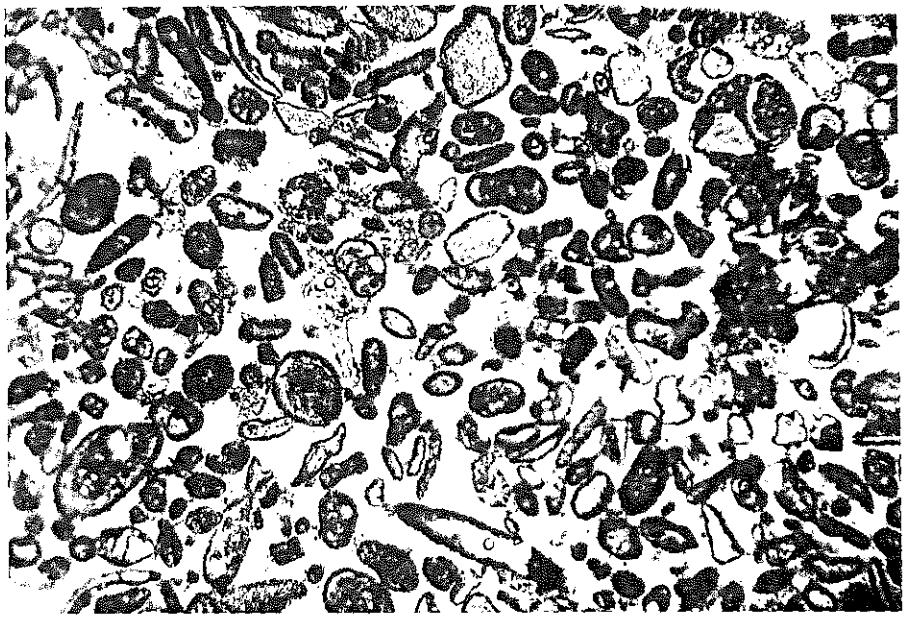
Zone X - This zone includes four feet of very pure looking dense limestone with a few fine oolites present. The impurities have changed in ratio, the fine quartz is now definitely in a minor percentage. Clay, organic matter and muscovite mica are the predominanting impurities. The limestone is more permeable than the preceding zone but is still impermeable by our standards. The fine grained character persists with the tendency to rounded particles shown by the accompanying photomicrograph.



Zone XI - This zone is made up of six feet, very similar, in color and texture, to Zone X. The impurities have changed again and oolites occupy small areas in an otherwise dense limestone. Quartz has again become prominent, occurring in angular and rounded fragments. Iron stains are common throughout the entire zone. At 59 ft. the presence of coal is unique. The appearance of coarse rounded quartz grains points to the nearness of an ancient shore-line and may be correlated with the quartz appearing in Quarry No. Three. It averages 2.70 Specific Gravity and 4.3% insoluble residue.

Zone XII - This zone is composed of three feet of light gray, dense, near lithographic limestone, which is characterized by the veins and pockets of crystalline calcite. At the center of this zone, a partly permeable silicious layer is encountered. The impurities are high in organic matter and the unique feature that is common to all this zone is the presence of "balled-up" quartz particles. It averages 2.65 Specific Gravity and 4.5% insoluble residue.

Zone XIII - This zone marks the beginning of the Gasper "oolite" which is the top geologic member of this quarry. It is composed of fifteen feet of very pure oolitic limestone corresponding to the "Bowling Green Quarry Rock". It is uniformly permeable for the first nine feet at which point it fluctuates to very permeable at the completion of sedimentation. The limestone is characteristic in appearance, being white, chalky looking and highly friable. The zone averages 2.48 Specific Gravity and 1.6% insoluble residue. A photomicrograph is attached to show the pureness of the matrix in this oolite.



Zone XIV - This zone is composed of four feet of brownish magnesium limestone. It is introduced by a very permeable layer. The limestone is irregular with organic streaks occurring haphazardly. Impurities are dominated by a very fine quartz sand. The entire zone is partly permeable. It averages 2.55 Specific Gravity and 2.3% insoluble residue.

Zone XV - This zone is composed of four feet of slightly permeable limestone. The arrangement is again irregular with very fine crystals of calcite dominating the field surrounded by impure matter. There is a sharp increase in the amount of residue with quartz still being the predominant member. It averages 2.65 Specific Gravity and 9.6% insoluble residue.

Zone XVI - This zone is composed of ten feet of variable limestone ranging from permeable to impermeable and from oolitic to non-oolitic. The zone is introduced by a partly permeable oolite and ranges to a fine-grained macro-crystalline non-oolitic limestone. Coarse, rounded quartz grains are common to the entire zone. The nuclei for oolites are predominately rounded and sub-rounded quartz grains. Likewise, quartz is the predominate member in the insoluble residue ranging up to 85% of the residue. Organic matter tends to be grouped in layers and pockets throughout the zone. The zone averages 2.64 Specific Gravity and 5.4% insoluble residue.

Zone XVII - This zone is composed of four feet of light greenish-gray, very oolitic limestone. Occasional pockets of crystalline calcite are common to the entire zone. The tenacity is good and the limestone fractures across the oolites. Organic matter is prominent and well distributed. Impurities are again mainly angular, rounded and sub-rounded quartz. It averages 2.66 Specific Gravity and 3.2% insoluble residue.

Zone XVIII - This zone is composed of three feet of highly fossiliferous, non-oolitic limestone. The fossils are macro size accompanied by algal growths. The zone is impermeable, highly friable with yellowish, angular fragments of magnesian looking limestone scattered through the samples. Organic matter is zoned. It averages 2.69 Specific Gravity and 3.4% insoluble residue.

Zone XIX - This zone is composed of four feet of permeable, vugular partially oolitic limestone. Structure is principally rounded quartz fragments in a crystalline calcite matrix. There is a slight trace of oil in this zone. Principal feature of the residue is rounded and sub-rounded milky quartz fragments. It averages 2.59 Specific Gravity and 2.6% insoluble residue.

Zone XX - This zone is composed of five feet of very highly organic, partly oolitic limestone. The structure is approximately the same as that of the previous zone with the limestone becoming less vugular. The residue is composed principally of clay and organic materials. It averages 2.69 Specific Gravity and 2.[illegible]% insoluble residue.

Zone XXI - This zone is composed of eleven feet of vugular, permeable, organic limestone. The structure is irregular, crystalline looking in spots. There are large, rounded and sub-rounded quartz fragments, coated occasionally with

Zone XXIV - This zone is composed of one foot of dark-greenish gray, irregularily colored, fossiliferous limestone. It is faintly permeable and has an impure calcite matrix surrounding angular chert fragments. The chert also replaces fossils. Organic matter gives the matrix a dark, slightly yellow cast. Its Specific Gravity is 2.66 and its insoluble residue is 5.5%.

Quarry No. Three
Source No. 06-1L-Q

This quarry is located in Carter County, about three-fourths of a mile east of Olive Hill, Kentucky. It is an open pit type quarry, composed of the Ste. Genevieve and its Ohara member overlain by the Gasper formation. The quarry was sampled August 9, 1946, by Bob Brown, Chemist, and the author, a total of 65 feet being quarried. Although this quarry is identical in geologic age with Quarry No. Two, some obvious changes have occurred between Rockcastle and Carter Counties. The Ste. Genevieve has thinned, become more and more argillaceous, and contains an abundance of quartz sand in varying sizes. Its Ohara member is about half as thick as it was in the Mt. Vernon quarry. The whole Ste. Genevieve, while retaining some of its features such as oolites, has done an abrupt change in lithology and argillaceous content. The Ste. Genevieve elsewhere averages 95% $CaCO_3$ and is used in the manufacture of lime, but is supposedly used for ballast and road metal at this source.

The Gasper oolite overlying the Ste. Genevieve has been reduced from 95 feet (Mt. Vernon) to 40 feet at this rouce. It, more than the Ste. Genevieve, has retained something of its character as at Mt. Vernon, being in the main a compact yellowish limestone.

This quarry has been rated as <u>poor</u> in our standards of classification. All contacts are conformable and individual phenomena will be indicated. The quarry was sampled from the quarry floor through a vertical distance of about 65 feet at which point the stripping operations commenced. (The quarry has been abandoned for a number of years.

TABLE NO. IV

Geologic Formation	Zone Number	Elevation	Bulk Sp.Gr.	Insoluble Residue	Zone Ave.
Gasper	6	35	2.30	25.5	I.R. 13.1%
		34	2.30	26.5	Sp.G. 2.49
Gasper	5	33	2.57	8.5	
		32	2.66	7.5	
		31	2.44	6.0	I.R. 10.1%
		30	2.50	11.0	
		29	2.58	13.5	Sp.G. 2.56
		28	2.61	14.0	
Gasper	4	27	2.60	11.5	
		26	2.67	6.0	I.R. 11.5%
		25	2.67	4.5	
		24	2.67	13.0	Sp.G. 2.65
		23	2.65	20.0	
		22	2.65	14.0	
Ohara	3	21	Shale parting		I.R. 43.8%
		20	2.64	28.0	Sp.G. 2.64
		19	2.64	59.5	
Ste. Genevieve	2	18	2.67	11.5	
		17	2.66	7.5	
		16	2.67	14.5	
		15	2.69	9.0	I.R. 12.2%
		14	2.68	8.5	
		13	2.68	12.0	Sp.G. 2.67
		12	2.67	19.5	
		11	2.67	13.0	
		10	2.68	11.0	
		9	2.65	15.0	
		8	2.67	20.0	
		7	2.67	4.5	
Ste. Genevieve	1	6	2.69	9.0	
		5	2.67	14.5	I.R. 11.4%
		4	2.68	12.5	
		3	2.68	10.5	Sp.G. 2.68
		2	2.69	9.5	
		1	2.68	12.5	

TABLE NO. IV (Continued)

Geologic Formation	Zone Number	Ele- vation	Bulk Sp.Gr.	Insoluble Residue	Zone Ave.
- -	- - - -	- stripping	- - -	- - - -	
Gasper	10	65	2.64	1.5	I.R. 2.1% Sp.G. 2.58
		64	2.64	2.5	
		63	2.63	2.0	
		62	2.52	1.5	
		61	2.48	3.0	
Gasper	9	60	2.63	5.0	I.R. 6.5% Sp.G. 2.61
		59	2.57	4.0	
		58	2.56	4.5	
		57	2.63	8.0	
		56	2.64	4.0	
		55	2.66	6.5	
		54	2.53	10.5	
		53	2.68	4.0	
		52	2.54	11.0	
		51	2.69	9.5	
		50	2.51	14.0	
Gasper	8	49	2.51	11.5	I.R. 17.8% Sp.G. 2.59
		48	2.59	20.5	
		47	2.56	17.0	
		46	2.63	16.0	
Gasper	7	45	2.61	20.0	I.R. 19.0% Sp.G. 2.60
		44	2.60	19.5	
		43	2.59	17.5	
Gasper	6 (con't)	42	2.62	4.5	I.R. 13.1% Sp.G. 2.49
		41	2.56	10.0	
		40	2.55	7.0	
		39	2.62	8.0	
		38	2.56	8.5	
		37	2.57	11.5	
		36	2.40	16.0	

Lab. No. 14
Dept. of Highways Div. of Tests Page 1 QUARRY NO. 3 State of Kentucky

County CARTER Prop. Owner CENTRAL ROCK COMPANY Operator CENTRAL ROCK CO. Date Sampled 12-14-39
Location 3/4 Mi. E. of OLIVE HILL ON RT. 60 TURN RT. AND GO 300 YDS. Date Received --
Sampled by DAVID L. ARNALL Date Reported 1-10-40

PHYSICAL TESTS					PASSED FOR	Lab. No.	LEDGE		QUARRY LOG
Specific Gravity	Soundness	% LA Wear	Deval	Absorption %			No.	Thickness	
					Stripping			16-18"	Stone and Soil. Weathered.
2.68	2.9	29.0			ALL USES	75869	1	6'	Coarse grain gray to brown crystalline oolitic limestone. Thick bedded.
2.64	8.1	36.0			CONCRETE AND BASE COURSE ONLY.	75870	2	5'	Medium to coarse grain brown with streaks of gray, flaky limestone. 1 bed. Weathers brown.
2.69	3.2	28.3			ALL USES	75871	3	4'	Fine grain gray to tan limestone. Nettled toward bottom.
2.65	9.1	26.4			ALL USES	75872	4x	3-1/2'	Medium grain brown and gray limestone.
2.67	28.8	32.8			FAILED FOR ALL USES	75873	5	3'	Fine grain purple to gray limestone.
					WASTE				Gray shaly limestone shale very shaly
2.55	42.2	39.4			FAILED FOR ALL USES	75874	6	10'	Fine grain powdery white limestone. Darker in color at top. Weathers badly. Thick bedded.
					WASTE			1½ to 2½'	Green shale. Waste.
2.69	22.9	28.2			FAILED FOR ALL USES	75875	7	6'	Fine grain gray to white limestone. Has large red spots in stone. Thick bedded. Weathers gray.
2.67	68.5	29.2			FAILED FOR ALL USES	75876	8	7½'	Fine grain gray limestone with green and red streaks in stone. Shaly toward bottom. Bottom nodular.
2.67	0.3	27.2			ALL USES	75877	9	1½ to 3'	Medium grain gray limestone. Has a sandy appearance in places and greenish cast.
2.67	5.2	28.2			" "	75878	10	1'	Fine grain gray to brown cherty limestone with jasper.

Lab. No. 14
Dept. of Highways Div. of Tests Page 2 QUARRY NO. 3 State of Kentucky

County CARTER Prop. Owner CENTRAL ROCK CO. Operator CENTRAL ROCK CO. Date Sampled 12-14-39
Location 3/4 Mi. E. of OLIVE HILL ON RT. 60 TURN RT. AND GO 300 YDS. Date Received -
Sampled by DAVID L. ARNALL Date Reported 1-10-40

PHYSICAL TESTS					PASSED FOR	Lab. No.	LEDGE		QUARRY LOG
Specific Gravity	Soundness	% LA Wear	Deval	Absorption %			No.	Thickness	
2.68	1.0	25.4			ALL USES	75879	11	4'	Fine grain gray flaky limestone.
2.70	1.7	27.8			" "	75880	12	3½'	Fine grain smooth brown cherty limestone Gray toward bottom. Very brittle.
2.68	2.2	30.0			" "	75881	13	4'	Fine to medium grain gray flaky limestone. In places smooth. Others granular.
2.69	0.8	27.8			" "	75882	14	3'	Medium gran gray granular limestone. Has small green and red spots in stone. Flaky in places.

-------- Green and red shale. --------

Remarks: Samples taken from East end of quarry back to center of quarry.
Some of the thicknesses shown vary because of the pinching in and out of some beds.
This quarry must be rechecked before using.

Zone No. I - Consists of six feet of light gray, dense looking, impermeable, sandy limestone. At the base of the zone, the sand grains are coarse, rounded and frosted; and are spoken of as "pebbles" by some authors. They range to a fine sand at the top of the zone, still showing rounding and frosting. The zone averages 11.4% insoluble residue, about 90% of which is quartz sand. It averages 2.68 Specific Gravity. No other unusual features were observed. The whole points to the nearness of a shore-line in depositional times, with the sandy shore-line contributing some of its clastics to the sediments here.

A photomicrograph is submitted here to show the included rounded quartz grains.

The quartz grains are the rounded darker masses. They are surrounded by crystalline calcite ($CaCO_3$) showing some impurities in the lower half of the film. The very bright patches are pure calcite pockets relatively free from impurities.

Zone II - The zone is composed of 12 feet of oolitic limestone to which subrounded sand and rounded sand are common. It averages 2.67 Bulk Specific Gravity and 12.16% insoluble residue. The close of this period is very positive and is indicated by sharp breaks in every aspect.

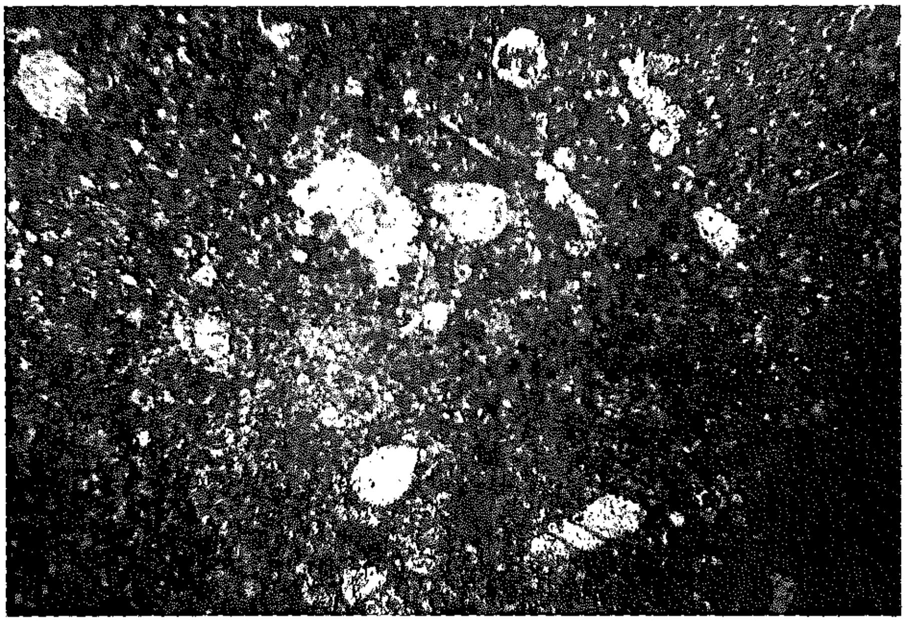
Zone No. II is marked by the introduction of an oolitic limestone rudimentary at first but steadily gaining impetus, with fluctuations. It received a larger amount of clastics from the ancient shoreline than did Zone No. I. Also the evidence is that conditions were slightly more stable in this time than in the time of Zone No. I as evidenced by the formation of oolites, with accompanying fluctuations as mentioned. Toward the latter part of this period of deposition, more staple times were the rule with fewer large clastics being contributed.

Zone III - This zone is introduced by a sharp break in the permeability, rock character and insoluble residue. It very nearly meets the requirements for a shale and at 21 feet an actual shale occurs. The zone is composed of three feet (including the shale parting), two feet of which were collected. It averages 2.64 bulk Specific Gravity and 43.75% insoluble residue. The limestone is near concholidal in fracture due to an abundance of chert, but has a crystalline calcite matrix. Coloring is irregular with organic matter furnishing the main color in an irregular distribution. This is the shaly Ohara member.

Zone IV - This zone is composed of six feet of non-fossiliferous, fairly dense limestone, with an accompanying variation in color. It is highly silicious, with quartz in fine grains, with chert accompanying at regular intervals. Organic materials and clay content are apparently low. The zone averages 2.65 Specific Gravity and 11.5% insoluble residue.

At the introduction of the zone, there is a slight tendency for oolites to form, indicating fairly stable conditions; but at 24 feet this condition is reversed, and an apparent speeding up occurred in the rate of sedimentation. The zone is closed by a partially permeable layer with oxidized iron giving a yellow tint to the sample. Exposure above sea-level would be indicated with accompanying weathering, oxidizing conditions and some small amount of recrystallization. This introduces the Gasper oolite, which is not a true oolite at this point.

Zone V - This zone is composed of six feet of yellowish, permeable, non-fossiliferous, fine grained limestone. There is a tendency for the permeability to fluctuate to its highest value at the center of the zone. The zone averages 2.56 Specific Gravity and 10.1% insoluble residue. Its structure is a fine crystalline calcite matrix surrounding rounded quartz particles. The limestone is apparently high in magnesium but exhibits no dolomite crystals. The break between this zone and zone No. VI is sharp and a chemical change in environment is indicated. A photomicrograph is submitted:

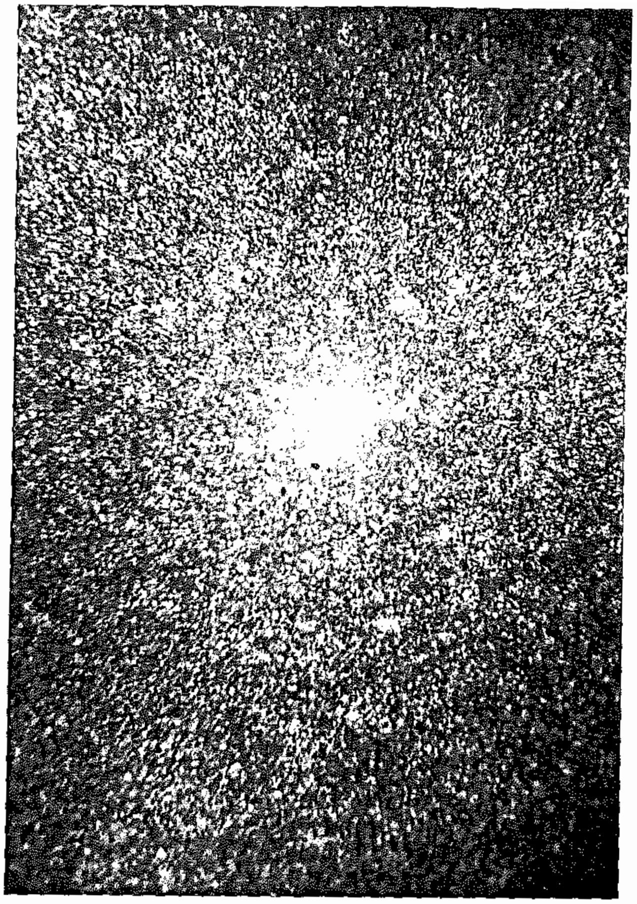


In this photomicrograph, the quartz particles appear lighter due to the very impure appearance of the limestone surrounding them.

Zone VI - This zone is composed of nine feet of light gray, finely crystalline, soft non-fossiliferous limestone which is introduced by a very highly permeable layer about three feet in thickness. The first three feet are very impure and highly silicious, a fact which might point to shallow water deposition with the silt being all clastics and no chemical deposition.

Small fragments of yellowish magnesium looking limestone persist throughout this zone. The permeability decreases as the sedimentation record is completed, with an accompanying decrease in insoluble residue. The zone averages 2.49 Specific Gravity and 13.05% insoluble residue

The fine pure looking calcite crystals are deceptive as they point to an apparently pure limestone. Such is not the case as the impurity is light covered silica in the form of fine quartz sand, not readily visible in the picture shown. (See following page for photomicrograph).



Photomicrograph Illustrating Zone VI

Zone VII - This zone is composed of three feet of medium dark brown, organic, fossiliferous, finely crystalline limestone, containing coarsely crystalline calcite in pockets and veins. The limestone is fairly permeable, which fact coupled with the coarsely crystalline calcite points to resolutional and recrystallization effect. The zone averages 2.60 Specific Gravity and 19.0% insoluble residue.

Zone VIII- This zone is composed of three feet of permeable limestone, colored a light dun brown, chalky looking and fossiliferous. It is separated from its neighbors on the basis of texture. Organic matter has a tendency to be grouped in a fine impure crystalline calcite matrix. Occasionally a small pocket of pure calcite is found, with a tendency for organic matter to group around the outer edges of the calcite. It averages 2.59 Specific Gravity and 17.83 insoluble residue. It is high in clay and organic content.

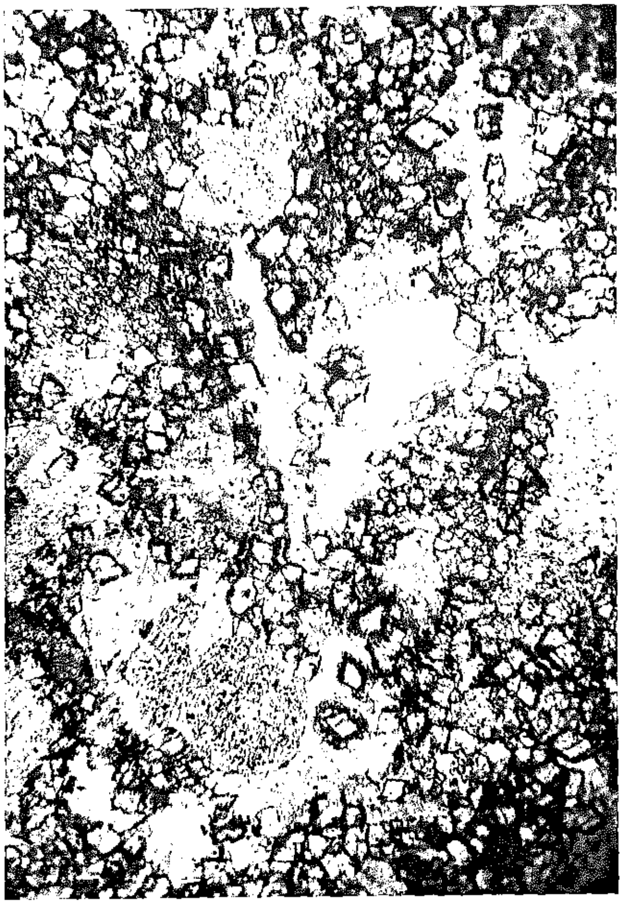
Zone IX - This zone is composed of thirteen feet of light yellowish tan fluctuating limestone, ranging to a light gray in color and ranging from permeable to impermeable. The insoluble residue definitely links these differing limestones together, and thin sections show comparable structures. The crystallization is again individual small calcite crystal's, but the size of crystals is increased and remains constant throughout. Organic matter surrounds the individual crystal form and is densest at the crystal boundaries giving every crystalline the appearance of being framed.

The initial zone of deposition is fossiliferous and crystallization is incomplete but with the following foot, crystallization is perfected and remains so throughout.

The impurities are small sand grains with enough organic material present to give a brown color to the residue. The organic material is streaked in veins occasionally. Towards the end of this period, some recrystallization is shown accompanying the lowering of permeability.

A photomicrograph is submitted to illustrate the above described phenomena. (See following page for photomicrograph)

Zone X - This zone is composed of four feet of irregular highly organic limestone. The organic matter is well grouped giving a mottled appearance. The limestone is partly permeable, nonfossiliferous and the organic matter has effected its tenacity apparently. Tt averages 2.60 Specific Gravity and 2.0% insoluble residue.



Photomicrograph Illustrating Zone IX

FUTURE WORK

In order that the investigation be carried to a more complete understanding of limestone, more comprehensive tests have been scheduled. These are designed to explore the following physical properties of limestone:

1. Absolute Specific Gravity
2. Hygroscopic Moisture
3. Permeability
4. Porosity
5. Tenacity
6. Tensile Strength
7. Coefficient of Thermal Expansion
8. Insulation (Conductivity of Heat)
9. Effect of Frost Action
10. Effect of Water
11. Capillarity

To further an understanding of why a limestone has these express properties, the following chemical and mineralogical tests will be performed on the impurities present in the limestone tested.

1. Moisture
    a. Firmly held
    b. Hygroscopic Water
2. Analysis of Insoluble Residue
3. Organic Content
    a. Simultaneous Determination of Water and Total Carbon.
    b. Carbon Dioxide*
4. Spectrography
5. Fluorescence
6. Relative Solubilities
7. Size of Particles in Insoluble Residue
8. Heavy Mineral Content
9. Other Mineral Content
10. Dielectric and Electrostatic Separation

Specific Gravity

There are several methods by which the specific gravity of sedimentary materials may be determined, each method being more or less adapted to a particular type of material and also to some extent to particular conditions. Specific gravity is ordinarily determined of dry materials, but in some cases it is necessary or desirable to determine the specific gravity of substances as they occur in nature, that is, with the contained natural waters or gases.

Specific gravity as previously determined is inaccurate. The method spoken of as the "Bulk Specific Gravity Method" is a hybrid of the Hydrostatic method. It is principally attractive as it gives a comparative value for the permeability when saturation is incomplete, a higher than normal Sp.G. is recorded. No quantitative determination may be made this way.

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* The chemist considers CO_2 as organic matter.

The method we intend to use is the volumetric flask type which has corrections for temperature and in which precautions are taken to evacuate air from the flask. This will give a value which is the "absolute" specific gravity or density. These figures compared against the Sp.G. of calcite 2.72 should be a good criterion for placing a limestone in a proper category.

A further consideration presents itself. These two determinations can lead to a third determination. The percentage of impermeable voids can be calculated from the foregoing determinations. While not an absolute value again, it should be a quick check against the permeability of a limestone.

Moisture Content

It has been determined in different unpublished tests that moisture content can be a definite influence in behavior of aggregate. Specifically, tests run on one source showed the aggregate caused failure of the beams from 20 to 30 freezing and thawing cycles. Later tests on rock exposed to air and weathering influence on the quarry floor for at least six months showed improvement up to and over 100 freezing and thawing cycles. As no definite collection methods were used, these tests are of no value other than for disucssion.

The difficulty of tests along these lines is that no correlation may be made. There is no way of knowing what time interval exists between quarrying and use of aggregate, nothing known of temperature and humidity at the stock pile, how much moisture was retained and how much evaporated.

The moisture determination can be divided into two types, (1) hygroscopic or physically held water, and (2) firmly held or water of crystallization.

Hygroscopic water would represent the bulk of the water in the limestone. Two different methods of testing are scheduled. The first, under way at the present, consists of a determination of the finely ground material coupled with another test (the determination of CO_2 and other organic matter). The second will consist of a determination of a chip sample in which the pore space is not disturbed.

Firmly held water is the determination of water of crystallization which in most cases will be held by clay minerals and zeolites. This would give some criterion as to mineral content.

Permeability

The permeability of a solid may be defined as the rate of flow of a given fluid through a unit cross section of the solid under a unit pressure gradient and conditions of viscous flow; permeability is therefore a measure of fluid conductivity of a solid. The standard unit of permeability as defined by the American Petroleum Institute (tentatively) is the "darcy" which is the rate of flow in milliliters per second, of a fluid of one centipoise viscosity through a cross section of one square centimeter of a porous medium, under a pressure gradient of one atmosphere (76.0 cm. Hg.) per centimeter and conditions of viscous flow.

Exclusive of joints, fractures and local zones of recrystallization, an ordinary limestone is usually saturated to the full extent of its permeability and under all other than extreme conditions is put in a concrete mix that way.

As observed in several cases a highly permeable limestone was the agent in one type of failure.

The various methods of measuring the permeability of consolidated materials are all based upon the quantity of fluid that will pass through a test block of a specific diameter and thickness in a given time. Therefore, the methods differ only in the type of fluid used - generally air or water - and in the complexity or refinement of the apparatus. In the case of limestone, a gas is the most practical medium. It is hoped that these tests can be run on a simple adaption of the equipment described by Wycoff, Botset, Muskat and Reed in the Feb. 1934 Bulletin A.A.P.G.

Porosity

Porosity may be defined as the percentage of the total volume of a sample that is occupied by pore space. Numerous methods have been devised for its determination; the method used in any particular case depends upon the type of material, the accuracy of results desired, and the time available for analysis.

Size of pores is also a good criterion, for if the pore size falls within the limit of capillary action, a powerful action is instigated for movement of water.

A study of porosity may involve very few laboratory supplies, but it is expected to supplement the standard methods with a dye penetrated thin section of the rock, in which size and also shape of pores may be studied.

This can be determined by comparison of the dry volume with the pulverized volume.

Tenacity

In the case of some types of limestones, such as an oolitic lime, the failure is obviously one of tenacity. The Los Angeles Wear test is high and direct observation reveals the chalky nature of the rock. The obviously poor retention this would give with the mortar would result in rapid failure under any load or possibly in time due to fatigue alone. This has been a possible cause of failure as regards scaling too. The poor retention again would cause the finished surface to break away from the aggregate and disintegrate after repeated pavement flexures under heavy loads. This lack of tenacity is not limited to an oolitic limestone, but may be observed in many limestones.

The obvious thing would be to retain the Los Angeles Wear Test with some improvements to discriminate to a finer extent. A special testing method may be called for and will be considered later.

Tensile Strength

Tensile strength of the average limestone should be characteristic of its purity. Although the limestone of lowest tensile strength would probably never be required to exceed its minimum (shearing/fracturing) stress in a highway, the failure of this limestone when compared with that of other limestones should be a reasonable criterion of its value as an aggregate.

It is intended that small beams be prepared representing each zone of each quarry. After other significant tests have been run on these beams, they will be broken in a testing machine. The break will be performed as a tension break. The beam will be center loaded and supported on each end.

Coefficient of Thermal Expansion

A fundamental concept of rock failure should be a heterogenous admixture of minerals having differing coefficients of thermal expansion. Any thermal influence brought to bear on this admixture would produce differing rates of expansion and hundreds of different sets of leverages which should in a period of time cause the rock to fail.

Different limestones tested from all over the country yield wide variations in their coefficients of thermal expansion. This is as should be expected. The variation in type of impurity would serve to produce this effect. Dolomitic limestones have a high coefficient, possibly indicating that Magnesium might be the cause; argillaceous limestones are high; whereas the purer "birds-eye" limestones are low, and some listed as Pale Gray Limestones are low.

Thermal studies at low temperatures are possible and not too complicated. A convenient method described in publications ranges from room temperature to 212°F. It is thought that this method will be used.

Insolation

Insolation is the conductivity of heat of a rock. It is usually spoken of as the linear distance per degree per unit time as: one degree Centigrade per inch per minute under a temperature influence of 100°C.

It is the principle upon which Indians relied to make flint arrowheads. Namely, the flint is heated, but the penetration of heat is very shallow. A drop of water causes the heated film to pop off due to rapid change in volume as opposed to the stable interior. If heating and cooling are carried on for a period of time on flint, chert, jasper and agate, the phenomena will be the same, although not so rapid. The same is true to a lesser extent in the case of all rocks. A silicious limestone would deteriorate more rapidly by this method under extreme conditions of temperature than a uniform limestone.

Therefore, it is more desirable to have uniform conductivity of rock than poor conductivity.

Effect of Frost Action

This would depend on a number of properties, the most important of which would be permeability or the percentage of permeable voids carrying water. Water can exert a powerful action when frozen in a void.

It is assumed that roughly this property would compare with the beams made of this aggregate in their freezing and thawing cycles.

Effect of Water

Whether water, carrying no especial compounds or acids in solution, can exert an influence on rock is not known. Theoretically several reactions should occur when a rock is immersed in water. Whether this effect is measurable remains to be seen. Possibly an increase in volume will occur and an attempt to measure this will be made. The water will change from neutral to alkaline, it is thought.

Capillarity

Capillarity is a direct dependent on surface tension and a fluid with higher surface tension will displace a fluid with lower surface tension. Water, for instance, having a surface tension 50 percent greater than crude oil (average A.P.I.), tends to be drawn into fine openings with half again as much force as that drawing fine oil into openings.

The force of capillarity is tremendous and will cause entire oil pools to migrate toward the surface from one stratum to the next.

Any size opening above 0.2 mm is free from capillary action of water with dissolved salts.

CHEMICAL AND MINERALOGICAL TESTS

Moisture - Firmly Held

Combined water may be determined ordinarily on a dry sample by heating the sample in a tube of combustion glass and collecting the water in a calcium chloride tube with specific precautions. From the result thus found it is necessary to deduct the separately determined hygroscopic water. It is to be remembered that the result will be in error by the amount of water afforded by the hydrogen of any organic matter which there may be in the limestone.

Moisture - Hygroscopic Water

One to several grams of the air dry powder is heated in a current of air dried by Calcium Chloride or some suitable desiccant to 100° to 105° and the escaping water collected in the same kind of desiccant. This method is said to give higher and more accurate results than those obtained by drying in a crucible at the same temperature.

Insoluble Residue

When the insoluble residue is large, it is sometimes desirable to analyze it separately.

It will be remembered that the insoluble residue is again a complex mixture of minerals, all of which may be present in various degrees of subdivision.

If a precise analysis is to be made, the residue may be obtained in the usual manner and analyzed as silicate rock.

Qualitative determinations of a great number of the minerals present may be made microscopically or by any means by which the constituents may be isolated and identified.

Organic Content

Since a definite ratio between organic content and particle size has been proposed, a determination of organic content may provide an indirect determination of particle sizes. With due consideration of the influence of particle sizes on the properties of limestone as an aggregate, the value of any results thus gained becomes obvious.

a. Simultaneous Determination of Water and Total Carbon

Ignite in a current of air one gram of the rock in a tube of very hard glass and collect the water and carbon dioxide with suitable absorption tubes. It is necessary for the success of the operation that the temperature be sufficient to drive out all of the CO_2, but insufficient to decompose the sulfates.

The water found represents that in the rock, as well as that derived from the hydrogen contributed by the organic matter.

A separate determination of CO_2 permits calculation of the carbon of the organic matter.

Carbon Dioxide

Place .5 gram of the sample in a small flask equipped with a small dropping funnel and small reflux condenser. The apparatus should not be over six inches tall and should not weigh over 150 grams. A sufficient quantity of HCL is introduced into the dropping funnel and the entire apparatus weighed. The acid is dropped into the flask slowly. When the reaction is complete the apparatus is re-weighed and the loss in weight represents the weight of CO_2 in the sample.

Spectrography

Spectrographic analysis is almost a science within itself and even though it is subject to several limitations, it is to be considered as both a quanitative and qualitative method of analysis. It is particularly applicable to the analysis and identification of certain minerals.

Its use is somewhat over-shadowed by the cost of the instrument.

Theory: At high temperatures, elements which become incandescent emit light rays of definite wavo lengths which are characteristics of the element. A spectrograph columnates the light, passes it through a prism and spreads the light out according to wave length on a photographic film. Careful reading of the film permits analysis of the material burned.

Fluorescence

Visual inspection of an insoluble residue using a microscope and ultra violet lighting may lead to the identification of many of the minerals present. Some minerals fluoresce under ultra violet and many others can be made to fluoresce by treatment with various reagents. Not only is it possible to ascertain the identity of many components, but also to estimate the quantity.

Relative solubilities

The chemical nature of limestone as an aggregate is more or less an obscure subject. The exact chemical changes which take place in the setting and hardening of concrete containing limestone as the coarse aggregate are not definitely known. If such were known, it would be possible to label certain ingredients as deleterious and introduce a correction.

$MgCO_3$ has long been considered as one of the highly reactive ingredients and in many cases called deleterious. Its presence in the aggregate is not conclusive proof that the aggregate is bad. The activity of $Ca_3(PO_4)_2$ is also questionable.

These points are cited merely to show that the rate of chemical change taking place may be proportional to the amount of moisture, the acidity or alkalinity of the moisture or leaching water. It is possible that certain materials pass into solution, concentrate in certain voids, re-crystallize and expand the void. Other ingredients may be completely leached out of the stone, leaving additional spaces for infiltration of foreign materials or water itself.

Any such change which reduces the strength and durability of the aggregate is undesirable.

These possibilities will be considered in future study although no definite process is in mind.

Size of Particles in Insoluble Residue

Materials ranging in dimensions from 2 mm to the largest dimensions are classified as coarse-grained clastics and are termed gravel; those in the range from 1/16 to 2 mm are medium grained clastics and form sands; those in the range from 1/16 to 1/256 mm form the silts; and those smaller than 1/256 mm, that is, the clays, are the fine grained clastics. In general, these terms are applied irrespective of composition, but the application cannot be made too rigorous, and if the particles in the range from clay to silt are composed of calcite or dolomite, the terms silt and clay are not applied. Since the possibility of calcite is excluded, with the use of Hydrocloric acid, the specifications can be more rigidly held.

Any determination of size will determine the material present in the residue in a group classification.

Particle size and organic content are related in sediments. The organic content of clay is twice that of silt and four times that of fine sand. This indicates an exponential relationship between size and organic content. In general, sands may have from essentially none to 0.6 percent organic matter, whereas clays have up to 8 or 10 percent.

What the influences of organic matter in a lithified sediment are is not known. This remains to be investigated in some more detail than is known at present, and will be discussed under special chemical tests.

Due to the extremely fine size of the insoluble residue, a sieve analysis is impractical. The only distinguishment that may be made is the division of silt and clay from the sand and other mineral suite present.

The problem of determining the distribution of particle size of fine grained sediments is far more complex than that encountered in coarser materials. Most methods of mechanical analysis of fine grained materials consist of preparing a suspension of the sediment in a dispersed state so that each particle acts as an independent unit in settling. The sediments are allowed to settle in water for various units of time and the quantity of material which has settled a unit distance per unit of time is recorded in some way.

A dry method of sorting consists of separation in varied air stream velocities, the sample being blown over a crook in a glass tube and collected in a receptacle. By varying the velocities, a size gradation is assured.

Heavy Mineral Content

As distinctly related to special chemical tests on the insoluble residue, the heavy mineral content should be mentioned here.

Heavy minerals are usually spoken of as those with a Specific Gravity of 2.90 or better. Although a mineral with a gravity rating of better than 2.90 is thought of as stable, such may not be the case every time. An investigation to determine if the appearance of any one mineral in poor type aggregate is characteristic should be included in this study. Other geologists with whom I have talked have mentioned this without holding forth too much hope, but it was agreed that without this information, the study would be incomplete.

The method of recovering heavy minerals, incorporates the use of a heavy liquid, into which is dropped the oven dry sample. All minerals having gravities higher than the liquid used will sink while the rest of the material floats.

Other Mineral Content

The special term used above has no scientific basis. It is a term coined to include the fine clastics with gravities below 2.90 and for this consideration will not include the clay minerals as they have already been considered. It will include the finest clastics present in the insoluble residue.

In addition to differences in particle size, water content, organic content, etc., sediments differ in their mineralogical composition, and hence in their susceptibility to chemical change. This susceptibility ranges from the comparative stability of quartz sand to relatively active clays or finely divided non-clastics with their large total surface areas. Chemical changes in part are a function of the size distribution of the sediment; base exchange, for example, may play a prominent role among very fine sediments, but is generally negligible in coarser sediments.

As this consideration must be stated so generally, no effort will be made to enumerate the detailed processes entailed in this complex determination. Suffice it to say, it will be an impractical method for the laboratory and will be retained until it is necessary to eliminate all possibilities.

Dielectric and Electrostatic Separation

Differing minerals possess different dielectric constants. The dielectric constant varies to some extent with the crystallographic direction and is influenced by inclusions within the mineral grains. In the case of several minerals, the duration of immersion has an effect on the dielectric constant.

Dielectric separation of mineral particles is based on the principle that oppositely charged poles attract each other with a force that varies inversely with the square of the distance between them. The force is considerably diminished if the oppositely charged poles are placed in a nonconducting, or dielectric medium. The dielectric strength of this medium is that property by which it resists the passage of a spark between the two oppositely charged poles and the numerical expression of this property is termed the dielectric constant. This is equal to the ratio of the force of attraction of the oppositely charged poles in a vaccum to their force of attraction in the medium. Any foreign substance in a medium of given dielectric value is attracted to the electric field between the poles if it possesses a dielectric constant greater than the medium. In the practical application for separating mineral particles the medium is necessarily liquid.

Electrostatic. Minerals that are good conductors of electricity may be separated readily from those that are poor conductors by the use of an electrostatically charged body, such as a glass rod on which a charge has been induced by rubbing with silk, or an ebony or sealing wax rod rubbed with catskin or rough flannel. A positive charge is developed on the glass rod and a negative one on the ebony or sealing wax rod.

After the particles have been sized by screening, they should be spread evenly and thinly over a clean thoroughly dry copper plate. The particles should be thoroughly dry, otherwise the nonconducting particles will become conducting. The ebonite rod should be 35 to 50 mm long and about 18 mm in diameter. The rod is charged by rubbing with fur or flannel and then is held over the particles and gradually lowered until the particles attach themselves to it. The rod is then moved over the particle-strewn surface and rotated slowly at the same time. After all the conducting particles have been attracted to the rod, they are brushed off into a suitable receptacle.

APPENDIX 1

Sampling

<u>Possibility of Error</u>. The main possibility of error lies in the human element involved in the selection of a face to be tested. The selection of individual specimens is a specialized case of this. Due to oxidation, solution and all the processes that combine to weather a rock, a "core" taken a few feet behind the vertical face of a quarry would eliminate this error. The lateral gradation in beds would be eliminated as a source of error by taking several "cores" so that an average might be obtained.

<u>Conclusion</u>. If conducted by a qualified operator the sampling operation should be reasonably accurate, and a fair average struck. The cost of taking "cores" is prohibitive in practically every case.

Separation

<u>Possibility of Error</u>. While not in error, the zones assigned two to five years ago do not agree with those that are apparent today principally because of "pinching out" of strata, etc. Also, the bulk specific gravity will vary both horizontally and vertically in any zone so of necessity correlation will be poor in any case.

<u>Conclusion</u>. Correlation, even if not positive, will be interesting and relevant for the specific gravity used to determine qualifications of aggregate. Comparison with results obtained in this study should be of value.

Crushing

<u>Possibility of Error</u>. Some criticism has been brought to bear on the size of the crushed material. What change could be effected by changing the particle size is not known. However, it is known that the use of a powerful magnet on the material yields no crusher fragments.

<u>Conclusion</u>. Until such time as the size of the particles is known to have more influence than the speed of the reaction of the acid, this method will be used. By using fragments of this size, the disclosure of the presence of silicious fossils and all silicious replacements was facilitated.

Sample Splitting

<u>Possibility of Error</u>. The operation seems quite comprehensive but it must be admitted that no control has been run on these in order to determine accuracy of operation. Until such time as an accurate check is made, no certainty is assured.

Conclusion. As stated, this operation must be checked to assure complete confidence in results. However, it is an accepted method of petrographers and results may be assumed to be reasonably accurate.

Thin Sectioning

Possibility of Error. Any factor contributing to error would occur in study of the thin section.

Conclusion. The quality of the thin section lies in the inherent skill of the operator which should come with a small amount of practice.

Insoluble Residue Process

Possibility of Error. The balance used was accurate to one-tenth of a gram. Due to the size of the sample the maximum error was one part in two hundred. The filter used was a medium Pyrex (Gooch type) fritted filter. Due to a negative charge developed at the filter by a difference in potential, there is a repulsion of all positively charged ions in suspension. Thus, the material passing the filter was estimated at only one-tenth of one percent. Room temperature was used for temperature of reaction and did not vary enough to be of consequence. When dolomite is tested, it is necessary to heat the reaction to drive it to completion.

Conclusion. No certainty exists as to the accuracy of this method. It is not known what intricacies of chemical reaction occur on digestion of the sample. Results point to the fact that some insoluble chlorides were formed. What other reactions took place was not certain. A deviation of from one to two percent in results may be expected. Although a lateral variation occurs in every ledge, it is not known if the variation is of sufficient amount to cause this method to be untenable. Results in other endeavors in the past seem to substantiate our methods. Research is progressing in this direction. Results will be reported later. Until such time as this method is justified, no definite conclusions may be made.

Clay Mineral Recovery

Possibility of Error. Recovery of the clay mineral fraction was never complete. There is no known method that is designed for this. This method assures recovery of a representative fraction of the clay mineral content. However, this size was not limited to the clay mineral alone so the sample was never pure. The extraneous material diffracts some lines of the pattern that tend to confuse and must be ignored. It is the most practical method and must be accepted.

Conclusion. While not efficient, as mentioned, the first aim was satisfied as this method permits identification of the clay mineral fraction. The first premise was that it was the type and not the amount of clay mineral that was important.

X-Ray Diffraction

Possibility of Error. An error in this process would produce a film that was not readable. Therefore, no serious error could be made from this, only from errors in study of the film.

Conclusion. Due to availability of equipment, tests have been limited thus far to only preliminary evaluation.

APPENDIX 2

ANALYSIS OF LIMESTONE

Silica Place 0.5000 g. of limestone in a 150 ml. beaker and moisten with water. Cover the beaker with a watch glass, add 10 ml. of HCl, heat on the hot plate for a few minutes and add 3 ml. of HNO_3. When most of the reaction ceases, wash and remove the watch glass, wash down the side of the beaker and dilute to 50 ml. Evaporate the solution to dryness and bake to dehydrate silica. Add 5 ml. of concentrated HCl to the covered beaker and heat until basic salts have dissolved. Wash and remove the cover, dilute the solution to 50 ml. and heat for 15-20 minutes. Filter the solution through Whatman No. 40 paper into a 250 ml. beaker, transfer the silica to the filter and wash with hot water. (Repeat the evaporation, take up the material in HCl and water as before, and filter through a second paper). Reserve the filtrate. Place the filters in a platinum crucible, burn off the paper, and ignite to constant weight. Add a few drops of water, a few drops of 50% H_2SO_4, and 4-5 ml. of Hydroflouric Acid. Evaporate to dryness, ignite the residue and weigh. The loss in weight due to treatment with HF (Hydroflouric Acid) is the weight of SiO_2.

$$\% \ SiO_2 = 200 \times \text{Wt } SiO_2$$

Iron and Aluminum Oxides Fuse the residue remaining in the crucible from the silica determination with 1-2 g of Na_2CO_3. Place the crucible in a 150 ml. beaker and dissolve the fusion in 10 ml. of dilute HCl added in two portions. Wash and remove the crucible, and add to the filtrate reserved from the silica determination. If the solution of the fusion is not perfectly clear it should be filtered through a Whatman No. 2 paper. Add 2-3 drops of Methyl Red indicator and make the hot solution just alkaline with NH_4OH and boil for two minutes. If the pink color returns add another drop of NH_4OH. Filter the solution through a Whatman No. 40 paper into a 400 ml. beaker and wash three times with 2% NH_4Cl. Place the original beaker under the funnel and dissolve the precipitate with hot dilute HCl. Wash with hot water until the iron color has been removed, and wash twice with 2% NH_4OH. Finally wash 5-6 times with hot water. Re-precipitate the iron and aluminum, filter through the original paper, and transfer and wash the precipitate. Reserve the filtrate. Place the paper containing the precipitate in a platinum crucible which has been weighed with cover. Burn off the paper and ignite to constant weight.

$$\% \ R_2O_3 = 200 \times \text{Wt } R_2O_3$$

Calcium Carbonate The filtrate from the determination of iron and aluminum should have a volume of 250-300 ml. Add about 20 drops of NH_4OH, heat to boiling and add 30 ml. of a saturated solution of $(NH_4)_2C_2O_4$ which has been heated to boiling. Boil the solution with the beaker covered until the precipitate is well formed and allowed to stand overnight. Filter the solution through Watman No. 42 paper into a 600 ml. beaker, transfer most of the precipitate to the filter and wash once with cold water. With a jet of hot water transfer the precipitate to the original beaker, heat on the hot plate and dissolve the precipitate by adding HCl. Use no more than necessary. To the solution, having a volume of about 50 ml, add 1 ml of saturated $(NH_4)_2C_2O_4$, heat to boiling and add NH_4OH with about 20 drops in excess. Boil for a few minutes and allow to stand on the hot plate for about two hours. Filter the solution through the original paper and receive the filtrate in the beaker containing the first filtrate. Wash the filter three times with cold water. Reserve the filtrate. Place the filter containing the precipitate in a platinum crucible which has been weighed with cover. Burn off the paper and ignite to constant weight. The percent of calcium carbonate as determined from the precipitation of calcium oxalate should be reduced by the calcium carbonate equivalent of the calcium phosphate.

$$\% \; CaCO_3 = 357 \times Wt \; CaO$$

Magnesium Carbonate

Evaporate the solution remaining from the calcium determination to approximately 150 ml and cool to room temperature. Add 5 ml of 10% $(NH_4)_2HPO_4$ for each 7% $MgCO_3$ in the sample, and slowly add NH_4OH until it is in about 10% excess. The solution should be frequently stirred during the first hour and allowed to stand overnight with the beaker covered. Filter the solution through Whatman No. 42 paper, wash out the beaker and wash the paper five times with 2% NH_4OH. Place the original beaker under the funnel and dissolve the precipitate with hot dilute HCl. Wash the paper five times with hot water and twice with 2% NH_4OH. Wash the sides of the beaker with hot dilute HCl and hot water. Add 1 ml of 10% $(NH_4)_2HPO_4$ and add NH_4OH as in the first precipitation. The solution should be frequently stirred during the first hour and allowed to stand two hours. Filter the solution through the original filter, transfer the precipitate and wash the filter five times with 2% NH_4OH. Place the paper containing the precipitate in a tared platinum crucible and ignite and weigh.

$$\% \; MgCO_3 = 151.2 \times Wt \; Ppt$$

Iron Oxide

Place 1.000 g of limestone in a 250 ml beaker and moisten with water. Cover the beaker with a watch glass, add 10 ml of HCl, heat on the hot plate for a few minutes and add 3 ml of HNO_3. When most of the reaction ceases, wash and remove the watch glass, and wash down the sides of the beaker. Evaporate to dryness. Make two evaporations with 5 ml portions of HCl, washing and removing the cover and washing the sides of the beaker each time. Add 15 ml of

HCl, heat for a few minutes, and wash with about 15 ml of water. Reduce the iron by the dropwise addition of $SnCl_2$ to the hot solution. Add 1-2 drops in excess after the solution becomes colorless. Cool under the water tap and add 25 ml of a saturated solution of $HgCl_2$. Stir and allow to stand five minutes, add 15 ml of dilute H_2SO_4, and dilute to about 200 ml. Titrate the solution with 0.1 N $KMnO_4$ solution to a faint pink color.

$$\% Fe_2O_3 = 7.98 \times \text{Ml } KMnO_4 \times \text{Normality}$$

Calcium Phosphate

Place 1.000 g of limestone in a 150 ml beaker, add 10 ml of HNO_3, cover and heat for 30 minutes on the hot plate, add 15 ml of HCl, heat with cover on until violent action ceases, then wash cover and sides of beaker with water and evaporate to 10 ml. Add 50 ml of water, filter through Whatman No. 40 paper into a 400 ml beaker, and wash the residue with hot water. Burn off the paper, ignite the residue, and destroy SiO_2 as above. Fuse the residue with 1-2 g of Na_2CO_3, and dissolve the material in hot water. Filter the water extract through a Whatman No. 1 paper into the beaker containing the main solution. Evaporate to dryness, add 10 ml of HNO_3 and heat with the beaker covered until basic salts have dissolved. Dilute to 50 ml with hot water and heat until all material is in solution, and until nitrous fumes have been driven off. Transfer to a 300 ml erlenmeyer flask and dilute to 100 ml. Start a blank by diluting 10 ml of HNO_3 to 100 ml in a flask.

With the solution at a temperature of 40°-50° add 50 ml of molybdate reagent. Shake the flask for 10 minutes and allow to stand 30 minutes. Filter the solution through a Whatman No. 7, 9 cm paper, and wash the flask with three portions of 1% KNO_3. Wash the filter from the top down with ten portions of 1% KNO_3. All mineral acid should be removed, but since the precipitate is slightly soluble in the washing solution, washing must not be carried to extremes. Place the filter in the original flask, add 2-3 ml of 0.1 N NaOH in excess from a burette, and shake until all the yellow precipitate has dissolved. Dilute to 100 ml, add three drops of phenolphthalein indicator, and titrate to an end point with 0.1 N HNO_3. Calculate the ml of NaOH equivalent to the phosphorus.

$$\% Ca_3(PO_4)_2 = 0.675 \times \text{ml NaOH} \times \text{Normality}$$

$$\% CaCO_3 = 0.968 \times \% Ca_3(PO_4)_2$$

Possibility of Error. These methods are subject to the usual experimental errors. When approximations are made, they will be so stated and treated as such.

Conclusions, These methods are applicable to carbonate rock if no separate determinations are to be made. Any determination made represents the total amount present, without regard to its nature of occurrence. The total of the determinations approaches 100% of the sample and the results are suitable for many comparative studies.

REPORT OF CHEMICAL ANALYSIS

Quarry #1
December 18, 1946

Five samples of limestone, representing the five geological zones assigned to the quarry by the geologist, Mr. Young, who provided the samples for analysis, were analyzed using standard procedures.

The results are included herein:

Sample	#1	#2	#3	#4	#5
SiO_2	3.51%	3.78%	2.15%	3.95%	2.26%
Fe_2O_3	.75%	.84%	.61%	.83%	.53%
Al_2O_3	1.76%	1.69%	1.46%	2.32%	1.53%
$Ca_3(PO_4)_2$	.93%	2.55%	2.61%	2.81%	2.93%
$CaCO_3$	86.10%	82.60%	85.80%	82.00%	37.40%
$MgCO_3$	6.94%	8.51%	7.28%	8.00%	5.29%
Total	99.99%	99.97%	99.91%	99.91%	99.94%
Bottom	0-5 ft.	6-11 ft.	12-18 ft.	19-24 ft.	25-30 ft.

It will be noted that there is a gradual increase in the percentage of $Ca_3(PO_4)_2$ from sample #1 through Sample #5.

Additional generalizations will not be attempted until further data have been obtained.

/s/ James H. Havens

Addendum: Sample #1 indicates that the Jessamine limestone may contain considerably less $Ca_3(PO_4)_2$ than the Benson series.

2nd Addendum: Phosphorous in the insoluble residue and soluble phosphorous were determined separately. Both are reported as $Ca_3(PO_4)_2$, but there is a possibility that that held in the residue exists as apatite $(Ca_5F(PO_4)_3)$.

Soluble	(1)	.66%	(2)	1.87%	(3)	2.11%	(4)	2.01%	(5)	2.43%
		.27%		.68%		.50%		.80%		.45%

Tests	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Immediate Immersion				[illegible]		[illegible]
Delayed Immersion	[illegible]		[illegible]	[illegible]	[illegible]	
Three Minute Boiling				[illegible]		
Immersion Agitation	[illegible]		[illegible]	[illegible]	[illegible]	