A CHEMICAL METHOD FOR DETERMINING THE QUALITY OF LIMESTONES.[1]

BY ALFRED M. PETER.

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THE turnpike roads in the vicinity of Lexington, Kentucky, are built of the only stone which is conveniently within reach, namely: the limestone of the upper and middle beds of the Trenton formation. The character of the beds of this limestone is quite different at different levels, and it is common experience that the so-called "blue" layers are less valuable for any exposed construction than the "gray" because of their more rapid disintegration on exposure to atmospheric influences. Some beds which, when recently quarried, appear of fairly good quality are penetrated by thin layers of the blue material which disintegrate rapidly by weathering, causing the stone to separate into laminae of varying thickness. According to the writer's observation, the blue material is of two varieties; it may be quite shaly and moderately phosphatic or very phosphatic and not especially clayey, but it invariably contains easily soluble ferrous compounds and a small but very notable amount of organic matter which makes its presence known when the material is dissolved in dilute acids by the odor of petroleum imparted to the escaping gas and by the brown scum floating upon the liquid. The writer believes that the peculiar color of the so-called "blue" limestone is largely determined by the presence of a ferrous phosphate. He is of the opinion, also, that the rapid weathering down of blue material is due to the presence in it of easily oxidizing substances, such as ferrous compounds and organic matter, the oxidation of which is greatly favored by the greater porosity of this material, as compared with the gray limestone. The porosity of these blue limestones appears to increase with increasing amounts of phosphates and may in reality be dependent upon the presence of the minute spiral shell, *cyclora minuta* which, as has been shown by the writer and Professor A. M. Miller,[2] carries the phosphate. When this shell is present in very large numbers it gives to the rock a structure somewhat resembling that of chalk, though more compact. These soft limestones, and especially the shaly kind containing clay, also contain some finely granular pyrite which, by its oxidation, undoubtedly promotes disintegration.

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[1] Read before the Cincinnati Section of the American Chemical Society, October 8, 1902.

[2] Eighth Annual Report Kentucky Agricultural Experiment Station, p. 25.

For the general character of the Trenton limestones of Central Kentucky reference is here made to Report A of the Kentucky Geological Survey, Vol. 2, pages 123-4. In the analyses there published of 18 samples of limestone from Trenton group in Bourbon, Clark, Fayette, Franklin, Madison. Mercer and Woodford counties. Kentucky, by Dr. Robert Peter, the silica and silicates insoluble in hydrochloric acid of 1.15 sp. gr. vary from 1.88 to 14.18 per cent., the average being 5.36 per cent., and the phosphoric acid ranges from 0.118 to 0.860, the average being 0.434 per cent. Later analyses by Dr. Robert Peter showed much higher percentages of phosphates in certain specimens.

If the writer's view of the causes of disintegration of these rocks is correct, a very good index of the relative stability of different samples could be obtained by measuring their relative amounts of easily oxidizable matters. phosphoric acid and clay or insoluble matters.

THE METHOD OF ANALYSIS.

The writer proposes, therefore, to dissolve the limestone in dilute sulphuric acid in the presence of a known amount of potassium permanganate and determine how much permanganate has been reduced during that process, after which the solution is to be used for the determination of phosphoric acid by a rapid volumetric method, and the insoluble residue, for the determination of the insoluble matter and clay.

Determination of Oxidizable Matters.—The method was actually carried out as follows: 1-gram portions of the finely powdered samples, previously dried at 100 C., were weighed into 250 cc. Erlenmeyer flasks, and 25 cc. of N/10 potassium permanganate solution measured into each and shaken until the powder was moistened; 100 cc. of a 10 per cent. sulphuric acid (110 cc. H_2SO_4 of 1.84 sp. gr. + 1800 cc. of water) was then added and the flasks again shaken. If the color of the permanganate appeared to be nearly all discharged, as happened in some of the limestones examined, a second 25 cc. of permanganate solution was added at once. Two other flasks were charged with the same amounts of permanganate and sulphuric acid to serve as checks upon the decomposition of the permanganate due to heat and acid alone. All the flasks were immediately placed upon a boiling water-bath and allowed to remain there for half an hour, with occasional shaking, after which 30 cc. of N/10 oxalic acid was run into each, or more, if necessary, and the flasks allowed to remain on the bath a few minutes longer, until the brown manganic compounds had entirely disappeared. It is well to adjust the quantity of oxalic acid added, so that there will be at least 8 or 10 cc. in excess of what is actually oxidized, as otherwise the disappearance of the manganic compounds will be slow. Where 25 cc. of permanganate had been used, 30 cc. of oxalic acid were enough, if the reduction by the limestone had been considerable, but not if this had been only slight. The flasks were then removed from the bath and the excess of oxalic acid titrated back with permanganate solution. The amount of permanganate reduced by the easily oxidizable matters in the limestone was thus ascertained, due allowance having been made in each case for the amount reduced in the control experiments.

The presence of pyrite in these limestones has already been mentioned and it was observed in several of the samples, after the acid had been poured on. After the titrations were finished, the residues were, in every instance, examined by means of a lens, before filtering, but in no case was any pyrite apparent. It is believed that it was completely oxidized. A qualitative test with finely powdered pyrite showed that it reduced the acid permanganate solution rapidly, even in the cold, but in a quantitative experiment with 0.02 gram of pyrite, 50 cc. of permanganate and 100 cc. of 10 per cent. of sulphuric acid, only about two-thirds were oxidized, probably because the mineral was not ground sufficiently fine.

The writer proposed to make a separate determination of the pyrite in these limestones by a rapid method based upon the reaction observed by A. Rollet[1] but time did not permit.

To ascertain whether one-half hour digestion with the sulphuric acid and permanganate was long enough to obtain the whole reducing effect of the samples, a set of duplicates was made upon six of the samples, digesting them one-half and one hour respectively. The results were substantially the same, as shown below.

Cubic centimeters permanganate solution reduced by 1 gram of sample (1 cc. permanganate = 0.00078 gram available oxygen).

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[1] Ref. in *Am. Chem. J.*, **2**, 69 to Dingler's *poly. J.*, **233**, 124.

	Blank.	1.	2.	3.	4.	5.	6.	Blank.
1 hour digestion	1.95	3.85	2.45	29.85	11.65	6.45	6.05	2.25
½ hour digestion	1.1	3.1	2.1	28.2	10.7	5.6	5.4	1.3
Gross difference	0.85	0.75	0.35	0.65	0.95	0.85	0.65	0.95

As the average increase of decomposition in the blank experiments is 0.9 cc., it is evident, therefore, that the oxidation was complete in half an hour. Indeed it is probable that the reaction is practically complete in the cold, or that heating for a shorter time than one-half hour would suffice, but no experiments were made to test this supposition. It is noteworthy that, when the acid is poured upon the limestone, in the presence of permanganate, the petroleum-like odor is very slight and there is no floating carbonaceous matter observable, whereas, with the acid alone, these are both very evident, as already mentioned.

Determination of Insoluble Matter and Clay.—After the titration, a drop or two more of oxalic acid was added to remove traces of permanganate, and 10 to 15 cc. of hydrochloric acid of reagent strength (20 per cent) to retard crystallization of calcium sulphate, and the solutions filtered from the residues as quickly as possible. It was difficult to obtain a perfectly clear filtrate without too much waste of time. so a slight opalescence of the liquid from suspended clay was disregarded in most cases. The residues were washed, first with a little warm, dilute hydrochloric acid, finally with water, burned and weighed as total insoluble residue. A comparison of the amounts of insoluble residue obtained in the half-hour and one-hour digestion already described, shows only a very slight decrease by the longer digestion.

PER CENT. OF INSOLUBLE MATTER.

	1.	2.	3.	4.	5.	6.
½ hour digestion....	2.94	1.45	18.75	8.22	2.29	2.43
1 " "	2.88	1.48	(17.08)	8.05	2.25	2.42
Difference..........	0.06	—0.03	(1.67)	0.17	0.04	0.01
Average............	2.91	1.46	(17.92)	8.14	2.27	2.43

Some of the residue from the one-hour digestion of No. 3 was accidentally lost before weighing, so that the difference in this case is not really as great as it appears.

In order to separate the sand and clay, the residue obtained from a duplicate determination of the easily oxidizable matter was transferred, together with the filter, without burning, to a platinum dish of about 100 cc. capacity. and gently boiled with 10 cc. of concentrated sulphuric acid for several hours, the dish being covered with a watch-glass during the operation. A small amount of potassium nitrate was added to hasten the oxidation of the filter-paper. After cooling, about 50 cc. of water were added and the contents of the dish boiled a few minutes, allowed to settle, and filtered, leaving as much of the residue as possible in the dish.

After washing this residue, it was boiled with three successive portions of a saturated solution of sodium carbonate to separate soluble silica, thoroughly washed, burned and weighed. This weight was designated sand and the difference between this and the total insoluble residue previously determined was considered clay. Qualitative tests of some of these residues showed that they were not pure quartz sand, but still contained silicates, probably feldspathic in character, as a very notable amount of potassium was present.

Determination of Phosphoric Acid.—The phosphoric acid was determined by A. L. Emery's modification of the volumetric method of the Association of Official Agricultural Chemists.[1] For this purpose, half of the solution obtained by dissolving the limestone in the sulphuric acid permanganate was used. When it is not desired to weigh the insoluble matter, this solution may be used without filtering. An independent determination of phosphoric acid was made for comparison upon the first six samples by the same volumetric method, using the solution obtained by dissolving 0.5 gram of the sample in nitric acid. The results are given below and show a reasonable agreement between the two methods.

PER CENT. OF PHOSPHORIC ACID.

	1.	2.	3.	4.	5.	6.
Solution in H_2SO_4 and $K_2Mn_2O_8$	1.00	0.18	2.42	1.98	0.60	0.62
" " HNO_3	1.02	0.14	2.32	1.80	0.54	0.48
Difference	—0.02	0.04	0.10	0.18	0.06	0.14
Average	1.01	0.16	2.37	1.89	0.57	0.55

The molybdic precipitates obtained from the sulphuric acid solutions were easier to filter and wash than those from the nitric acid solution, the latter showing a great tendency to run through the filters.

DESCRIPTION OF THE SAMPLES.

In this investigation 18 samples of limestone were analyzed,

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collected by the writer from stone in use upon roads near Lexington or from quarries which had been worked for such stone. The samples were chosen especially with reference to presenting the best, the worst and about the average quality of the material now actually in use for road construction in this locality. They may be described briefly as follows:

No. 1. Gray, crystalline, fossiliferous limestone; very hard; broken from an eight-inch ledge which appeared to have resisted the weather. From an old quarry on the Nicholasville road.

No. 2. Hard, gray, crystalline stone selected from a pile of broken stone on the roadside, Nicholasville road.

No. 3. Blue, slaty, soft stone, selected from the same pile as No. 2. It was already disintegrating, although it had only been exposed a few months.

No. 4. Blue limestone from the roadside; not as shaly as No. 3, but weathering in places to a soft pinkish material.

No. 5. Hard, gray, compact stone, selected from the road now in process of construction at the Lexington Fair Grounds. The superintendent of the Construction Company considers this the best stone for the purpose he has used about Lexington.

No. 6. Average of small pieces taken from the same road as No. 5.

No. 7. Hard, gray, crystalline stone, selected from a pile by the roadside on the Tates Creek pike.

No. 8. Thin, blue, slaty piece from the same pile as No. 7.

No. 9. Another slaty, blue piece from the same pile.

No. 10. Compact, hard, gray stone selected from the roadbed near the same place as No. 7.

No. 11. Average from the same place as the preceding, obtained by taking small pieces from the surface of the road where it had been exposed by washing; mostly blue limestone.

No. 12. Average of small pieces taken from a pile of crushed rock by the roadside on the Bryan's Station pike. The superintendent of the Construction Company states that the stone used on this pike is the worst he has met with about Lexington.

No. 13. Representative sample of the thin, soft, blue layers in the quarry on the Bryan's Station pike.

No. 14. Representative pieces from the thicker, soft, blue layers in the same quarry.

No. 15. Selected piece of the harder blue layers in the same quarry.

No. 16. Nearly white, very hard, concretionary masses occurring in the soft, blue layers in the same quarry.

No. 17. Thin, slaty layers from the same quarry. Disintegrate very rapidly.

No. 18. Selected piece from the hard layers in the upper part of the same quarry, which seem to have resisted weathering.

RESULTS.

The results of the analyses were as follows, calculated as per cent. of the samples dried at 100° C.

	Number.	Oxygen consumed.	P_2O_5.	Sand.	Clay.	Total insoluble.
Tough, hard, compact stone, resisting weathering, mostly gray.	1	0.143	1.01	2.26	0.65	2.91
	2	0.048	0.16	1.34	0.13	1.47
	5	0.341	0.57	1.63	0.64	2.27
	6	0.318	0.55	1.76	0.66	2.42
	7	0.137	0.18	...	...	1.33
	10	0.133	0.22	...	...	1.50
	15	0.207	0.98	...	...	0.88
	16	....	0.20	...	...	4.15
	18	0.160	0.47	...	...	1.44
	Average,	0.165	0.48	1.75	0.52	2.04
	Highest,	0.341	1.01	2.26	0.66	4.15
	Lowest,	0.048	0.16	1.34	0.13	0.88
Soft, porous or shaly stone, weathering rapidly, mostly blue.	3	2.120	2.37	7.73	10.19	17.92
	4	0.743	1.89	6.23	1.91	8.14
	8	0.952	1.90	17.43	7.64	25.07
	9	0.948	1.68	17.42	8.24	25.66
	11	0.666	0.96	4.20	4.08	8.28
	12	0.843	4.62	...	...	2.59
	13	0.710	6.24	...	...	2.06
	14	1.139	9.10	...	...	2.10
	17	2.044	4.52	12.53	10.23	22.76
	Average,	1.129	3.70	10.92	7.05	12.73
	Highest,	2.120	9.10	17.43	10.23	25.66
	Lowest,	0.666	0.96	4.20	1.91	2.06

A study of these results shows that the soft, blue, rapidly weathering limestones are characterized by the presence of high percentages of easily oxidizable matter and phosphates, accompanied in the shaly kinds by a high percentage of insoluble matter containing a large proportion of clay. In three instances there is some appearance of a deviation from this rule. Sample No. 1 was selected as being very hard and apparently resistant to weathering, nevertheless it contains 1 per cent. of phosphoric anhydride, which is more than the average for good limestone. However, the "oxygen consumed" is not large. In samples 5 and 6, taken from a road in process of construction, the material of which was considered very good, the "oxygen consumed," while not excessive, is distinctly larger than in most of the selected gray rock, and the phosphoric acid is over 0.5 per cent., or slightly above the average. However, the uniform character of this stone is shown by the close agreement betwen the figures obtained from the selected piece, No. 5, and the average sample, No. 6. On this account the favorable opinion as to its quality may be considered to have been confirmed by this test.

CONCLUSION.

The conclusion would seem justified that the limestone which consumes much more than 0.3 per cent. of oxygen and at the same time contains as much as 1 per cent. of phosphoric acid, more especially if it contains also several per cent. of clay, will disintegrate rapidly upon exposure to air and moisture and will be undesirable for road building or other exposed construction.

While this method of analysis has not been tried upon other rocks than the Trenton limestone, it is probably of much more general application, especially that part of it which takes into account easily oxidizable constituents of rocks.

The writer is indebted to Mr. S. D. Averitt of this laboratory for assistance in the determinations of phosphoric acid and sand and the weighing of the total insoluble matter.

KENTUCKY AGRICULTURAL EXPERIMENT STATION,
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[CONTRIBUTIONS FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE DETERMINATION OF ATMOSPHERIC CARBON DIOXIDE BY THE WALKER METHOD.

BY A. G. WOODMAN.

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DETERMINATIONS of carbon dioxide in atmospheric air or in the air of rooms, where results must be obtained with a considerable degree of accuracy, are usually made by the well-known