greater rate than the other, or of selectively adsorbing to an extent easily determined quantitatively.

The nature of the surface of the constituents of a soil is such that the cation is adsorbed at a much greater rate than the anion.

The presence of bases of the soil (Ca, Mg, etc.) in solution, after contact of certain salt solutions with a soil, is not due to a direct chemical reaction of the salt in solution with the silicates of the soil, but to a secondary reaction of free acid, resulting from the selective adsorption of the cation, with the mineral constituents of the soil.

In general, the smaller the soil particles, the greater the selective adsorption of the cation.

The selective adsorption of the cation from a solution of an electrolyte by a soil increases with the concentration up to a certain point, and then remains practically constant, the surface of the soil particles having taken up all that it is able at this point. At very low concentrations the adsorption of the cation is practically complete.

The presence of other substances may or may not affect the selective adsorption by a soil.

BUREAU OF SOILS
WASHINGTON

THE ESTIMATION OF THE LIME REQUIREMENT OF SOILS BY MEANS OF THE HYDROXIDE OF THE ALKALIN EARTHS¹

By C. R. MOULTON AND P. F. TROWBRIDGE

The methods which are in use for estimating the acidity of soils are not proving to be entirely satisfactory and this gives rise to new methods and proposals for new methods. The old provisional method of the Association of Official Agricultural Chemists—shaking out the acids and acid salts with normal potassium nitrate—is open to criticism both on the score of the length of time needed for the determination and because the process does not bear any direct relation to the practice of liming soils. The method in use now, that of Veitch,² is not open to the last objection but is to the first—according to some critics—as it frequently takes a large number of determinations to fix the lime-absorbing power of the soil.

In order to cut down the length of time involved in the Veitch method, Bizzell and Lyon³ have proposed a modification of R. Albert's method. The essential points of the new method are boiling the soil with an excess of *N*/10 barium hydroxide solution and measuring the excess by means of ammonia set free from added ammonium chloride. The ammonia is distilled off and caught in *N*/10 acid. The barium hydroxide is standardized by direct titration against the acid and a correction is made for the power of the soil to set free ammonia from ammonium chloride. Fifty cc. of barium hydroxide are used and 25 g. of soil. A fixed amount is consequently always present which may greatly exceed the amount needed by the soil or may not exceed it materially.

Now in the Veitch method it is tacitly admitted that an excess of lime water will cause more calcium oxide to be absorbed by the soil, and so the least amount that will show an excess is used as the lime requirement. Some of the effects of this mass reaction have been studied in the laboratories here in the past when an attempt was made to modify the Veitch method by titrating back the excess of lime water. The lime requirement was determined by the Veitch method. Then to fresh samples of soil various amounts of lime water were added, as 5, 10, 15, 20, 25 and 30 cc. Thus in some cases there was an excess of lime water amounting to 10 cc. and in other cases the same deficiency. It was found that when evaporating the solution with phenolphthalein a considerable deficiency required but a very few cc. more lime water to give a color than did a slight deficiency. Likewise, a great excess required but little more acid to neutralize than did a small excess. In some cases but 2 or 4 drops of acid or lime water represented a difference of 10 cc. of lime water.

An attempt was made to determine what ingredients of the soil were using this excess of lime water. It was found that thoroughly washed and ignited sea sand when used in place of soil with the Veitch method used up considerable lime water as shown by the few drops of tenth-normal acid needed to destroy the color when 5, 10, or even 15 cc. of lime water were used. Sand treated once with lime water would use up considerable amounts of lime water added subsequently after decanting and washing free of the previous addition.

Enough of this unpublished work has been quoted to show that in this laboratory it was considered to be demonstrated that an excess of calcium hydroxide increased the lime requirements of soils. It was the results of this work that led us to investigate the work of Bizzell and Lyon to determine if barium hydroxide acted any differently than did calcium hydroxide.

Lime requirements were determined on a sample of soil by the method of Bizzell and Lyon, using 50 and 100 cc. of barium hydroxide. No blanks were run on the soil as they would not effect the results found. Table I shows the results of this soil.

The Veitch method gave a lime requirement of 10,420 pounds of lime per acre foot. The Bizzell and Lyon method accurately followed gave only 85 per cent

TABLE I

G. soil No. 7b	Cc. Ba(OH) ₂	Cc. Ba(OH) ₂ used by soil	G. CaO	Parts per million	Pounds per acre foot
25	50	30.40	0.06958	2783	8,350
25	50	32.90	0.07530	3012	9,036
25	50	27.29	0.06246	2498	7,495
25	100	60.00	0.13734	5494	16,481
25	100	59.14	0.13537	5415	16,244
25	100	61.20	0.14008	5604	16,811
25	35	9.80	0.02243	896	2,688
25	35	6.34	0.01451	580	1,741

of this amount, varying from 7,500 to 9,000 lbs. When double the amount of barium hydroxide called for by the Bizzell and Lyon method was used the lime requirement was increased to over 16,000 lbs., thus doubling the lime requirement.

Since about 30 cc. of hydroxide were sufficient to satisfy the soil when the determination was made as directed by the Bizzell and Lyon method, duplicate samples were run, using 35 cc. of hydroxide. In this

¹ Read before the University of Missouri Section of the American Chemical Society, March 6, 1914.

² *J. Amer. Chem. Soc.*, **24**, 1120.

³ *THIS JOURNAL*, **5**, 1011.

case the lime requirement fell to about one-fourth of the first value.

The method was further tested with a different soil and by different chemists, using various amounts of barium hydroxide water, the treatment otherwise being the same as in the Bizzell and Lyon method. Table II shows the results on this second soil. A blank was run on this soil in order to be able to make a better comparison with the Veitch method. Enough ammonia was freed by the soil to represent 1.05 cc. of $\text{Ba}(\text{OH})_2$ solution and this correction was made on the following determinations:

TABLE II					
G. soil No. 3b	Cc. $\text{Ba}(\text{OH})_2$	Cc. $\text{Ba}(\text{OH})_2$ used by soil	G. CaO	Parts per million	Pounds per acre foot
CHEMIST A					
25	00	1.17	1.05 blank	..	..
25	00	0.92		..	..
25	5	3.16	0.00858	343	1,030
25	5	3.49	0.00947	379	1,136
25	25	11.18	0.03035	1214	3,642
25	25	8.86	0.02405	962	2,866
25	50	14.11	0.03811	1523	4,597
25	50	10.41	0.02831	1130	3,391
CHEMIST B					
25	50	13.41	0.03641	1456	4,369
25	50	12.59	0.03418	1367	4,102
25	75	15.15	0.04113	1645	4,936
25	75	15.50	0.04208	1683	5,050
25	100	9.23	0.02506	1002	3,007
25	100	16.66	0.04523	1809	5,428
25	100	21.05	0.05715	2286	6,858
25	100	22.15	0.06014	2406	7,217

The Veitch method gave 6,855 lbs. of lime per acre foot, whereas the method of Bizzell and Lyon gave various amounts according to the amount of barium hydroxide used. In some cases the lime requirement found was not at all proportional to the barium hydroxide used but in general it increased as the hydroxide increased and frequently in strict proportion to the hydroxide.

In the third table the following variation of the method was used. The first two duplicates were treated as per the regular Bizzell and Lyon method until the digestion was complete when the soils were decanted upon a filter and washed three times by decantation with hot water. These washings were distilled with ammonium chloride as usual with the result that from 38 to 39 cc. of the 50 cc. of hydroxide added had not been washed out of the soil. The soil residue was again treated with 50 cc. of lime water as above and this time a further 35 to 36 cc. of the second 50 cc. of hydroxide remained with the soil. The soil residue holding about 75 cc. of barium hydroxide was then distilled and all but 13.90 cc. recovered by distillation, thus making the lime requirement comparable to that found when 75 cc. had been used in Table II.

TABLE III					
Soil 3b	Cc. $\text{Ba}(\text{OH})_2$	Cc. $\text{Ba}(\text{OH})_2$ used by soil	G. CaO	Parts per million	Pounds per acre foot
1st washing.....	50	39.30	..	..	..
1st washing.....	50	38.21	..	..	..
2nd washing.....	50	35.59	..	..	..
2nd washing.....	50	36.04	..	..	..
Soil.....	residue	15.34	0.04165	1666	4,998
Soil.....	residue	13.90	0.03774	1510	4,529

In Table II and all following work the barium hydroxide solutions used were standardized not by direct titration but by distillation exactly as in the determination but omitting the soil. It seems to the authors that this is the only logical method of standardization,

for then conditions are all alike in all cases. Any effect that boiling in the flasks has upon the barium hydroxide will have an influence upon both the standardization and the determination.

An extremely acid soil was selected for further study. In this case as the barium hydroxide was increased, the water added before distillation was decreased by the same volume so that the same amount of distillate would represent the same part of the whole. Otherwise the determination was carried out as usual.

TABLE IV					
G. soil 14-4-16	Cc. $\text{Ba}(\text{OH})_2$	Cc. $\text{Ba}(\text{OH})_2$ by soil	G. CaO	Parts per million	Pounds per acre foot
25	10	-2.20	..	..	..
25	10	-2.09	..	..	..
25	25	0.60	0.00120	48	144
25	25	4.46	0.00892	357	1,071
25	50	11.43	0.02286	914	2,742
25	50	10.86	0.02172	869	2,607
25	100	30.14	0.06028	2411	7,233
25	100	Lost	..	..	..

Table IV gives the results on this soil. The Veitch method gave a lime requirement of 17,250 lbs. per acre foot. When 10 cc. of hydroxide were used more ammonia was recovered in the distillate than corresponded to the hydroxide. Had a blank been run on this soil it might account for the difference. The sample of soil was exhausted, and so no blank could be run. The lime requirement increases much more rapidly than does the barium hydroxide used, but not even with 100 cc. does the lime requirement reach more than a third of that found by the Veitch method.

Exactly similar results were obtained from another strongly acid soil. The Veitch method gave 18,630 lbs. of lime needed per acre foot and the Bizzell and Lyon method gave 681 and 1,032 lbs. per acre foot. A soil which was alkaline by the Veitch method at no cc. of lime water was next studied. The blank by the Bizzell and Lyon method was 56.05 cc. of acid used by the ammonia freed by the soil. Table V gives the results of this work. In all cases the soil showed a lime requirement, that is, in no case was sufficient ammonia recovered in the distillate to represent the power of

TABLE V					
G. soil 14-1-109	Cc. $\text{Ba}(\text{OH})_2$	Cc. $\text{Ba}(\text{OH})_2$ used by soil	G. CaO	Parts per million	Pounds per acre foot
25	10	10.72 (a)	0.029105	1,164	3,492
25	10	15.32 (a)	0.041590	1,664	4,992
25	25	15.86	0.04306	1,722	5,166
25	25	12.21	0.03315	1,326	3,978
25	50	20.82	0.05652	2,261	6,783
25	50	18.23	0.04949	1,980	5,940
25	50 (b)	7.56	0.02052	821	2,463
25	50 (b)	10.43	0.02832	1,133	3,399
25	100	28.55	0.07751	3,100	9,300
25	100	30.78	0.08356	3,342	10,026

(a) The cc. of $\text{Ba}(\text{OH})_2$ used by the soil is expressed in terms of a tenth-normal acid which is weaker than the $\text{Ba}(\text{OH})_2$ solution.

(b) These two determinations were run by a chemist other than the one making the others.

both the $\text{Ba}(\text{OH})_2$ and the soil to free ammonia from ammonium chloride. Consequently when the soil blank was accounted for there remained some of the $\text{Ba}(\text{OH})_2$ which was held back by the soil. So even with an alkaline soil some of the added hydroxide solution will be held back on distillation and will not free ammonia from ammonium chloride. The so-called lime requirement we find by this method is considerably greater for this alkaline soil than it was for the other strongly acid soils.

The behavior of some of the determinations above

was such as to raise the question whether the lime requirement could not be varied by the length of distillation of the ammonia. Some of the samples at the end of 20 minutes had used up all the hydrochloric acid in the receiving flask, showing an alkaline reaction. Five cc. more of acid were added and again the solution in the flask turned alkaline at the end of 25 minutes, necessitating a second addition of acid which was largely used up. To further test this continued freeing of ammonia, some determinations were made and the distillate was caught in different receiving flasks by means of an adapter having a two-way stopcock between condenser and receiving flask. About 450 cc. of water were used and an 800 cc. Kjeldahl. Table VI gives results on both the acid and alkaline soil.

TABLE VI

Soil	Time	Cc. Ba(OH) ₂	G.	Parts per	Pounds per
14-4-16	Minutes.	used by soil	CaO	million	acre foot
25 g. and 50 cc. Ba(OH) ₂	20	24.32	0.04864	1,946	5,838
	40	13.29	0.02658	1,063	3,189
	60	7.38	0.01476	590	1,770
	75	3.97	0.00794	318	954
	90	0.79	0.00158	63	189
	20	35.86	0.07172	2,870	8,610
	40	21.31	0.04262	1,705	5,115
	60	13.24	0.02648	1,060	3,180
	75	6.99	0.01398	560	1,680
	90	3.12	0.00624	250	750
14-1-109 25 g. soil and 50 cc. Ba(OH) ₂	20	39.90	0.10833	4,333	12,999
	35	24.30	0.06597	2,639	7,919
	50	13.80	0.037466	1,499	4,497
	65	7.41	0.02012	805	2,415
	80	4.63	0.01257	503	1,509
	20	33.89	0.092005	3,680	11,040
	35	16.38	0.04447	1,779	5,337
	50	7.46	0.020254	810	2,430
	65	0.42	0.001140	46	138
	80	0.27	0.000733	29	87

The figures shown are for the total time given. As more ammonia was freed the barium hydroxide held by the soil was decreased until at the end of 80 or 90 minutes it had been decreased to an insignificant amount which in the acid soil might have been reduced to nothing if a blank had been run on this soil. The total volume of distillate was about 450 cc. and was distributed among the aliquots about in proportion to the time of each separate collection.

A brief survey of the data presented seems to establish the fact that the lime requirement found by the method of Bizzell and Lyon is proportionate to the barium hydroxide used and not to the acidity of the soil. The lime requirement is considerably lower than when the Veitch method is used. The lime requirement varies with the length of time of the distillation and volume of distillate until a zero lime requirement is obtained.

No consideration of the speed of a method is worth while when its performance is such as is indicated by this study. However, the experience in this laboratory shows that at least as much attention on the part of the operator is needed for the method of Bizzell and Lyon as for the Veitch method. The time consumed in evaporating, and so forth, does not enter into consideration when a chemist has other work in progress.

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A STUDY OF THE DOLOMITIC LIMESTONES OF THE ALLENTOWN QUADRANGLE

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Received June 16, 1914

The Allentown Quadrangle is located in the extreme

eastern part of Pennsylvania and is included between the parallels of 40° 30' and 40° 45' and the meridians 75° 15' and 75° 30' west, covering an area of about 226 square miles. It lies in Lehigh and Northampton counties with its southeastern corner in Bucks county. Most of the rocks in this section are more or less crystalline, being either sediments which have changed to slates, quartzites, schists and gneisses by varying degrees of metamorphism, or igneous rocks, such as granite and diabase which have solidified from a molten magma.

The basal complex¹ of the region consists chiefly of gneisses and schists. Following the formation of these deep-seated rocks occurred a long period of erosion, after which a portion of the land was submerged beneath the sea, and sand, gravel, mud and calcareous ooze were laid down in the form of marine sediments. In these deposits, now hardened to sandstone, conglomerate, shale and limestone, are to be seen fragments of waste from the igneous and metamorphic rocks of the adjacent land. Those strata are not continuous sheets, for portions of the sea bottom were, at times, uplifted into land and the sediments that had been deposited were subjected to erosion, while other portions were still submerged. The sea in which these sediments were laid down was a body of water occupying the interior of the American continent and its eastern shore oscillated back and forth across what is known as the Appalachian province, in the eastern part of which the Allentown Quadrangle is situated. Submergence began at least as early as the Cambrian, probably as early as the Algonkian, and continued to the close of Carboniferous Time.

Several great cycles of sedimentation are recorded in the rocks of this region. The first sedimentary rocks—conglomerates, sandstones and shales—were laid down early in Cambrian time along the eastern border of the interior sea as it encroached on the sinking land. As the land was worn down and erosion became less active, the sediments became finer until in late Cambrian time very little mechanical detritus reached the sea and the deposits were mainly carbonates of lime and magnesia. This condition continued into Ordovician time with no marked break in sedimentation. During Silurian time, however, great beds of quartz sand and pebbles were laid down over the limestones of the preceding age. The Carboniferous began with the formation of marine deposits, in large part limestone, which, in the southern part of the province, are of great thickness.

The sedimentary rocks of the Quadrangle are those laid down in pre-Cambrian, Cambrian and Ordovician time.

The pre-Cambrian formations of the Quadrangle are known as the Shimer graphite schist and the Franklin limestone and are of no importance in this investigation.

The Cambrian formations are known as the Hardy-ston quartzite, the Leithsville limestone and the Allentown limestone.

Of the Ordovician formations, the only one of importance to us is the Coplay limestone.

¹ G. W. Stose, Mercersburg-Chambersburg Folio, *Geological Atlas of the United States*, No. 170.