THE REMOVAL OF "BLACK ALKALI" BY LEACHING.[1]

BY F. K. CAMERON AND H. E. PATTEN.

Received August 24, 1906.

THE reclamation of soils containing "black alkali," or soluble carbonates, presents unusual difficulties. These difficulties are due in large part to the fact that soils generally show decidedly higher absorptive powers toward bases present in alkaline solutions than when the solutions are neutral or acid;[2] and that the presence of hydroxides or carbonates of the alkali metals frequently induces a "puddling" of the soil, preventing a thorough penetration by water and subsequent removal of the water with its dissolved contents by drainage. Consequently, a laboratory investigation was deemed advisable of two soils which contain "black alkali" and which are now in process of reclamation. One, a sample from North Yakima, Washington,[3] was from the surface eight inches of the experimental tract north of Wide Hollow Creek. The second sample,[4] from the Toft-Hansen tract at Fresno, California, was from the surface eight inches of a spot plainly showing "black alkali" at the surface. When collected there were a few scattering spears of grain on this spot, although all about it the grain had made a good stand. When the crust formed by the "alkali" was broken grain was found which had sprouted but had not been able to push through the crust. A calcium carbonate hard pan was found about three feet below the surface, but was also found at the same depth in adjoining fields on which there was a good stand of barley.

TABLE I.—WATER-SOLUBLE CONSTITUENTS IN SOILS FROM NORTH YAKIMA AND FRESNO, EXTRACTED BY DIGESTING ONE PART OF SOIL WITH FIVE PARTS OF WATER.

	North Yakima. Per cent.	Fresno. Per cent.
Ca	trace	trace
Mg	0.02	trace
Na	0.24	0.13
K	0.03	0.02
SO_4	0.18	0.09
Cl	0.03	0.03
HCO_3	0.27	0.16
CO_3	0.10	0.02
Total	0.87	0.45

---

[1] Published by permission of the Secretary of Agriculture.

[2] See Bulletins Nos. 30 and 32, Bureau of Soils, U. S. Dept. Agric.

[3] Sample No. 14,413, Bureau of Soils collection; Soil Survey.

[4] Sample No. 14,402, Bureau of Soils collection; Soil Survey.

Chemical analyses of the water-soluble salts in these samples by the conventional method[1] of digesting the sample with five times its weight of water gave the foregoing results.

It will be observed that both samples were of the same type of alkali soils, containing beside the soluble carbonates, notable quantities of sodium sulphate, with much lesser amounts of other sulphates and chlorides.

From the mechanical analyses of these samples together with their field properties, both the Yakima and Fresno soils would be classified as fine sandy loams.

TABLE II.—MECHANICAL ANALYSES OF SOILS FROM NORTH YAKIMA, WASHINGTON, AND FRESNO, CALIFORNIA.

Diameter. mm.	Conventional name.	North Yakima. Per cent.	Fresno. Per cent.
2–1	Fine gravel	trace	0.1
1–0.5	Coarse sand	1.3	2.1
0.5–0.25	Medium sand	2.5	3.7
0.25–0.1	Fine sand	12.8	24.7
0.1–0.05	Very fine sand	21.2	33.6
0.05–0.005	Silt	48.6	29.5
0.005–0	Clay	13.5	6.2

Experimental Methods.—The method of percolation was essentially the same as described by Schreiner and Failyer in Bulletin No. 32 of this Bureau (1906), "The Absorption of Phosphates and Potassium by Soils,"[2] with the exception that a constant water pressure was used instead of attempting to maintain the rate of percolation constant. One hundred grams of soil were placed in a paraffined brass tube fitted below with a short section of a Pasteur-Chamberland filter tube, and distilled water allowed to percolate through the soil under a constant water pressure of 199 cm., or 6.5 feet.

The volume of each percolate was measured, its electrical conductivity taken with a field bridge, and its time of flow recorded. Normal carbonates (CO_3) and bicarbonates (HCO_3) were then determined volumetrically with standard acid potassium sulphate solution, and the chlorine titrated with tenth-normal silver nitrate solution, using potassium chromate as indicator. Sulphates were not determined because the amounts here involved are too small to have any great agricultural significance, and the analytical

---

[1] Bull. No. 18, p. 65, Bureau of Soils, U. S. Dept. Agric. (1901).

[2] See also J. Physic. Chem. 10, 239, 361 (1906).

difficulties in handling quantities of this magnitude would be unjustifiably great.

Results with Soils from North Yakima.—The data obtained with the Yakima soil are given in Table III. The first column gives the time during which percolation has been progressing; the second column the volume of percolate which has passed; the third column the conductivity of the successive percolates, at 25°, expressed in reciprocal ohms multiplied by 1000, which may be converted to "specific conductivity" by multiplying by the cell factor, 3.57. The next three columns give concentrations in the successive leachings and the last three columns show the total amounts of the several constituents removed from the soil.

An inspection of the results presented in this table (III) shows that while the water which was passed through the soil was kept under a constant head, the rate of percolation was not constant but varied somewhat from time to time. The first water entering the dry soil ran through quite rapidly, but as soon as the soil became saturated, it moved much more slowly. Subsequent variations in the rate of percolation were observed, undoubtedly due in some cases, to "channeling" in the soil, in some cases probably to "silting up" of channels, and in part to the fact that as the percolation proceeded with a consequent decrease in the amount of alkali present, the strongly deflocculating action of this material became less and less, so that the soil behaved as though it underwent a change in texture as well as in structure. For these reasons the concentrations of the successive portions of the percolates, as evidenced by the conductivity as well as the analyses, did not show a *regularly* progressive change, although on the whole, the concentrations became lower and lower as percolation proceeded. These results are in harmony with many field observations where it has been found that the concentration of a drainage water may vary over quite a wide range, depending upon the rate at which the applied water moves through the soil, and upon whether a sufficient length of time had elapsed for equilibrium to result between the salts dissolved and the salts remaining in the soil.[1]

In the present case, chlorides had practically disappeared after 778 hours, when 829 cc. of water had passed through the soil.

---

[1] See Bull. No. 33, p. 10, Bureau of Soils, U. S. Dept. Agric. (1906); and this Journal, 28, 1229 (1906).

TABLE III.—EXPERIMENTAL DATA FROM NORTH YAKIMA SOIL.

Time in hours.	Volume of percolate passed.	Conductivity of successive portions of percolate $\times 10^3$. T = 25° C.	Concentration of successive portions of percolate in parts per million of solution.			Total grams constituents leached from 100 grams of soils.		
			CO_3.	HCO_3.	Cl.	CO_3.	HCO_3.	Cl.
48	37	.....	84	1,160	193	0.00304	0.0424	0.00715
120	101	.....	196	1,586	110	0.0156	0.1439	0.01420
216	170	5.76	171	753	152	0.0274	0.1962	0.0247
264	242	3.62	223	406	4	0.0433	0.2252	0.02498
312	312	4.07	168	445	2	0.0550	0.2563	0.02512
360	383	3.98	128	403	3	0.0641	0.2849	0.02533
432	473	3.38	89	385	4	0.0722	0.3199	0.02569
480	539	2.94	64	388	4	0.0764	0.3451	0.02595
558	629	2.80	73	321	1	0.0829	0.3740	0.02606
726	739	2.49	73	263	0.7	0.0909	0.4029	0.02615
778	829	2.17	73	218	trace	0.0974	0.4225	
827	917	2.04	67	221		0.1034	0.4420	
873	992	1.90	78	158		0.1093	0.4538	
940	1,097	1.71	78	130		0.1173	0.4675	
988	1,184	1.77	50	170		0.1219	0.4823	
1,065	1,314	1.63	42	185		0.1273	0.5065	
1,114	1,398	1.51	34	164		0.1301	0.5203	
1,163	1,485	1.33	22	170		0.1322	0.5352	
1,210	1,562	1.24	27	145		0.1343	0.5470	
1,259	1,642	1.03	22	127		0.1361	0.5583	
1,306	1,716	1.03	6	139		0.1365	0.5683	
1,378	1,831	1.00	8	130		0.1372	0.5733	
1,443	1,951	0.91	11	109		0.1385	0.5864	
1,499	2,050	0.93	11	115		0.1396	0.5978	
1,566	2,138	0.83	8	103		0.1404	0.6069	
1,614	2,216	0.74	6	94			0.6142	
1,665	2,306	0.71	6	85			0.6214	
1,711	2,378	0.68	6	79			0.6271	
1,785	2,490	0.61	6	73			0.6353	
1,836	2,586	0.59	0	79			0.6429	
1,884	2,673	0.59	0	67			0.6487	
1,932	2,768	0.51	0	67			0.6551	
2,004	2,908	0.45	0	67			0.6645	
2,076	3,028	0.48	0	61			0.6718	
2,148	3,148	0.43	0	55			0.6784	
2,340	3,378	.....	0	51			0.6900	
2,460	3,583	.....	0	47			0.6996	
2,580	3,813	0.51		42			0.7093	
2,772	4,088			42			0.7209	
2,887	4,276			39			0.7283	

Normal carbonates failed to appear in the percolate after 1,614 hours when 2216 cc. of solution had passed. This does not mean, however, that no normal carbonates remained in the soil for, as has been previously shown in this laboratory,[1] dilution of a normal carbonate causes a change with formation of more bicarbonate. It is certain that the amount of normal carbonates in the solution has been reduced to a point below that dangerous to plant growth. The alkali in the form of bicarbonates, however, continued to be leached from the soil after percolation had proceeded for 120 days and a total volume of over 4200 cc. had passed through the soil. The results are readily seen in Fig. 1, where the abscissas are total volume of percolate and the ordinates, total grams of the several constituents removed from the soil. It will be observed that the curves are asymptotic. In the case of the chlorides and normal carbonates, as noted above, the amounts in the successive portions of percolate soon become too small to determine accurately, but in the case of the bicarbonate amounts could still be readily determined, while the run of the figures in the table and the shape of the curve show that at the time the experiment was terminated the amount in the successive portions

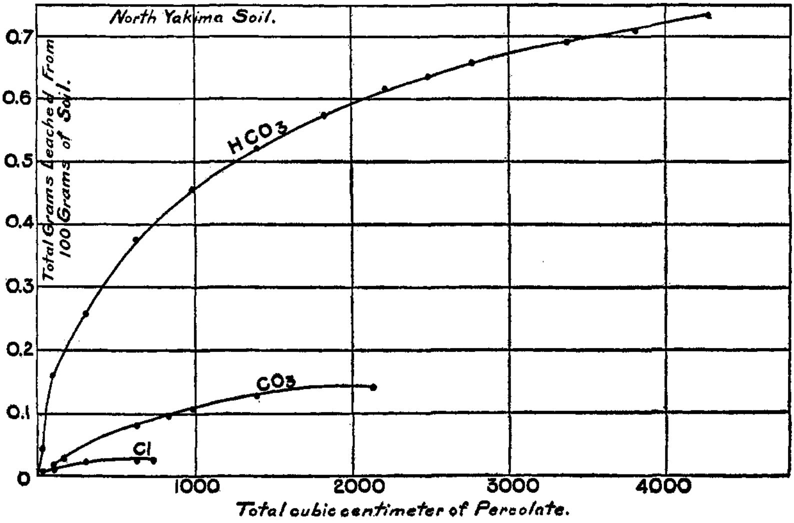

Fig. 1.

---

[1] Cameron and Briggs: Bull. No. 18, p. 14, Bureau of Soils, U. S. Dept. Agric. (1901); J. Physic. Chem. 5, 537 (1901).

of percolate was diminishing so slowly as to be almost constant. This is brought out more clearly in Fig. 2, in which the ordinates represent the concentrations in parts per million in successive portions of the percolate. The results in this chart are calculated from the curve in Fig. 1, rather than from the actually observed values, in order to avoid the accidental experimental errors noted above, and thus obtain a more accurate idea of the nature of the curve. This result is analogous to former leaching experiments made in this laboratory. An inspection of the results for bicarbonates shows, moreover, that, if the first few observations be disregarded, the leaching curve is described with fair accuracy by the equation

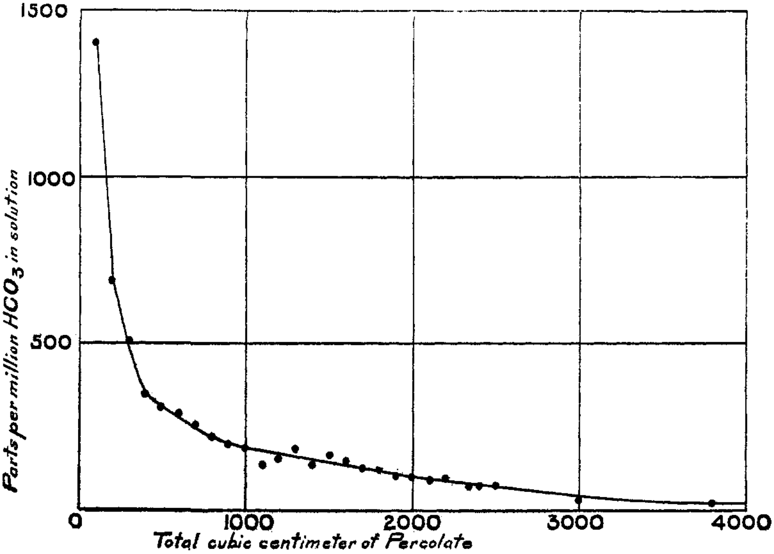

Fig. 2.

$$\frac{dy}{dv} = K(A-y),$$

proposed by Schreiner and Failyer.[1]

Results with Soils from Fresno.—In working with the Fresno sample the same experimental difficulties were encountered as with the Yakima sample, in that changes in flocculation and channeling materially affected the rate of leaching. In Table IV

---

[1] Bull. No. 32, p. 23, Bureau of Soils, U. S. Dept. Agric. (1906).

are given the rates of leaching during the earlier part of the experiment. The results are more clearly shown in Fig. 3. It will be seen that at first there was a rapid fall in the rate, and then as percolation proceeded with the formation of channels and an increase in the flocculation due to the alkali there is an increase in the rate of percolation, becoming quite regular after about 300 cc. had passed through the soil. It is believed that these changes in the physical condition of the soil as affecting percolation in these experiments are very helpful in showing what may be expected in field practice, although it must be remembered that the intermittent leaching to which the soil is subjected in the field should be more effective than the laboratory results, in so far at least as respects the volume of water required.

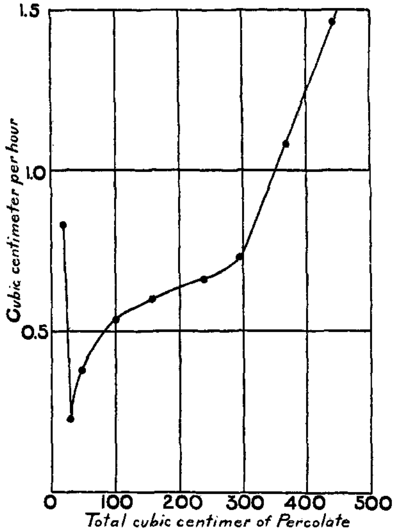

Fig. 3.

TABLE IV.—RATE OF LEACHING IN SOIL FROM FRESNO.

Total cc. percolate.	Cc. per hour.
20	0.83
31	0.23
49	0.38
101	0.54
159	0.60
238	0.66
295	0.73
368	1.08
443	1.46

In Table V are given the data obtained from the leachings of the Fresno soil, which are also shown in Figs. 4 and 5.

TABLE V.—EXPERIMENTAL DATA FROM FRESNO SOIL.

Time in hours.	Volume of percolate passed.	Conductivity of successive portions of percolate × 10³. T = 25° C.	Concentration of successive portions of percolate in parts per million of solution.			Total grams constituents leached from 100 grams of soil.		
			CO_3.	HCO_3.	Cl.	CO_3.	HCO_3.	Cl.
24	20	......	...	1,514	352	....	0.0303	0.0070
72	31	......	...	4,125	961	....	0.0757	0.0176
120	49	......	...	2,860	489	....	0.1268	0.0264
216	101	7.87	81	1,370	101	0.0042	0.1981	0.0317
312	159	3.31	45	475	0	0.0068	0.2256	
432	238	2.37	23	297		0.0086	0.2489	
510	295	1.603	12	206		0.0092	0.2606	
578	368	1.243	12	137		0.0100	0.2706	
630	444	0.842	3	112		0.0102	0.2791	
679	514	0.680	1	105		0.0103	0.2865	
724	572	0.59	0	79			0.2911	
791	656	0.52		73			0.2972	
839	724	0.53		67			0.3017	
916	833	0.49		64			0.3087	
964	912	0.401		55			0.3131	
1,014	1,000	0.366		33			0.3160	
1,061	1,083	0.361		33			0.3187	
1,110	1,162	0.351		33			0.3214	
1,157	1,230	0.376		43			0.3242	
1,229	1,345	0.417		42			0.3291	
1,301	1,459	0.400		42			0.3340	
1,357	1,558	0.370		37			0.3376	
1,424	1,667	0.334		27			0.3406	
1,472	1,744	0.307		21			0.3422	
1,523	1,829	0.312		19			0.3437	
1,569	1,905	0.283		15			0.3449	
1,643	2,017	0.296		12			0.3462	
1,694	2,104	0.293		15			0.3475	
1,742	2,185	0.293		18			0.3490	
1,790	2,271	0.292		18			0.3506	
1,862	2,393	0.235		15			0.3524	
1,934	2,513	0.209		15			0.3542	
2,006	2,626	0.202		15			0.3559	
2,198	2,856	......		17			0.3598	
2,318	3,061	......		18			0.3635	
2,438	3,291	0.362		18			0.3677	
2,630	3,575			25			0.3745	
2,745	3,756			15			0.3773	

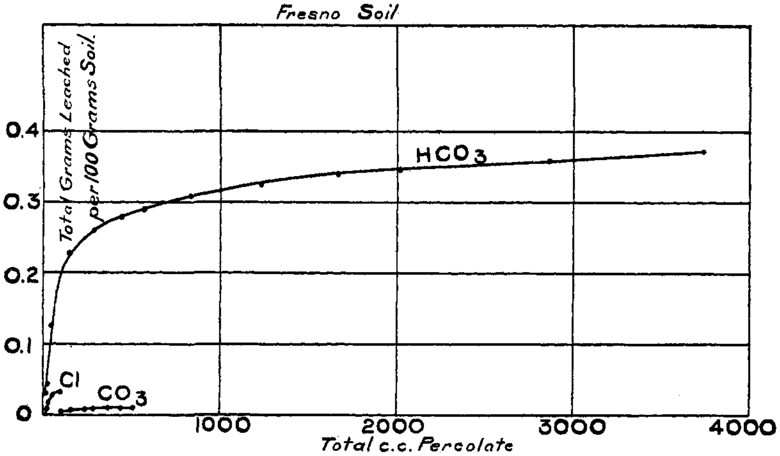
Fresno Soil
Total Grams Leached per 100 Grams Soil.
0.4
0.3
0.2
0.1
0
HCO3
Cl
CO3
1000
2000
3000
4000
Total c.c. Percolate

Fig. 4.

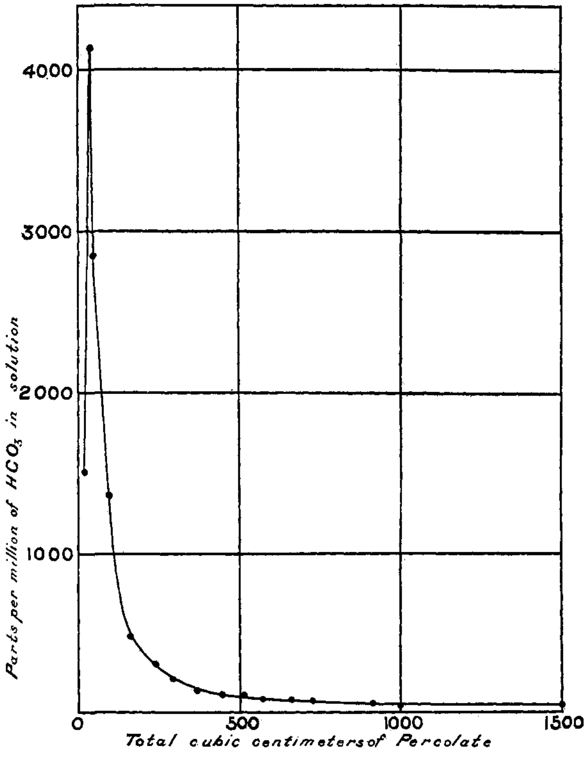
Parts per million of HCO3 in solution
4000
3000
2000
1000
0
500
1000
1500
Total cubic centimeters of Percolate

Fig. 5.

It will be observed that in general the results are very similar to those obtained with the heavier soil from Yakima, but, as might reasonably be expected, the soluble salts disappear more rapidly from the lighter soil. It will be interesting to observe also that in the case of the Fresno soil the curve for chlorides (Fig. 4) lies above that for normal carbonates while the reverse is the case with the Yakima soil (Fig. 1). This might seem to illustrate a selective absorption, which soils undoubtedly possess, but nothing of the kind can be predicted in this case, since the Yakima soil probably contained, initially, much more normal carbonates than did the Fresno sample, while both contained approximately the same amounts of chlorides. It will be further observed that the later leachings, while approaching a constant composition with respect to bicarbonates, are more dilute than in the case of the heavier Yakima soil, indicating a higher absorptive power in the latter.

The Extraction of Soluble Salts from Soils.—It will be observed that the leachings from the two soil samples here described has resulted in the removal of larger total amounts of soluble salts than the standard method of analysis shows to be originally present. The amounts of carbonates removed by the leaching process agrees with the amounts found present by digesting the soil with five times its weight of water even within the limits of experimental error. In the case of normal carbonates, the continuous leaching as compared with the digestion used in the analytical procedure, showed slightly more in the Yakima soil and somewhat less in the Fresno sample. The differences are, however, so small as to be quite possibly ascribed to analytical errors, but it should be remembered that the addition of much water has the effect of converting a part of the normal carbonates into bicarbonates, and it is in respect to this constituent that the leaching process yields much higher results than does the empirical method employed in the analytical procedure which cannot take proper cognizance of absorption effects. The results on the whole indicate that the analytical procedure, with its known inherent defects, nevertheless gives a very fair idea of the soluble constituents of the soil, where the generally impracticable method of leaching cannot be employed.

SUMMARY.

In the foregoing pages results have been presented which indicate the following conclusions:

(1) Neutral salts such as the chlorides in the presence of carbonates can be comparatively readily and completely leached from the soil.

(2) With continued leaching of soils containing "black alkali" there is an increase in the rate at which percolation takes place, due probably to the reduction of the amount of alkali present and its effect on the physical structure of the soil.

(3) With continued leaching there is a comparatively rapid reduction of normal carbonates in the soil water, due in large measure to conversion into bicarbonates.

(4) Bicarbonates are rapidly removed at first and then continue to be slowly removed in the soil water in very small amounts, diminishing so slowly as to be practically constant for an indefinite period.

(5) Soils containing "black alkali" can be reclaimed by leaching, but the time and the amount of water required are probably much greater than in the case of "white alkali."

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

THE CRYSTALLINE SUBSTANCES OF PRICKLY ASH BARK.[1]

BY H. M. GORDIN.

Received August 11, 1906.

THE discovery of a crystalline substance in northern prickly ash (*Xanthoxylum fraxineum*, s. *X. Americanum*) is due to E. Staples.[2] The same crystals were later isolated by J. U. Lloyd[3] and more fully examined by G. Eberhardt.[4] To this substance the name of xanthoxylin (xanthoxyline) was given by Staples.

Another crystalline substance was isolated by G. Colton[5] from southern prickly ash (*Xanthoxylum Carolinianum*, s. *X. Clava-Herculis*) and was shown by Eberhardt[6] to be different from the

[1] A preliminary report of this work was read before the A.Ph.A. in 1903.

[2] Am. J. Pharm. 1829, 163.

[3] Ibid. 1890, 229.

[4] Ibid. 1890, 231.

[5] Ibid. 1890, 191.

[6] Loc. cit.