# HILGARDIA

A Journal of Agricultural Science Published by the California Agricultural Experiment Station

**VOLUME 8** 

**JANUARY**, 1934

NUMBER 5

CONTENTS

# PRINCIPLES GOVERNING THE RECLAMATION OF ALKALI SOILS

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## PRINCIPLES GOVERNING THE RECLAMATION OF ALKALI SOILS<sup>1, 2</sup>

W. P. KELLEY<sup>3</sup> AND S. M. BROWN<sup>4</sup>

#### INTRODUCTION

OUR PRESENT UNDERSTANDING of alkali soils is based on two lines of investigation. Hilgard<sup>(14)</sup> was chiefly responsible for the first of these. He showed that the peculiar properties of alkali soils are caused by excessive concentrations of soluble salts; and that while high concentrations of soluble calcium, magnesium, and potassium salts are often found, sodium salts usually predominate. The other phase of the subject, developed during the past twenty years by a considerable number of investigators, is concerned with the principles of base exchange. It has been found that soluble sodium salts, upon accumulating in the soil, react by base exchange with certain constituents of the soil, thus altering the ratio of its replaceable bases. The importance of this discovery inheres in the fact that the replacement by sodium of the bases which normally occur in soils profoundly affects the chemical, physical, and crop-producing powers of the soil. Generally speaking calcium is the dominant replaceable base of normal soils. Alkali soils, on the other hand, often contain much replaceable sodium. This fact has a very important bearing on the reclamation of alkali soils.

*Hilgard's View.*—As is well known, Hilgard<sup>5</sup> devoted extended study to the origin and mode of accumulation of the soluble salts in soils; to

<sup>&</sup>lt;sup>1</sup> Received for publication July 13, 1933.

<sup>&</sup>lt;sup>2</sup> Paper No. 283, University of California Graduate School of Tropical Agriculture and Citrus Experiment Station, Riverside, California.

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<sup>&</sup>lt;sup>5</sup> The data on which Hilgard's book on soils<sup>(14)</sup> is based were taken chiefly from the numerous papers which he and his associates published originally in the various Bulletins and Annual Reports of the California Agricultural Experiment Station from 1877 to 1904.

the tolerance of plants for the soluble salts that occur in alkali soils, and to methods of alkali-soil reclamation. He found that the soluble salts are chiefly chlorides, sulfates, carbonates, and bicarbonates of sodium, and that these salts arise, either directly or indirectly, through the natural weathering process to which rock masses are subjected in the state of nature. The ratios of the different salts vary widely from place to place, and the effects produced on plants by different salts also vary greatly. Hilgard found that  $Na_2CO_3$  is extremely toxic, NaCl somewhat less so, and  $Na_2SO_4$  still less toxic. Hence special emphasis was placed on the soluble anions of alkali soils.

When the soluble salts have been removed, as by leaching, Hilgard believed that an alkali soil would be restored to a normal state. He recognized, however, that the physical properties of alkali soils are sometimes extremely adverse. This was attributed to the deflocculating effect of  $Na_2CO_3$ . If  $Na_2CO_3$  is present, he held that it may be necessary to apply gypsum, or some substance which produces similar effects, before it is possible to leach out the soluble salts. Hilgard assumed that the chemical effect of gypsum would be that of the well-known chemical reaction which takes place when a soluble calcium salt is added to a solution of  $Na_2CO_3$ , as follows:

$$CaSO_4 + Na_2CO_3 \neq CaCO_3 + Na_2SO_4$$
.

Thus upon applying gypsum the alkaline and therefore deflocculating  $Na_2CO_3$  will be converted into insoluble  $CaCO_3$  and neutral  $Na_2SO_4$ ; consequently, the soil will become flocculated and then the soluble salts can be effectively leached out.

Hilgard subdivided alkali soils into two classes, namely, "white alkali" and "black alkali." The soluble salts of the former are neutral compounds, chiefly chlorides and sulfates, while the latter contain  $Na_2CO_3$ and may also contain high concentrations of NaCl and  $Na_2SO_4$ .

Present View.—Consideration of the researches of de Mondesir,<sup>(21)</sup> Hissink,<sup>(15)</sup> Gedroiz,<sup>(7)</sup> de 'Sigmond,<sup>(24)</sup> de Dominicis,<sup>(6)</sup> Cummins and Kelley,<sup>(5, 18)</sup> and other students of base exchange, shows that there is an important deficiency in Hilgard's views. He failed to take into consideration the extremely important fact that under certain conditions the soluble sodium salts react by base exchange with the clay and humus of the soil. The Na-clay and Na-humate thus formed, being insoluble in water, are not readily removed from the soil by leaching. Moreover, it is now known that Na-clay and Na-humate cause special difficulties in the practical reclamation of alkali soil. Hence the mere removal of the soluble salts will not necessarily restore the soil to a normal condition.

It is well established that soil containing replaceable sodium tends

to become highly deflocculated and more or less alkaline upon leaching, owing to hydrolysis of Na-clay and Na-humate.<sup>(5, 7, 8, 11, 21, 22)</sup> The soluble product of the hydrolysis, NaOH, becomes converted into Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> by CO<sub>2</sub>. When the concentration of soluble sodium salts has been reduced to a low level, interaction sets in between Na-clay or Na-humate and CaCO<sub>3</sub>, which also results in the formation of Na<sub>2</sub>CO<sub>3</sub>. Thus the soil solution of an alkali soil will tend to be alkaline in a chemical sense as long as sodium constitutes a high percentage of the total replaceable cations.

Gedroiz,<sup>(7, 8)</sup> Hissink,<sup>(15)</sup> de 'Sigmond,<sup>(24)</sup> and others <sup>(5, 18)</sup> have found that base exchange has an important effect on the physical properties of the soil. According to Gedroiz,<sup>(10)</sup> the pronounced deflocculation that develops upon leaching Na-saturated soil is due to the OH ions that are formed through hydrolysis. He concluded that the consequence of this deflocculation is the gradual development of peculiar morphological structures within the soil profile. Since leaching a sodium saline soil promotes the formation of Na<sub>2</sub>CO<sub>3</sub> and produces adverse physical effects on the soil, Gedroiz<sup>(7, 8)</sup> concluded that leaching may produce actual injury rather than benefit to the soil.

Relation of Black Alkali and White Alkali to Solonetz and Solonchak.—For many decades Russian investigators have subdivided alkali soils into two classes, namely, solonetz and solonchak. These two terms are now widely used in the soil literature of the world, but not always in precisely the sense of the original Russian usage. Strictly speaking, solonetz denotes an alkali soil which contains a relatively low content of soluble salts. However, Glinka<sup>(12)</sup> and other soil morphologists in Russia, and more recently students of soil classification in the United States, have used the term solonetz to denote certain morphological features of the soil profile, but without special regard either to the soluble salt content or the specific base that is held by the exchange complex of the soil. On the other hand, Gedroiz<sup>(8, 11)</sup> employed the term solonetz to denote soil containing replaceable (absorbed) sodium.

Solonchak denotes a soil high in soluble salts. Generally speaking white-alkali soils belong to the solonchak class, but solonchak may contain  $Na_2CO_3$  as well as chlorides and sulfates. The profile of solonchak does not show characteristic morphological structures. The solonchaks are subdivided into sodium solonchaks, calcium solonchaks, chloride solonchaks, sulfate solonchaks, etc., depending upon the specific kind of salt that predominates.

Gedroiz showed that solonetz is derived from solonchak through leaching, but that only one kind of solonchak can be converted into solonetz, namely, sodium solonchak. Calcium solonchak does not pass into solonetz

upon leaching because the formation of Na-clay does not take place under these conditions. Although Gedroiz<sup>(8, 11)</sup> pointed out that sodium solonchak must necessarily contain more or less replaceable (absorbed) sodium, his usage of the term solonetz in various places in his publications is, as pointed out above, in the sense of soil containing replaceable (absorbed) sodium. Thus it is evident that Gedroiz has placed special emphasis on the cations of alkali soils, whereas Hilgard placed the emphasis on the soluble anions.

Gedroiz'(10) views as to the origin of the solonetz morphological structures are briefly as follows: Soluble sodium salts, upon accumulating in the soil, react with the base-exchange complex of the soil. This leads to the formation of simple calcium and magnesium salts and of Na-clay and Na-humates (absorbed sodium). The Na-clay and Na-humates thus formed remain in a state of flocculation as long as the soil contains a high concentration of soluble salts, but when the soluble salts have been leached out the clay constituents pass into a condition of high dispersion or deflocculation. The dispersed particles then gradually become elutriated downward, in consequence of which relatively dense subsoil horizons are formed. The zones, in which the elutriated particles accumulate, being relatively rich in Na-clay, develop the peculiar morphological structures that are characteristic of solonetz, owing to the inherent properties of Na-clay when largely freed from soluble electrolyte. Thus the solonetz morphological structures arise from sodium salines through leaching.

Solonetz is also relatively unstable chemically. Its chemical instability is due to the fact that Na-clay and Na-humate undergo hydrolysis upon leaching out the soluble salts, giving rise to H-clay and H-humate. Gedroiz holds that H-clay is itself relatively unstable and that it may gradually disintegrate into simple oxides. The pronounced development of this disintegration Gedroiz looks upon as the degradation stage of solonetz for which he employed the term *solodi*. However, if CaCO<sub>3</sub> be present in the soil, Ca ions will pass into solution upon leaching out the soluble salts and these ions will then begin to replace Na from the exchange complex with the consequent formation of Na<sub>2</sub>CO<sub>3</sub> and stable Ca-clay. Hence CaCO<sub>3</sub> tends to prevent the decomposition of the clay constituents of a solonetz. Therefore, solonetz may either pass into solodi upon prolonged leaching or into a condition similar to that of normal soil.

Black-alkali soil, as defined by Hilgard, is related to solonetz but is not necessarily identical with solonetz. As stated already, the morphological structures that are characteristic of solonetz arise through the leaching of sodium salines, and it is probable that the solonetz structures arise only in this way. As stated above, the formation of Na<sub>2</sub>CO<sub>3</sub> sets in when the concentration of soluble sodium salts becomes reduced to a low level by leaching, owing to hydrolysis of Na-clay and Na-humate, or to the reaction of these constituents with CaCO<sub>3</sub>. However, the occurrence of Na<sub>2</sub>CO<sub>3</sub> in the soil is not necessarily proof that leaching of that particular soil has actually taken place. Sodium carbonate may be transported by means of water from one place to an entirely different location. Gedroiz<sup>(11)</sup> has pointed out that soil into which Na<sub>2</sub>CO<sub>3</sub> arises by capillarity inevitably acquires the chemical property of solonetz, whether it be subjected to leaching or not. Moreover, since NaCl and Na<sub>2</sub>SO<sub>4</sub> may arise into the surface soil from the subsoil by capillarity along with Na<sub>2</sub>CO<sub>3</sub>, black-alkali soil may have the chemical properties without the morphological structures of solonetz. Thus it follows that a sodium solonchak may contain Na<sub>2</sub>CO<sub>3</sub> and therefore conform to Hilgard's definition of black-alkali soil.

Briefly, then, black alkali denotes soil which contains  $Na_2CO_3$ , while solonetz has a twofold significance, namely morphological and chemical, i.e., it refers to certain morphological features of the soil profile and to the presence of replaceable (absorbed) sodium. Since soils which contain  $Na_2CO_3$  also probably always contain more or less replaceable (absorbed) sodium, black alkali is equivalent to solonetz in a chemical sense, but not necessarily so in a physical sense.

#### EXPERIMENTAL RESULTS

The results of the authors' investigations on two widely different types of alkali soil will be presented as a basis for discussion of the important principles that are involved in the reclamation of alkali soils in general.

#### BLACK-ALKALI SOILS

Description of the Fresno Type.—The black-alkali soil of the Fresno area of California is a fine sandy loam low in organic matter. The soil and subsoil are approximately uniform in texture to a depth of 2 to 3 feet, below which there is a compact layer 2 to 6 inches in thickness, which is rich in  $CaCO_3$ . Immediately below this calcareous layer, soil material is found similar to that on or near the surface of the soil, and this extends down to variable depths where another compact calcareous layer is encountered. This succession of sandy loam materials and calcareous horizons extends to a relatively great depth. The surface soil contains somewhat less than 0.1 per cent  $CaCO_3$ . The profile of this soil does not present a clearly defined sequence of soil horizons such as occur

in more mature soils of other localities. Moreover, the morphological structures that are characteristic of solonetz are also absent from it. This soil is therefore a sodium solonchak. The alkalinity of this soil is due primarily not to hydrolysis of Na-clay and Na-humate of the soil, but to  $Na_2CO_3$  that has accumulated by capillary rise from subsoil horizons. This fact has some bearing on the experimental results, as will be pointed out later.

Treatments.—In 1920 a series of plot experiments was begun on an area of this soil on the Kearney Ranch near Fresno. At that time the soil was extremely toxic to cereals, alfalfa, and other crops. The soil contained a relatively high concentration of soluble sodium salts consisting chiefly of chloride, sulfate, carbonate, and bicarbonate. The total concentration of soluble salts was greatest near the surface of the soil. The clay and humus of the soil had been largely converted, through base exchange, into sodium compounds. It was expected, therefore, that leaching would cause more or less hydrolysis of the base-exchange constituents. Further reference to this point will be made later.

The discussion of the Fresno experiments will be confined to three plots, namely, plot 4, treated with 15 tons per acre of gypsum, 9 tons of which were applied in 1920 and 6 tons in 1921; plot 5, a check plot, to which no material other than irrigation water has been applied; and plot 10, which was treated in 1921 with 3,600 pounds per acre of elemental sulfur.

After applying gypsum to plot 4 this plot and also plot 5 were flooded with water, and were kept submerged by repeated applications of water, for two successive periods of approximately three weeks each in the summer of 1920 and again in 1921. The sulfur plot No. 10, was flooded for a period of about three weeks in September, 1921. Subsequently no material other than irrigation water has been applied to any of these plots. The amount and frequency of irrigation has been somewhat in excess of that usually practiced in this locality.

Effect of Gypsum and Sulfur.—The crop records are reported in table 1. It is shown that both the gypsum and the sulfur plots have produced good yields of crops for a period of several years. The data presented in tables 2 and 3 confirm those reported in 1928,<sup>(16, 19)</sup> in showing that the concentration of water-soluble salts<sup>6</sup> has been greatly reduced by the treatments. In fact the gypsum and sulfur plots do not now contain injurious concentrations of soluble salts at any depth above 48 inches. The data on replaceable bases reported in tables 4 and 5 show that replaceable sodium has also been chiefly removed from these plots.

<sup>&</sup>lt;sup>6</sup> The water-soluble constituents were determined in 1:5 water extracts of the soil.

Year	Сгор	Plot 4; treated with gypsum, 1920	Plot 5; leached	Plot 10; treated with sulfur, 1921
1921	Barley hay	2,865	1,770	
1922	Barley hay	3,216	2,584	300
1923	Melilotus indica	Plowed under as		
1924	Melilotus alba	green manure Plowed under as green manure	••••••	
1925	Alfalfa	5,955	3,585	18,467
1926	Alfalfa	Uncropped	Uncropped	23,658
1927	Alfalfa	11,742	6,255	20,138
1928	Alfalfa	18,858	15,446	5,873*
1929	Alfalfa	16,785	15,617	10,570
1930	Alfalfa	19,082	17,494	18,902
1931		Uncropped	Uncropped	Uncropped
1932	Cotton	1,622	1,874	

# TABLE 1 CROP RECORDS OF THE FRESNO EXPERIMENTS (Pounds per acre)

\* Barley hay.

#### TABLE 2

## WATER-SOLUBLE SALTS, PLOT 4; TREATED WITH GYPSUM

#### (Milliequivalents per 100 grams)

Depth in inches	CO <sup>8</sup>	HCO <sub>8</sub>	Cl	SO4	Ca	Mg	K	Na
			Before tre	atment (19	20)			
0-12	0.94	0.80	0.32	0.20	trace	trace	0.20	2.06
12-24	0.49	0.51	0.46	0.21	trace	trace	0.20	1.47
24-36	0.43	0.34	0.39	0.14	trace	trace	0.21	1.09
36-48	0.15	0.40	0.32	0.13	trace	trace	0.18	0.82
· · · · · ·		<u> </u>	After trea	tment (193	1)	· · · · · · · · · · · · · · · · · · ·		
0-12	0.00	0.40	0.05	0.02	0.23	trace	trace	0.24
12-24	0.00	0.32	0.08	0.04	0.17	trace	trace	0.27
24-36	0.15	0.35	0.08	0.04	0.12	trace	trace	0.50
36-48	0.15	0.50	0.10	0.04	0.07	trace	trace	0.67

#### TABLE 3

### WATER-SOLUBLE SALTS, PLOT 10; TREATED WITH SULFUR

(Milliequivalents per 100 grams)

Depth in inches	CO3	HCO <sub>8</sub>	Cl	SO4	Ca	Mg	к	Na
			Before tre	atment (19	21)			
0–12	1.15	0.90	1.53	0.65	trace	trace	0.17	4.06
12-24	0.60	0.64	1.24	0.41	trace	trace	0.17	2.72
24-36	0.53	0.68	0.70	0.19	trace	trace	0.20	1.90
36–48	0.42	0.57	0.50	0.12	trace	trace	0.20	1.41
			After trea	atment (19	31)			
0-12	0.00	0.25	0.05	0.04	0.10	trace	trace	0.24
12-24	0.00	0.30	0.05	0.05	0.12	trace	trace	0.28
24-36	trace	0.50	0.07	0.07	0.07	trace	trace	0.57
36-48	0.30	0.62	0.07	0.10	trace	trace	trace	0.79

#### TABLE 4

#### REPLACEABLE BASES, PLOT 4; TREATED WITH GYPSUM

Milliequ	ivalents per 10	Na as per cent		
Ca + Mg	K Na		of total	pH
Befo	re treatment (1	1920)		
1.08	0.23	3.13	70	9.67
0.42	0.98	2.87	67	9.42
1.78	0.28	2.41	54	9.59
2.57	0.34	1.59	35	9.11
Afte	er treatment (1	931)		
	0.00	0.27	5	7.53
4.59	0.00	0.40	8	8.10
	0.00 .	0.43	8	8.30
. 4.13	0.00	1.00	19	8.70
	Ca + Mg Befo 1.08 0.42 1.78 2.57 Afte 5.05 4.59 4.63	Ca + Mg         K           Before treatment (1            1.08         0.23           0.42         0.98           1.78         0.28           2.57         0.34           After treatment (1            5.05         0.00            5.05         0.00            4.63         0.00	Before treatment (1920)           I.08         0.23         3.13           0.42         0.98         2.87           1.78         0.28         2.41           2.57         0.34         1.59           After treatment (1931)            5.05         0.00         0.27            5.05         0.00         0.40            4.63         0.00         0.43	Ca + Mg         K         Na         Na as per cent of total           Before treatment (1920)           1.08         0.23         3.13         70            0.42         0.98         2.87         67         67           1.78         0.28         2.41         54          2.57         0.34         1.59         35           After treatment (1931)            5.05         0.00         0.27         5          4.59         0.00         0.43         8

#### TABLE 5

#### REPLACEABLE BASES, PLOT 10; TREATED WITH SULFUR

	Milliequ	ivalents per 1	Na as per cent	pH	
Depth in inches	Ca + Mg	u + Mg K Na			of total
	Befo	re treatment (	1921)		
0–12	1.35	0.44	2.51	. 58	9.67
12–24	1.21	0.34	2.90	65	9.20
24–36	3.19	0.20	2.00	37	8.98
36-48	3.61	0.13	1.26	25	9.43
	Afte	er treatment (1	931)	<b>b b</b>	
0–12	4.06	0.29	0.21	5	7.05
1224	3.75	0.15	0.44	10	7.50
24-36	4.05	0.37	0.38	8	8.80
36-48	3.66	0.30	0.85	17	9.30

Before the experiments were begun, sodium comprised from 60 to 70 per cent of the total replaceable bases of the soil. The treatments with sulfur and gypsum have, however, brought about the replacement of practically all the sodium by calcium. Therefore, the soil of neither of these plots can now be properly regarded as alkali soil. It has become normal in every essential particular. Effect of Leaching.—Although good results were obtained within a comparatively brief period following the application of gypsum or sulfur, the check plots failed to produce satisfactory yields of crops for several years. In fact certain parts of the check plots remained totally unproductive for some time after these experiments were begun, notwithstanding the fact that the leaching, to which they were subjected, was effective in removing the principal part of the soluble salts. During the course of the experiment it was noted, however, that the size of the unproductive spots within the check plots diminished from year to year.



Fig. 1. Barley, plot 5 of the Fresno experiment, after it was leached in 1920. The barley crop failed to grow on much of this plot. Photographed April 20, 1921.

These spots finally disappeared entirely in 1928, when a complete stand of alfalfa was obtained over practically all parts of the check plots. Subsequently the check plots have produced large yields of crops. In 1932 cotton was planted on these plots. The cotton seeds germinated uniformly, and fully as large yields were obtained from the check plots as from the gypsum plots (table 1 and figs. 1, 2, 3).

Gedroiz, <sup>(7, 8)</sup> as stated already, concluded that the suitability for crop growth of a sodium saline soil, such as that of these experiments, would be adversely affected rather than benefited by leaching, owing to deflocculation and the excessive alkalinity that would be produced through the formation of Na<sub>2</sub>CO<sub>3</sub>. As is well established, the formation of Na<sub>2</sub>CO<sub>3</sub> will not take place as long as the soil contains a high concentration of soluble sodium salts owing to the effect of a common ion on hydrolysis, but when the concentration is reduced sufficiently through leaching, it is reasonable to expect that more or less Na<sub>2</sub>CO<sub>3</sub> would be formed in the

soil. The crop yields obtained during the early years of this experiment seemed to support Gedroiz' hypothesis, for, as pointed out already, the check plots failed to produce satisfactory growth of crops for several years (figs. 1 and 2).

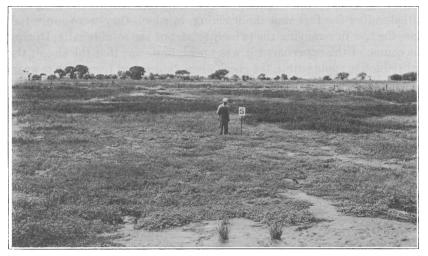


Fig. 2. Alfalfa, plot 5, after having been leached in 1920 and 1921. The plants shown in the foreground are alkali weeds consisting chiefly of *Tissa salina*. When this photograph was taken (September 16, 1925) the practical failure of alfalfa shown thereon indicated that this plot had not been benefited by leaching.

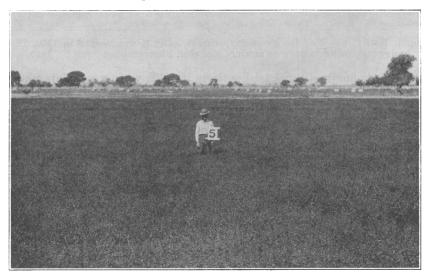


Fig. 3. Alfalfa, plot 5, photographed August 23, 1930. The normal growth of alfalfa presents a striking contrast to that of 1925 (see fig. 2). No material other than irrigation water has been applied to this plot. Jan., 1934]

The data reported in tables 6 and 7 show the transformations that have been produced by leaching. It will be noted that the water-soluble salts and the replaceable sodium have been largely removed from the upper two feet of the soil. On the other hand, the content of replaceable sodium in the subsoil (36–48 inches) of this plot has been increased slightly, probably because of the leaching down of the soluble sodium salts that originally occurred near the surface of the soil.

Depth in inches	$\mathbf{CO}_3$	HCO3	CI	SO4	Ca	Mg	к	Na
		·	Before le	aching (192	20)			
0-12	1.05	0.73	0.62	0.33	trace	trace	0.14 ·	2.59
12-24	0.49	0.52	0.62	0.26	trace	trace	0.11	1.78
24-36	0.42	0.38	0.54	0.17	trace	trace	0.24	1.27
36–48	0.15	0.38	0.34	0.10	trace	trace	trace	0.97
			After lea	ching (193	L)			
0–12	trace	0.52	0.05	0.05	0.06	trace	trace	0.56
12-24	0.15	0.45	0.07	0.06	0.04	trace	trace	0.69
24–36	0.55	0.50	0.07	0.03	trace	trace	trace	1.15
36–48	0.70	0.65	0.12	0.05	trace	trace	trace	1.52

TABLE 6
WATER-SOLUBLE SALTS, PLOT 5, AS AFFECTED BY LEACHING
(Milliequivalents per 100 grams)

#### TABLE 7

#### REPLACEABLE BASES, PLOT 5, AS AFFECTED BY LEACHING

	Milliequi	valents per 10	Na as per cent		
Depth in inches	Ca + Mg	Ca + Mg K Na		of total	pН
	Befo	ore leaching (19	920)		
0–12	1.21	0.33	2.90	65	9.18
12-24	1.17	0.33	3.61	70	9.15
24-36	2.89	trace	2.49	46	8.61
36–48	3.46	0.23	1.43	28	8.59
	Afte	er leaching (19	31)		
0-12	4.66	0.00	0.30	6	8.07
2-24	4.44	0.00	1.20	21	8.70
4-36	4.35	0.00	1.54	26	9.03
36-48	3.07	0.00	3.45	53	9.30

Since the subsoil of the check plot still contains considerable soluble carbonate and replaceable (absorbed) sodium, it has not yet been completely restored to a state of normality. However, the data strongly indicate that a continuation of ordinary methods of soil management, provided it includes the liberal application of irrigation water, will ultimately bring about the complete elimination of sodium carbonate and replaceable sodium from the subsoil of the check plot, just as has already taken place in the gypsum and sulfur plots. Moreover, there is no evidence that this plot has been actually injured by leaching. The results, therefore, are not in harmony with Gedroiz' conclusion.

	Well water, Fresno experi- mental tract	Colorado River water*
HCO3	2.54	2.99
C1	0.42	3.20
SO4		7.94
Са	1.50	4.90
Mg	1.00	2.86
Na		6.44

TABLE 8
Composition of Irrigation Water
(Milliequivalents per liter)

\* Mean on 41 analyses of samples taken at Yuma, Arizona, as reported in: Scofield, C. S., and L. V. Wilcox. Boron in irrigation waters. U. S. Dept. Agr. Tech. Bul. **264**: 58, 1931.

#### COMPOSITION OF IRRIGATION WATER

The salt content of the irrigation water is important in connection with the reclamation of alkali soil, as was pointed out previously by Scofield and Headley,<sup>(23)</sup> and by Kelley and Brown.<sup>(17)</sup> The experiments of Gedroiz, (7) de Dominicis, (6) Cummins and Kelley, (5) and others, showing that extremely adverse chemical and physical conditions develop in sodium saline soils upon leaching out the soluble salts, were all conducted with the aid of distilled water. On the other hand, irrigation waters usually contain more or less dissolved salts. Hibbard<sup>(13)</sup> showed that water containing even a relatively low concentration of dissolved salts is more effective as a leaching agent than distilled water. American irrigation waters not only contain more or less dissolved salts, but, what is still more important, they commonly contain considerable calcium salts. When an alkali soil is leached with water of this kind much less hydrolysis takes place than with distilled water; the Ca ions and Mg ions of the water tend to replace sodium from the exchange complex, and the electrolytes flocculate the soil colloids. The net result is that the soil tends to remain in a flocculated condition.

The effectiveness of irrigation water in the reclamation process is dependent both on its total content of soluble salts and on the ratio of its divalent to monovalent bases. The irrigation water used in the Fresno experiments contains about 250 p.p.m. total salts with a ratio of sodium to divalent bases of approximately 1:3 (see table 8). Many other irrigation waters are still more favorable, since they contain considerably higher concentrations of calcium and magnesium salts.

It is not possible to assign a quantitative value to the effects produced by the irrigation water that was used in the foregoing experiments, owing to the complexity of the components of the systems under consideration. However, in addition to serving as a vehicle for the removal of soluble salts, it is highly probable that the irrigation water, through its content of calcium salts has, nevertheless, contributed something towards the conversion of Na-clay into Ca-clay.

#### THE ROLE OF CaCO<sub>3</sub> IN THE RECLAMATION PROCESS

The high concentration of sodium salts, which had accumulated in the Fresno soil before the experiments were begun, undoubtedly brought about the replacement of a large part of the replaceable calcium and magnesium by sodium. However, the calcium and magnesium thus replaced were not converted into soluble calcium and magnesium salts, but were probably precipitated in the soil mass principally as carbonates, through combination with soluble  $CO_3$  ions, and to a lesser extent as silicates. Consequently, the leaching process has not removed any important amount of calcium and magnesium from the soil. The available data justify the conclusion that, upon reducing the concentration of soluble sodium salts by leaching, the labile calcium minerals (probably chiefly  $CaCO_3$ ) began to react with the sodium exchange complex (Na-clay and Na-humate). Consequently sodium has been gradually replaced by calcium with the formation of  $Na_2CO_3$  and  $NaHCO_3$ . A possible explanation of the reactions is as follows:

 $Na-clay + CaCO_3 \rightleftharpoons Ca-clay + Na_2CO_3$ 

 $Na_2CO_3$ , thus formed, would be converted, partially at least, into  $NaHCO_3$  by the action of  $CO_2$  of the soil.

Or, it may be assumed that hydrolysis first intervened and that the H-clay thus formed reacted with CaCO<sub>3</sub> as follows:

$$\begin{split} & \text{Na-clay} + \text{HOH} \rightleftarrows \text{NaOH} + \text{H-clay} \\ & \text{H-clay} + \text{CaCO}_{\text{s}} \rightleftarrows \text{Ca-clay} + \text{H}_{2}\text{CO}_{3} \\ & \text{H}_{2}\text{CO}_{3} + \text{NaOH} \rightleftarrows \text{NaHCO}_{3} + \text{H}_{2}\text{O} \end{split}$$

Therefore, the end products would be essentially the same whether CaCO<sub>3</sub> reacted directly with Na-clay or indirectly with H-clay formed

by hydrolysis of Na-clay. In either case these reactions would bring about the replacement of sodium and a corresponding increase in replaceable calcium. Sodium carbonate and  $NaHCO_3$  formed by these reactions have been leached down into the subsoil and partially into the underdrainage.

As Cummins and Kelley<sup>(5)</sup> pointed out, the extent to which Na-clay undergoes hydrolysis in pure water is limited by two factors, namely, the low ionization of water and the concentration and composition of the soluble sodium salts that are present. Theoretically we would expect that at the equilibrium point of this reaction the ionization constant of the Na-clay would equal that of the NaOH formed. Since the former is relatively low, the total concentration of NaOH will also be low. However,  $CO_2$ , which is commonly present in soils to some extent, exerts a potent influence, first through increasing the ionization of water and secondly through converting NaOH into NaHCO<sub>3</sub>. Thus carbonated water will be more effective than pure water in the conversion of Naclay into H-clay.

That  $CaCO_3$  has played the important role indicated above is shown by the determination of the insoluble  $CO_3$  of the soil. It has been found (table 9) that the content of insoluble  $CO_3$  has been materially altered as a result of these treatments. It will be noted that the check plot, No. 5, has lost a large part of its insoluble  $CO_3$ . It is logical to conclude, therefore, that the changes which have taken place in the replaceable bases of the check plot have been produced, partially at least, by  $CaCO_3$ .

	Pla	ot 4	Plo	ot 5	Plot 10	
Depth in inches	Before treatment (1920)	After treat- ment with gypsum (1931)	Before leaching (1920)	After leaching (1931)	Before treatment (1921)	After treat- ment with sulfur (1931)
0-12 12-24	0.0294 0.0729	0.0372 0.0989	0.0419 0.0562	0 0121 0.0025	0.0728 0.0120	0 0

TABLE 9

#### PERCENTAGE OF INSOLUBLE CO3 AS AFFECTED BY VARIOUS TREATMENTS

It will also be noted that the insoluble  $CO_3$  of the gypsum plot has been increased slightly. This was probably due to the formation of  $CaCO_3$  through the interaction of  $CaSO_4$  (gypsum) and soluble  $CO_3$  of the soil. In this connection it may be pointed out that these results afford strong evidence that this soil actually contains  $Na_2CO_3$ , despite the claim of Breazeale and McGeorge<sup>(3)</sup> that black-alkali soils do not contain  $Na_2CO_3$ . Jan., 1934]

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The theoretical reactions, which are expected to take place upon applying sulfur, readily account for the loss of insoluble  $CO_3$  from the sulfur plot. As is well known, sulfur undergoes biological oxidation in soil, which leads to the formation of  $H_2SO_4$ . The acid thus formed reacts with  $CaCO_3$ . The following equations illustrate these reactions:

$$2 S+3 O_2+2 H_2O=2 H_2SO_4$$
$$H_2SO_4+CaCO_3 \rightleftarrows CaSO_4+H_2CO_3$$
$$H_2CO_3+CaCO_3 \rightleftarrows Ca(HCO_3)_2$$

Therefore sulfur, upon oxidation,<sup>7</sup> converts  $CaCO_3$  into  $CaSO_4$  and  $Ca(HCO_3)_2$ . The calcium thus made soluble functions in the replacement of sodium from the exchange complex. Or it is possible that  $H_2SO_4$  reacted with Na-clay and Na-humate, converting the same into H-clay and H-humate and Na<sub>2</sub>SO<sub>4</sub>, and that H-clay and H-humate then reacted with  $CaCO_3$ , as was discussed above.

Obviously the sulfur oxidation product  $(H_2SO_4)$  and gypsum also converted Na<sub>2</sub>CO<sub>3</sub>, originally present in the soil, into Na<sub>2</sub>SO<sub>4</sub>.

As long as an alkali soil contains a high concentration of soluble sodium salts,  $CaCO_3$  is unable to bring about the replacement of sodium, owing to the high concentration of Na ions that are continually present in the soil solution. However, when the concentration of Na ions is reduced sufficiently by leaching, Ca ions furnished by the solution of  $CaCO_3$  begin to replace sodium, and thus a gradual increase in replaceable calcium and a corresponding diminution in the replaceable sodium are brought about.

Dialysis Experiments.—That  $CaCO_3$  has played the role indicated above has been further confirmed by dialysis experiments. Samples of soil artificially saturated with sodium and which were free from watersoluble salts, were mixed with  $CaCO_3$  and then subjected to dialysis. The dialyzate was removed daily from the external chamber of the dialyzer. After the dialysis had been continued for two weeks, the soil was found to be free from replaceable sodium and its base-exchange complex was calcium saturated. Analysis showed that sodium was the chief base which diffused through the semipermeable membrane, the amount thus removed from the soil being approximately equal to the original content of replaceable sodium. Similar results were obtained with a sample of the Fresno soil and also with an alkali soil from Utah.

*Electrodialysis Experiments.*—Electrodialysis experiments have also been made with these soils. In these experiments the rate of the reaction between  $CaCO_3$  and the sodium-saturated soil (Na-clay) was much more

<sup>&</sup>lt;sup>7</sup> These equations are intended to represent the end results of sulfur oxidation. It is probable that the oxidation passes through one or more intermediate stages before the sulfate form is reached.

rapid than that which took place in the dialysis experiments referred to above, but the final result was the same. It was found that the replaceable sodium was removed from the soil quantitatively and that calcium took its place in the exchange complex. It was necessary, of course, to discontinue the electrodialysis before the last traces of  $CaCO_3$  were decomposed; otherwise the soil would probably have become base unsaturated.

The validity of the foregoing argument as to the role of  $CaCO_3$  in the leaching of a sodium saline soil rests essentially on two principles: (1) The replacing power of Ca ions is considerably greater than that of Na ions. Students of base exchange generally accept this as a fact. As soon as the concentration of soluble sodium is sufficiently reduced by leaching, Ca ions furnished by  $CaCO_3$  gradually effect the replacement of sodium. (2) H-clay and H-humate, whether formed by hydrolysis or by the action of acids, react actively with  $CaCO_3$ . The result is the replacement of H ions by Ca ions and the consequent augmentation of replaceable calcium. Generally speaking, it is well agreed that this is the most important reaction which takes place when acid soils are limed.

The importance of CaCO<sub>3</sub> in the process of alkali soil reclamation has been strikingly confirmed by investigations in Hungary. Arany<sup>(1)</sup> and de 'Sigmond<sup>(28)</sup> have shown that an important type of alkali soil of Hungary has been markedly ameliorated by the application of sugar beet lime. Before the sugar beet lime was applied the Hungarian soil did not contain CaCO<sub>3</sub>. It was in fact somewhat acid. Nevertheless, the soil contained relatively much replaceable sodium. It appears that this soil has been subjected to conditions in the state of nature which leached away the soluble products of the hydrolysis of its Na-clay, with the result that the soil mass has become slightly acidic owing to the accumulation of H-clay. Hence the soil contains both Na-clay and H-clay. It is probable that upon applying lime a reaction was set up with the H-clay of the soil which brought about the formation of Ca-clay and  $Ca(HCO_3)_2$ . The calcium thus made soluble replaced sodium from the exchange complex with the consequent conversion of Na-clay into Ca-clay. Thus the application of lime brought about a diminution in replaceable sodium and an increase in replaceable calcium. These chemical transformations produced marked flocculation of the soil, and hence an improvement in its physical properties and in the growth of crops.

It is important to state in this connection that the beneficial effect of lime as a treatment for alkali soil is probably limited to acid (the so-called degraded) types of alkali soil, for it is obviously unreasonable to expect any important effect from liming, if the soil already contains  $CaCO_3$ . In unpublished investigations at Fresno, for example, E. E.

Thomas has obtained no benefit whatever from the application of  $CaCO_3$ , either in the form of ground limestone or as sugar beet lime, but as stated above, this soil contains considerable  $CaCO_3$ . It may also be mentioned in passing that  $CaCO_3$  is widely distributed in the semiarid regions of America. Generally speaking, the alkali soils of the American continent contain much more  $CaCO_3$  than the Fresno soil. It is not probable, therefore, that lime will be useful in their reclamation.

From the foregoing discussion it is evident that any agency which will bring about an increase in the solubility of the calcium minerals of the soil will promote the reclamation of a sodium saline soil. This is true because the rate of replacement of sodium by calcium is roughly proportional to the concentration of the Ca ions in the soil solution. It is largely for this reason that decaying organic matter and the generation of  $CO_2$ in the soil by microörganisms and by plant roots exert a favorable influence on the reclamation process. Consequently the growth of alkaliresistant crops as green manures may be utilized as a practical means of promoting the reclamation process.

The above interpretation of the role played by  $CaCO_3$  in alkali soil reclamation is in agreement with the views of Gedroiz as set forth in detail in his publication of 1928.<sup>(11)</sup> However, he again emphasized the view that when subjected to leaching an alkali soil will remain toxic to plants as long as it contains important amounts of replacement sodium, owing to the fact that a toxic concentration of Na<sub>2</sub>CO<sub>3</sub> will be continually present. Moreover, he pointed out that, since CaCO<sub>3</sub> promotes the formation of Na<sub>2</sub>CO<sub>3</sub> through replacement of sodium by calcium from the base-exchange complex, the soil might even become less favorable for crop growth when leached than if CaCO<sub>3</sub> were absent. The authors' experimental results do not support this conclusion.

From the preceding discussion it follows that the development of alkalinity as a result of leaching a sodium saline soil, should not be interpreted to mean that the soil has necessarily been injured by the leaching process. If the soil contains  $CaCO_3$ , the formation of  $Na_2CO_3$  as a result of leaching denotes that sodium has been replaced by calcium, and therefore the leaching process has changed the base-exchange constituents in the direction of a normal soil. It is, of course, essential to remove the  $Na_2CO_3$  thus formed, otherwise toxic concentrations of OH ions will ensue, and unless this be done the replacing action of  $CaCO_3$  will be brought to a standstill owing to the low solubility of  $CaCO_3$  and the high concentration of soluble sodium that will ensue.

The principal objection to the leaching process as a practical method of reclaiming sodium saline soil lies in two facts: (1) The soil may become so highly deflocculated, owing to the removal of soluble electro-

lytes and hydrolysis, as seriously to retard the penetration of water; (2) the rate of the reactions are relatively slow. The dialysis experiments referred to above have indicated that, were it possible to remove  $Na_2CO_3$  from the soil speedily, the rate of the reaction between  $CaCO_3$  and Na-clay would be very rapid, but unfortunately sodium-saturated soils become excessively dispersed upon leaching. The result is that the removal of  $Na_2CO_3$  may become impossible unless some flocculating substance is applied.

The leaching method also has been objected to on the ground that the high dispersion of the clay constituents of the soil will cause the mechanical transfer, through elutriation, of the base-exchange constituents from the surface soil into the subsoil, and thus will impoverish the upper part of the soil profile of these important components.<sup>(6, 9)</sup> This conclusion, based on laboratory leaching experiments, has not been confirmed by the authors' studies on the Fresno soil. It has been found, for example, that the base-exchange capacity of this soil has not been diminished by leaching (table 7).

Gedroiz<sup>(10, 11)</sup> and de 'Sigmond<sup>(26, 27)</sup> hold that when sodium saline soil is subjected to prolonged leaching, there is developed first the solonetz structure, and later the solodi, or degredation condition, the latter denoting that more or less of the base-exchange complex has been decomposed. However, if the soil contains CaCO<sub>3</sub>, Gedroiz<sup>(11)</sup> concluded that leaching will not produce decomposition of the inorganic constituents of the base-exchange complex except to a very limited extent. The authors' results indicate that the base-exchange complex of soil containing CaCO<sub>3</sub> undergoes no important decomposition upon leaching. This must be true, since H-clay, formed by hydrolysis from Na-clay, will immediately react with CaCO<sub>3</sub> and thus be converted into stable Ca-clay. It is a fact, however, that Na-clay becomes excessively deflocculated upon leaching and this is a serious objection to the leaching method. With heavy clay types of sodium saline soil, it is not probable that reclamation can be effected simply by leaching with water. It is also not probable that the leaching method, when unaccompanied by other treatment, will be successful with alkali soils having the physical structure of a solonetz, owing to the extremely impervious character of the subsoil.

Various theories have been proposed to explain the deflocculation of Na-clays.<sup>(30)</sup> The most generally accepted view is that OH ions, formed by hydrolysis, cause dispersion of the soil particles. However, the behavior of soil colloids saturated with different bases, as revealed by studies with the use of the petrographic microscope, suggests that some additional factor is involved. This subject will be more fully discussed in a separate paper. Finally, it is of interest to note that the pH of the Fresno soil has not been increased, but rather it has been definitely decreased by leaching (table 7). Soil samples, drawn from the check plot immediately after the termination of the leaching periods of 1920 and 1921, showed that leaching had materially reduced the pH of the upper part of the soil profile. Samples drawn at later dates showed still further reduction in the pH values. This was probably due both to the leaching out of the native Na<sub>2</sub>CO<sub>3</sub> of the soil and to the replacement of sodium by calcium. The authors do not believe that leaching will cause an increase in the OH-ion concentration of soil which contains considerable Na<sub>2</sub>CO<sub>3</sub>.

#### WHITE-ALKALI SOILS

The alkali soil of the Imperial Valley, California, differs from the Fresno soil, discussed in the preceding section of this paper, in three important particulars: (1) It is free from soluble  $CO_3$ ; (2) it is a Ca-Na saline containing a high concentration of soluble calcium; (3) the soil is a heavy clay loam. The soil and subsoil are fine-textured down to a depth of about 8 feet, below which a porous, sandy substratum is found. There are no well-defined structural horizons within the profile. It is therefore a Na-Ca solonchak.

In 1929 a series of plots were prepared for irrigation on a barren area of this soil near El Centro. Certain of these plots were treated with gypsum, others with sulfur, and still others with gypsum or sulfur and barnyard manure. Three plots were left untreated as checks. All of the plots were flooded with water from the Colorado River, analysis of which is reported in table 8, for three successive periods between December, 1929, and May, 1930. Alfalfa was sown in October, 1930. In 1931 and 1932 good yields of alfalfa were obtained from all the plots (figs. 4 and 5).

It was found that leaching without other treatment produced as good results as the application of gypsum or sulfur. The data reported in table 10 show that the leaching has removed the chief part of the soluble salts to a depth of at least 48 inches. Table 11 shows that this soil does not contain important amounts of replaceable sodium. Although the content of soluble sodium salts was originally very high, the concentration of soluble calcium and magnesium was sufficient to prevent base replacement by sodium. These results confirm the conclusions which Gedroiz<sup>(8, 11)</sup> and de 'Sigmond<sup>(25)</sup> drew chiefly on the basis of theoretical reasoning.

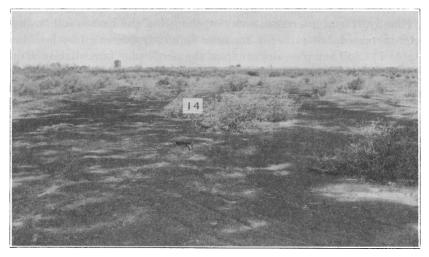


Fig. 4. This photograph, taken June 17, 1929, illustrates the general condition of the Imperial Valley soil before the reclamation experiment was begun.



Fig. 5. This photograph (June 7, 1932), taken from the same place as that of figure 4, shows the growth of alfalfa after leaching the Imperial valley soil. In 1930 and 1931 good growth of alfalfa was also obtained on this plot.

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This soil also contains about 10 per cent  $CaCO_3$ , but this constituent has played no important part in the reclamation process because of the abundance of soluble calcium salts which it contained. For the same reason it seems logical to assume that the calcium content of the irrigation water has played but little part in the experimental results. The reclamation of this type of alkali soil is, therefore, merely a matter of leaching out the excess of soluble salts.

Depth in inches	CO3	HCO3	Cl	SO4	Са	Mg	K	Na
		· · · · · · · · · · · · · · · · · · ·	Before	e leaching				
0-12	0.0	0.3	80.2	11.7	26.0	14.0	2.4	50.8
12-24	0.0	0.4	20.8	4.1	4.7	4.3	1.6	14.7
24-36	0.0	0.3	11.7	3.2	2.8	2.1	1.3	9.0
36-48	0.0	0.4	8.4	3.4	1.8	1.9	1.0	7.5
			After	leaching				
0-12	0.0	0.5	0.5	1.6	0.7	0.5	0.6	0.8
12-24	0.0	0.5	0.7	2.4	0.5	0.4	0.6	2.1
24-36	0.1	0.6	0.6	2.0	0.2	0.7	0.5	1.9
36-48.	0.1	0.7	0.9	3.5	0.2	0.5	0.5	4.0

#### TABLE 10 WATER-SOLUBLE SALTS, IMPERIAL VALLEY SOIL (Milliequivalents per 100 grams)

TABLE	11
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#### REPLACEABLE BASES, IMPERIAL VALLEY SOIL

	Milliequ	Na as per cent			
Depth in inches	Ca + Mg	К	Na	of total	
	Before le	aching			
0–12	13.70	0.00	0.00	0	
12-24	14.55	0.00	0.20	1	
24–36	11.30	0.04	1.80	13	
36–48	17.92	0.11	1.70	9	
	After les	aching			
0-12	17.36	0.19	0.70	4	
12-24		0.24	1.25	7	
24–36		0.29	2.40	14	
36-48	17.29	0.63	4.65	20	

#### BASE-EXCHANGE CONSTITUENTS OF ALKALI SOILS

It seems desirable to present a brief discussion in this connection on the base-exchange constituents of alkali soils and of methods for the determination of the replaceable bases. Alkali soils commonly differ from normal soils not alone in containing an excess of soluble salts and replaceable sodium, but also in that the former may contain abnormal amounts of precipitated silicates and carbonates. It is well established that the base-exchange property of normal soils is due chiefly to the clays, which are alumino-silicates, and to the humates. It is believed that the importance of base exchange in alkali soils is also largely controlled by the clay and humus constituents, but the replaceable (absorbed) bases that are held by the clay and humus of alkali soils can be determined only by the use of special methods.

As Hilgard showed, the soluble salts of alkali soils are derived from the soluble products formed by the weathering of the rock masses within a given watershed. These soluble products become concentrated in certain places owing to the periodic nature and quantity of the precipitation. The soluble products of weathering are chiefly chlorides, sulfates, carbonates, bicarbonates, and small amounts of silicates. Soluble carbonates and bicarbonates may also be formed in the soil as a result of the hydrolysis of Na-clays and Na-humates.

As is well known,  $Na_2CO_3$  is a solvent for  $SiO_2$ . The result is that more or less soluble silicate is likely to be formed within the soil mass wherever high concentrations of  $Na_2CO_3$  accumulate. Alkali soils usually contain considerable CaCO<sub>3</sub>. This substance, being soluble to some extent in solutions of NaCl and Na<sub>2</sub>SO<sub>4</sub>, gives rise to more or less dissolved Ca ions. Ca ions and Mg ions are also brought into solution by base exchange. Moreover, the soluble products of weathering may also include considerable calcium and magnesium. Therefore, the conditions that obtain in black alkali soils inevitably lead to the formation and precipitation within the soil mass of more or less calcium and magnesium as silicates and carbonates. Silicates and carbonates of the divalent bases may also accumulate in the soil to some extent in the absence of  $Na_2CO_3$ , since, upon concentrating the soluble products of weathering, the solubility of calcium and magnesium silicates and carbonates may be exceeded. It follows, then, that alkali soils of various kinds are likely to contain more or less precipitated silicates and carbonates. These facts must be taken into consideration if one is to arrive at an intelligent understanding of alkali soils.

With normal soils the replaceable bases are usually determined by extraction with a salt solution, or a dilute acid, or by electrodialysis. All these methods bring into solution more or less base from relatively simple silicates and carbonates of calcium and magnesium as well as from the clay and humus constituents. If, for example, precipitated calcium silicate or magnesium silicate be treated with a solution of BaCl<sub>2</sub>, true base exchange ensues in which a part of the calcium and magnesium is replaced by Ba ions with the formation of CaCl<sub>2</sub> or MgCl<sub>2</sub> and insoluble barium silicate. However, if an ammonium or sodium salt be used instead of BaCl<sub>2</sub>, calcium and magnesium are also brought into solution, but NH<sub>4</sub> ions are not absorbed to an important extent by these silicates, owing to the fact that ammonium silicate is unstable, and sodium silicate is, of course, soluble in water. Therefore, calcium silicate or magnesium silicate will not be converted into sodium or ammonium absorption compounds by reaction with soluble sodium or ammonium salts. On the other hand, the NH<sub>4</sub>-clays and NH<sub>4</sub>-humates and the corresponding sodium compounds are relatively stable and insoluble. The authors have taken advantage of these facts as a means of distinguishing between base exchange due to the clay and humus constituents, on the one hand, and reactions set up by the silicates and carbonates, on the other hand.

It is also well established that the absorption of cations by colloids is some function of the OH-ion concentration. Soils absorb greater amounts of cations from alkaline than from neutral solutions. In view of this fact, Bradfield<sup>(2)</sup> and Mattson and Hester<sup>(20)</sup> have suggested that base-exchange capacity should be defined in terms of pH. The term base-exchange capacity is used by the authors to denote the maximum amount of  $NH_4$  the soil is able to absorb upon prolonged leaching with neutral normal ammonium acetate. The determination is made as follows: A sample of soil is leached with a solution of ammonium acetate as long as base is extracted from the soil. The uncombined ammonium acetate is then leached out with methyl alcohol, which practically prevents hydrolysis, after which the absorbed  $NH_4$  is determined by aeration. The details of the method were described by Chapman and Kelley.<sup>(4)</sup>

Sodium and potassium are determined in the ammonium acetate extract of the soil, but calcium and magnesium are disregarded owing to the impossibility of measuring the extent to which precipitated silicates and carbonates have contributed to the base content of the extract. The content of water-soluble sodium and potassium must of course be subtracted from the results. This correction is not highly accurate owing to hydrolysis. Moreover, since leaching a black-alkali soil with neutral ammonium acetate changes its pH toward neutrality, its con-

tent of absorbed cations  $(NH_4)$ , after having been leached with neutral ammonium acetate, will probably be less than the equivalent of the total bases that were removed from the soil. However, this method affords a means of determining the total content of absorbed sodium.

Gedroiz<sup>(9)</sup> suggested that replaceable (absorbed) calcium can be determined in alkaline soils by subtracting the calcium equivalent of the dissolved carbonate from the calcium found in the extract. This correction obviously rests on the assumption that  $CaCO_3$  is the only carbonate present. A similar assumption underlies the titration method of Tjurin.<sup>(29)</sup> This assumption is not always justified, since MgCO<sub>3</sub> is sometimes present in soils. Moreover, black-alkali soils may also contain basic carbonate of magnesium.

In view of the above discussion, replaceable calcium and magnesium have not been determined individually, but, instead, the sum of the replaceable potassium and sodium was subtracted from the base-exchange capacity as determined by the absorbed  $NH_4$ . The result is reported as calcium and magnesium collectively.

#### DISCUSSION

There seems to be good reason for the belief that either one or the other of the above-named methods of reclamation, that is the application of a soluble calcium salt, or of some substance which will increase the solubility of the calcium minerals of the soil, or leaching without applying any soil amendment, is applicable to alkali soils everywhere, with the possible exception of the so-called degraded types of alkali soils. In connection with these investigations soil samples have been studied from many alkali areas of California and other states. In certain localities both farmers and scientific workers have been able to secure complete reclamation of important areas of alkali soil by applying the principles of one or the other of the above-named methods. Many of these soils contain considerable water-soluble calcium salts, and wherever this is the case leaching has proved to be a successful method of reclamation.

Black-alkali soils may or may not require the application of some substance, such as gypsum or sulfur. As shown already, the Fresno type of black-alkali soil can be reclaimed by mere leaching with water, but this soil responds to the leaching process too slowly to justify placing complete reliance on leaching as a practical method of reclamation. Certain other types of black-alkali soil, however (for example east and north of Great Salt Lake, Utah), respond to leaching readily. In this case the effectiveness of leaching is probably due to a combination of two fortunate circumstances, namely: (1) The composition of the irrigation water which is relatively rich in calcium and magnesium salts and (2) the occurrence of precipitated CaCO<sub>3</sub> and calcium silicate, which are thoroughly disseminated throughout the profile of this soil.

The difficulty that must be overcome in the reclamation of alkali soils in general lies in their content of soluble salts and replaceable sodium, but alkali soils are usually not deficient in total calcium. Rather, replaceable forms of calcium may have been converted into other forms through base exchange and precipitation. Both  $CaCO_3$  and calcium silicates may be caused to play an important role in the reclamation process. Any agency which will increase the solubility of these calcium minerals of the soil will promote the replacement of absorbed sodium by calcium and thus convert Na-clays and Na-humates into normal Caclays and Ca-humates. Among such agencies are elemental sulfur,  $CO_2$ formed by plant roots and the decomposition of organic manures, iron sulfate, and soluble aluminum salts.<sup>(16)</sup> Obviously the absorbed sodium can also be replaced by applying a soluble calcium salt either as a constituent of the irrigation water or as a soil amendment.

From the foregoing it follows that the important properties of alkali soils are dependent on not only the soluble salts, as was emphasized by Hilgard, and the replaceable sodium, as was emphasized by Gedroiz, but also on the calcium minerals of the soil other than the base-exchange constituents. Furthermore,  $CaCO_3$  of the soil and the calcium and magnesium salts of the irrigation water may play important parts in the reclamation process.

Other conditions being equal the facility of reclamation will be inversely proportional to the clay content of the soil. Heavy types of alkali soil may prove to be extremely difficult to reclaim, especially if the clay is largely saturated with sodium. Solonetz or solonetz-like subsoil horizons, which are high in absorbed sodium, will probably be exceedingly difficult to ameliorate. With alkali soils of this type the application of a calcium salt of high solubility should, on theoretical grounds, produce the best results.

The removal of the soluble salts and the complete replacement of sodium by calcium from the base-exchange complex of the soil are dependent on the possibility of leaching the soil, and it is obviously impossible to effect leaching if the ground water level remains near the surface, or if the soil is impenetrable to water. The drainage conditions are therefore exceedingly important in alkali soil reclamation. However, a general discussion of drainage would be inappropriate in this paper, since the drainage conditions do not alter the essential nature of the chemical principles which govern the reclamation process. For a similar reason a discussion of methods of practical management and of the sys-

tems of cropping and irrigation that will give the best results with a given alkali soil are also omitted from this publication, although the authors fully recognize that practical success of reclamation may largely depend on the observance of special care with respect to methods of irrigation and soil management.

#### SUMMARY

The history of present views as to the essential nature of alkali soils has been briefly reviewed. It was shown that alkali soils contain either an excess of soluble salts or abnormal amounts of replaceable (absorbed) sodium. The clay and humus of normal soils are combined with calcium. With alkali soils, on the other hand, soluble sodium salts tend to bring about replacement of calcium by sodium and thus produce chemical and physical conditions that are extremely adverse to plant growth. Hence, successful reclamation of alkali soils depends on the removal of the soluble salts and the replacement of the absorbed sodium by calcium.

The Russian word solonetz is used by soil investigators in two senses, namely, chemically and physically. In order to avoid confusion it is suggested that this term be used to denote both chemical and physical properties of the soil. Accordingly solonetz is defined as alkali soil containing replaceable (absorbed) sodium the profile of which presents certain morphological structures.

This paper reports the results of investigations on the reclamation of two important types of alkali soil, namely, the black-alkali soil of the Fresno area of California and the white-alkali soil, Imperial Valley, California. It has been shown that the application of gypsum or sulfur has produced markedly effective results on the Fresno black-alkali soil, while leaching without other treatment has been equally effective with the Imperial Valley white-alkali soil. The Fresno soil can also be reclaimed by simple leaching, but only at excessively slow rates. The Fresno soil contains much replaceable sodium (60 per cent or more of the total replaceable bases), while the white-alkali soil of the Imperial Valley of California, contains almost no replaceable sodium.

The important aspects of the chemistry of alkali soil as affected by treatments with gypsum and sulfur and by leaching are discussed in detail.

The composition of the irrigation water is an important consideration in connection with the reclamation of alkali soils.

The accomplishment of successful reclamation depends on the maintenance of effective drainage conditions.

The determination of replaceable calcium and magnesium in alkali

soil is especially difficult. A method is outlined for the determination of the replaceable divalent bases collectively.

The following points should be carefully considered before proceeding to reclaim an area of alkali soil: (1) The drainage conditions; (2) the composition of the soluble salts; (3) the content of replaceable (absorbed) sodium in the soil; (4) the nature and content of the calcium minerals of the soil; (5) the composition of the available irrigation water.

#### LITERATURE CITED

<sup>1</sup> ARANY, SÁNDOR.

- 1926. The effect of lime cake on our alkali soils. Kisérletügyi Közlemények. 29: 1-32.
- <sup>2</sup> BRADFIELD, RICHARD.

1924. The importance of hydrogen ion concentration control in physico-chemical studies of heavy soils. Soil Sci. 17:411-422.

<sup>3</sup> BREAZEALE, J. F., AND W. T. MCGEORGE.

1926. Sodium hydroxide rather than sodium carbonate the source of alkalinity in black alkali soils. Arizona Agr. Exp. Sta. Tech. Bul. 13:307-335.

4 CHAPMAN, H. D., AND W. P. KELLEY.

1930. The determination of the replaceable bases and the base-exchange capacity of soils. Soil Sci. 30:391-406.

<sup>5</sup> CUMMINS, ARTHUR B., AND W. P. KELLEY.

1923. The formation of sodium carbonate in soils. California Agr. Exp. Sta. Tech. Paper 3:1-35.

<sup>6</sup> DOMINICIS, A. DE.

1918. Terreni Salsi e Terreni Alcalini. Staz. Sper. Agr. Ital., 41:103-161.

#### 7 GEDROIZ, K. K.

1912. Colloidal chemistry as related to soil science. I. Colloidal substances in the soil solution. Formation of sodium carbonate in the soil. Alkali soils and saline soils. Zhur. Opit. Agron. 13:363-420.

8 GEDROIZ, K. K.

1917. Saline soils and their improvement. Zhur. Opit. Agron. 18:122-140.

9 GEDROIZ, K. K.

1918. Contribution to the method of determining the zeolytic bases in the soil. Zhur. Opit. Agron. 19:226-244.

#### 10 GEDROIZ, K. K.

- 1925. Soil absorbing complex and the absorbed cations as a basis of genetic soil classification. Nossovsk Agr. Exp. Sta. Paper 38:1-29.
- 11 Gedroiz, K. K.
  - 1928. Alkali soils, their origin, properties and improvement. Nossovsk Agr. Exp. Sta. Paper 46:1-73.

12 GLINKA, K. D. (Translation by C. F. Marbut.)

1927. The great soil groups of the world and their development. 150 p. Edwards Bros., Inc., Ann Arbor, Michigan.

13 HIBBARD,	Р.	$\mathbf{L}$ .	
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1922. Some experiments on reclamation of infertile alkali soils by means of gypsum and other treatments. Soil Sci. 13:125-134.

14 HILGARD, E. W.

1907. Soils. The Macmillan Co., New York. 593 p.

<sup>15</sup> HISSINK, D. J.

1922. Beitrag zur Kenntnis der Adsorptionsvorgänge im Boden. Methode zur Bestimmung der austauschfähigen oder absorptiv gebundenen Basen im Boden und die Bedeutung dieser Basen für die Prozesse, die sich im Boden abspielen. Internatl. Mitt. Bodenk. 12:81-172.

16 KELLEY, W. P., AND ALEXANDER ARANY.

1928. The chemical effect of gypsum, sulfur, iron sulfate and alum on alkali soil. Hilgardia 31:393-420.

- 17 KELLEY, W. P., AND S. M. BROWN. 1926. Base exchange in relation to alkali soils. Soil Sci. 20:477-495.
- <sup>18</sup> KELLEY, W. P., AND A. B. CUMMINS. 1921. Chemical effects of salts on soils. Soil Sci. 11:139–159.
- 19 KELLEY, W. P., AND E. E. THOMAS.
  - 1928. Reclamation of the Fresno type of black alkali soil. California Agr. Exp. Sta. Bul. 455:1-37.
- 20 MATTSON, SANTE, AND JACKSON B. HESTER.

1932. The laws of colloidal behavior: X. Exchange neutrality and combining capacity. Soil Sci. 34:459-482.

#### <sup>21</sup> MONDESIR, PAUL DE.

1888. Sur le rôle du pouvoir des terres dans la formation des carbonates des soude naturels. Compt. Rend. 160:459-462.

- 22 PRESCOTT, J. A.
  - 1922. Base exchange and alkalinity in Egyptian soils. The Cairo Sci. Jour. 10: 58-64.
- 23 SCOFIELD, C. S., AND F. B. HEADLEY.
  - 1921. Quality of irrigation water in relation to land reclamation. Jour. Agr. Research 21:265-278.
- 24 'SIGMOND, ALEXIUS A. J. DE.
  - 1926. Contribution to the theory of the origin of alkali soils. Soil Sci. 21:455-475.
- 25 'SIGMOND, ALEXIUS, A. J. DE.
  - 1927. Hungarian alkali soils and methods of their reclamation. California Agr. Exp. Sta. Special Publication. 156 p.
- <sup>26</sup> 'SIGMOND, ALEXIUS, A. J. DE.
  - 1928. The chemical characteristics of soil leachings. Proceedings First International Congress of Soil Science 1:60-90.
- 27 'SIGMOND, ALEXIUS, A. J. DE.
  - 1928. The classification of alkali and salty soils. Proceedings First International Congress of Soil Science 1:330-344.
- 28 'SIGMOND, ALEXIUS, A. J. DE.
  - 1932. The reclamation of alkali soils in Hungary. Imperial Bureau of Soil Science, Technical Communication 23:5-26.

Jan., 1934]

29 TJURIN, I. W.

1927. Method of determination of exchangeable calcium and magnesium in soils containing alkaline earth carbonates. La Pedologie 22:5-24.

<sup>30</sup> WIEGNER, GEORG VON.

1925. Dispersität und Basenaustausch (Ionenaustausch). Ergänzungsband zur Kolloid Ztschr. 36:341-369.