Exchangeable Cation Hydrolysis and Soil Weathering as Affected by Exchangeable Sodium[1]

J. D. OSTER AND I. SHAINBERG[2]

ABSTRACT

The specific conductance and chemical composition of aqueous soil suspensions were measured as a function of time on suspensions prepared from three arid soils pretreated with acidified salt solutions to remove lime. The release of Ca^{2+}, Mg^{2+}, and K^{+} from silicate minerals and the hydrolysis of exchangeable Na^{+} occurred rapidly and prevented the preparation of homoionic Na soils. Crystalline ion release and hydrolysis of exchangeable Na^{+} and Ca^{2+} continued after the soils were suspended in distilled water. The rate was enhanced by increasing exchangeable NA^{+}. The combination of Ca^{2+} hydrolysis and its release from silicate minerals was sufficient, when coupled with Na^{+} hydrolysis, to cause the solution phase of the suspension to be supersaturated with lime for one soil.

Separate experiments with untreated soil and its silt fraction indicated that silt weathers rapidly and contributes significantly to the increase in soil conductance. Silt weathering was enhanced by increasing exchangeable Na^{+}.

Additional Index Words: **silt weathering, soil lime solubility, cation exchange capacity, specific conductance.**

Oster, J. D., and I. Shainberg. 1979. Exchangeable cation hydrolysis and soil weathering as affected by exchangeable sodium. Soil Sci. Soc. Am. J. 43:70–75.

EXCHANGEABLE and crystalline cations are released from soil minerals as a result of hydrolysis and weathering. Cummins and Kelley (1923) first demonstrated the hydrolysis of exchangeable Na^{+}, or the replacement of exchangeable Na^{+} by H^{+} supplied by the dissociation of water. They found that, in the absence of $CaCO_3$ and CO_2, a Na-saturated soil leached with distilled water yielded a NaOH solution; an equivalent concentration of Na_2CO_3 was obtained in the presence of CO_2. Barshad (1960) found that the adsorbed H^{+} in this reaction was replaced by Mg^{2+} and Al^{3+} from the crystal. He proposed that the H^{+} was able to penetrate the interior of the crystal structure and displace ions in the octahedral and tetrahedral sheets. Apparently the hydrolysis of Na soils and soil clays that do not contain $CaCO_3$ is accompanied by clay decomposition, or weathering, in a manner analogous to the acidic attack mechanism usually associated with hydrogen-saturated clays (Coleman and Craig, 1961).

In the same paper, Barshad (1960) reported that Ca^{+}, present in clay-sized plagioclase feldspars, also replaced exchangeable Na^{+}. More Na^{+} was replaced by Ca^{2+} when the soils contained $CaCO_3$ because of the double decomposition reaction between Na clay and $CaCO_3$ (Cruz-Romero and Coleman, 1975). Rhoades et al. (1968) demonstrated the release of Ca^{+} plus Mg^{2+} from several soils extensively leached with chloride solutions of different compositions [$0.002 > M < 0.02$ (kmol m^{-3}); $5 > \text{SAR}$[3] < 20 (mol $m^{-3})^{1/2}$]. Divalent ion release increased with increasing SAR, which, because the soils contained lime ($CaCO_3$), was a consequence of either lime dissolution or the weathering of soil minerals or both. In a related experiment, the release of divalent ions also occurred from specimen plagioclase feldspars, hornblende, and common mafic minerals. Consequently, the source of divalent ions was attributed to the weathering of unstable Ca, Mg-silicates present in the sand and silt fractions.

The reaction mechanisms and rates involved in the hydrolysis and decomposition of montmorillonite clays have been studied in greater detail than have those for soil-clays and soils. In an experiment with Na-montmorillonite, where the hydrolysis products were continuously removed, Bar-On and Shainberg (1970) found the Na^{+} concentration in the effluent was 0.11 mol m^{-3}. Based on Donnan equilibrium, the Na^{+} concentration required a surface pH of between 5 and 6, which closely corresponds to the expected pH for a system buffered by aluminum hydroxy polymers (Jackson, 1963). Shainberg (1973) demonstrated the instability of Na-montmorillonite even when the reaction products were not removed. He found the specific conductance of the clay suspension was proportional to the square root of time. The proportionality constant increased with increasing octahedral substitution (Shainberg et al., 1974), which is compatible with the observation that the chemical stability of a H clay decreases with increasing MgO content and cation exchange capacity (Barshad and Foscolos, 1970). These observations are consistent with a hydrolysis mechanism (Shainberg, 1973) consisting of two consecutive reactions: (i) a rapid exchange between exchangeable Na^{+} and H^{+} in solutions, which should result in an acidic surface ($pH < 4$); and (ii) a slower, first-order transformation of H clay to Mg or Al clay, which buffers the pH to about 5 and increases the amount of exchangeable Na^{+} released.

The hydrolysis of exchangeable Ca^{2+} from montmorillonite has also been reported by Frenkel and Saurez (1977). They found the extent and rate of hydrolysis were comparable to those for exchangeable Na^{+}, and concluded that Al hydroxy polymers controlled surface pH. Since these polymers are generally present in soils, the rate of soil weathering may be independent of the exchange and solution composition if the results obtained for montmorillonite are representative of other clay minerals, and clay weathering is the predominant mechanism in soil weathering. If, on the other hand, weathering of Ca, Mg-silicates in the silt and sand fraction is dominant, the chemical composition could affect the rate; based on equilibrium considerations, the lower the divalent ion concentration, the greater the expected rate of their release. The purpose of this work was to determine rates of hydrolysis and the resultant changes in the cation ex-

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[1] Contribution from U. S. Salinity Laboratory, USDA, Riverside, CA 92501, and Agricultural Research Organization, The Volcani Center, Bet Dagan, Israel. Financial support by the ARO of the senior author is gratefully acknowledged. Received 8 May 1978. Approved 26 Sept. 1978.

[2] Soil Scientists, U. S. Salinity Laboratory, and Physical Chemist, The Volcani Center, respectively.

[3] $SAR = Na/(Ca + Mg)^{1/2}$ where all concentrations are expressed in mol m^{-3}.

change composition of three lime-free arid zone soils as affected by different levels of exchangeable Na^+.

MATERIALS AND METHODS

Two of the soils used in this study were from the coastal plain of Israel and one was from the Central Valley of California. The cation exchange capacity, determined using the Na-NH_4OAC procedure (U. S. Salinity Laboratory Staff, 1954) and other soil properties are given in Table 1. The Grangeville soil formed on alluvial fans or flood plains of granite-rock sediments from outwash of the Sierra Nevada Range in California. The Nahal-Oz soil developed on loessial wind-blown material from the Sinai Desert and the Netanya soil formed on coastal sand and calcareous sandstone. The genesis of the last two soils has been influenced by aeolian additions. For the Nahal-Oz region, the calculated rate of dust deposition in recent years is 100 – 200 t yr^{-1} km^{-2} (Ganor, 1975).[4]

Soil preparation included lime removal and adjustment of the exchangeable Na^+ level. Lime was removed by suspending 100 to 300 g of each soil in 1*M* NaCl (0.5 to 1 liter) and adding HCl as needed, while stirring, to maintain the suspension pH between 4 and 5. The acid additions were continued until the pH remained less than 5 for 30 min. The soil was then allowed to settle and the clear supernatant was decanted. The procedure was repeated until the pH remained less than 5 after the first acid addition. Contact time with acidified solutions ranged from 24 to 72 hours. The soils were then freeze-dried and thoroughly mixed. Subsamples were equilibrated (two washes, >25 symmetries per wash) in 1*M* chloride salt solutions with different ratios of Na^+ to Ca^+ corresponding to SAR's of 5, 20, and ∞, washed twice in 0.1*M* solutions of the same SAR, and again freeze-dried.

The chemical stability of the silt fraction of the lime-free Nahal-Oz soil was also studied. The silt fraction was obtained by semidentation, equilibrated with 1*M* chloride solutions of SAR 20 and ∞, washed twice in 0.1*M* solutions of the same SAR and freeze-dried.

The remaining excess salt was removed on the day the hydrolysis experiments were started. Six, 2-g samples of a given soil were weighed into plastic vials and quickly rinsed with 33 ml of 0.01 solution having the appropriate SAR and with 33 ml of distilled water. Sufficient distilled water was added to three plastic vials to make a suspension with a soil to water ratio (by weight) of 2:12. The soil material was quickly suspended using a vortex stirrer, after which the initial specific conductance and pH of the suspension were determined. The suspensions were shaken in a water bath at 25 ± 2°C, and the specific conductance and pH were determined periodically during the following 7-14 days. The suspensions were then centrifuged and the final chemical composition of the liquid and exchange phases determined. Because the vials were opened frequently to measure conductance and pH, the partial pressure of carbon dioxide during the experiment was about 0.04 kPa (0.04% vol/vol). The initial chemical composition of both phases was determined on the remaining three soil samples and three samples of the final distilled water rinse. The base exchange composition was determined by treating the soils with 1*M* NH_4OAC, pH7. Concentrations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ were determined with an atomic absorption spectrometer (Unicam SP-90), using standards prepared in 1*M* NH_4OAC. For Ca^{2+} and Mg^{2+} the samples and standards contained 1% $LaCl_3$. The same instrument was used to determine the cation composition of the liquid phase, using standards prepared in distilled water (Na^+ and K^+) or 1% $LaCl_3$ solutions (Ca^{2+} and Mg^{2+}). Chloride and bicarbonate concentrations were determined using a chloride titrimeter and Metrohm potentiometric titrator.[5] The colorimetric molybdate procedure was used to determine silica.

Table 1—General properties of soil.

Soil	Cation exchange capacity	Clay	Silt	$CaCO_3$	Clay mineralogy
	mmol$_c$ kg^{-1}†		%		
Grangeville (USSL #3623, Aquic calcic Haploxeroll, coarse-loamy mixed thermic)	90	6.0	12	tr	Montmorillonite Vermiculite Kaolinite
Nahal-Oz (Calcic Haploxeralf)	237	26.0	30	13	Montmorillonite Kaolinite
Netanya (Typic Rhodoxeralf)	44	7.5	5	0.1	Montmorillonite Kaolinite Illite

† mmol$_c$ kg^{-1} represents 1 mmol of charge kg^{-1} and is equal to 0.1 meq/100 g.

The Nahal-Oz soil was exceptionally unstable. To determine the possible effect of the lime removal treatment, we also studied the chemical stability of a natural soil. Two soil samples were obtained, one from a field irrigated with sodic water to give a soil ESP of 21, and one with an ESP of 5. The air-dried soil was mixed with distilled water (soil/water ratio of 1:10) and centrifuged, and the supernatant solution was kept for chemical analysis. The soil was mixed again with distilled water (ratio of 2:12), shaken, and the specific conductance recorded as a function of time.

RESULTS AND DISCUSSION

Significant amounts of Ca^{2+} and Mg^{2+} were released during the two final washing steps with 0.01*M* chloride solutions and distilled water. This was particularly evident from the initial cation exchange compositions (Table 2) obtained in the attempt to prepare the homoionic Na soils. For the Na- Nahal-Oz, the initial exchangeable Na^+, Ca^{2+}, and Mg^{2+} percentages were 59, 34, and 6, respectively. Significant Mg^{2+} also was released in the Nahal-Oz soils with lower initial exchangeable Na^+ percentages; however, these percentages were about equal to the SAR of the preparation solution. For Grangeville and Netanya, the amount of Ca^{2+} released was considerably smaller and there was little or no release of Mg^{2+}. Because $CaCO_3$ was removed from the soils before they were equilibrated, the source of the Ca^{2+} was limited to the silicate minerals. The release of Ca^{2+} and Mg^{2+} was also rapid. The soils were exposed to dilute salt solutions ($0.0002 > M < 0.01$) for only 1 to 2 hours during their preparation. Ion release continued after the soils were suspended in distilled water.

During the first 24 hours the specific conductance increased for 5 to 60 mS m^{-1}.[6] The increase was dependent on the soil (Nahal-Oz>Grangeville>Netanya), as shown in Fig. 1, and on the initial exchangeable Na^+ percent, ESP_i, as illustrated for Nahal-Oz in Fig. 2. In every case, the specific conductance increased for the duration of the experiment. With the exception of the Nahal-Oz, $ESP_i = 1.3$, two linear segments were evident in the plots of specific conductance vs. the square root of time, $t^{1/2}$. The two slopes are presumed to represent rates of different individual or groups of weathering and hydrolysis reactions. The slope of segment 1, the initial rate (Table 3), $0 > t < 60$ hours, was 2 to 30 times greater than the second. Both the initial and final rates were greatest for the Nahal-Oz soil. The second rates for Grangeville and Netanya were about the same as the single rate (0.1 to 0.9 mS m^{-1} hour$^{-1/2}$) obtained in suspensions of comparable clay concentration of Na and Ca montmorillonites (Shainberg et al., 1974; Frenkel and

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[4] E. Ganor. 1975. Atmospheric dust in Israel. Ph.D. Thesis, Hebrew Univ., Jerusalem, Israel.

[5] Trade names are included for the benefit of the reader and do not reflect endorsement by the U. S. Department of Agriculture.

[6] A mS m^{-1} is equivalent to 10 µmho/cm.

Table 2—The cation exchange composition of the soil samples before (i) and after (f) the kinetics experiments.

Soil	SAR of preparation solution†	Exchangeable cation Na$^+$ i	Na$^+$ f	K$^+$ i	K$^+$ f	Ca^{2+} i	Ca^{2+} f	Mg^{2+} i	Mg^{2+} f
	(mol m^{-3})$^{1/2}$	%							
Nahal-Oz	0	1.3	1.0	2.0	2.0	95.0	93.1	1.7	3.9
	5	5.7	2.0	0.5	1.2	91.5	92.1	2.3	4.7
	20	14.1	7.4	0.4	0.9	83.1	86.5	2.4	5.2
	∞	59.2	47.9	0.5	0.8	34.4	43.9	6.0	7.4
Grangeville	5	6.7	5.6	0.7	1.8	92.4	90.8	0.1	1.8
	20	14.7	14.3‡	0.9	1.9‡	84.4	83.6‡	0.0	1.7‡
	∞	93.6	81.0	1.4	2.0	5.0	15.4	0.0	1.3
Netanya	5	14.3	6.8	0.6	2.2	85.2	81.1	0.0	3.8
	20	25.3	8.8	0.6	1.0	73.4	88.4	0.7	1.8
	∞	88.8	66.0	0.3	1.4	10.9	31.7	0.0	0.4

† The solutions were prepared from NaCl and CaCl$_2$; they did not contain Mg^{2+}.

‡ Data was obtained from an hydrolysis experiment performed at 40°C. The chemical composition of the solution phase at both temperatures were very similar.

Suarez, 1977). Increasing ESP$_i$ caused increases in: i) the initial rate for Nahal-Oz, ii) the final rate for Grangeville, and iii) the duration of the initial rate for Netanya.

Based on studies with clay suspensions, the multirate character of the soil suspension conductance and the effect of ESP$_i$, were unexpected. The complex mineralogy of a soil suspension could be the cause: soil minerals could vary in stability, or exchangeable ions adsorbed on different clay minerals could hydrolyze at different rates, or both. We also investigated the possibility that the chemical treatment to remove lime resulted in the formation of an unstable material. Because of its instability, the Nahal-Oz was chosen for further study to determine the effects of mineralogy and pretreatment.

This soil was developed on wind-blown material, high in silt, which originated in the Sinai and Egyptian Desert. The mineralogical composition of a typical dust storm in the region consists of 50 - 60% quartz, 10 - 30% feldspar, and 20 - 40% calcite (Ganor, 1974)[4]. The results of grain size analyses indicate a bimodal dis-

Table 3—Hydrolysis rates of acid-treated soil suspensions.

Soil	SAR	ESP$_i$	Initial specific conductance†	Segment 1 Duration	Segment 1 Slope‡	Segment 2 Duration	Segment 2 Slope‡
	(mole m^{-3})$^{1/2}$	%	mS m^{-1}§	hr	mS m^{-1}hr$^{-1/2}$	hr	mS m^{-1}hr$^{-1/2}$
Nahal-Oz	0	1.3	1.7	270.0	1.7	–	–
	5	5.7	2.6	9.0	4.7	330	0.9
	20	14.1	3.2	2.6	15.6	260	1.1
	∞	59.2	8.6	6.2	19.0	210	1.9
Grangeville	5	6.7	3.9	1.7	3.4	188	0.1
	20	14.7	3.0	0.8	3.4	172	0.3
	∞	94.2	3.9	1.7	3.4	210	0.7
Netanya	5	14.3	2.1	9.6	0.8	250	0.5
	20	25.3	2.3	29.2	2.7	232	0.4
	∞	88.8	2.0	59.3	1.3	160	0.4

† Obtained by linear interpolation to t = 0.

‡ The parameters of the straight lines relating the specific conductance of the suspensions to the square root of time.

§ A mS m^{-1} is equivalent to 10 μmho/cm.

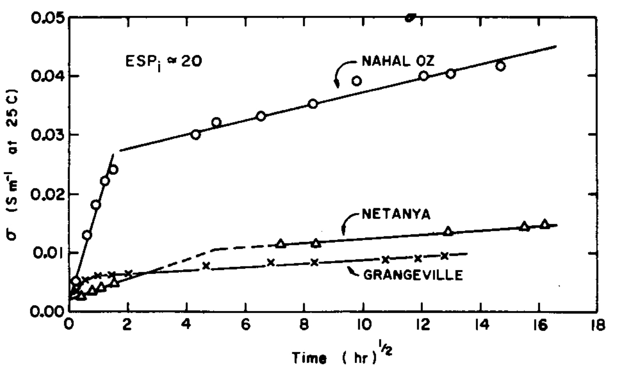

Fig. 1—The relation between specific conductance (σ) and time for aqueous suspensions of different soils with an initial exchangeable sodium percent of about 20.

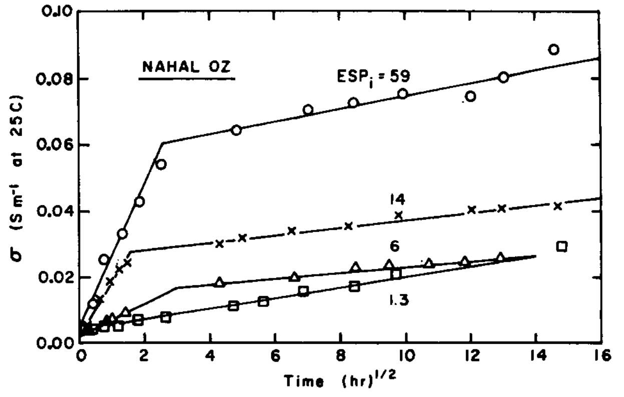

Fig. 2—The relation between specific conductance (σ) and time for aqueous suspensions of Nahal-Oz with different initial exchangeable sodium percentages.

Table 4—Hydrolysis rates of acid-treated, Nahal-Oz silt and untreated Nahal-Oz soil.

Soil	SAR	ESP_i	Initial specific conductance	Segment 1 Duration	Segment 1 Slope	Segment 2 Duration	Segment 2 Slope
	$(mole\ m^{-3})^{1/2}$	%	$mS\ m^{-1}$	hr	$mS\ m^{-1}hr^{-1/2}$	hr	$mS\ m^{-1}hr^{-1/2}$
Nahal-Oz	20	–	22.8	5	6.6	165	2.9
(Silt fraction)	∞	–	50.1	1	38.0	165	4.6
Nahal-Oz	–	5	12.4	250	1.8	–	–
(Natural soil)	–	21	23.0	250	2.2	–	–

tribution with a large peak in the silt fraction (70%), and a second mode in the clay fraction. The high proportion of silt in the dust is the cause for the high percentage of silt in the soil profile and the probable cause of high rates of hydrolysis and weathering because of the unweathered state of the silt. The lime-free Nahal-Oz silt was less stable than the natural soil (Table 4), and the instability increased with increasing ESP_i. Three of the four slopes exceed those for the lime-free Nahal-Oz soil (Table 3) initially equilibrated with the same SAR solutions.

The silt fraction of the Nahal-Oz soil was X-rayed before and after the hydrolysis reaction. The detailed data are presented elsewhere (Kreit, 1978)[7]. In the untreated silt fraction, the peaks corresponding to the plagioclase family (3.20Å) and K-feldspars (3.27Å) were sharp. However, following the hydrolysis treatment, the Ca-plagioclase peak was attenuated, and the orientation of the K-feldspars was less ordered. Thus we may conclude that the main source for Ca-hydrolysis is the Ca-plagioclase dissolution.

The conductance-time characteristics of two untreated Nahal-Oz samples were studied to determine the consequences of the treatment used to remove lime. It is evidenced from Fig. 3 that, although the rate is affected by ESP_i, the first segment disappeared and the slopes of the lines (Table 4) were greater than those found for the second segment in the lime-free Nahal-Oz soil. The presence of $CaCO_3$ is probably responsible for the greater slope (Cruz-Romero and Coleman, 1975). It is evident that exchangeable Na affects the hydrolysis and weathering of Nahal-Oz soil. This is in contrast to results obtained with montmorillonite (Frenkel and Suarez, 1977), where the rate of adsorbed Ca hydrolysis equaled that of adsorbed Na. It seems that the rate of silt weathering, which is the dominant fraction that weathered in Nahal-Oz soil, is enhanced by the presence of exchangeable Na.

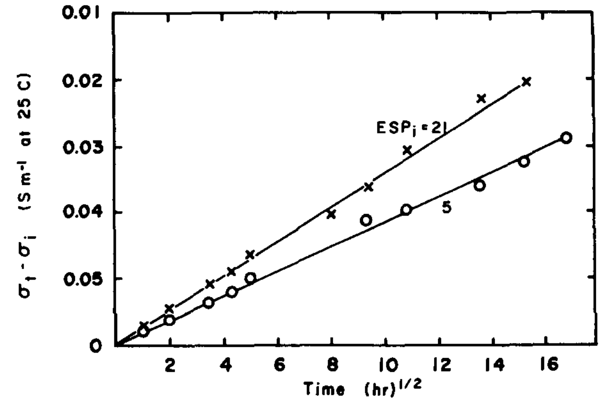

Fig. 3—The relationship between change in specific conductance (σ) and time for aqueous suspensions of two untreated Nahal-Oz soils. The subscripts t and i represent time and initial time, respectively.

The method of preparing the lime-free soil apparently is responsible for the reaction represented by the first segment in the kinetic experiments (Fig. 3 and 4). Nash and Marshall (1957) demonstrated the sensitivity of feldspars to slightly acidified solutions (pH~6.0). Thus, during the preparation of the lime-free soil, the feldspar weathered to intermediate unstable complexes, which dissolved rapidly to give the high slope of the first segment. In the second part of the reaction, the dissolution of both aluminosilicate clays and feldspars and hydrolysis of exchangeable cations is responsible for the increase in the specific conductance of the suspensions.

As can be seen in Table 5, the final total exchange-

Table 5—Total initial and final exchangeable bases and changes in exchange ion composition.

Soil	ESP_i	Total exchangeable bases Initial	Total exchangeable bases Final	Change in exchange composition (final—initial) Na	K	Ca	Mg
	%			$mmol_c\ kg^{-1}$			
Nahal-Oz	1.3	249 + 4* − 5	237 + 18 − 19	− 1.0	−0.2	−16.0	5.0
	5.7	241 + 12 − 10	135 + 14 − 12	−11.0	0.4	−96.0	1.0
	14.1	245 + 10 − 21	170 + 12 − 11	−22.0	0.6	−57.0	3.0
	14.1‡	245 + 10 − 21	190 + 18 − 12	−10.0	0.4	−47.0	2.0
	59.2	235 + 5 − 5	182 + 46 − 5	−52.0	0.3	− 1.0	−1.0
Grangeville†	6.7	80 + 2 − 2	72 + 9 − 14	− 1.0	0.9	− 1.0	1.0
	14.7§	76 + 1 − 1	79 + 4 − 6	0.0	0.8	− 1.0	1.0
	14.7‡	76 + 1 − 1	86 + 3 − 4	7.0	0.9	− 9.0	1.0
	94.2	70 + 1 − 1	82 + 2 − 2	−10.0	0.5	8.0	1.0
Netanya†	14.3	47 + 6 − 5	40 + 1 − 1	− 3.0	0.7	1.0	2.0
	25.3	45 + 3 − 4	61 + 5 − 5	− 7.0	0.2	7.0	0.0
	25.3	45 + 3 − 4	44 + 7 − 4	− 2.0	0.2	1.0	1.0
	88.8	40 + 1	34 + .3	−10.0	0.5	9.0	0.0

† Change in exchange composition calculated using the average of initial and final total exchangeable bases. Values for Grangeville and Netanya were 78.0 and 44.0 $mmol_c\ kg^{-1}$.

‡ Soil suspension prepared from a 0.01*M* salt solution with an SAR of 20.

§ Data was obtained from an hydrolysis experiment performed at 40°C. The chemical composition of the solution phase at both temperatures were very similar.

* The positive and negative numbers represent the maximum deviations of the individual replicates from the mean.

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[7] J. F. Kreit. 1978. Chemical stability of Na and Ca clays in dilute solutions. Ph.D. Thesis (in preparation), The Volcani Center, P.O.B. 6, Bet Dagan, Israel.

Table 6—Final solution composition.

Soil	Number ESP_i	Ca	Mg	Na	K	HCO_3	Cl	Si	pH_S†	SAR	pIAP‡
		mole m^{-3}						gm/m^3		(mole m^{-3})$^{1/2}$	(kmol m^{-3})^2
Nahal-Oz	1.3	1.32	0.03	0.32	0.08	2.35	0.56	--	6.8	0.3	7.5
	5.7	1.68	0.06	1.09	0.02	2.52	0.52	17	7.7	1.3	7.7
	14.1	0.14	0.04	3.58	0.01	4.02	0.52	6	8.0	8.5	8.0
	14.1§	1.84	0.08	10.10	0.01	2.39	9.10	16	7.8	10.5	7.8
	59.2	0.16	0.15	9.27	0.06	7.98	1.05	11	8.8	16.5	7.6
Grangeville	6.7	0.27	0.08	0.57	0.04	0.56	0.54	36	6.8	1.0	9.3
	14.7	0.23	0.07	0.75	0.06	0.83	0.69	36	7.3	1.4	9.0
	14.7§	0.31	0.07	8.33	0.08	0.21	8.60	44	6.5	13.4	10.2
	94.2	0.34	0.11	1.99	0.08	1.34	0.39	46	7.7	2.9	8.5
Netanya	14.3	0.37	0.06	0.59	0.08	1.09	0.67	26	7.4	0.9	8.6
	25.3	0.34	0.05	0.99	0.03	1.24	0.56	6	7.6	1.6	8.6
	25.3§	0.45	0.05	10.15	0.30	0.81	10.15	16	7.3	14.3	9.0
	88.8	0.23	0.36	2.02	0.24	1.83	0.55	26	8.1	2.6	8.4

† pH_S is the pH of the suspension.
‡ pIAP is the negative logarithm of the activity product, $A_{Ca}A_{CO_3}$.
§ Suspensions prepared for a 0.01*M* salt solution with an SAR of 20.

able bases for the Nahal-Oz soil were significantly lower than the initial values. The hydrolysis of both exchangeable Na^+ and Ca^{2+} are both involved as demonstrated by the changes in exchangeable ion composition (Table 5). For Grangeville and Netanya, the differences between initial and final exchangeable bases were not significant; but, for Grangeville, the initial exchangeable bases were less than the cation exchange capacity (Table 1). This indicates that most of the hydrolysis occurred during the final washings before the hydrolysis experiment was started. Afterwards, the release of crystalline K^+ and Mg^{2+} offset the hydrolysis of exchangeable Na^+ and Ca^{2+}. For Netanya, crystalline ion release offset the effects of hydrolysis.

The chemical composition of the solution phase is given in Table 6. In all cases the silicate concentrations are significant, as are the low SAR's. SAR also decreased significantly in suspensions made from dilute salt solutions (0.01*M*, SAR $=$ 20). Because the reaction vessels were opened to the atmosphere, the compensating anion for the cations released was HCO_3^-.

The Na^+ concentrations did equal those calculated from the initial soluble concentration (0.52 to 1.29 mol m^{-3}) and the changes in exchangeable Na^+ which occurred. This was not true for Ca^{2+} concentrations obtained for Nahal-Oz. Based on the changes in exchangeable Ca^{2+}, the final soluble Ca^{2+} concentrations should have been 1.4, 7.75, 4.65, and 0.12 mol m^{-3} for the ESP_i values of 1.3, 5.7, 14.1, and 59.2, respectively. Expectations were realized for ESP_i of 1.3 and 59.2. However, for ESP_i of 5.7 and 14.1, the calculated Ca^{2+} concentrations exceed those measured by 7.05 and 4.5 mol m^{-3}. Likewise, when the suspension was prepared from a 0.01*M* salt solution (SAR $=$ 20), the excess was 3 mol m^{-3}. Apparently, $CaCO_3$ precipitation occurred. Since any $CaCO_3$ dissolved by 1*M* NH_4OAC, pH 7, was regarded as exchangeable Ca^{2+}, the estimates of precipitation are too low. The water phase of the Nahal-Oz suspension was also supersaturated with respect to $CaCO_3$. The negative logarithm of the product of the calculated activities (pIAP) of Ca^{2+} and CO_3^{2-} (Table 6) was calculated, after correction for ion pair formation (Oster and Rhoades, 1975), by assuming the solution was in equilibrium with 0.04 kPa of CO_2. The calculated pIAP's may not be appropriate for soil suspensions due to ion-soil charge interactions. However, correction for anion exclusion effects would result in lower values or greater degrees of supersaturation. The low pIAP values suggest that exchangeable Ca^{2+} hydrolyzes faster than it precipitates as $CaCO_3$.

The precipitation of $CaCO_3$ also explains the increased hydrolysis of exchangeable Ca^{2+} at an ESP_i of 5.7 as compared with that at an ESP_i of 1.3. With increased levels of exchangeable Na^+, its hydrolysis increased, resulting in a higher level of HCO_3^- and pH, thereby lowering the solubility of $CaCO_3$ and limiting the activity of Ca^{+2} in solution.

CONCLUSIONS

The release of Ca^{2+}, Mg^{2+}, and K^+ from silicate minerals and the hydrolysis of exchangeable Na^+ and Ca^{2+} for three arid-zone soils occurred at rates sufficient to prevent the preparation of homoionic Na soils and caused the relationship between suspension conductance with the square root of time to exhibit two linear rates. We concluded that the first rate, the more rapid of the two and dependent on exchangeable Na, was controlled by intermediates formed while removing $CaCO_3$ with acidified salt solutions, and the second by a slower decomposition exchange of adsorbed H^+ with the crystalline cations of soil silicates. A single rate, which increased with increasing exchangeable Na, was obtained with suspensions prepared from untreated samples of the most unstable soil. Weathering of the silt fraction was the dominant reason for the increase in soil conductance. Apparently silt weathering is enhanced by increasing exchangeable Na.

The rate of exchangeable Ca^{2+} hydrolysis and release from silicate materials was sufficient to cause the solution phase to be supersaturated with lime for the soil with the highest cation exchange capacity. That this occurred, indicates the rate of Ca^{2+} release from soils can exceed that of lime precipitation.

ACKNOWLEDGEMENT

We wish to thank R. Ben Zaken and J. F. Kreit for their expert technical assistance.

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