NOTES

KINETICS OF HYDROLYSIS OF SOME PALYGORSKITE-CONTAINING SOIL CLAYS IN DILUTE SALT SOLUTIONS

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INTRODUCTION

Some soils in arid and semi-arid areas contain palygorskite in their clay fraction. The absence of palygorskite in soils in humid areas is attributed to the acid nature of these soils. Palygorskite is known to be unstable even in very dilute acid (Singer, 1977). As shown recently, decomposition of palygorskite occurs also under neutral conditions (Neaman and Singer, 2000).

Palygorskite is the most Mg-rich among common clay minerals (Singer, 1989). Based on leaching experiments of palygorskite, Mg is preferentially released into solution over Fe and Al under both acid and neutral conditions (Abdul-Latif and Weaver, 1969; Singer, 1977; Corma *et al.*, 1987, 1990; Gonzalez *et al.*, 1989; Myriam *et al.*, 1998; Neaman and Singer, 2000).

Nearly all palygorskite-containing soils are found in dry regions, where irrigation is indispensable for profitable agriculture. For proper irrigation practices, the physical behavior of wetted soils is of great importance. Mg, when released into the soil solution, is known to affect the dispersivity of the soil clay fractions (Shainberg *et al.*, 1988; Keren, 1991). No studies have been performed to examine Mg-related chemistry of palygorskite-containing soils.

Models suggested by Neaman and Singer (2000) for decomposition of standard palygorskite clays under neutral conditions may be applicable also to palygorskite-containing soil clays. Standard palygorskite clays are defined as clays obtained from deposits in which palygorskite is the major mineral phase, and differ from soil clays, which contain other minerals besides palygorskite. To determined the effect of palygorskite in soil clays, we have investigated the hydrolysis of

some palygorskite-containing soil clays using the same procedure as Neaman and Singer (2000).

MATERIALS AND METHODS

Subsoils from five irrigated fields in the Jordan (Nos. 7 and 9) and Bet-She'an (Nos. 11, 13, and 16) Valleys, Israel, were collected for the study. According to USDA taxonomy (Soil Survey Staff, 1996), these soils are classified as Haplocalcids.

The samples were air-dried and ground to pass a 2-mm sieve. The soils were ultrasonically dispersed in water and the <2-μm fraction was separated by sedimentation under gravity. The clays were then treated by 0.1 M HCl (sample/solution ratio of 1/100) for the removal of carbonates. The samples were rapidly heated in the acid to boiling, then the pH values of the suspensions were immediately adjusted to pH 7 by addition of 0.1 M NaOH. Organic matter was removed by H_2O_2 treatment (heated overnight at 60°C). Free iron oxides were extracted by the dithionite-citrate-bicarbonate method (Kunze and Dixon, 1986). Na-saturated clays were prepared by washing and centrifuging the clay-size faction three times with 1 M NaCl solution; washing and centrifuging with ethyl alcohol until the electrical conductivity of equilibrium solution was <10 dS/m. The clays were then freeze-dried.

X-ray diffraction (XRD) data were obtained using a Rigaku diffractometer with CuKα radiation. Oriented specimens of Na-saturated clays were prepared for XRD analysis by sedimentation of clay suspension onto a glass slide, and then solvated in ethylene glycol vapor (65°C for 24 h). The clay fractions of the soils were of similar mineralogy. The clays from the Jordan Valley soils (Nos. 7 and 9) contained smectite, palygorskite, kaolinite, quartz, and feldspar. In the clays from Bet-She'an Valley soils (Nos. 11, 13, and 16),
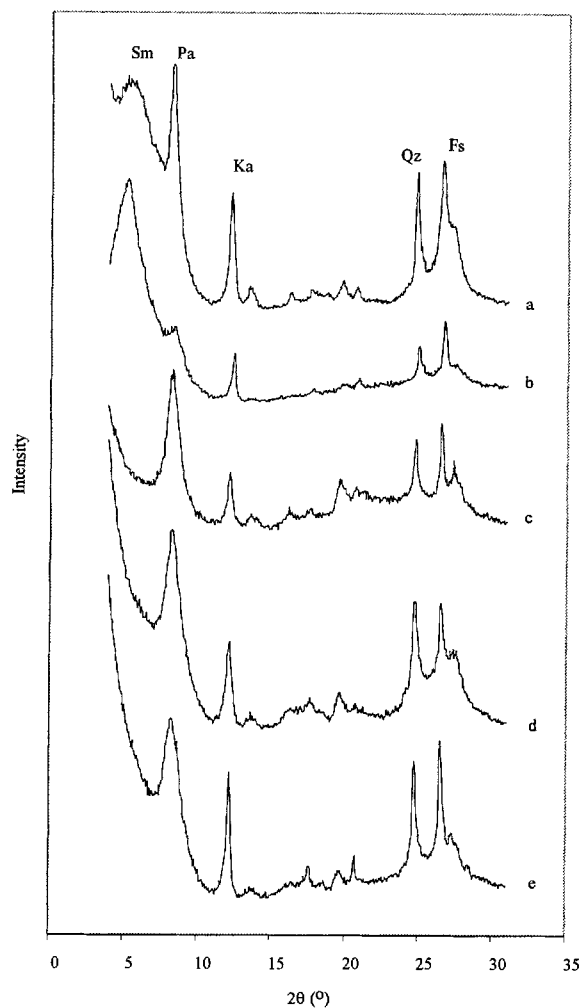
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Figure 1.   X-ray diffractograms of the <2-μm size fractions (oriented specimen, Na-saturated, ethylene-glycol solvated): (a) soil 7, (b) soil 9, (c) soil 11, (d) soil 13, (e) soil 16. Sm = smectite, Pa = palygorskite, Ka = kaolinite, Qz = quartz, Fs = feldspar.

Figure 2.   X-ray diffractograms of the <2-μm size fractions (unoriented specimen): (a) soil 7, (b) soil 9, (c) soil 11, (d) soil 13, (e) soil 16. Qz = quartz, Sm = smectite.

interstratified clay (probably smectite-illite) is present instead of smectite (Figure 1). To determine whether the smectite present in the clays is dioctahedral or trioctahedral, unoriented samples were scanned from 59 to 63 °2θ (Figure 2). A narrow reflection at 1.54 Å belongs to quartz (211); a broad reflection at 1.50 Å belongs to smectite (060) and shows the smectite to be dioctahedral.

Batch experiments in dilute salt solutions (0.001 M NaCl) under neutral conditions in the presence of cationic resin were conducted to study the kinetics of clay hydrolysis. The presence of the cationic resin prevents equilibrium from being attained, and dilute salt solutions are a better approximation to soil solution than deionized water. The procedure was described in detail in Neaman and Singer (2000). Batch experiments were
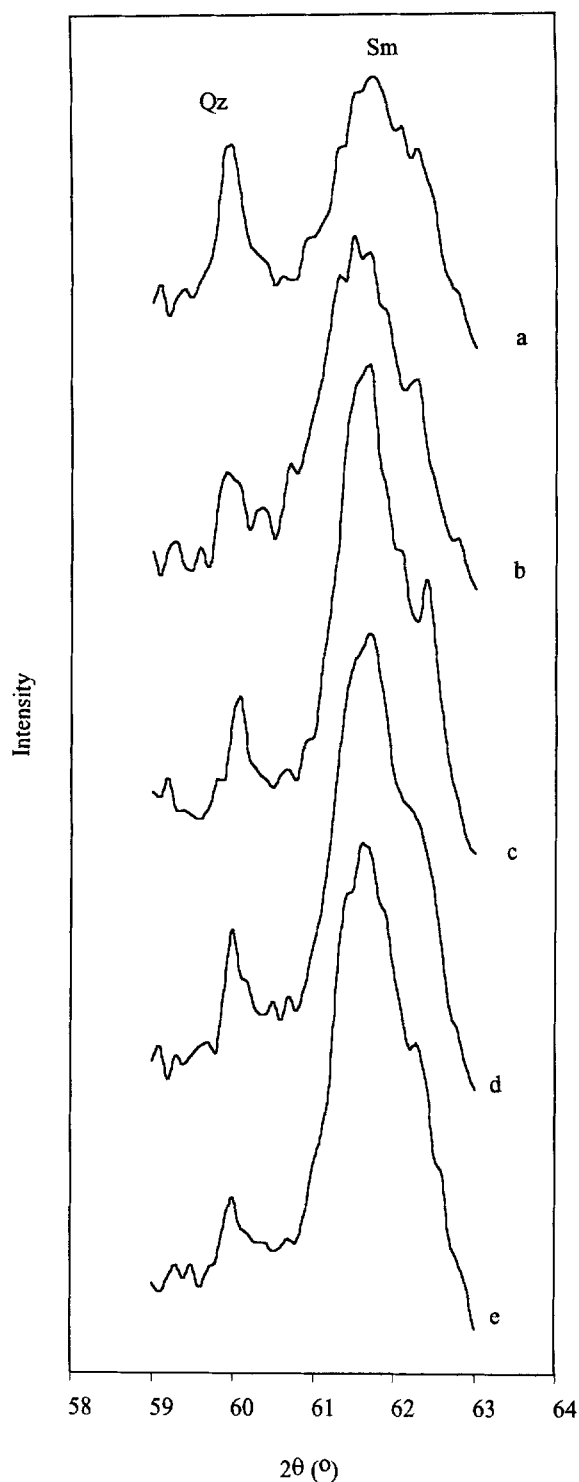
Table 1. Mg and Si released from the clays and the pH of the solution as a function of shaking time.

Sample	Shaking time days	Element released, Mg	mg/100 g of clay Si	pH
7	7	64.6	140.2	7.6
	15	81.2	169.4	7.6
	21	85.4	174.7	7.5
	35	92.3	180.5	7.5
	42	98.0	202.8	7.3
9	7	41.5	233.2	7.6
	15	47.1	265.2	7.4
	21	55.8	263.1	7.3
	35	60.0	290.0	7.2
	42	63.6	301.9	7.3
11	7	38.9	153.5	7.4
	15	44.1	175.9	7.2
	21	45.9	175.5	7.2
	35	51.8	205.8	7.1
	42	53.6	223.9	7.1
13	7	24.9	122.4	7.8
	15	26.6	130.4	7.4
	21	27.8	134.3	7.3
	35	31.5	158.2	7.2
	42	33.5	196.8	7.2
16	7	29.4	162.8	7.5
	15	32.2	189	7.2
	21	32.5	186.6	7.3
	35	36.4	215.2	7.1
	42	35.6	218.6	7.1

Table 2. Chemical composition and specific surface areas of the clays.

	Sample 7	Sample 9	Sample 11	Sample 13	Sample 16
Chemical composition, wt. %					
SiO_2	60.51	55.51	55.41	53.00	55.40
Al_2O_3	15.83	17.17	17.78	19.83	19.03
MgO	5.99	5.34	5.37	4.31	4.47
Fe_2O_3	7.69	10.72	9.26	9.47	10.00
CaO	0.15	0.50	0.24	0.08	0.10
Na_2O	1.49	2.24	1.48	1.98	2.09
K_2O	1.91	2.31	2.20	2.04	1.92
TiO_2	0.82	1.27	1.22	1.43	1.23
H_2O	5.82	6.04	7.35	7.06	7.15
Total	100.20	101.10	100.30	99.19	101.39
Specific surface area, m^2/g					
EGME	469	390	399	412	412

performed in duplicate. The deviations in the values obtained from the duplicate runs were ≤10%. The average values are shown here.

Chemical analysis of the clays was performed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Samples (in two replicates) were decomposed by fusion with lithium metaborate (Wilson, 1987). Specific surface areas (SSAs) were determined by ethylene glycol monoethyl ether (EGME) adsorption (in two replicates) with 24-h oven drying (105°C) as a pretreatment according to Rather-Zohar *et al.* (1983).

RESULTS AND DISCUSSION

Table 1 shows Mg and Si released from the clays and the pH of the solution as a function of shaking time. No Al and Fe were released from the clays in the present study. The pH of the solutions after 7 d of shaking is in the range of 7.4–7.8 for each sample, and the pH remains nearly constant. The amount of Si and Mg released from the clay increases with time, and a straight line was obtained when the amount of element released (mg/100 g of clay) was plotted as a function of time (days). The slope of the line is referred to as the "release rate". Release rates of Mg and Si differ significantly among samples.

Table 2 shows the chemical composition of the clays. Palygorskite is the major source of Mg in the clays. Kaolinite, quartz, and feldspar do not contain Mg. The clays used do not contain dolomite or Mg-rich calcite, as they were treated with 0.1 M HCl. Smectite does not contribute significantly to Mg content because the smectite is dioctahedral. Thus, differences in Mg content in the clays is related to differences in the palygorskite content of the clay. Assuming that the MgO content in palygorskite in each soil clay is identical, palygorskite contents in the soil clays can be evaluated. Assuming that the MgO content in palygorskite is equal to 12.28 wt. %, the value for common Mg-rich palygorskite from Florida (Neaman and Singer, 2000), palygorskite content in soil clay ranges from 35% (sample 13) to 50% (sample 7).

Neaman and Singer (2000) reported that differences in the Mg release rate among standard palygorskite clays were related to differences in the chemical composition and the SSA of the clays: MgO and Fe_2O_3 contents and SSA had a positive, and Al_2O_3 content a negative effect on the Mg release rate. Thus, the Mg release rate was higher in palygorskites with high SSA and high Mg and Fe contents than in palygorskites with low SSA and high Al content. When linear regression analysis for Mg release rate *versus* SSA or Mg release rate *versus* chemical composition was performed, the correlation coefficients were relatively low. In the present study, however, linear regressions for Mg release rate *versus* MgO content in the clay show a relatively high correlation coefficient ($R^2 = 0.87$), because the SSAs of the clays are similar to each other (Table 2).

We suggest that palygorskite is the only significant source of Mg released from the clays in the present study. Results reported by Neaman and Singer (2000) showed that the Mg release rate from the Cheto montmorillonite, which is high in Mg content among dioctahedral smectites (Grim and Kulbicki, 1961), was four times lower than that from Mg-rich palygorskite varieties. Thus, dioctahedral smectite present in the

Table 3. Mg and Si released from the clays after 42 d of shaking calculated as a percentage of element content in the untreated clay and Si/Mg molar ratios in the solid phase and in the solution.

Soil	Released, % of total		Si/Mg molar ratio	
	Mg	Si	In solid	In solution
7	2.73	0.72	6.7	1.8
9	1.99	1.17	6.9	4.1
11	1.66	0.87	6.9	3.6
13	1.29	0.80	8.2	5.0
16	1.33	0.85	8.3	5.3

clays can not contribute significantly to the release rate of Mg.

The release rate of Mg from soil clay was from 0.18 mg 100 g^{-1} d^{-1} (sample 16) to 0.84 mg 100 g^{-1} d^{-1} (sample 7). Correlations obtained for Mg release rate *versus* MgO content are in accord with results reported by Neaman and Singer (2000) for standard palygorskite clays because palygorskite is the major source of Mg in the clays (see above).

Neaman and Singer (2000) reported for standard palygorskite clays that the Si release rate depended on the SSA of the mineral only and was not related to chemical composition. Si release rate decreased with increasing SSA. In the present study, however, no significant correlations of this type were obtained because all minerals present contained Si in their structure.

Table 3 shows Mg and Si released from the clays after 42 d of shaking, as calculated as a percentage of element content in the untreated clay. Mg release varies from 1.33 to 2.73%. Release of Si, however, is much lower than that of Mg and varies from 0.72 to 1.17%. It is interesting to compare the results obtained for soil clays in the present study with those reported by Neaman and Singer (2000) for standard palygorskite clays. For the latter clays, release of Mg was reported to be similar to release of Si when calculated as a percentage of element content in the untreated clay. Release of both Si and Mg was 1.7 to 2.4% for Mg-rich palygorskites and 0.9 to 1.0% for Al-rich varieties. Values of Mg release obtained in the present study for soil clays are close to those for Mg-rich standard palygorskites clays, suggesting that palygorskite in the soil clays used in the study is Mg-rich.

Based on the results reported for standard palygorskite clays, release of Si from palygorskite is expected to be similar to release of Mg. Release of Si, however, is much lower than that of Mg (Table 3). The maximum amount of Si released in the present study was 301.9 mg Si/100 g of clay (Table 1, sample 9, 42 d of shaking), which is equal to a Si concentration in solution of 37.7 ppm or 1.35×10^{-3} M or pSi = 2.87 (pSi = $-\log$ a$_{H_4SiO_4}°$, where a$_{H_4SiO_4}°$ is the activity of H$_4$SiO$_4$°). This value is below 50.9 ppm Si or pSi = 2.74, the solubility of amorphous silica in pure water

(Lindsay, 1979). Thus, in the present study, the system was far from saturation, and precipitation of Si released from palygorskite is unlikely.

As suggested above, palygorskite is the only significant source of Mg released from the clays in the present study. With regards to silica, all minerals present contained Si in their structure and may release Si into solution. Results obtained suggest that release of Si from smectite, kaolinite, quartz, and feldspar is lower than that from palygorskite. Thus, release of Si, when calculated as a percentage of Si content in the untreated clay, is much lower than the release of Mg.

Table 3 also shows Si/Mg molar ratios in the solid phase and in solution. The Si/Mg ratio in solution after 42 d of shaking under neutral conditions is much lower than that in the solid phase. Neaman and Singer (2000) reported for standard palygorskite clays that the Si/Mg ratio in solution after 70 d of shaking under neutral conditions was close to that in the solid phase. Based on the results reported for standard palygorskite clays, the Si/Mg ratio in solution is expected to be close to that in the solid phase of the palygorskite-containing soil clays studied here. The Si/Mg ratio in solution is much lower than in the solid phase (Table 3), because release of Si from smectite, kaolinite, quartz, and feldspar is lower than that from palygorskite (see above). Thus, dissolution of Mg is strongly favored over that of Si for soil clays. For standard palygorskite clays, however, the dissolution of Si and Mg is close to congruent.

CONCLUSIONS

Decomposition of palygorskite takes place in soils under neutral conditions. The models suggested by Neaman and Singer (2000) for the hydrolysis of standard palygorskite clays are applicable for Mg release from palygorskite-containing soil clays. Si release from the soil clays, however, is not in accord with these models.

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