



Differences in sodication and desodication processes influenced by type of clay minerals and clay contents

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Abstract

The processes of sodication and desodication in soil influences agricultural productivity. We explored sodication and desodication processes in montmorillonite and illite with varying ratios of clay contents in 5% and 25 % on sodium adsorption ratios (SAR) of 7, 13, and 20 of equilibrated solution with 10 mmol_c L⁻¹. The sodication and desodication processes were observed to vary considerably, depending on the type of clay, clay content, and equilibrated solution. Sodication and desodication processes were different even for the same clay under similar conditions. The differences in clay sodication based on SAR of equilibrated solution were observed, and it was found that sodication progressed comparatively more rapid in illite than in montmorillonite. The desodication processes varied according to the type of clay and clay content. In montmorillonite, desodication progressed comparatively better at low clay content than at high clay content. In contrast, it progressed more rapid at high clay content than at low clay content in illite. However, desodication processes in illite with low clay content had similar tendencies as SAR of an equilibrated solution. As a result, the Gapon equilibrium constant was different for clay sodication and desodication processes even in the same clay mineral and clay content. The clay sodication and desodication processes as well as final exchangeable sodium percentage values were affected not only by SAR of the equilibrated solution but by the type of clay minerals and clay contents as well.

Keywords: Arid regions; cation exchange; exchangeable sodium percentage; sodic soil; sodium adsorption ratio

Introduction

Saline soils are characterized by the accumulation of high levels of soluble salts and can be further classified according to the specific salt composition (Abrol, 1988). In saline soils, the high salinity of the soil water solution inhibits plant water absorption. Saline soils are defined as having an electrical conductivity (EC) of the saturated soil paste extract (EC_e) of ≥ 4 dS m⁻¹ and an exchangeable sodium percentage (ESP) $< 15\%$. On the other hand, sodic soils are defined as having an EC_e < 4 dS m⁻¹ and an ESP $\geq 15\%$ (US. Salinity Lab. Staff, 1954). Sodic soils contain a large concentration of sodium ions (Na⁺). High ESP can degrade soil physical properties, enhance soil structure collapse, and generate a potential for strong alkalinity (pH ≥ 8.5), thus comprehensively worsening the soil environment and significantly inhibiting crop growth as a consequence of clay dispersion and inhibition of nutrient absorption due to high pH (Läuchli and Grattan, 2012). It is major global conundrum that severely impacts agricultural productivity.

The amount and composition of exchangeable cations adsorbed onto the soils solid phase of the soil are strongly correlated with the concentration and composition of cations in the saturation paste extract. The sodium adsorption ratio (SAR) is the main diagnostic tool for evaluating Na⁺ hazards, such as dispersion, flocculation, and crustification of soils, in irrigation water or soil solution (Sumner, 1993; Rengasamy and Churchman, 1999; Quirk, 2001; Abbaslou *et al.*, 2020). The SAR of the extracted soil solution is easy to obtain and can be used as an indirect indicator of soil Na⁺ hazards in arid regions (Paliwai and Gandhi, 1976; Jurinak *et al.*, 1984; Yeilagi *et al.*, 2021). SAR is calculated using the following equation (US. Salinity Lab. Staff, 1954):

$$SAR = Na^+ / [(Ca^{2+} + Mg^{2+}) / 2]^{0.5} \quad (1)$$

where ionic concentrations are expressed in mmol_c L⁻¹, and the unit of SAR is (mmol L⁻¹)^{0.5}, however, unit will be omitted hereafter. SAR is related to the exchangeable sodium ratio (ESR) of the soil. ESP and ESR can be calculated from the concentrations of Na⁺, calcium, and magnesium in the soil solution using the following formulae (Bohn *et al.*, 1985):

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$$\text{ESR} = \text{ESP}/(100 - \text{ESP}) = K_G \times \text{SAR} \quad (2)$$

where K_G is the Gapon exchange coefficient (Gapon, 1933). The Gapon equation (3) is widely used in research concerning sodic and saline-sodic soils (US. Salinity Lab. Staff, 1954):

$$[\text{NaX}]/[\text{Ca}_{1/2}\text{X}] = K_G \times [\text{Na}^+]/[\text{Ca}^{2+}]^{0.5} \quad (3)$$

where exchangeable cation concentrations are in $\text{mmol}_c \text{ kg}^{-1}$, and soluble cation concentrations are in $\text{mmol}_c \text{ L}^{-1}$. The exchangeable sodium status of soils can be predicted quite well from SAR and a Gapon type exchange equation such as the one below:

$$\text{ESR} = 0.01475 \times \text{SAR} - 0.0126 \quad (4)$$

Sodic soils will have a soil solution SAR value of approximately 13 and an ESP value of 15%; therefore, the SAR value can be used as a rough estimation of ESP.

Furthermore, useful correlations between ESP and SAR values have been established using soil–water solutions of specific soil types (Rashidi and Seilsepour, 2008; Seilsepour *et al.*, 2009; Chi *et al.*, 2011). However, cation exchange selectivity coefficients vary widely, which poses a major problem for using the ESR–SAR relationship to estimate the exchangeable Na^+ (Sinanuwong and El-Swaify, 1974; Oster and Sposito, 1980; Jurinak *et al.*, 1984; Miller *et al.*, 1990; Keshavarzi *et al.*, 2016; Gharaibeh *et al.*, 2021).

Results on the completely exchange between $\text{Na}^+/\text{Ca}^{2+}$ have been discussed in many previous studies (Sinanuwong and El-Swaify, 1974; Endo *et al.*, 2002; Kopitke *et al.*, 2006; Hedstrom and Karnland, 2011; Singh *et al.*, 2018). Shainberg *et al.* (1980) studied the effect of salt concentration and exchanger composition on $\text{Na}^+/\text{Ca}^{2+}$ exchange in montmorillonite and illite suspensions. Their results showed that ion affinities differed with clay minerals

Table 1: Chemical properties of the equilibrated solution

Treatments	pH	EC dS m ⁻¹	Na ⁺	Ca ²⁺	SAR (mmol L ⁻¹) ^{0.5}
			mmolc L ⁻¹		
SAR7	5.50	1.14	7.61	2.30	7.11
SAR13	5.66	1.10	8.98	0.97	12.89
SAR20	5.53	1.13	9.63	0.47	19.87

EC: Electrical conductivity, SAR: Sodium adsorption ratio

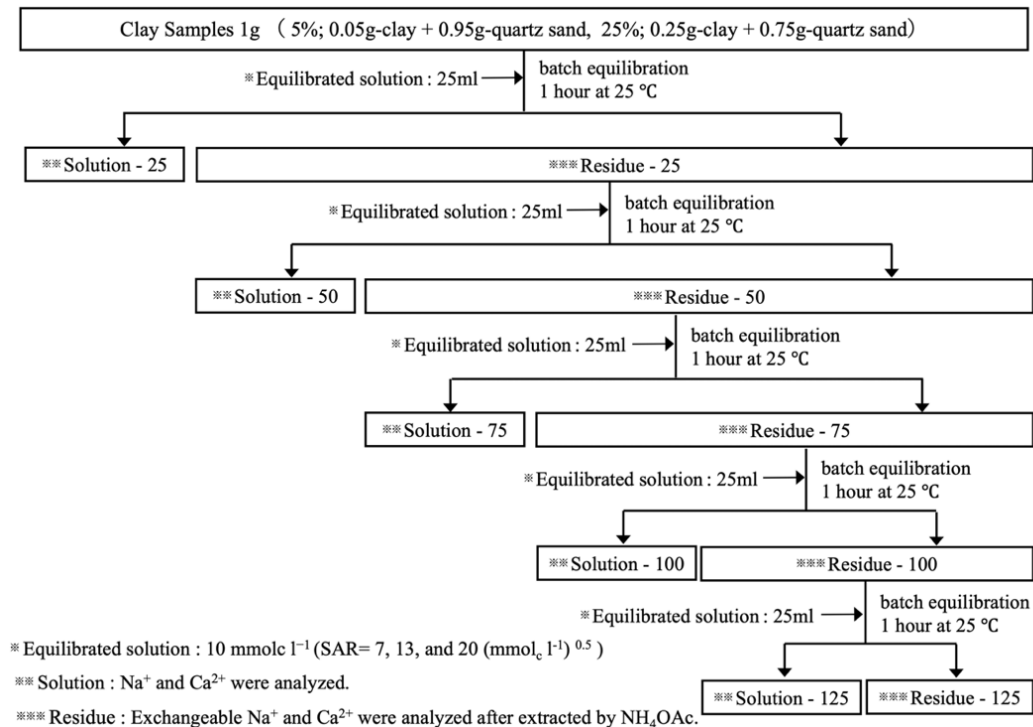


Figure 1: Experimental design



and ion concentrations of the clay suspension. The same has been reported for different clay minerals, clay contents, and different equilibrating solutions of varying SAR ratios (Sumner, 1993; Toze, 2006). Sodium hazards in soils may be predicted on the basis of these approaches. However, during actual irrigation events, the status of the soil colloid surfaces changes. Very few farmlands reach the equilibrated state between irrigation water and the soil solid phases, probably because the status of complete $\text{Na}^+/\text{Ca}^{2+}$ exchange and that of farmland management are different; thus, salt quantity and composition in soils changes with irrigation. Therefore, it is important to understand the cation status in the soil by sodication and desodication processes for a better farmland soil management. In turn, the two processes depend on the soil characteristics.

We conducted this study as the first step to understand the processes of sodication and desodication and how they are influenced by the type of clay mineral, clay content, and by the quantity and quality of water added. We evaluated the differences in sodication and desodication processes according to the type of clay mineral and clay contents using two clay minerals, montmorillonite and illite. Montmorillonite is the predominant clay mineral in semi-arid and arid regions (Amézketa, 1999; Mamedov *et al.*, 2010) and is characterized as having a problematic, high swelling-potential (Pérez *et al.*, 2021). Illite was used for comparison with montmorillonite because it is the 2:1 clay mineral with the same of montmorillonite and is widely distributed in arid regions (Mamedov *et al.*, 2010). For this purpose, the effect of mineral type and content on each stage of the sodication and desodication processes was assessed quantitatively.

Materials and Methods

Experiment layout

We used montmorillonite and illite for this study. Commercial (Nichika Inc., Japan) montmorillonite from Yamagata, Japan, and illite from Iowa, USA were used for our experiments. Clay fractions less than 2 μm in size were obtained using the sedimentation techniques by the pipette method according to Stoke's law (Gee and Bauder, 1986). Sodium-saturated clays and calcium-saturated clays were prepared by exchanging Na^+ or Ca^{2+} on the clay surface with 1 $\text{mol}_\text{c} \text{L}^{-1}$ solutions of NaCl and CaCl_2 (Shainberg *et al.*, 1980). Next, the clay was washed by centrifugation with distilled water until an AgNO_3 test indicated that the equilibrated solution was free of chloride. The homo-ionic clays were air-dried and sieved through a 100-mesh sieve (< 0.15 mm, purity > 98.0%) prior to use. Exchangeable cations in clay minerals were extracted with 1 $\text{mol}_\text{c} \text{L}^{-1}$ NH_4 acetate (NH_4OAc) (Sumner and Miller, 1996). The

Na^+ and Ca^{2+} in the NH_4OAc -extracted solutions were analyzed using an atomic absorption spectrophotometer (Z-2000; Hitachi, Japan). Cation exchange capacity (CEC) was estimated by adding exchangeable Ca^{2+} and Na^+ . The chemical properties of the prepared clay are shown in Table 1. CEC values of Na^+ -saturated clay were greater than those of Ca^{2+} -saturated clay in both montmorillonite and illite. The ESP values of illite were greater than those of montmorillonite in both Na^+ - and Ca^{2+} -saturated clays. Sodium-calcium selectivity was determined by batch equilibration as follows (Figure 1): 1 g samples (clay + quartz sand) were placed in pre-weighed 50 mL centrifuged tubes with varying ratios of clay to quartz sand (clay contents with air-dried weight: 5% and 25%). These were equilibrated with 25 mL of 10 $\text{mmol}_\text{c} \text{L}^{-1}$ salinity solution with SAR levels of 7, 13, and 20 ($\text{mmol} \text{L}^{-1}$)^{-0.5} by shaking for 1 hour at 25 °C. Salinity hazard of the concentration level for equilibrated solution was high (US. Salinity Lab. Staff, 1954). Sodic soils yield a soil solution with SAR values of approximately 13 to an ESP value of 15%, according to US. Salinity Lab. Staff (1954). We prepared SAR20, which was higher than SAR13, and SAR7 which was lower than SAR13, as equilibrated solutions. The solutions were prepared using NaCl and CaCl_2 , and the Na^+ and Ca^{2+} in the solutions were analysed using an atomic absorption spectrophotometer (Z-2000; Hitachi, Japan). The chemical properties of equilibrated solution are shown in Table 1. We prepared three different SAR levels with same concentration of 10 $\text{mmol}_\text{c} \text{L}^{-1}$. The solutions were analysed after equilibration. The tubes and wet samples were weighed and the amounts of soluble Na^+ and Ca^{2+} which remained in the tubes were estimated by calculation. Exchangeable and soluble cations were extracted from the wet clay with 1 $\text{mol}_\text{c} \text{L}^{-1}$ NH_4OAc . Na^+ and Ca^{2+} in the equilibrated and NH_4OAc -extracted solutions were analysed using an atomic absorption spectrophotometer (Z-2000; Hitachi, Japan). To observe the process of ion exchange selectivity change, 25 mL of the equilibrated solutions were added to the extraction residues and replacement by NH_4OAc was conducted. Exchangeable cation composition was calculated after making allowance for soluble Na^+ and Ca^{2+} carried over in the extract obtained by NH_4OAc solution extraction. CEC values were estimated by adding exchangeable Na^+ and Ca^{2+} . These equilibrium processes were repeated five times sequentially. Although irrigation events are quite different from this batch equilibration, it might still be useful to clarify the sodication and desodication processes. Sequential extractions were conducted on the residue samples from each step. The $\text{Na}^+/\text{Ca}^{2+}$ exchange selectivity of each sample was evaluated using the each same quantity of the equilibrated solution to identify differences in the sodication and desodication processes.



Table 2: Chemical properties of the clay samples

Clay properties	Ex-Ca	Ex-Na	CEC	ESP
	cmol _c kg ⁻¹			%
Ca ²⁺ montmorillonite	83.07	0.53	83.60	0.63
Na ⁺ montmorillonite	14.42	84.51	98.93	85.42
Ca ²⁺ illite	12.90	1.00	13.90	7.19
Na ⁺ illite	0.00	25.03	25.03	100.00

Ex-Ca: Exchangeable calcium ion, Ex-Na: Exchangeable sodium ion, CEC: Cation exchangeable capacity, ESP: Exchangeable sodium percentage

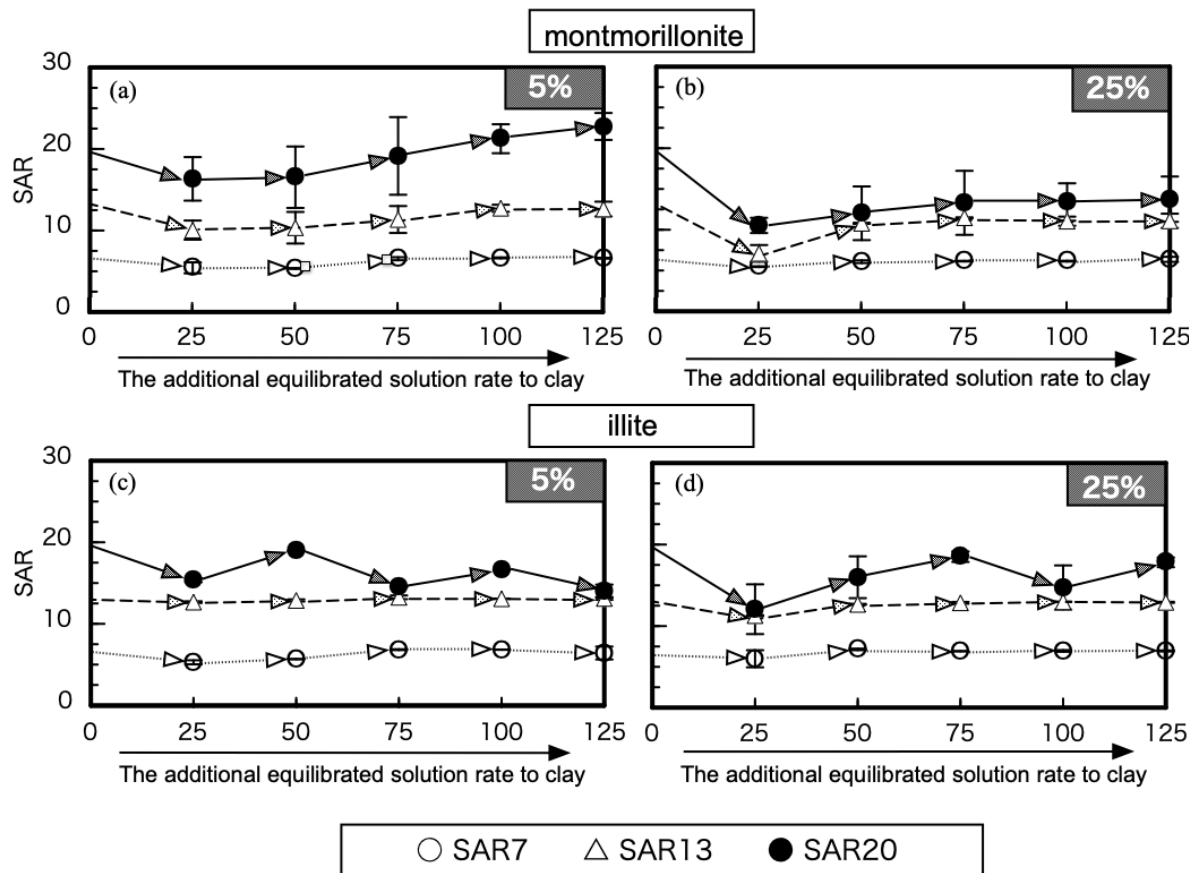


Figure 2: The processes of SAR change with clay sodication as influenced by clay mineral type and clay content. (a) calcium-saturated montmorillonite, 5%; (b) calcium-saturated montmorillonite, 25%; (c) calcium-saturated illite, 5%; (d) calcium-saturated illite, 25%. SAR7, SAR13, and SAR20 represent the values of sodium adsorption ratio in each equilibrated solution. Vertical bars indicate standard error. There were significant differences among samples at $p \leq 0.05$ by analysis of variance (ANOVA) at each solution rate to clay for each SAR

Statistical analysis

Data shown are means \pm standard deviation (S.D.) of four replicates. Statistical results were obtained by one-way analysis of variance (one-way ANOVA) with a Tukey's HSD (honestly significant difference) test ($p < 0.05$) using IBM® SPSS® statistics software (version 27.0).

Results

Chemical properties of clay minerals

The chemical properties of the prepared clay are shown in Table 2. CEC values of Na⁺-saturated clay were greater than those of Ca²⁺-saturated clay in both montmorillonite



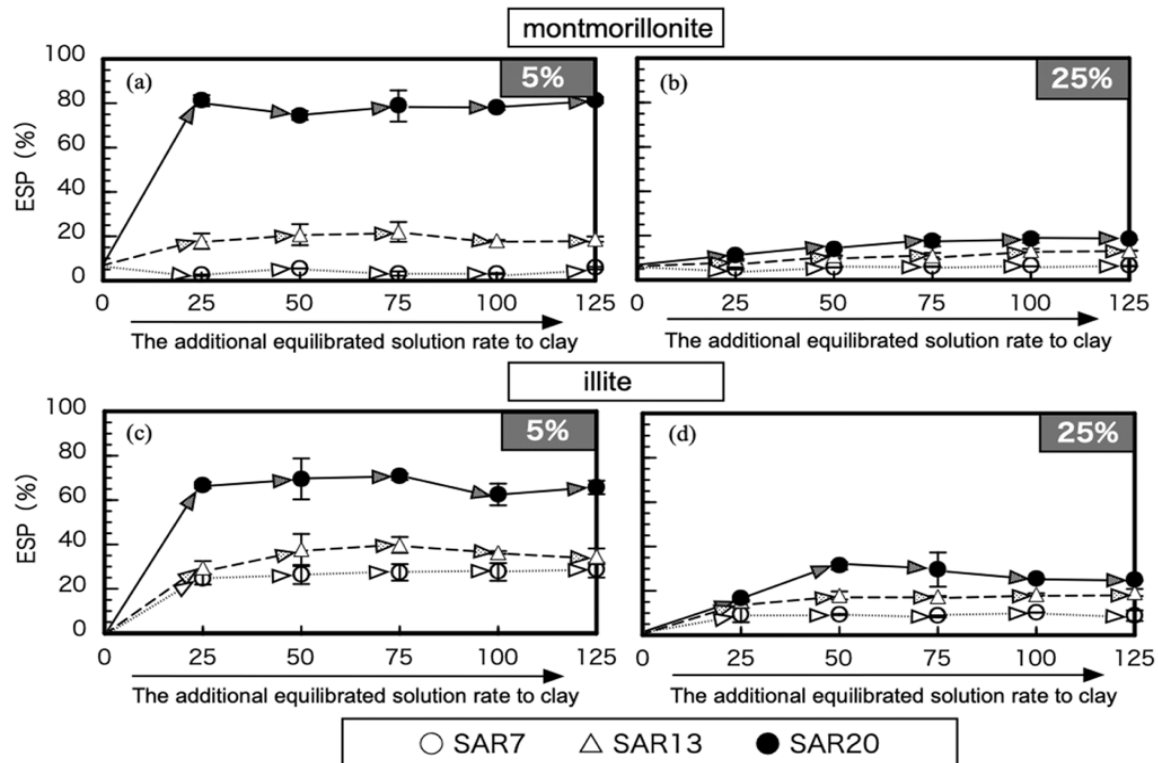


Figure 3: The processes of ESP change with clay sodication as influenced by clay mineral type and clay content. (a) Calcium-saturated montmorillonite, 5%; (b) Calcium-saturated montmorillonite, 25%; (c) calcium-saturated illite, 5%; (d) calcium-saturated illite, 25%. SAR7, SAR13, and SAR20 represent the values of sodium adsorption ratio in each equilibrated solution. Vertical bars indicate standard error ($n = 4$). There were significant differences among samples at $p \leq 0.05$ by analysis of variance (ANOVA) at each solution rate to clay for each SAR

and illite. The ESP values of illite were greater than those of montmorillonite in both Na^+ - and Ca^{2+} -saturated clays.

Changes in sodium adsorption ratio with clay sodication processes

The changes in SAR with clay sodication processes as influenced by clay minerals and clay contents are shown in Figure 2. At the initial stage (i.e., at the equilibrated status by first adding 25 mL equilibrated solution to samples), with the clay content of 25% and an equilibrated solution of SAR 20, the SARs of the equilibrated solution of montmorillonite and illite decreased by 47.4% and 39.7%, respectively. Thereafter, the SAR of montmorillonite and illite continued to increase when equilibrated solution of SAR20 was added; the final SAR were 13.8 and 17.8, respectively. On the other hand, it decreased to 14.0 in illite at the final SAR with clay content of 5% when equilibrated solution of SAR20 was added. However, the final SAR was slightly increased to 22.8 in montmorillonite with clay

content of 5% when equilibrated solution of SAR20 was added. A nearly constant process was observed in clay sodication of SARs and the SAR converged to similar values.

Changes in exchangeable sodium percentage with clay sodication processes

The changes in ESP with clay sodication processes as influenced by clay minerals and clay contents are shown in Figure 3. The ESP values varied depending on the clay minerals and clay contents. Clay sodication tended to progress at low-clay content. The sodication in montmorillonite with low clay content progressed rapidly in the equilibrated SAR20 solution. However, the ESP values remained almost same and the clay sodication proceeded gradually when equilibrated SAR7 and SAR13 solution was added to montmorillonite. The final ESP value was dependent on the SAR of the equilibrated solution. On the other hand, the change in ESP value of illite differed with

Table 3: The differences of Gapon exchange coefficient as influenced by clay minerals and composition with clay sodication (mean \pm standard deviation, $n = 4$)

The additional equilibrated solution rate to clay	Gapon exchange constants					
	SAR7		SAR13		SAR20	
-----	Calcium-saturated montmorillonite 5% -----					
25	0.02264	± 0.0007 a	0.02220	± 0.0089 bc	0.26833	± 0.0670 a
50	0.01079	± 0.0006 c	0.02695	± 0.0141 a	0.08279	± 0.1072 e
75	0.00502	± 0.0021 d	0.02597	± 0.0117 ab	0.11922	± 0.0270 e
100	0.00361	± 0.0004 e	0.01732	± 0.0016 d	0.16676	± 0.0074 e
125	0.00493	± 0.0008 d	0.01833	± 0.0032 cd	0.19407	± 0.0313 e
-----	Calcium-saturated montmorillonite 25% -----					
25	0.00962	± 0.0007 c	0.01430	± 0.0031 a	0.01155	± 0.0012 b
50	0.00985	± 0.0005 c	0.01138	± 0.0017 ab	0.01396	± 0.0033 ab
75	0.01034	± 0.0008 a	0.01054	± 0.0020 b	0.01689	± 0.0078 a
100	0.01062	± 0.0005 a	0.01390	± 0.0004 a	0.01704	± 0.0048 a
125	0.01045	± 0.0002 a	0.01376	± 0.0012 a	0.01651	± 0.0032 a
-----	Calcium-saturated illite 5% -----					
25	0.10436	± 0.0092 d	0.03319	± 0.0062 bc	0.13117	± 0.0189 d
50	0.18640	± 0.0141 a	0.04839	± 0.0178 ab	0.13273	± 0.0276 cd
75	0.05218	± 0.0101 e	0.05644	± 0.0074 a	0.16493	± 0.0008 a
100	0.08884	± 0.0208 d	0.03025	± 0.0073 c	0.10193	± 0.0110 e
125	0.05010	± 0.0012 e	0.04064	± 0.0147 ab	0.13797	± 0.0011 c
-----	Calcium-saturated illite 25% -----					
25	0.01663	± 0.0023 a	0.01626	± 0.0008 c	0.01735	± 0.0006 e
50	0.01439	± 0.0008 d	0.01727	± 0.0026 ac	0.04861	± 0.0012 a
75	0.01341	± 0.0010 d	0.01639	± 0.0003 c	0.02325	± 0.0096 c
100	0.01633	± 0.0033 a	0.01735	± 0.0013 ac	0.02339	± 0.0004 c
125	0.01387	± 0.0052 d	0.01843	± 0.0018 a	0.01846	± 0.0010 d

SAR: Sodium adsorption ratio. Values with the same letter within each column are not significantly different at $p \leq 0.05$ by Tukey's HSD (honestly significant difference) test of variance (ANOVA).

the SAR of the equilibrated solution. The process of clay sodication was different based on the type of clay and clay contents (Figure 3). Particularly, the rate of increase of ESP was gradual until achieving the final ESP when SAR7 equilibrated solution was added to low-clay content montmorillonite. The sodication processes of ESP with a clay content of 25% were observed the same tendency for both montmorillonite and illite. However, a large difference in the sodication processes of ESP with a clay content of 5% were observed for both clays. The final ESPs of SAR7, SAR13, and SAR25 with a clay content of 5% of montmorillonite were 5.6, 18.7, and 81.4, while the final ESPs of SAR7, SAR13, and SAR25 with a clay content of 5% of illite were 28.4, 34.6, and 65.7. Comparing montmorillonite and illite, ESP of illite remained high in SAR 7 and 13.

Differences in sodium-calcium exchange selectivity with clay sodication processes

The differences in K_G with clay sodication processes as influenced by clay minerals and clay contents are shown in Table 3. Although US. Salinity Lab. Staff (1954) concluded that the value of K_G is 0.01475, these results show the difference of K_G values by sodication process by SAR despite being of same clay mineral. Shainberg *et al.* (1980) showed the difference of K_G values by mineralogy. The K_G values of this study were also different by mineralogy. Moreover, this result shows the difference of K_G values by sodication process in spite of same clay mineral. The K_G values were dependent on the SAR of the equilibrated solution, the type of clay, and clay content. K_G values were high under high SAR of the equilibrated solution and lower clay content.

Changes in sodium adsorption ratio with clay desodication processes



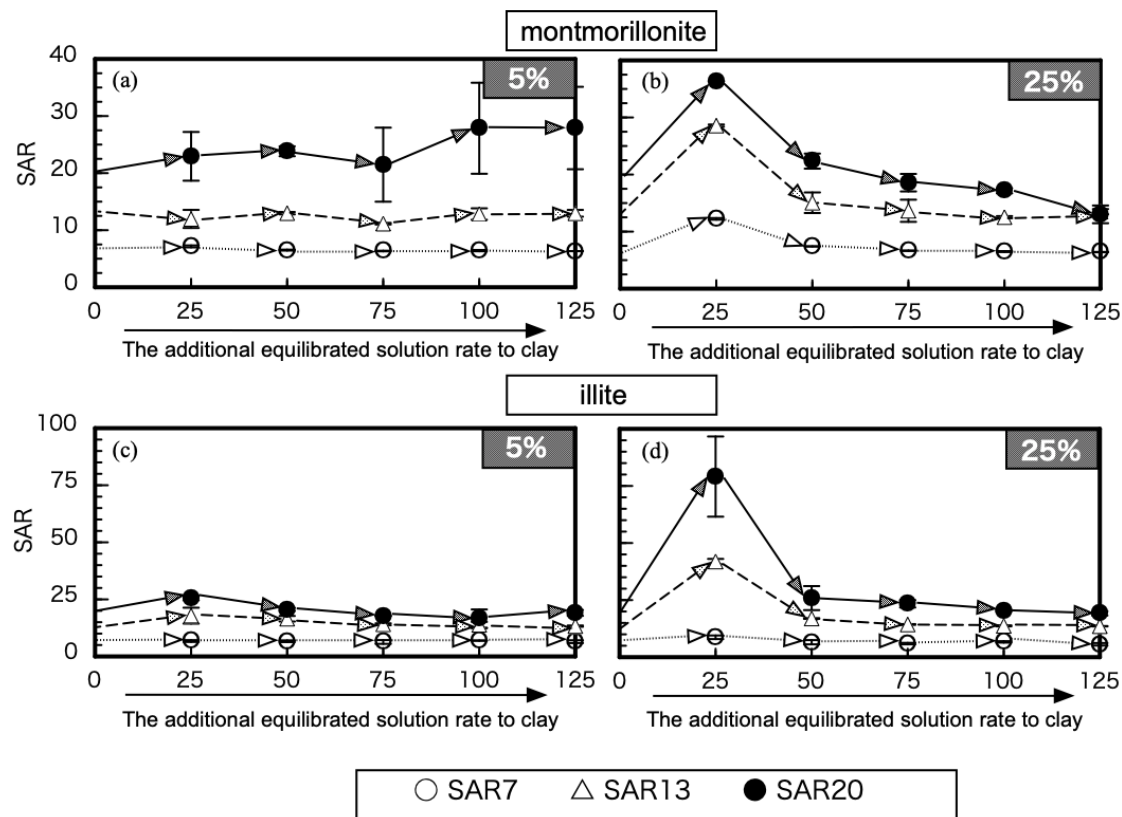


Figure 4: The processes of SAR change with clay desodication as influenced by clay mineral type and clay content. (a) sodium-saturated montmorillonite, 5%; (b) sodium-saturated montmorillonite, 25%; (c) sodium-saturated illite, 5%; (d) sodium-saturated illite, 25%. SAR7, SAR13, and SAR20 represent the values of sodium adsorption ratio in each equilibrated solution. Vertical bars indicate standard error ($n = 4$). There were significant differences among samples at $p \leq 0.05$ by analysis of variance (ANOVA) at each solution rate to clay for each SAR

The changes in SAR with clay desodication processes as influenced by the clay minerals and clay contents are shown in Figure 4. The process of SAR change was dependent on the type of clay minerals and clay contents. At low clay content, the SAR values were similar in both montmorillonite and illite to those of the equilibrated solution, remaining almost constant. On the other hand, the SAR values increased at high clay content in the initial stage. At the initial stage, the SARs of the equilibrated solutions of SAR7, SAR13, and SAR20 with the clay content of 25% of montmorillonite were 12.2, 28.6 and 36.4, respectively. And, the SARs of the equilibrated solutions at the initial stage of SAR7, SAR13, and SAR20 with the clay content of 25% of illite, the SARs were 8.7, 41.9 and 79.1, respectively. Thereafter, SAR values decreased and remained almost constant and equal to those of the equilibrated solution.

Changes in exchangeable sodium percentage with clay desodication processes

The changes in ESP as influenced by clay minerals and/or clay contents with clay desodication are shown in Figure 5. In montmorillonite the degree of ESP change with clay desodication was influenced by SAR of equilibrated solution. The clay desodication process was influenced by clay flocculation. That is, the degrees of clay dispersion under SAR20 of equilibrated solution remained high during desodication process. The clay desodication gradually progressed in equilibrated solutions of SAR7 and SAR13. We observed a greater and more rapid ESP decrease in the initial stage at low clay content. The process of clay desodication differed according to the type of clay and clay contents. The decreasing rate of ESP was particularly observed on adding SAR20 equilibrated solution to illite with high clay content where it progressed from initial stage and maintained low ESP values throughout.

Differences in sodium-calcium exchange selectivity with clay desodication processes

The differences in K_G with clay desodication processes as influenced by the clay minerals and clay contents are shown in Table 4. In montmorillonite, there was preferential Na^+ adsorption/ Ca^{2+} release due to the high K_G values in the high SAR of equilibrium solution. The K_G values were

remained low under high clay content, regardless of the equilibrium solution. These results indicate a preferential Na^+ release/ Ca^{2+} adsorption and subsequent ESP decrease. The K_G values with desodication under SAR7 and SAR13 of the equilibrium solution remained higher than those of sodication. The adsorption of Ca^{2+} was suppressed by the large amount of Na^+ in the clay for desodication. These results, along with the difference between the final ESP

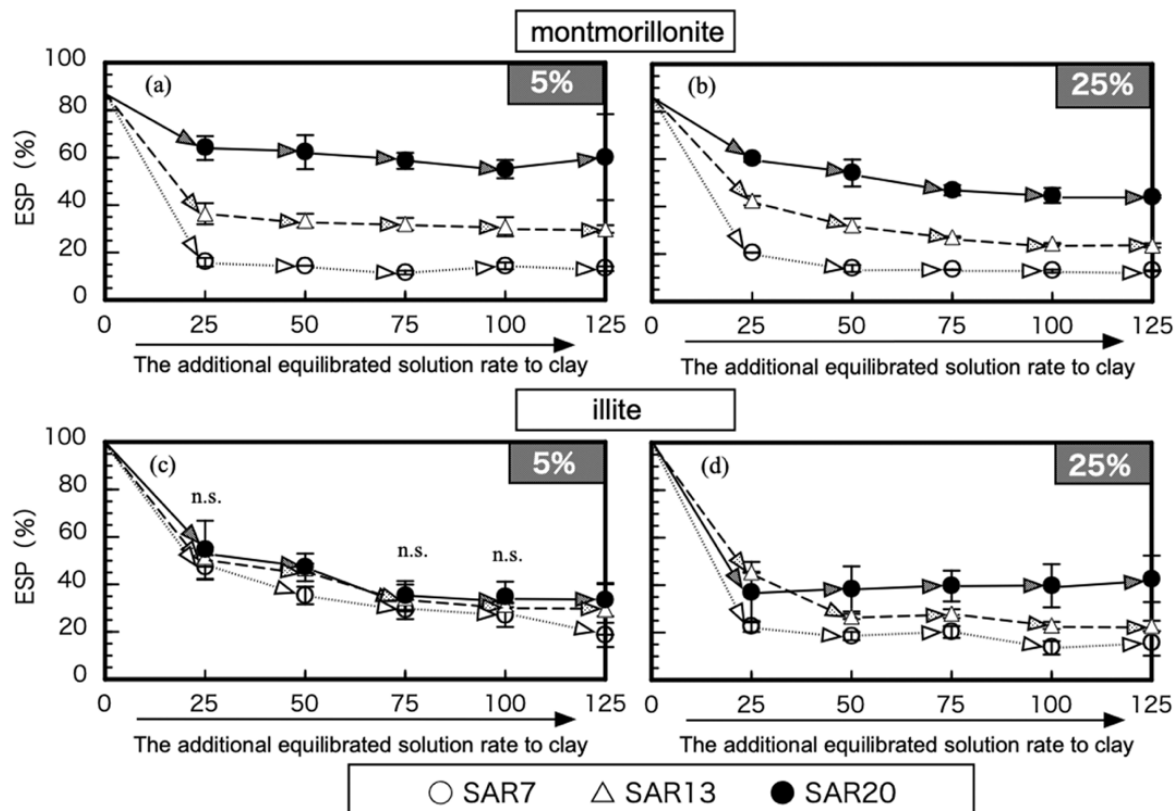


Figure 5: The processes of ESP change with clay desodication as influenced by clay mineral type and clay content. (a) sodium-saturated montmorillonite, 5%; (b) sodium-saturated montmorillonite, 25%; (c) sodium-saturated illite, 5%; (d) sodium-saturated illite, 25%. SAR7, SAR13, and SAR20 represent the values of sodium adsorption ratio in each equilibrated solution. Vertical bars indicate standard error ($n = 4$). There were significant differences among samples at $p \leq 0.05$, and n.s. indicate not significant by analysis of variance (ANOVA) at each solution to clay ratio for each SAR

almost constant with the process of change. The higher the SAR of the equilibrium solution, the higher the K_G values of the clay. Therefore, the final ESP values were dependent on the SAR of the irrigation water and the clay composition. In low clay content illite, the changes in K_G varied widely depending on the equilibrium solution. This can be attributed to the activation of the exchange reaction due to the large layer charge of illite. The reaction between the liquid phase and the solid phases was changed by the clay content and SAR of the equilibrium solution. The K_G

values of sodication and desodication, suggest that the change in cation exchange is largely reflected in the ion composition originally adsorbed to the soil.

Discussion

The changes of SAR with the sodication process were dependent on the type of clay minerals and clay contents. SAR decreased at the initial stage with adding the equilibrated solution to samples with high clay contents. The Na^+ in the equilibrated solution was absorbed to the



clay and Ca^{2+} was released to the equilibrated solution temporally in the initial stage. On the other hand, the concentration of Na^+ in the equilibrated solution that was replaced by Ca^{2+} on the clay was small under low-clay content because of a paucity of Ca-saturated clay. The Ca^{2+} on the clay was exchanged with Na^+ , which was adsorbed in large amounts in the high SAR equilibrated solution in the initial stage. This was the result of the immediate saturation

significantly affected by low clay content, reaching the equilibrium state in the initial stage. We observed a constant ESP under low and moderate SAR in montmorillonite with high clay content, even as there was a slight increase observed at initial stage (Figure 3). The final SAR value did not differ much depending on the clay content in illite. The exchange equilibrated solution SAR converged in all illite treatments. The ESP value increased to $\geq 15\%$ with the

Table 4: The differences of Gapon exchange constant as influenced by clay minerals and composition with clay desodication (mean \pm standard deviation, n= 4)

The additional equilibrated solution rate to clay	Gapon exchange constant		
	SAR7	SAR13	SAR20
----- Sodium-saturated montmorillonite 5% -----			
25	0.02646 \pm 0.0029 a	0.04771 \pm 0.0157 a	0.07763 \pm 0.0024 a
50	0.02595 \pm 0.0002 a	0.03869 \pm 0.0057 abc	0.06938 \pm 0.0019 a
75	0.02056 \pm 0.0014 b	0.04230 \pm 0.0044 ab	0.07672 \pm 0.0016 a
100	0.02614 \pm 0.0026 a	0.03484 \pm 0.0009 bc	0.04417 \pm 0.0006 c
125	0.02398 \pm 0.0021 a	0.03285 \pm 0.0010 c	0.05417 \pm 0.0065 c
----- Sodium-saturated montmorillonite 25% -----			
25	0.02117 \pm 0.0002 b	0.02031 \pm 0.0017 d	0.05261 \pm 0.0026 e
50	0.02181 \pm 0.0027 ab	0.03141 \pm 0.0079 a	0.05282 \pm 0.0090 e
75	0.02317 \pm 0.0003 a	0.02725 \pm 0.0044 ab	0.04752 \pm 0.0081 e
100	0.02252 \pm 0.0010 ab	0.02579 \pm 0.0007 bc	0.04706 \pm 0.0048 e
125	0.02311 \pm 0.0003 a	0.02291 \pm 0.0019 cd	0.06076 \pm 0.0058 a
----- Sodium-saturated illite 5% -----			
25	0.17315 \pm 0.0162 a	0.05955 \pm 0.0032 a	0.02198 \pm 0.0087 c
50	0.07157 \pm 0.0035 e	0.05323 \pm 0.0038 ad	0.01116 \pm 0.0004 d
75	0.05879 \pm 0.0057 e	0.03703 \pm 0.0050 d	0.04376 \pm 0.0050 a
100	0.12696 \pm 0.0068 d	0.03305 \pm 0.0064 d	0.03729 \pm 0.0032 bc
125	0.18193 \pm 0.0067 a	0.03137 \pm 0.0068 d	0.02643 \pm 0.0016 c
----- Sodium-saturated illite 25% -----			
25	0.03349 \pm 0.0014 ab	0.01985 \pm 0.0003 e	0.00743 \pm 0.0003 d
50	0.03475 \pm 0.0009 ab	0.02157 \pm 0.0015 e	0.02410 \pm 0.0023 c
75	0.04264 \pm 0.0039 a	0.02714 \pm 0.0022 a	0.02805 \pm 0.0010 bc
100	0.02343 \pm 0.0068 c	0.02179 \pm 0.0015 e	0.03227 \pm 0.0023 ab
125	0.03251 \pm 0.0016 bc	0.02178 \pm 0.0029 e	0.03875 \pm 0.0018 a

SAR: Sodium adsorption ratio. Different lowercase letters within a column indicate significant differences at $p \leq 0.05$ by Tukey's HSD (honestly significant difference) test of variance (ANOVA) between the additional equilibrated solution rate to clay.

of a certain amount of Na^+ on the clay, which was also affected by the low clay content (Endo *et al.*, 2002; Dawes and Goonetilleke, 2006). As the amounts of exchanged ion sites in internal surfaces are low under low clay contents, the ratio of external surfaces to internal surfaces increases. The affinity of Na^+ adsorption is higher at the external than at the internal surface (Shainberg and Otoh, 1968; Sposito *et al.*, 1983). Hence, ESP of montmorillonite with low clay content increased with high SAR equilibrated solution at the initial stage. Subsequently, SAR of equilibrated solution was constantly high with high ESP values. ESP was

increase of equilibrated solution in the SAR13 treatment.

As can be seen from the K_G values of montmorillonite (Table 3), the lower the clay content, the smaller the K_G under low SAR conditions. It suggested that Na affinity was low at low SAR unlike illite. On the other hand, it remained at a higher K_G with the low clay content and was under the tendency of Na^+ adsorption/ Ca^{2+} release in the equilibrium solution of the treatment of SAR13 and SAR20. It was suggested that the lower the clay content, the easier the clay sodication process progressed. K_G value was very high at



the initial stage on the low clay content and the high SAR of the equilibrium solution. It was considered that the clay sodication progressed rapidly due to the tendency of Na^+ adsorption/ Ca^{2+} release. After that, K_G decreased and it showed a relatively high constant value. This result was reflected in the degree of increase in ESP. ESP increased at the initial stage and subsequently remained at a constant value. It was considered to be the high final ESP due to the high K_G environment at the initial stage on the clay sodication process.

As can be seen from the clay sodication process of K_G in illite (Table 3), it was a tendency of the high K_G value on the low clay content rather than the high clay content. There was preferential Na^+ adsorption/ Ca^{2+} release on the low clay content of illite. It was suggesting that the difference in clay content affects clay sodication in illite regardless of the difference in SAR of equilibrium solution. The K_G value increased with the low clay content in illite. On the other hand, the K_G remained low on the high clay content in illite, suggesting that clay sodication progressed slowly with a high clay content in illite. It was suggested that the difference of clay content in illite affects sodication regardless of the difference of equilibrium solution.

In each of clay, although the K_G values at the initial stage were high in the low SAR of equilibrium solution, clay sodication was suppressed. Na^+ adsorption suppressed because of the low Na concentration in the equilibrium solution and high Ca^{2+} content in the clay. On the other hand, the K_G values at the initial stage were high in high SAR of equilibrium solution and Na^+ was easy to adsorb to clay. It was considered that K_G converged to an equilibrium as the amount of solution increased. Regardless of the type of clay and the SAR of the equilibrium solution, the K_G was high and Na^+ was preferentially adsorbed under the low clay content.

As demonstrated by the change of ESP in illite with low clay content, ESP increased rapidly in the initial stage with the high SAR of the equilibrated solution. In illite, ESP tended to be high in the initial stage, even with low and medium SARs. In this study, the K_G value in clay sodication was higher for illite than for montmorillonite suspensions, consistent with the findings of Shainberg *et al.* (1980). Moreover, K_G values were higher for low clay contents than for high clay contents. Therefore, illite was more likely to promote sodication than montmorillonite based on the ion affinity difference of clay minerals under low SAR of the equilibrated solution.

The process of changes in SAR with the clay desodication process was similar in illite and in

montmorillonite (Figure 4). An increase in SAR was observed at high clay content in both of clay minerals. The absolute amount of Na^+ released from the clay was reflected in the amount of clay. The amount of Na^+ released from the clay was higher in the initial stage at high clay content. This was due to the release of Na^+ from Na-saturated clay into the equilibrated solution, thus, Na^+ concentration in the solution became high. The amount of Na^+ released from clay subsequently decreased presumably due to the decrease of the clay ESP under the influences of the SAR of equilibrated solution, particularly under high SAR. These findings were not attributed to different type of clay mineral. However, the SAR of the equilibrated solutions eventually converged to reach equilibrium, even though a temporal SAR increase at high clay content was observed, which resulted in the equilibrium states between clay minerals and each equilibrated solution. Converged SARs in montmorillonite were slightly higher than those of illite. These results suggested that the change in SAR with clay desodication processes were almost the same for the two clay minerals but depended on the SAR of the equilibrated solution. Clay desodication progressed gradually with the equilibrated solution of high SAR because of the clay dispersion in montmorillonite (Figure 5). ESP values did not decrease excessively under montmorillonite dispersion with high external surface which has high affinity of Na^+ . On the other hand, Na^+ release/ Ca^{2+} adsorption progressed in the initial stage in illite and the ESP value decreased, regardless of the difference in equilibrated solutions.

The rate of sodication and desodication processes differed even for the same type of mineral, clay contents, and same equilibrated solution. The advance of sodication and desodication was more in illite than in montmorillonite. In the latter case, desodication rather than sodication progressed in low clay contents with equilibrated solutions of low SAR. These differences were observed due to the differences in cation compositions of clay and equilibrated solution. The effect of these differences was more significant in montmorillonite than in illite. Although the process of sodication in montmorillonite was suppressed by equilibrated solutions of low SAR, it progressed with equilibrated solutions of high SAR.

The K_G values also varied widely and it is thought that the SAR values of equilibrated solutions varied within a wide range with the same of clay sodication. The K_G values of desodication remained higher than those of sodication. These results, along with the difference between the final ESP values of sodication and desodication, suggest that the cation exchange status and processes are largely reflected in the initial cation saturation status for clay.



Final ESP values were high at high SAR of the equilibrated solution and low at low SAR of the equilibrated solution in both clay sodication and desodication processes. However, the final ESP values by clay sodication and desodication were different for each clay mineral and clay content. These differences are presumably due to the Na^+ and Ca^{2+} concentrations in the equilibrated solution. Ion exchanges of Na^+ and Ca^{2+} is limited under low concentrations of the equilibrated solution from high cation exchange sites (Kopittke *et al.*, 2006). ESP was not uniform during the process of clay sodication and clay desodication. K_G values are influenced by clay contents and SAR of the equilibrated solution in both clay sodication and desodication. The higher the K_G values were observed, the lower the clay contents, and the higher the SAR of the equilibrated solution. These findings suggest that the final ESP values vary depending on clay mineralogy.

Conclusions

Soil sodication and desodication processes were explored on the basis of the type of clay mineral and content. The processes of soil sodication and desodication were significantly affected not only by the SAR of the equilibrated solutions but by the type of clay mineral and clay content as well. The processes differed even when the equilibrated solutions and the SAR and ESP remained the same but the type of clay mineral and clay content changed. This study indicates that the processes of soil sodication and desodication are different at the initial stage of irrigation than in later stages. On farmLands, the process of soil sodication and desodication depends on factors such as clay minerals, soil clay contents, and irrigation water quality. Although it is important to understand the final degree of sodication and desodication that completely reaches equilibrium, it is equally important to understand the processes of sodication and desodication per se. To delay soil sodication or to produce soil desodication, it is helpful to reduce the SAR of irrigation water by adding Ca amendment at the initial stage, as shown in this study. Our results will surely prove useful for predicting the progression of sodication and desodication processes for farmLand management in arid regions.

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