Effect of Exchangeable Cation and Electrolyte Concentration on Mineralogy of Clay Dispersed from Aggregates¹

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ABSTRACT

The type of clay dispersed from aggregates of various arid land soils as influenced by sodium adsorption ratio (SAR) and electrolyte concentration was evaluated in Ca-Na and Mg-Na systems. It was observed that, in general, in the case of Fallbrook I, Fallbrook II, Pachappa, and Arlington soils, all the common clay minerals (kaolinite, clay mica, vermiculite, and montmorillonite) dispersed whenever disaggregation occurred inrrespective of SAR and electrolyte concentration levels. In Bonsall soil, kaolinite and mica clays were apparently more dispersive than montmorillonite, which, in turn, was more dispersive than mixed layer clays in Ca-NaCl solutions. More intense x-ray diffraction peaks were obtained, in general, in the Mg-Na system compared to the Ca-Na system.

Additional Index Words: clay mineralogy, disaggregation, aggregate stability.

Ali, O.M., M. Yousaf, and J.D. Rhoades. 1987. Effect of exchange-

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IFFERENT SOILS FREQUENTLY DISPLAY different clay dispersion characteristics when subjected to identical conditions of exchangeable sodium percentage (E_{Na}) and electrolyte concentration. Differences among the soils in their clay mineralogies are thought to partly account for this phenomenon. McNeal and Coleman (1966) and Yaron and Thomas (1968) postulated that the most susceptible soils to sodicity problems (i.e., reductions in permeability) are those dominated by the 2:1 layer silicates, especially montmorillonite, and the least susceptible soils are those dominated by kaolinite and sesquioxides. Similar conclusions were made by El-Swaify and Swindale (1969) for the soils of Hawaii. On the other hand, Elgabaly and Elghamry (1970) observed that arid land kaolinitic soils were quite sensitive to sodicity problems, especially at an E_{Na} of 10 or more when leached with distilled water. Valasco-Molina et al (1971) observed that, in the absence of electrolyte, the relative order of dispersibility of soil clays, at a given E_{Na} , was

¹ Contribution from the U.S. Salinity Laboratory, USDA-ARS, Riverside, CA, 92501. This research was supported by a grant from the United States-Israel (Binational) Agricultural Research and Development Fund (BARD). Received 29 May 1985.

montmorillonite > kaolinite and halloysite > clay mica, except at low E_{Na} where mica-dominated soils were more dispersive than those dominated by kaolinite. They further observed that for all these minerals, dispersion increased with increasing sodium adsorption ratio (SAR = Na/(Ca+Mg)^{1/2}, with all concentrations expressed in mmol L⁻¹) and decreasing electrolyte concentration.

Investigations of clay *flocculation* have often been made to evaluate the dispersion behavior of soils (El-Swaify, 1976; van Olphen, 1977; Arora and Coleman, 1979; Oster et al., 1980). El-Swaify (1976) observed that flocculation values of Na and Ca illite were 40 to 50 and 0.25 mmol_c L^{-1} for NaCl and CaCl₂ systems, respectively. Recently, Oster et al. (1980) observed that flocculation values of Na-Ca montmorillonite and illite were 3.0 and 4.0, 7.0 and 6.0 and 10.0 and 18.0 mmol_c L^{-1} , for E_{Na} values of 5, 10, and 20, respectively. The flocculation values of Oster et al. (1980) are lower than those reported by Arora and Coleman (1979). The latter investigators reported that the critical salt concentrations needed to flocculate montmorillonite and illite were 28 to 60 and 185 mmol_c L^{-1} for NaHCO₃, respectively. The apparent discrepancy between the two investigations may be related

to the different salts used (and hence pH conditions). Arora and Coleman concluded that clay mineral susceptibility to deflocculation by $NaHCO_3$ was in the decreasing order of illite, vermiculite, smectite, and kaolinite. These results imply that soils with illitic clay are more "dispersive" than soils dominated by mont-morillonite clays, especially at low levels of SAR.

Clays in natural soils usually occur as mixtures and in the assemblages making up aggregates; accordingly their behavior may be modified by their association with other minerals and/or materials. Illustrative of this is the decrease in the hydraulic conductivity of a kaolinitic soil observed by Frenkel et al. (1978) when 2% montmorillonite was added to the system and ascribed to increased dispersion of the kaolinite-montmorillonite mixture.

This study was undertaken to determine if the apparent different aggregate stabilities observed for soils is related to differences in their clay mineralogies and/ or to differences in the relative dispersibilities of the different clay minerals themselves.

MATERIALS AND METHODS

Selected physical and chemical characteristics of the experimental soils and their classification (U.S. system) were



Fig. 1. X-ray diffractogram of clay dispersed from Bonsall soil at various electrolyte concentrations and levels of SAR in Ca-NaCl solutions.

given in (Yousaf et al., 1987). The method used in the dispersion study is also described in this same reference. After collection of 25 mL of supernatant for determination of the amount of clay (reported in Yousaf et al., 1987), the remaining supernatant was centrifuged and the clays so obtained were subjected to x-ray analysis for clay mineralogy identification. Subsamples of the clays were saturated with Mg, Mg + glycerol, and K, and oriented samples were prepared on glass slides using the methods of Jackson (1974). X-ray analysis of the oriented clay samples (the same amount of clay was used for each determination) was made using a Norelco x-ray diffractometer with Cu K_a radiation ($\lambda = 1.5418$ Å), 1° pre-, 4° divergence-, and 1° receiving-slits, and 40 kW and 20 mA. Diffraction patterns were obtained for the following treatments: Mg saturated (air dry); Mg saturated and glycerated (30% relative humidity); K saturated (air dry); K saturated and heated at 310°C; and K saturated and heated at 550°C. X-ray patterns presented in the results section are only of Mg-saturated (air dry) samples. However, identification was made using all of the data.

RESULTS AND DISCUSSION

The x-ray diffraction patterns (Mg- saturation, airdried) obtained of the dispersed clays present in each successively diluted suspension at various SAR values for the Ca-Na system for Bonsall soil are presented in Fig. 1. Similar x-ray diffractograms were obtained for the Fallbrook I, II, Pachappa, and Arlington soils. The identified clays which had dispersed at the different electrolyte concentration and sodium adsorption ratios are summarized in Table 1.

In the case of Bonsall soil, insufficient clay was dispersed for x-ray analysis at concentrations of >30mmol_c L⁻¹. Significant amounts of dispersion occurred at concentrations of 30 mmol_c L⁻¹ at SAR levels of ≥ 10 ; for 10 mmol_c L⁻¹ concentration at SAR levels of ≥ 5 , and for 1 mmol_c L⁻¹ concentration at SAR levels of ≥ 0 . Irrespective of levels of electrolyte concentration and SAR, the clavs dispersed from Bonsall soil were predominantly kaolinite (7.3 Å) and clay mica (10.2 Å) (Fig. 1). Montmorillonite was not detectable in the first "dispersate" of Bonsall soil at an SAR level of 20 or less. With subsequent exposures of the undispersed sediment to more dilute electrolyte solutions, additional clay was dispersed from the Bonsall soil. Montmorillonite clay appeared in this latter clay, especially at the higher SAR levels. Mixed layer clay only appeared in the x-ray pattern of the clay that dispersed at SAR 40. The heights of the x-ray diffraction peaks were intense at a concentration of 4 mmol. L^{-1} . Montmorillonite was prominent in the x-ray patterns of the clay that dispersed at this level of concentration but kaolinite and clay mica were still present in substantial amounts. In Bonsall soil, kaolinite and clay mica appear to be more dispersible in the Ca-NaCl solutions than montmorillonite, which, in turn, is more dispersible than the mixed layer clay.

In the case of Fallbrook I soil, kaolinite, clay mica, vermiculite, and montmorillonite were present in the x-ray patterns of every dispersed clay sample and in about the same proportion irrespective of electrolyte

 Table 1. Mineralogical identity of the clays dispersed from the soils at different levels of electrolyte concentration and SAR, Ca-NaCl solutions.

	Electrolyte concentration, mmol _c L ⁻¹							
SAR	50	30	10	4	1	0		
			Bonsall					
40		K†,M,S,ML	K,M,S,ML	K,M,S,ML	K,M,S,ML	K,S,ML,M		
20		K,M	K,M,S,ML	K,S,M	K,M,S	K,S,M		
10		K,M	K,M,S	K,M,S	K,M,S	K,M,S		
5			K,M	K,M,S	K,M,S	K,M,S		
0					K,M,S	K,M,S		
			Fallbrook	Ĩ				
40		K,M,V,S	K,M,V,S	K,M,V,S	K,M,V,S,ML	K,M,V,S		
20		K,M,V,S	K,M,V,S	K.M.V.S	K,M,V,S	K,M,V,S		
10			K.M.V.S	K.M.V.S	K.M.V.S	K.M.V.S		
5			K.V.M	K.M.V.S	K,M,V,S	K.M.V.S		
0			••		K,M,V,S	K,M,V,S		
			Fallbrook I	Ι				
40		K.M.V.S.ML	K.M.V.S.ML	KMVSML	K.M.ML.V.S	K.ML.V.S.M		
20			K.M.V.S.ML	K.M.V.S.ML	K.M.ML.V.S	K.M.V.S.ML		
10				M.K.V.S	K.M.V.S.ML	K.M.ML.V.S		
5				K.M.V.S	K.M.ML.V.S	K.M.V.S.ML		
0						K,V,S,M,ML		
			Pachappa					
40	M	MSK	M S K	MSK	MSK	M.S.K		
20		MSK	SMK	MSK	MSK	MSK		
10			SMK	MSK	SMK	M.S.K		
5		_	MSK	MSK	SMK	MSK		
ŏ					S.M	M.K.S		
			Arlington					
40		VINI N V	V V V V	11 M 1 M 17		V MI MK		
40		V,IVIL,IVI,K,		V,ML,M,K		V MI M K		
20			V,ML,M,K	V, ML, M, K,	V ML MK	V MI M V		
10			V, WIL, WI, K	V ML MK		V MI MV		
о О			V,ML,M,K	V, IVIL, IVI, K	V,WL,W,K	V, WIL, M, K		
					v,IVIL,IVI,K	7, IVI, 1VI, N		

 $\dagger K$ = kaolinite, M = clay mica, S = smectite (montmorillonite), ML = mixed layer, V = vermiculite.

concentration and level of SAR. Kaolinite was the dominant clay mineral dispersed from Fallbrook I soil.

The clay minerals that dispersed from Fallbrook II soil at all combinations of electrolyte concentration and SAR were essentially identical. The soil aggregates were relatively stable at the higher concentrations but were relatively more dispersive than those of the other soils at concentrations of 4 mmol_c L^{-1} . The clay that dispersed in the greatest amount was kaolinite. The amounts of vermiculite and montmorillonite dispersed increased slightly with increase in SAR level. Mixed layer clay was more evident in the clay dispersed at high levels of SAR but was also present, in contrast to Bonsall soil, in the clay dispersed at lower levels of SAR as well.

Clay mica, montmorillonite, and kaolinite were present in the clays dispersed from Pachappa soil at each combination of concentration and SAR. Clay mica was predominant in most cases and kaolinite was less prevalent than in the Bonsall, Fallbrook I, and Fallbrook II soils.

Vermiculite was the dominant clay, followed by mixed layer clay, clay mica, and kaolinite, present in the clay dispersed from the Arlington soil. Little effect of SAR was observed in the x-ray patterns; peak intensities were higher at 4 $\text{mmol}_c L^{-i}$ than at other concentrations.

The results of x-ray analysis of the clays dispersed from Bonsall soil in Mg-Na chloride salt solutions at various concentrations and levels of SAR are presented in Fig. 2. Similar x-ray diffractograms were obtained for the other soils; the clay minerals identified are summarized in Table 2. More intense x-ray diffraction peaks were obtained, in general, in the Mg-Na system compared to the Ca-Na system. Otherwise, results were about the same in both systems, with a few exceptions. Montmorillonite was present in the clays that first dispersed from the Bonsall soil with Mg as the divalent counter-ion; this was not the case when Ca was the divalent counter-ion. In general, the proportions of montmorillonite increased as SAR increased and as electrolyte concentration decreased; mixed layer clay appeared in the clay dispersed at SAR 40 in both systems. Kaolinite and clay mica were present in relatively large amounts at all combinations of SAR and electrolyte concentration. In the case of Fallbrook I, Fallbrook II, Pachappa, and Arlington soils, the clay minerals dispersed in the Mg-Na system were



Electrolyte Concentration, mmol, L⁻¹

Fig. 2. X-ray diffractogram of clay dispersed from Bonsall soil at various electrolyte concentrations and levels of SAR in Mg-NaCl solutions.

		Electrolyte concentration, mmol _c L ⁻¹							
SAR	50	30	10	4	1	0			
			Bonsall						
40	K†.M.S	K.S.M	K.M.S	K.M.S.ML	K.S.M.ML	K.S.M.ML			
20	K.M.S	K.M.S	K.M.S	K.M.S	K.M.S	K.S.M.ML			
10		K.M.S	K.M.S	K.M.S	K.M.S	K.M.S			
5			K.M.S	K.M.S	K.M.S	K.M.S			
0				K,M,S	K,M,S	K,M,S			
			Fallbrook I						
40	KVSM	KVSM	KVSM	KVSM	KVSM	KMVS			
20	KVSMLM	KVSM	KVSM	KMVS	KVSM	KVSM			
10		KVSM	KMVS	KMVS	KVSM	KMVS			
5		IX, V , C, IVI	KMVS	KMVS	KVSM	KMVS			
Ő	_			KVSM	KVSM	KMVS			
v			Fallbrook II	11, 1, 0,011	11, 1, 5,111	11,111, 1,15			
40	K.V.S.ML.M		K.V.S.M.ML	K.V.S.M.ML	K.V.S.M.ML	K.ML.V.S.M			
20				K.V.S.M.ML	K.V.S.ML.M	K.ML.V.S.M			
10				K.V.S.M.ML	K.V.S.ML.M	K,M,ML,V,S			
5				K.M.V.S	K,V,S,ML,M	K,ML,V,S,M			
0					K,V,S,ML,M	K,V,S,ML,M			
			Pachappa						
40	S.M.K	S.M.K	S.M.K	S.M.K	M,S,K	M,S,K			
20	S.M.K	S,M,K	S,M,K	M,S,K	M,S,K	M,S,K			
10	S.M.K	S.M.K	M.S.K	M.S.K	M.S.K	M,S,K			
5		S.M.K	S.M.K	M,S,K	M,S,K	S,M,K			
0				M,S,K	S,M,K	M,S,K			
			Arlington						
40		V,ML,M,K	V,ML,M,K	V,ML,M,K	V,ML,M,K	V,ML,M,K			
20		V,ML,M,K	V,ML,M,K	V,ML,M,K	V,ML,M,K	V,ML,M,K			
10		V,ML,M,K	V,ML,M,K	V,ML,M,K	V,ML,M,K	V,ML,M,K			
5				V,ML,M,K	V,ML,M,K	V,ML,M,K			
0	••		-		V,ML,M,K	V,ML,M,K			

Table 2. Mineralogical identity of the clays dispersed from the soils at different levels of electrolyte concentratio
and SAR, Mg-NaCl solutions.

 $\dagger K$ = kaolinite, M = clay mica, S = smectite (montmorillonite), ML = mixed layer, V = vermiculite.

analogous to those in the Ca-Na system except that more intense x-ray diffraction peaks were observed in the case of the Mg-Na system.

The amounts of clay dispersed with Mg as the divalent counter-ion were greater than when Ca was the divalent counter-ion (Yousaf et al., 1987); likewise, the amounts of the individual clay minerals dispersed were greater in the Mg-Na system compared to the Ca-Na system. The soils also showed slightly more sensitivity to dispersion with Mg compared to Ca as the divalent counter-ion, with the exception of the Fallbrook II soil. Pachappa soil was far more dispersive with Mg at low levels of SAR. It appears that the high sand content of Pachappa, in conjunction with its montmorillonitic clay mineralogy, enhances the aggregate stability of the Ca-Na system relative to the Mg–Na system.

CONCLUSIONS

The mineralogy of clay dispersed from several of the arid land soils studied was essentially independent of SAR and electrolyte concentration. If dispersion occurred, all clay minerals present in these soils dispersed approximately equally. Sodium-Ca saturated Bonsall soil was an exception. Kaolinite and mica dispersed preferentially and montmorillonite was only detectable in the clay dispersed from this soil at high levels of SAR. Thus the observed differences in the aggregate stabilities of these soils are apparently not due to differences in their clay mineralogies or to differences in the relative dispersibilities of the different

clay minerals. Other factors besides clay mineralogy appear to be more influential in controlling aggregate stability.

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