

EFFECT OF SATURATING CATION, pH, AND ALUMINUM AND IRON OXIDE ON THE FLOCCULATION OF KAOLINITE AND MONTMORILLONITE

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Abstract—The effect of pH on the flocculation-dispersion behavior of noncrystalline aluminum and iron oxides, kaolinite, montmorillonite, and various mixtures of these materials was investigated. The clays were Na- or Ca-saturated and freeze-dried before use. Critical coagulation concentrations (CCC) of all materials and mixtures were found to be pH dependent. The Al oxide was flocculated at pH >9.5 and the iron oxide was flocculated between pH 6.0 and 8.2; i.e., flocculation occurred at pHs near the point of zero charge (PZC). The CCC of both the Na- and Ca-clay systems increased with increasing pH. The effect of pH was greater for the Na-kaolinite (flocculated at pH 5.8 and having a CCC of 55 meq/liter at pH 9.1) than the Na-montmorillonite system (having a CCC of 14 meq/liter at pH 6.4 and a CCC of 28 meq/liter at pH 9.4). A 50/50 mixture of Na-kaolinite and Na-montmorillonite behaved more like montmorillonite (having CCCs of 13 and 33 meq/liter at pH 6.2 and pH 9.0, respectively). The presence of either noncrystalline oxide decreased the CCC over that of the clay(s) alone; the decrease occurred at pHs >7 for Al oxide and at pHs >6.5 for Fe oxide. Aluminum oxide produced a greater decrease in CCC than Fe oxide, especially at pHs >8. The effect of each oxide on CCC was greatest near the PZC, 9.5 and 7.2 for Al and Fe oxide, respectively.

Key Words—Aggregation, Aluminum oxide, Critical coagulation concentration, Dispersion, Flocculation, Iron oxide, Kaolinite, Montmorillonite.

INTRODUCTION

Reductions of soil permeability and loss of soil structure are often due to high sodium concentrations on the soil exchange complex. Soil texture, clay mineralogy, and salt concentration of irrigation water influence the sensitivity of soil structure to the adverse effect of Na ions (Shainberg and Letey, 1984); however, consideration of these variables has not yet resulted in a quantitative prediction of this effect. Additional factors such as solution pH and soil aluminum and iron oxide content, apparently, must also be considered.

Many pure clay mineral-solution systems have been studied under laboratory conditions. These studies are relevant to soil systems because migration of dispersed clay in irrigation water leads to plugging of soil pores and reduced soil permeability (Frenkel *et al.*, 1978).

The dispersion of Na-saturated systems has been studied previously; however, research is needed to establish the effect of the pH variable on clay mineral dispersion of Ca-saturated systems and clay mixtures. Although much is known about the interaction of Al and Fe oxides with clay minerals, the role of pH in these reactions has been ignored almost completely. Many of the discrepancies between previous studies regarding the ability of Al and Fe oxides to reduce swelling of soils and promote flocculation of clays apparently exist because the experiments were carried out at different pHs.

The present investigation was therefore undertaken

to determine the effect of pH on the flocculation-dispersion behavior of kaolinite, montmorillonite, and a 50/50 mixture of these clays. The effect of 2% and 10% noncrystalline Al and Fe oxide sols on the flocculation-dispersion behavior of the clay systems was also examined.

BACKGROUND

Flocculation values for phyllosilicates are available (see, e.g., El-Swaify, 1976). The flocculation value or critical coagulation concentration (CCC) is the minimum concentration of an electrolyte required to cause flocculation of a given colloidal dispersion in a given time (van Olphen, 1977). Conversely, if the salt concentration is below the CCC, dispersion occurs. CCC values for Na-montmorillonite range from 7 to 20 meq/liter NaCl (Arora and Coleman, 1979), and those for Ca-montmorillonite range from 0.17 meq/liter (van Olphen, 1977) to 0.25 meq/liter CaCl₂ (Greene *et al.*, 1978; Oster *et al.*, 1980). For Na-kaolinite CCC values range from 0 to 5 meq/liter NaCl; however, Ca-kaolinite is stable even in distilled water (Arora and Coleman, 1979).

Effect of pH on flocculation-dispersion behavior of clays

The flocculation-dispersion behavior of phyllosilicates (Swartzen-Allen and Matijevic, 1976; Arora and Coleman, 1979) and two arid-zone soils (Suarez *et al.*,

1984) has been found to depend on pH. Arora and Coleman (1979) found that in electrolyte solutions of NaCl at pH 7.0, NaHCO₃ at pH 8.3, and Na₂CO₃ at pH 9.5 the CCC for most of the Na-clays studied was highest in the NaHCO₃ solution; however, interpretation of these data is difficult because pH was not measured in the presence of the clays. Swartzen-Allen and Matijevic (1976) found that the CCCs for both Na-montmorillonite and Na-kaolinite in NaNO₃ solution increased with increasing pH from 1 meq/liter at pH 3.8 to 10 meq/liter at pH 10 and from 2 meq/liter at pH 4.1 to 40 meq/liter at pH 10.1, respectively. Thus, the pH effect was much greater for Na-kaolinite. Suarez *et al.* (1984) found that hydraulic conductivity of two arid-zone soils containing mixtures of clays decreased from pH 6 to 9; dispersion increased with increasing pH for both the predominantly kaolinitic and the montmorillonitic soil. These authors suggested that the pH effect in their soils was due to the presence of variable charge minerals and organic matter. At low pHs these materials were positively charged and bonded to the negatively charged faces of the phyllosilicates. At high pHs, however, they underwent charge reversal, contributed negative charge to the system, and thereby increased dispersion of the system.

The predominant variable charge minerals in soils are the noncrystalline and crystalline Al and Fe oxides (Bohn *et al.*, 1979). These materials exhibit a point of zero charge (PZC) at pH 6 to 9 (see Table 2 of Kiniburgh and Jackson, 1981). For the phyllosilicates, PZCs are much lower due to the presence of permanent negative charges. The PZCs of kaolinite clays are at pH 2.8 to 4.8 (see, e.g., Tschapek *et al.*, 1974), whereas the PZC of montmorillonite is so low that it cannot be measured without dissolving the material (Sposito, 1984). Variable charge is located at the edges of phyllosilicate particles. The PZC of the edge surfaces of kaolinite ranges from pH 7.3 (Rand and Melton, 1977) to 7.8 (Michaels and Bolger, 1964).

Effect of oxides on flocculation-dispersion behavior of clays

The stabilizing effect on soil structure produced by the presence of Al and Fe oxides was demonstrated by Deshpande *et al.* (1964), El Rayah and Rowell (1973), and Shanmuganathan and Oades (1982). After depositing Al and Fe oxides onto dispersed and aggregated soil samples, El Rayah and Rowell (1973) found greater permeabilities for hydroxide-treated than for untreated soils. Aluminum hydroxide-treated soils were more stable than iron hydroxide-treated soils. By precipitating Al and Fe oxides onto air-dry aggregates of Australian soils, Deshpande *et al.* (1964) found that Al oxide reduced swelling but Fe oxide did not. They concluded that Al oxide was acting as a cement and that Fe oxide was present as discrete particles.

Interactions of phyllosilicates with Al and Fe oxides have been studied extensively. McAtee and Wells (1967), for example, found that the addition of gibbsite produced flocculation at an oxide:clay ratio of 0.009:1 for kaolin and 0.5:1 for Wyoming bentonite. They observed that gibbsite was adsorbed on the edges of kaolin and on the basal surfaces of bentonite. Because the Wyoming bentonite redispersed at oxide additions greater than the flocculation value, McAtee and Wells (1967) concluded that the bentonite particles had acquired a positive charge from large amounts of oxide adsorption. Transmission electron micrographs verified that the clay particles were coated with gibbsite.

Greenland (1975) found little interaction between goethite precipitated at pH 8.5 and a kaolinite surface. He also found that at pH 3 lepidocrocite had precipitated on the kaolinite surface in needle-shaped clusters and cemented the clay crystals into larger particles. From studies of the extent of aggregation produced in dispersions of kaolin and bentonite exposed to ferric chloride solutions, Blackmore (1973) reported that ferric chloride was an effective cementing agent for bentonite, but was much less effective for kaolin. Effectiveness of aggregation was decreased markedly when clay was added later than 2 min after the start of ferric chloride hydrolyzation. At that point, the aggregates formed were not homogeneous but visibly a mechanical mixture of clay and oxide (Blackmore, 1973). Aggregation was improved with increasing oxide content to as much as 50%.

By adding Al and Fe hydroxides into a clay dispersion, onto clay aggregates, or onto oriented clay flakes, El Rayah and Rowell (1973) showed that the presence of Al or Fe hydroxide reduced clay swelling at all electrolyte concentrations and lowered the electrolyte concentration at which dispersion began. Al hydroxide was more effective than Fe hydroxide in preventing swelling and dispersion (El Rayah and Rowell, 1973). Frenkel and Shainberg (1980) found that Al polymers could stabilize montmorillonite suspensions against the adverse effects of Na ions better than could Fe polymers. Moreover, Oades (1984) found Al polymers to be more efficient than Fe polymers in reducing the swelling of montmorillonite. He suggested that this difference was a result of polymer morphology. Aluminum polymers occur as sheets and can therefore neutralize clay layer charge more completely than can the spherical Fe polymers. Alperovitch *et al.* (1985) found that the presence of both Al and Fe polymers reduced the adverse effect of Na ions on the hydraulic conductivity of columns containing a montmorillonite-sand mixture.

MATERIALS AND METHODS

Material preparation

Samples of a Ca-montmorillonite from Cheto, Arizona (SAZ-1) and a well-crystallized kaolinite from

Table 1. Critical percent transmittance (%T) values for clays, oxides, clay mixtures, and clay-oxide mixtures.

	Pure	+2% Al oxide	+10% Al oxide	+2% Fe oxide	+10% Fe oxide
Clay					
Na-montmorillonite	73	73	72	70	60
Na-kaolinite	51	51	51	48	47
Ca-montmorillonite	52	52	57	52	45
Ca-kaolinite	39	39	40	53	45
Na-montmorillonite-Na-kaolinite 50/50	49	50	50	45	49
Ca-montmorillonite-Ca-kaolinite 50/50	40	40	47	50	45
Oxide					
Al oxide in NaCl	51				
Al oxide in CaCl ₂	51				
Fe oxide in NaCl	8.5				
Fe oxide in CaCl ₂	12				

Georgia (KGa-1) were obtained from The Clay Minerals Society's Source Clays Repository. X-ray powder diffraction (XRD) analysis indicated no impurities for the montmorillonite, but detected traces of vermiculite and feldspar in the kaolinite. The <2- μ m fraction of both clays was collected by sedimentation. To collect the kaolinite, the pH of the settling suspension was raised to 9.6 using NaOH to disperse the material. Subsamples of the <2- μ m fraction of both clays were saturated with Na, Ca, or Mg using 1 N NaCl, CaCl₂, or MgCl₂. The materials were washed free of Cl⁻ and freeze dried.

Noncrystalline Al and Fe oxide materials were prepared using a modification of the method developed by McPhail *et al.* (1972). For the Al oxide synthesis, AlCl₃ was substituted for Al(NO₃)₃ and the shaking time increased to 15 min. For the Fe oxide synthesis, Fe(NO₃)₃ and NaOH concentrations were doubled, and the water bath heating time was increased to 15 min. Each oxide was washed in deionized water and centrifuged three times. The Fe oxide was amorphous to X-rays, but the Al oxide contained traces of gibbsite and bayerite. Suspension density was determined by drying a known volume of oxide suspension to constant weight. Prior to use, each suspension density was reduced to 1.0% (10.0 g solid/liter) by adding deionized water.

Critical coagulation concentration determinations

The CCC is herein defined as the salt concentration at which percent transmittance (%T) corresponds to 20% of the solids remaining in solution after 3 hr. CCCs were measured for the above materials and mixtures in the pH range 5.5 to 9.5. The same CCC procedure was used in all parts of this study. Solutions (7 ml) of different salt concentrations were pipeted into ten 10-ml spectrophotometer cuvettes. Solutions of NaCl, CaCl₂, or MgCl₂ were used to match the cation saturation of the clay(s).

A 1.0% suspension of pure clay, mixed clay, oxide, or clay-oxide mixture was added to a 50-ml polypro-

pylene centrifuge tube and shaken for 5 min. The clay suspensions were prepared by combining 100 mg of clay with 10.0 ml deionized water. For the Ca- and Mg-saturated clays and clay mixtures, it was necessary to sonicate the suspension for 15 s at 75–85 watts prior to shaking. The 1.0% clay mixtures consisted of 50% montmorillonite and 50% kaolinite clay. Subsamples of the 1.0% Al and 1.0% Fe oxide suspensions were diluted with deionized water to produce 0.2% oxide suspensions (2.0 g solid/liter solution). It was necessary to sonicate the Fe oxide suspension for 15 s at 75–85 watts prior to shaking. The 2% clay-oxide suspension was prepared by combining 98 mg of clay(s), 9.0 ml of deionized water, and 1.0 ml of 0.2% oxide suspension. The 10% clay-oxide suspension was prepared by combining 90 mg of clay(s), 9.0 ml of deionized water, and 1.0 ml of 1.0% oxide suspension.

The suspensions of clays, clay mixtures, and clay-oxide mixtures were prepared just prior to use. For the Na systems, the pH was adjusted by adding small volumes (<0.2 ml) of 0.1 N HCl or NaOH to the 1.0% suspensions prior to shaking. For the Ca and the Mg systems, the pH was adjusted by adding HCl, Ca(OH)₂, or Mg(OH)₂ to the salt solutions prior to pipeting into the cuvettes. The amounts of Na, Ca, Mg, or H used in pH adjustment were included in the CCC calculations.

A 0.50-ml aliquot of the 1.0% clay, clay mixture, oxide, or clay-oxide mixture was pipeted into each cuvette containing the salt solution. The cuvettes were sealed with Parafilm, mixed on a vortex mixer for 15 s, and allowed to settle. After 3 hr, the %T of each cuvette was read at 420 nm wavelength. Deionized water was used as the 100%T blank.

Before determining the CCC for each system, the %T corresponding to 20% of the solids remaining in solution was established. This "critical %T" was established for each clay, clay mixture, oxide, and clay-oxide mixture and is indicated in Table 1. The pHs of the suspensions were measured near the critical %T. For calculating the CCC and the corresponding pH for

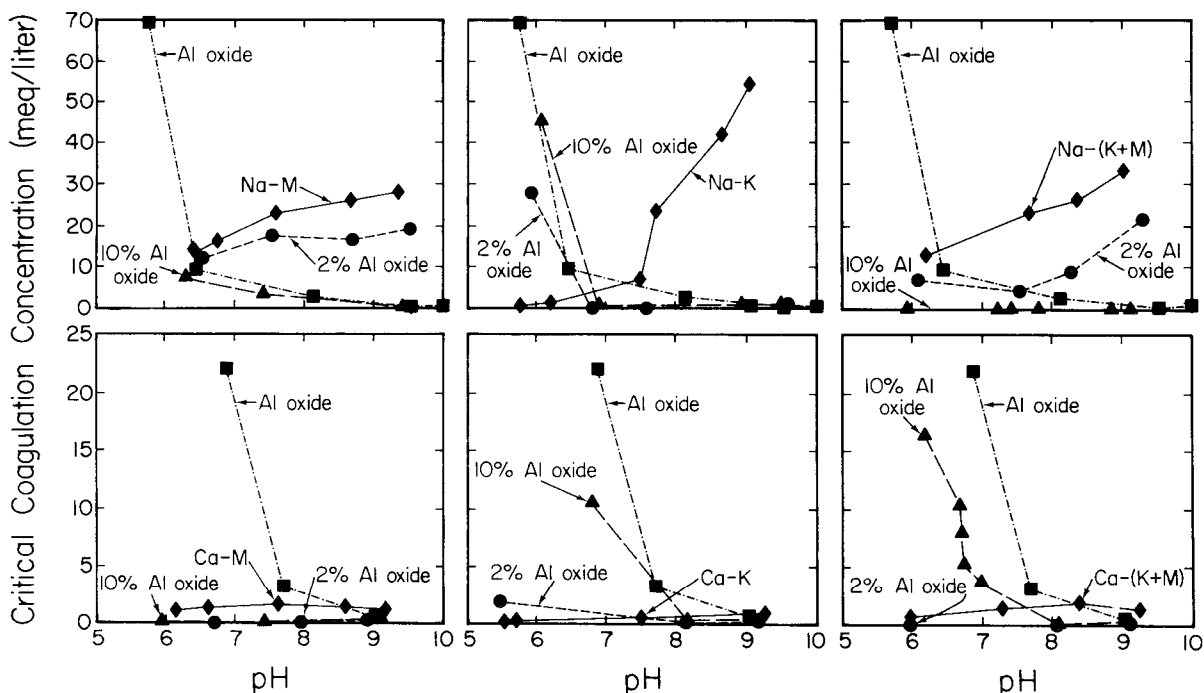


Figure 1. Critical coagulation concentrations of Al oxide-clay(s) mixtures: (a) Na-montmorillonite, (b) Na-kaolinite, (c) Na-montmorillonite-kaolinite 50/50, (d) Ca-montmorillonite, (e) Ca-kaolinite, (f) Ca-montmorillonite-kaolinite 50/50. The Na systems (a-c) were determined in NaCl solution. The Ca systems (d-f) were determined in CaCl_2 solution.

each run, a linear relationship was assumed between the two data points bracketing the critical %T.

To verify the validity of %T light transmittance measurements for the study of clay mixtures, the clay mineralogy of the resultant flocs was analyzed directly. Proportions of kaolinite and montmorillonite in the flocs at the CCCs were determined by quantitative XRD analysis using peak areas. These proportions were compared with those obtained from XRD peak areas of equivalent mechanical mixtures of the two minerals. The XRD analysis of each mixture was carried out in triplicate. The percentages of montmorillonite in the flocs are provided in column 4 of Table 3. These direct measurements show that the mineral proportions in the flocs are almost identical to those in the initial solutions, clearly indicating that the mixed systems are interacting and flocculating as mixtures.

Additional material characterization

Particle-size distributions of the Al and Fe oxides were determined by sedimentation using a Horiba CAPA 300 particle size analyzer. All Al oxide particles were $<1 \mu\text{m}$, and 93.5% were $<0.5 \mu\text{m}$ in size. For the Fe oxide, all particles were $<10 \mu\text{m}$, 81.8% were $<2 \mu\text{m}$, 42.3% were $<1 \mu\text{m}$, and 14.9% were $<0.5 \mu\text{m}$ in size. The median diameter was $0.16 \mu\text{m}$ for the Al oxide and $0.88 \mu\text{m}$ for the Fe oxide particles.

For the Al and Fe oxide materials, the PZC was determined by microelectrophoresis using a Zeta-Me-

ter 3.0 system. The electrophoretic mobility of suspensions containing 0.01% Al or Fe oxide in 0.001 N NaCl was determined at various pHs. The PZC was obtained by interpolating the data to zero electrophoretic mobility; PZC occurred at pH 9.5 for Al oxide and at pH 7.2 for Fe oxide.

RESULTS AND DISCUSSION

CCCs for all clay, mixed clay, and clay-oxide systems at all pHs investigated are given in Table 2. The effect of pH on the flocculation of montmorillonite, kaolinite, and a 50/50 mixture of these clays is indicated in Figures 1 and 2. The CCCs for kaolinites are much more pH dependent than those for montmorillonites. This difference was observed by Swartz-Allen and Matijevic (1976) for Na-montmorillonite and Na-kaolinite and is due to the greater proportion of pH-dependent charge of kaolinite. The CCCs for the 50/50 mixtures are about the same as those for the montmorillonites. The presence of kaolinite was expected to decrease the CCCs of the montmorillonite-kaolinite mixtures at pHs less than its edge PZC; however, this effect was slight because the charge density of kaolinite per gram is much less than that of montmorillonite. At pHs greater than its edge PZC, no flocculating effect of kaolinite was found. The CCCs for the 10/90, 25/75, and 50/50 mixtures of montmorillonite and kaolinite (Table 3) demonstrate that even small amounts of montmorillonite can deflocculate kaolinite. This ef-

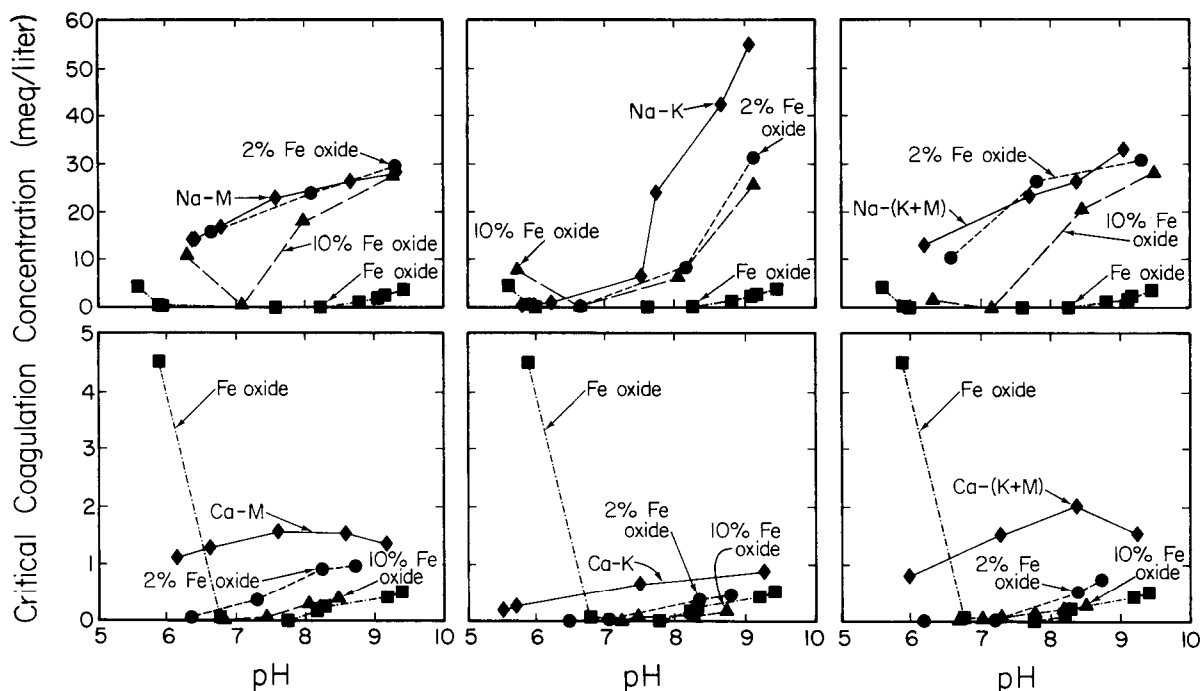


Figure 2. Critical coagulation concentrations of Fe oxide-clay(s) mixtures: (a) Na-montmorillonite, (b) Na-kaolinite, (c) Na-montmorillonite-kaolinite 50/50, (d) Ca-montmorillonite, (e) Ca-kaolinite, (f) Ca-montmorillonite-kaolinite 50/50. The Na systems (a-c) were determined in NaCl solution. The Ca systems (d-f) were determined in CaCl₂ solution.

fect is much greater than merely a percentage-weighted average, especially for the Na system. Precise interpretation of these data is difficult because of the variation in pH. The flocculation behavior of Mg-montmorillonite is not significantly pH dependent (Table 2). The drop in CCC of some of the Ca systems at pH > 9 may have been due to charge neutralization and aggregation resulting from precipitation of CaCO₃ on the clay particle surfaces.

Table 4 lists CCCs for Al and Fe oxides in contact with solutions of NaCl or CaCl₂ at different pHs. The materials coagulated in a broad region around their PZC value (pH 9.5 for Al oxide and pH 7.2 for Fe oxide). It is reasonable that less salt is required to flocculate the materials when they have lower charge density. Similarly, Yopps and Fuerstenau (1964) reported that coagulation was most rapid near the PZC. In the CaCl₂ solutions, the CCC minima shifted to higher pHs. This behavior was probably due to specific Ca adsorption which shifted the PZC of oxide minerals (Huang and Stumm, 1973). The lack of increase in CCC of the Fe oxide system in the CaCl₂ solution at pH > 9 may have been due to CaCO₃ precipitation on the oxide particles.

The effect of the presence of Al or Fe oxides on CCCs (Table 2) of the clays and clay mixtures as a function of pH is indicated in Figures 1 and 2. The presence of oxides in the montmorillonite systems (Figures 1a, 1d, 2a, and 2d) reduced the CCCs of the mixtures below

the CCC of montmorillonite alone. The ameliorative effect on flocculation was greater for Al oxide than for Fe oxide. An addition of 2% Fe oxide had no effect on the CCCs of Na-montmorillonite. The decrease in CCC when Al oxide was added was such that the CCCs for some of the mixtures were lower than those for either material alone. The CCC reductions were greater for the 10% than for the 2% oxide additions. The same amount of oxide material was a more effective flocculant in the Ca systems than the Na systems. Inasmuch as Ca-montmorillonite occurs as tactoids, not as single particles like Na-montmorillonite (Shainberg and Letey, 1984), less charge is exposed and less oxide is required to neutralize the charge and thereby flocculate the system.

The effect of oxides on the flocculation of the kaolinite systems appears to be additive (Figures 1b, 1e, 2b, and 2e); i.e., the CCCs of the mixtures are intermediate between those of the end-member materials. At low pH all oxide-kaolinite mixtures exhibited high CCCs, with the exception of the Fe oxide-Na-kaolinite mixtures which exhibited high CCCs only at high pH. These CCC increases of the mixtures correspond to increases in the CCC of Al oxide and Na-kaolinite, respectively. The presence of Al oxide apparently induced flocculation at pHs as high as 10, whereas Fe oxide was less effective at pH > 8. These results indicate that the oxide materials were most effective as flocculants at pHs near their PZC.

Table 2. Critical coagulation concentrations (CCC) for clays and clay mixtures.

Sample	CCC (meq/liter)	pH	CCC 2% Al oxide (meq/liter)	pH	CCC 10% Al oxide (meq/liter)	pH	CCC 2% Fe oxide (meq/liter)	pH	CCC 10% Fe oxide (meq/liter)	pH
Na-montmorillonite	14.0	6.38			7.40	6.26	15.8	6.65	10.5	6.27
	13.8	6.42	12.2	6.53						
	16.2	6.74			3.46	7.39			0.25	7.10
	22.9	7.59	17.6	7.53			23.7	8.11	17.6	7.99
	26.1	8.67	16.8	8.69	<0.15 ¹	9.40	29.2	9.33	26.9	9.26
28.0	9.38	19.7	9.52							
Na-kaolinite	<0.19	5.76	28.0	5.92	44.8	6.04	c ²	6.62	7.43	5.71
	1.03	6.20	<0.02	6.80	0.81	6.89			c	6.62
	6.58	7.50	<0.04	7.58						
	23.6	7.71	0.90	9.08	1.00	8.94	8.51	8.14	5.71	8.00
	42.0	8.66	1.76	9.61	1.08	9.50	31.0	9.12	25.0	9.10
54.6	9.07									
Ca-montmorillonite	1.09	6.13			c	5.92	0.08	6.34		
	1.28	6.61	c	6.70					c	6.82
	1.56	7.60	<0.07	7.94	<0.07	7.40	0.38	7.31	<0.05	7.44
	1.54	8.58	<0.19	8.88			0.92	8.24	0.28	8.04
	1.34	9.17			<0.20	9.12	0.98	8.72	0.39	8.48
Ca-kaolinite	<0.19	5.48	1.97	5.44	48.0	6.53	c	6.46	c	7.20
	0.28	5.67			10.3	6.76	<0.05	7.02	<0.05	7.42
	0.63	7.46	<0.07	8.12	<0.14	8.12	0.38	8.32	<0.10	8.22
	0.85	9.26	<0.19	9.16	<0.20	9.10	0.47	8.77	<0.15	8.70
	13.2	6.17	7.11	6.08	c	5.90	10.9	6.56	1.62	6.28
Na-montmorillonite-Na-kaolinite 50/50			c		c	7.20			0.07	7.14
	23.3	7.68	4.61	7.54						
					c	7.40				
	26.3	8.37	9.28	8.28	<0.04	7.80	26.6	7.79		
	33.2	9.04	21.9	9.31	<0.11	8.86			20.5	8.44
Ca-montmorillonite-Ca-kaolinite 50/50	0.80	5.95	c	5.96	<0.12	9.12	31.0	9.29	28.0	9.46
					16.3	6.16	c	6.16	c	6.64
					10.3	6.67				
					8.04	6.68				
					5.21	6.71				
Mg-montmorillonite	1.52	7.27	<0.07	8.06	3.72	6.97	<0.05	7.18	<0.05	7.28
	2.02	8.36	<0.19	9.12	<0.14	8.08	0.54	8.38	0.15	7.75
	1.54	9.25			<0.20	9.10	0.76	8.72	0.26	8.51
	0.93	6.12								
	1.09	6.60								
1.00	8.40									
0.88	9.01									
0.91	9.30									

¹ The symbol < indicates coagulation at the concentration given which is the lowest salt concentration that could be achieved for that particular pH.

² Coagulated in distilled water.

Table 3. Critical coagulation concentrations (CCC) for clay mixtures.

Montmorillonite-kaolinite (%/%)	CCC (meq/liter)	pH	Montmorillonite in floc (% \pm σ)
Na system			
100/0	14.0	6.38	
50/50	13.2	6.17	48.0 \pm 1.27
25/75	11.4	5.91	22.4 \pm 1.33
10/90	2.33	5.71	8.5 \pm 0.13
0/100	<0.19 ¹	5.76	
Ca system			
100/0	1.09	6.13	
50/50	0.80	5.95	50.6 \pm 0.79
25/75	0.37	5.82	23.1 \pm 0.74
10/90	0.07	6.18	9.6 \pm 0.54
0/100	<0.19	5.48	

¹ The symbol < indicates coagulation at the concentration given which is the lowest salt concentration that could be achieved for that particular pH.

The effect of oxide addition on the CCCs of the montmorillonite-kaolinite 50/50 systems is apparently additive as well (Figures 1c, 1f, 2c, and 2f). Here also, the CCCs of the mixtures are intermediate between those of the clay(s) systems and the oxides. The CCCs of the 50/50 clay mixtures in the presence of oxides are intermediate between those of montmorillonite and kaolinite in the presence of oxides, but closer to the CCCs of montmorillonite. The presence of 2% Al oxide in the Ca-50/50 systems and 10% Al oxide in the Na-50/50 systems reduced the CCCs to less than those of either end-member material. As in the Na-montmorillonite system, the presence of 2% Fe oxide had no effect on the CCC of the Na-50/50 system; the same amount of oxide was more effective in coagulating the Ca system than the Na system, and the Al oxide was a more effective flocculant than the Fe oxide. The Ca-50/50 mixture was less stable at low pH in the presence of the larger amount of Al oxide. This effect was likely due to an excess of positive charge from both the oxide mineral and the edges of the kaolinite particles.

SUMMARY AND CONCLUSIONS

Critical coagulation concentrations of all clays, clay mixtures, oxides, and oxide-clay(s) mixtures were found to be pH dependent. The pH dependence for kaolinite was greater than that for montmorillonite, with the 50/50 mixture behaving more like montmorillonite. The same amount of oxide material was more effective in promoting flocculation in the Ca system than in the Na system. The ameliorative effect of Al oxide was greater than that of Fe oxide, probably because of the size and the morphology of the oxide particles. The Al oxide material consisted of a greater proportion of sub-micrometer-size particles and would therefore possess a higher charge density than the Fe oxide material. As suggested by Oades (1984), the Al oxide sheets were

Table 4. Critical coagulation concentrations (CCC) for oxides.

Solid	CCC in NaCl (meq/liter)	pH	CCC in CaCl ₂ (meq/liter)	pH
Al oxide	292	5.28		
	69.1	5.74	82.3	6.10
	9.53	6.44	22.1	6.85
	2.66	8.13	3.24	7.69
	<0.60 ¹	9.54	<0.70	9.02
	<0.87	10.04		
Fe oxide	4.45	5.57		
	0.52	5.88	4.52	5.87
	<0.13	5.98	<0.08	6.74
	<0.09	7.58	c ²	7.74
	<0.07	8.24	<0.20	8.18
	1.37	8.80	<0.25	8.28
	2.14	9.08		
	2.64	9.17	<0.45	9.18
	3.90	9.44	<0.51	9.40

¹ The symbol < indicates coagulation at the concentration given which is the lowest salt concentration that could be achieved for that particular pH.

² Coagulated in distilled water.

apparently better able to neutralize charge than the spherical Fe particles. The PZC of noncrystalline Al oxide was found to occur at a higher pH than that of noncrystalline Fe oxide. Because the reduction in CCC was greatest near the PZC value of the oxide material, the Al oxide material was more effective at high pHs.

This research indicates that small amounts of noncrystalline Al or Fe oxides may greatly improve the flocculation of clay systems and that Al oxide is not only more effective than Fe oxide, but effective over a greater pH range. The role of Al and Fe oxides in stabilization of arid zone soils under conditions of variable pH should now be investigated.

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REFERENCES

- Alperovitch, N., Shainberg, I., Keren, R., and Singer, M. J. (1985) Effect of clay mineralogy and aluminum and iron oxides on the hydraulic conductivity of clay-sand mixtures: *Clays & Clay Minerals* **33**, 443-450.
- Arora, H. S. and Coleman, N. T. (1979) The influence of electrolyte concentration on flocculation of clay suspensions: *Soil Sci.* **127**, 134-139.
- Blackmore, A. V. (1973) Aggregation of clay by the products of iron(III) hydrolysis: *Aust. J. Soil Res.* **11**, 75-82.
- Bohn, H. L., B. L. McNeal, and G. A. O'Connor (1979) *Soil Chemistry*: Wiley, New York, 329 pp.
- Deshpande, T. L., Greenland, D. J., and Quirk, J. P. (1964) Role of iron oxides in the bonding of soil particles: *Nature* **201**, 107-108.
- El Rayah, H. M. E. and Rowell, D. L. (1973) The influence of iron and aluminum hydroxides on the swelling of Na-

- montmorillonite and the permeability of a Na-soil: *J. Soil Sci.* **24**, 137–144.
- El-Swaify, S. A. (1976) Changes in the physical properties of soil clays due to precipitated aluminum and iron hydroxides: II. Colloidal interactions in the absence of drying: *Soil Sci. Soc. Amer. J.* **40**, 516–520.
- Frenkel, H. and Shainberg, I. (1980) The effect of hydroxy-Al and hydroxy-Fe on montmorillonite particle size: *Soil Sci. Soc. Amer. J.* **44**, 626–629.
- Frenkel, H., Goertzen, J. O., and Rhoades, J. D. (1978) Effects of clay type and content, exchangeable sodium percentage, and electrolyte concentration on clay dispersion and soil hydraulic conductivity: *Soil Sci. Soc. Amer. J.* **42**, 32–39.
- Greene, R. S. B., Posner, A. M., and Quirk, J. P. (1978) A study of the coagulation of montmorillonite and illite suspensions by calcium chloride using the electron microscope: in *Modification of Soil Structure*, W. W. Emerson, R. D. Bond, and A. R. Dexter, eds., Wiley, New York, 35–40.
- Greenland, D. J. (1975) Charge characteristics of some kaolinite-iron hydroxide complexes: *Clay Miner.* **10**, 407–416.
- Huang, C.-P. and Stumm, W. (1973) Specific adsorption of cations on hydrous γ -Al₂O₃: *J. Colloid Interface Sci.* **43**, 409–420.
- Kinniburgh, D. G. and Jackson, M. L. (1981) Cation adsorption by hydrous metal oxides and clay: in *Adsorption of Inorganics at Solid-Liquid Interfaces*, M. A. Anderson and A. J. Rubin, eds., Ann Arbor Science, Ann Arbor, Michigan, 91–160.
- McAtee, J. L. and Wells, L. M. (1967) Mutual adsorption of clay minerals and colloidal hydrous aluminum oxide—An electron microscopy investigation: *J. Colloid Interface Sci.* **24**, 203–210.
- McPhail, M., Page, A. L., and Bingham, F. T. (1972) Adsorption interactions of monosilicic and boric acid on hydrous oxides of iron and aluminum: *Soil Sci. Soc. Amer. Proc.* **36**, 510–514.
- Michaels, A. S. and Bolger, J. C. (1964) Particle interactions in aqueous kaolinite suspensions: *Ind. Eng. Chem. Fundamentals* **3**, 14–20.
- Oades, J. M. (1984) Interactions of polycations of aluminum and iron with clays: *Clays & Clay Minerals* **32**, 49–57.
- Oster, J. D., Shainberg, I., and Wood, J. D. (1980) Flocculation value and gel structure of sodium/calcium montmorillonite and illite suspensions: *Soil Sci. Soc. Amer. J.* **44**, 955–959.
- Rand, B. and Melton, I. E. (1977) Particle interactions in aqueous kaolinite suspensions. I. Effect of pH and electrolyte upon the mode of particle interaction in homoionic sodium kaolinite suspensions: *J. Colloid Interface Sci.* **60**, 308–320.
- Shainberg, I. and Letey, J. (1984) Response of soils to sodic and saline conditions: *Hilgardia* **52**, 1–57.
- Shanmuganathan, R. T. and Oades, J. M. (1982) Effect of dispersible clay on the physical properties of the B horizon of a red-brown earth: *Aust. J. Soil Res.* **20**, 315–324.
- Sposito, G. (1984) *The Surface Chemistry of Soils*: Oxford University Press, New York, 234 pp.
- Suarez, D. L., Rhoades, J. D., Lavado, R., and Grieve, C. M. (1984) Effect of pH on saturated hydraulic conductivity and soil dispersion: *Soil Sci. Soc. Amer. J.* **48**, 50–55.
- Swartzen-Allen, S. L. and Matijevic, E. (1976) Colloid and surface properties of clay suspensions. III. Stability of montmorillonite and kaolinite: *J. Colloid Interface Sci.* **56**, 159–167.
- Tschapek, M., Tcheichvili, L., and Wasowski, C. (1974) The point of zero charge (pzc) of kaolinite and SiO₂ + Al₂O₃ mixtures: *Clay Miner.* **10**, 219–229.
- van Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry*: 2nd ed., Wiley, New York, 318 pp.
- Yopps, J. A. and Fuerstenau, D. W. (1964) The zero point of charge of alpha-alumina: *J. Colloid Sci.* **19**, 61–71.

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