

Hydraulic Characteristics of Depositional Seals as Affected by Exchangeable Cations, Clay Mineralogy, and Polyacrylamide

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Depositional seals, formed when turbid waters infiltrate into soils, lead to a reduction in the hydraulic conductivity (HC) of soils and increased runoff. In this study, the effect of anionic polyacrylamide (PAM) on the HC and flocculation of depositional seals made of three clay minerals (montmorillonite, illite, and kaolinite), saturated with either Na or Ca, was investigated. A silt loam soil was packed in columns and leached with 5 g L⁻¹ suspensions of the reference clays. Deposition of the clay particles on the soil surface formed seals. In the PAM treatment, dry granules of linear PAM were spread on the soil surface before the suspension application. Calcium seals were more permeable than Na seals in all the clay types, up to 26 times greater for montmorillonite. The HC of the seals for the clay minerals was in the order kaolinite (2.8–3.5 mm h⁻¹) > illite (0.6–3.0 mm h⁻¹) > montmorillonite (0.09–1.0 mm h⁻¹). The addition of PAM generally enhanced clay flocculation, with the magnitude of the enhancement depending on the type of the exchangeable cation. The Na-saturated seals in the three clay types had significantly higher initial HC with the PAM treatment. This increase, however, was transient except in Na-illite. The impact of PAM on the degree of clay flocculation and floc density partially explained the effects of PAM on the HC of the depositional seals. An increase in clay flocculation or a decrease in floc density caused by PAM resulted in an increase in depositional seal HC.

Abbreviations: DW, deionized water; ESP, exchangeable sodium percentage; FD, floc density; HC, hydraulic conductivity; HR, hydraulic resistance; PAM, polyacrylamide; RFI, relative flocculation index.

Surface seals that form on soils create problems by both reducing infiltration and, once dry, increasing the mechanical strength of the soil surface to the point where seedling emergence is inhibited. Two types of seals, differing by the mechanism of their formation, are recognized: (i) structural seals formed by raindrop impact, and (ii) depositional seals formed by fine soil particles transported

from another area (Chen et al., 1980; Southard et al., 1988). Depositional seals generally form where water carrying the particles slows down (Shainberg and Singer, 1985).

Depositional seals are characterized by high bulk density and a reduced pore volume and thus impede the infiltration of water through them. Shainberg and Singer (1985) studied the effect of electrolyte concentration (*C*) on the HC of depositional seals on a sandy loam and a loam, and found that when the *C* of the percolating solution was low (≤ 0.005 mol L⁻¹), the HC of the depositional seal was greatly reduced. The *C* of the soil solution affects the density and micromorphology of these seals (Southard et al., 1988; Bresson and Boiffin, 1990; West et al., 1992). A depositional seal formed from soil material suspended in deionized water had high bulk density as well as birefringent-oriented layers of clay, neither of which occurred in an electrolyte solution (Southard et al., 1988; Bresson and Boiffin, 1990; Fox et al., 1998).

The depositional seal HC is largely determined by the state of clay flocculation in the suspended material (Shainberg

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and Singer, 1985). Increasing the C of the suspension was shown to form a depositional seal with HC much higher than with low- C water and only one order of magnitude lower than that of the bulk soil (Shainberg and Singer, 1985; Southard et al., 1988). When C exceeded the flocculation value of the suspended clay, the seal formed consisted of flocculated particles that were deposited randomly in an open structure, resulting in a high permeability. When the C of the suspension was below the flocculation value of the soil clay, the seal formed was made of dispersed clay particles deposited in a dense structure oriented parallel to the soil surface (Southard et al., 1988).

Clay mineralogy has also been identified as playing a key role in seal formation, with 2:1 clays being more dispersive than 1:1 clays (Arora and Coleman, 1979; Chorom and Rengasamy, 1995; Lado et al., 2007) and likely to form denser seals. Soils with smectite are unstable and prone to structural seal formation; kaolinitic and illitic soils with no smectite are stable and less susceptible to seal formation (Stern et al., 1991). Increasing C was shown to increase HC for montmorillonite but not for illite, while increasing the exchangeable Na percentage (ESP) decreased HC for both (Lado et al., 2007). They found that when ESP = 0, montmorillonite, illite, and kaolinite had relatively high HC. Kaolinite seals were not affected by ESP, except when the pH was above 9, due to greater negatively charged edges of the clay particles and associated dispersion (Lado et al., 2007). The rheological properties of clay suspensions are also known to correlate with inter-clay-particle interactions (Van Olphen, 1977).

The application of high-molecular-weight, linear, anionic PAM to soils has been shown to significantly increase the aggregate and structural stability (Mamedov et al., 2007) and the infiltration rate (Wallace et al., 1986, Smith et al., 1990). Synthetic polymers have been shown to promote both coagulation and flocculation of soil particles in suspensions as well as stabilization of preexisting soil aggregates (Helalia and Letey, 1988; Aly and Letey, 1988). Texture, mineralogy, and extractable Fe were found to be highly correlated with PAM flocculation in suspensions of natural soils (McLaughlin and Bartholomew, 2007).

It is generally accepted that infiltration rates can be maintained by treating the soil surface or irrigation water with PAM (Sojka et al., 2007). This is because PAM maintains the soil structure and greatly reduces clay dispersion (Shainberg et al., 1992). Many studies on the effect of PAM on crusting have been related to structural crusts formed from raindrop impact (Levy and Agassi, 1995; Levy et al., 1992; Shainberg et al., 1990; Zhang and Miller, 1996). Improvements in infiltration rates and reduction of erosion in furrow irrigation suggests that PAM may be effective in improving the hydraulic properties of depositional seals as well (Lentz et al., 1992; Sirjacobs et al., 2000; Sojka et al., 1998). Sojka et al. (2007) suggested that seals formed in the presence of PAM are inherently more porous than the seals under untreated irrigation water.

The possibility of improving the HC of depositional seals with a small amount of flocculant could also contribute to the improvement of runoff farming technology. In runoff farming, runoff water from adjacent lands is directed to crop fields. The runoff water often carries sediment, which forms a depositional seal, reducing water infiltration to very low values and increas-

ing evaporation losses. Increasing the rate of water percolation decreases water loss to evaporation and more water is therefore available to the crops.

Polyacrylamide flocculates clay by forming bridges between the clay particles and binding them into large agglomerates (Laird, 1997). Bridging occurs when segments of the polymer chain adsorb to different particles and help particles aggregate. When added to a clay suspension, the anionic PAM can adsorb (i) directly on the positive edges of the clay particles, (ii) through cation bridging on the negatively charged clay surfaces, and (iii) by Van der Waals and entropy forces on the neutral surfaces of the particles (Laird, 1997; Luckham and Rossi, 1999). It is expected, therefore, that in the presence of PAM the suspended clay material will be in a flocculated state and consequently the HC of the seal formed with such a suspension will increase in comparison to a seal formed with a unflocculated clay material.

The objective of our study was to evaluate the effects of PAM on (i) the HC of depositional seals made of three homoionic (Na or Ca) reference clay suspensions, and (ii) the relationships between the flocculation characteristics of those clay suspensions and the HC of the depositional seals formed.

MATERIALS AND METHODS

A smectitic, calcareous silt loam (a Calcic Haploxeralf) from Be'er Sheva, Israel, was used as a base on the surface of which depositional seals were formed using different clay minerals. A detailed description of this concept was presented in Lado et al. (2007). The mechanical composition of the soil was 400, 355, and 245 g kg⁻¹ sand, silt, and clay, respectively. The soil CaCO₃ content was 180 g kg⁻¹ and organic matter content was 19 g kg⁻¹. We specifically selected this soil to serve as a mechanical support for the depositional seals formed because of its small pores, which limit the movement of clay particles into the soil surface, and thus depositional seals would be obtained that were distinctly separated from the underlying bulk soil (Chen et al., 1980; Lado et al., 2007). The soil was initially washed with excess 20 mmol L⁻¹ CaCl₂ solution, to reduce the ESP of the soil to <1.0, and air dried. Saturating the exchangeable complex of the soil with Ca ions was done to ensure that the HC of the soil would not change much on leaching with deionized water (DW) (Shainberg and Letey, 1984; Lado et al., 2007).

Three reference clays were used in this study: Wyoming montmorillonite, Fithian illite (both obtained from Ward's NSE, Rochester, UK), and Supreme kaolinite (English China Clay, Austell, UK). Homoionic Na- or Ca-saturated clays were prepared by the method of Harter and Stotzky (1971) as modified by Lado et al. (2007). We further modified the procedure of Lado et al. (2007) by discarding the >53- μ m fraction from the clays while suspended in DW. This was done to remove the impurities, particularly in illite and montmorillonite, which do not dissolve in DW and would have interfered with the results. The <53- μ m fraction was suspended in the NaCl or CaCl₂ solution (0.5 mol kg⁻¹) and centrifuged three times to obtain the homoionic clays. Excess Cl⁻ in the suspended homoionic clays was washed away with DW and thereafter by ethanol-water mixtures until the supernatants were tested Cl⁻ negative and

their electrical conductivity remained constant. The clay suspensions were centrifuged to a thick slurry and freeze-dried.

The PAM used in this study was an anionic PAM (A110, Cytec Inc., North Andover, MA) with a high molecular weight (12×10^6 Da) and 15% hydrolysis.

Hydraulic Conductivity Studies

The HC studies were conducted using soil columns. Air-dried soil samples (120 g) with aggregate size <2 mm were packed in Plexiglas columns (5.2-cm diameter) to a bulk density of 1.25 g cm^{-3} on top of a 2-cm layer of acid-washed coarse quartz sand with a metal screen at the bottom. The thickness of the soil layer in the columns was 43 mm. The soil columns were then wetted from below with DW until saturation at a wetting rate of 35 mm h^{-1} using a peristaltic pump.

Following saturation, the surfaces of the soils in the columns were either left untouched or spread with dry PAM granules at a rate of 20 kg ha^{-1} . Thereafter, the columns were leached with homoionic clay suspensions that were obtained by mixing the freeze-dried clay slurries with DW at a concentration of 5 g L^{-1} . The pH of the montmorillonite and illite suspensions was ~ 7 while that of the kaolinite suspension was ~ 6.5 . The clay suspensions were placed in Marriott bottles and stirred with a magnetic stirrer throughout the course of the leaching. The leaching was performed under a constant hydraulic head of 0.30 m. In addition, the HC of the base soil was determined by leaching columns of the saturated base soil with DW in the presence or absence of dry PAM granules at the soil surface. The results of this study served as reference.

In all the experiments, the leachate from each soil core was collected continuously in 30-mL glass tubes placed in a fraction collector; the volume, electrical conductivity, and pH of the leachate were measured. Leaching was continued until the leachate volume was relatively constant in at least 10 consecutive tubes.

The HC was calculated using Darcy's law:

$$K_s = q \Delta L / \Delta h \quad [1]$$

where K_s [L T^{-1}] is the saturated HC, q [L T^{-1}] is the flux through the column, L [L] is the soil thickness, and h [L] is the hydraulic head.

Specifically, three parameters were used for quantitative evaluation of the effects on the soil HC of the treatments studied: initial HC (HC_i; the HC measured at the beginning of the leaching from the top, ~ 0.1 pore volume), apparent steady-state HC (HC_{ss}; the HC that was asymptotically approaching a steady-state value), and the hydraulic resistance at steady state (HR_{ss}).

When the soil was leached with a clay suspension, a depositional seal was formed at the surface of the base soil due to the blocking of surface pores by the suspended clay particles. Thus, a two-layered system was obtained, with the permeability of the upper layer (the depositional seal) being expected to be lower than that of the lower layer (the base soil). Calculation of the HC of the depositional seal is not possible as its thickness cannot be accurately determined. We have opted therefore to use the hydraulic resistance (HR) of the depositional seal as an indicator of the hydraulic properties of this seal (Freebairn

et al., 1991; Fox et al., 1998). We have calculated the HR using the equation proposed by Lado et al. (2007):

$$\text{HR} = \Delta h / q - \Delta L / K_s \quad [2]$$

Flocculation and Floc Density Studies

The effects of PAM on flocculation and floc density were determined for both Ca- and Na-saturated clays. It was assumed that the effects of PAM on the HC of the seal can be linked to the effects of PAM on clay flocculation characteristics. A stock solution of 1000 mg L^{-1} PAM was prepared by adding polymer granules slowly to magnetically stirred DW, with stirring continuing for at least 24 h at room temperature. Suspensions of montmorillonite, illite, and kaolinite (the same clays as those used in the HC studies) were prepared by adding 5.0 g of Na- or Ca-saturated clay to 1000 mL of DW and mixing the suspension for 12 h.

Flocculation of the clay suspensions in the presence of different PAM concentrations was determined as follows. Given volumes of the stock solution of PAM were added by pipette to 200-mL portions of the clay suspensions that were placed in 330-mL Nalgene containers (63.75-mm i.d. and 104.95-mm depth) to obtain final PAM concentrations of 0, 0.01, 0.1, 0.5, 2.5, 5, or 10 mg L^{-1} , and the suspensions were then hand shaken for 10 s. A nephelometer (Analite 152, McVan Instruments, Mulgrave, Australia) probe was inserted into each suspension to a depth of 25 mm and the turbidity (in nephelometric turbidity units) was recorded after 1 min. The pH and electrical conductivity of each suspension was also measured.

The relative flocculation index (RFI) was calculated from the turbidity data using the equation:

$$\text{RFI} = (T_i / T_0) 100 \quad [3]$$

where T_i is the turbidity of the suspensions with PAM and T_0 is the turbidity of suspensions without PAM but otherwise under the same conditions.

The floc density (FD) of the clay suspensions was determined using the settleable solids method as described by Eaton et al. (2005). One-liter clay suspensions that were prepared as for the flocculation study were magnetically stirred for 12 h and poured into Imhoff cones. For FD determination with PAM, before pouring the clay suspension into the Imhoff cone, 2.5 mg of dry PAM granules was added slowly to the suspension, which was then shaken for 10 s. The suspensions in the Imhoff cone were allowed to settle for 45 min; thereafter, the sides of the cones were gently agitated with a rod and the suspensions were allowed to settle for another 15 min. The volume of the settleable solids (flocculated clay) was then obtained by reading the volume markings on the Imhoff cone. In the cases where the flocs had settled, there was a clear separation between the settled flocs and the suspension, so that the volume occupied by the settled flocs and by the suspension could be easily determined (Fig. 1). After taking the volume readings, three 5-mL subsamples of the suspension above the flocculated material were taken at 100-, 150-, and 200-mm depths from the surface to get representative samples of the quantity of suspended solids. These subsamples were dried (105°C) and weighed. The

remaining liquid was decanted slowly without removing the settled solids (flocs), which were then transferred to a 53- μm sieve. The material retained on the sieve was dried (105°C) and the floc density (Mg m^{-3}) was determined by dividing the weight of the flocs by the volume occupied by the flocculated clay.

In addition, we calculated FD based on the concentration of the solids left in the suspension above the flocculated material. This FD, termed the *analytical FD*, was calculated as

$$\text{Analytical FD} = (5 \text{ g} - \text{TSS in suspensions}) / \text{total floc volume} \quad [4]$$

where TSS is the total suspended solids in the suspension above the flocculated material and total floc volume is the volume occupied by the flocculated and settled material after 1 h as measured in the Imhoff cone.

Statistical Analysis

All the treatments in the hydraulic conductivity experiments were conducted in three replicates. The flocculation and floc density studies were done on two replicates for each treatment combination (clay type, saturating ion, and PAM concentration). The effects of the main treatments (clay type, exchangeable cation, and PAM addition) and their interactions on the mean values of the HC, RFI, and FD were subjected to ANOVA as a completely randomized design. Separation of means was obtained by Tukey's honestly significant difference test (SAS Version 9.1, SAS Institute, 2004). All tests were performed at the 0.05 significance level.

RESULTS AND DISCUSSION

Hydraulic Conductivity of Depositional Seals

Changes in the HC of the base soil during leaching with DW or clay suspensions and in the presence or absence of PAM is presented in Fig. 2 to 4. Leaching the base soil with DW resulted in a slight decrease in the HC of the soil (Fig. 2–4). This decrease in the HC was probably due to slight clay swelling, which decreased the size of the water-conducting pores in the soil (Shainberg and Letey, 1984). The addition of PAM to the soil surface had minor effects on the HC of the base soil. These two HC curves are repeated for each clay treatment to illustrate changes relative to the base soil.

Addition of dry PAM to the soil surface before leaching with DW resulted in HC_i and HC_s values that were comparable to those obtained in the absence of PAM (Fig. 2–4). At the initial stage of leaching with DW (the first 1.5 pore volumes), however, the HC of the PAM-treated soil was stable and higher than that of the base soil, probably due to the stabilization effect of PAM on the aggregates at the soil surface. The aggregates of the silt loam are very weak (Shainberg et al., 2002) and the slight disturbance introduced by the initial addition of the DW was apparently mitigated by the PAM. After the passing of ~ 1.5 pore volumes, the HC for the PAM-treated soils started to decline gradually. The latter phenomenon was also observed by Ajwa and Trout (2006), who reported that leaching soil with PAM solutions decreased its permeability and ascribed the decrease to the apparent increase in the effective viscosity of the PAM-containing leaching solution. In our study, PAM was applied as dry granules at the soil surface, and on leaching, the dry PAM dissolved in the leaching solution and increased its viscosity. This increase in solution viscosity became apparently significant after ~ 1.5 pore volume of leaching and led to the observed reduction in HC of the PAM-treated soil with time (Fig. 2–4).



Fig. 1. Floc density studies using Imhoff cones: the clear demarcation between the settled flocs and the suspended sediments was used to calculate the floc density from the volume occupied by the settled flocs.

Changes in the HC following leaching with the clay suspensions appeared to depend on the clay mineralogy, the type of exchangeable cation, and the presence or absence of PAM at the soil surface (Fig. 2–4). The results of a multifactor ANOVA test indicated that the main treatments (clay type, exchangeable cation, and PAM addition) and their interactions had significant effects on the HC_i (Table 1). In the case of the HC_s, it appeared that PAM had no effect on these parameters, but the triple interaction (clay type \times exchangeable cation \times PAM) had a significant effect on the

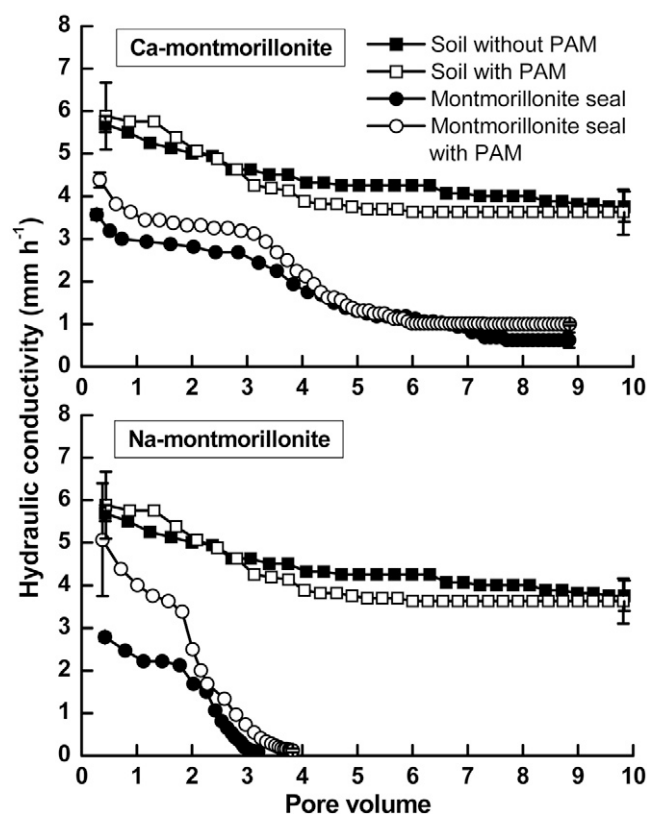


Fig. 2. Hydraulic conductivity curves of the bare soil leached with deionized water and with Ca- and Na-montmorillonite suspensions with and without the addition of polyacrylamide (PAM) to the soil surface. Bars indicate one standard deviation.

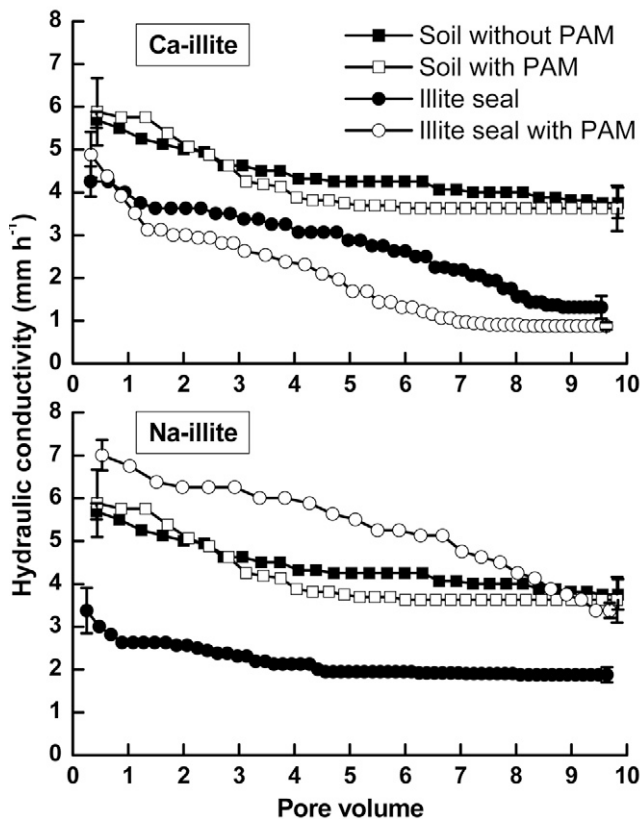


Fig. 3. Hydraulic conductivity curves of the bare soil leached with deionized water and with Ca- and Na-illite suspensions with and without the addition of polyacrylamide (PAM) to the soil surface. Bars indicate one standard deviation.

HCss (Table 1). For the HRss, only clay type and exchangeable cation and their interaction significantly affected this parameter; PAM alone and its interactions with the other two treatments had no effect on the HRss (Table 1).

Montmorillonitic Seals

Leaching the soil with montmorillonitic suspensions resulted in HC that was lower than that of the base soil (Fig. 2). The Na-montmorillonite suspensions produced depositional seals that reduced the HC of the soil column to near zero after fewer than four pore volumes of leaching. The development of the Ca-montmorillonite seal was much more gradual (Fig. 2). The HCi

Table 1. Significance of the effects of clay type (montmorillonite, illite, or kaolinite), exchangeable cation (ExCat: Ca or Na), and polyacrylamide (PAM) on the initial hydraulic conductivity (HC_i), apparent steady-state hydraulic conductivity (HC_{ss}), relative flocculation index (RFI), and hydraulic resistance at the HC_{ss} (HR_{ss}).

| Sources | <i>P</i> > <i>F</i> | | | |
|--------------------|---------------------|------------------|---------|------------------|
| | HC _i | HC _{ss} | RFI† | HR _{ss} |
| Clay | 0.0012 | <0.0001 | <0.0001 | <0.0001 |
| ExCat | 0.0177 | 0.0103 | <0.0001 | <0.0001 |
| PAM | <0.0001 | 0.4066 | <0.0001 | 0.1889 |
| Clay × ExCat | 0.0100 | <0.0001 | <0.0001 | <0.0001 |
| Clay × PAM | 0.0553 | 0.0293 | <0.0001 | 0.1073 |
| ExCat × PAM | 0.0003 | 0.0036 | <0.0001 | 0.3908 |
| Clay × ExCat × PAM | 0.0153 | 0.0038 | <0.0001 | 0.8787 |
| Error | <0.0001 | <0.0001 | <0.0001 | <0.0001 |

† RFI was compared for clay suspensions to which 0.5 mg L⁻¹ of PAM was added and turbidity was measured after 1.0 min from the beginning of settling.

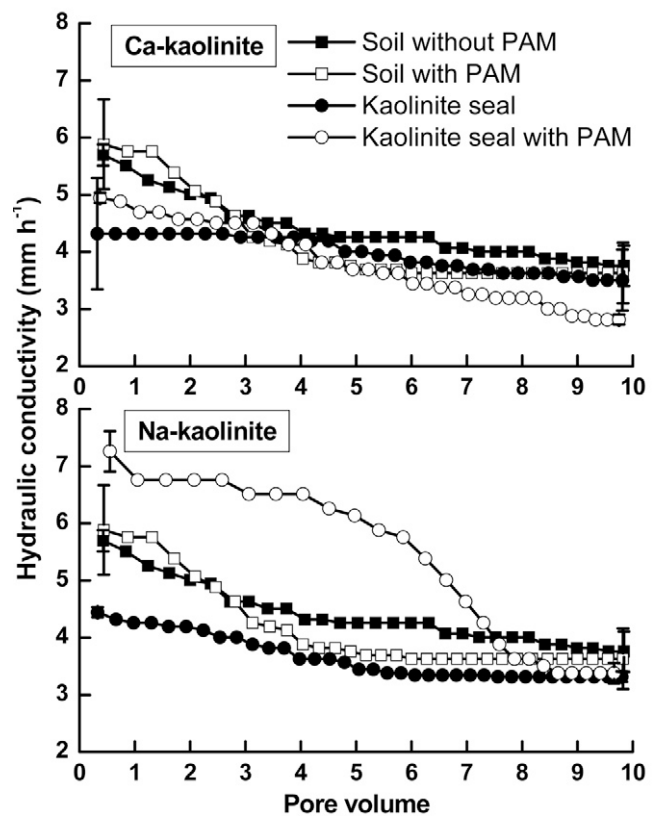


Fig. 4. Hydraulic conductivity curves of the bare soil leached with deionized water and with Ca- and Na-kaolinite suspensions with and without the addition of polyacrylamide (PAM) to the soil surface. Bars indicate one standard deviation.

values for leaching with Na-montmorillonite were significantly lower than that of Ca-montmorillonite (Table 2). After leaching with three pore volumes, the HC of the Ca-montmorillonite seal was 26 times that of the Na-montmorillonite seal, but the HC_{ss} of the Ca-montmorillonite seal obtained after leaching with approximately seven pore volumes was only seven times that of the HC_{ss} of Na-montmorillonite seal (Fig. 2, Table 2). In accordance with the latter, the HR_{ss} of the Ca-montmorillonite seal was approximately seven times lower than that of the Na-montmorillonite seal (Table 2).

The clay in the Na-montmorillonite suspension was completely dispersed, since the electrolyte concentration (0.46 mmol_c L⁻¹) was more than an order of magnitude lower than its flocculation value (12 mmol_c L⁻¹) (Shainberg and Letey, 1984; Goldberg and Glaubig, 1987). Consequently, the steady-state permeability of the depositional seal made of dispersed Na-montmorillonite platelets was only 0.09 mm h⁻¹. The extremely low permeability of the Na-montmorillonite seal (Table 2) probably resulted from two complimentary mechanisms: (i) the penetration of the suspended particles into the base soil that thus clogged water-conducting pores, and (ii) the settling of the dispersed clay platelets at the soil surface in an orientation parallel to the soil surface, which formed a layer with high tortuosity (Southard et al., 1988). The PAM treatment significantly lessened the sealing effect of the

Na-montmorillonite initially, with an HCl of almost twice that of the untreated seal (Fig. 2). This effect was lost, however, after four pore volumes and the HC_s was not significantly improved (Table 2).

The Ca-montmorillonite suspension C was 0.5 mmol_c L⁻¹, which exceeds the flocculation value of Ca-montmorillonite (0.2 mmol_c L⁻¹; Shainberg and Letey, 1984). Furthermore, Ca-montmorillonite forms packets of five to 10 clay platelets with c-spacing of 1.9 nm between platelets (Shainberg and Letey, 1984; Chorom and Rengasamy 1995). These floccules of Ca-montmorillonite packets deposited at the soil surface, forming a seal with large pores and low tortuosity, which thus enabled high permeability. A similar observation was made by Lado et al. (2007). As a result, the addition of PAM did not significantly increase the HCl of the Ca-montmorillonite (Table 2).

Illitic Seals

Similar to montmorillonite, leaching the soil with a Na- or Ca-illite suspension resulted in a seal with HC (Fig. 3) and HC_s (Table 2) that were significantly lower than that of the base soil. The HC curves of the Ca- and Na-illite seals were higher than those of the corresponding montmorillonite seals (Fig. 2 and 3). Sodium- and Ca-saturated illite particles are bigger than those of Na- and Ca-montmorillonite and their flocculation values are higher (Van Olphen, 1977; Shainberg and Letey, 1984; Chorom and Rengasamy, 1995). The flocculation values of Na- and Ca-illites are 40 to 50 mmol_c L⁻¹ NaCl and 0.25 mmol_c L⁻¹ CaCl₂, respectively (El-Swaify, 1976; Arora and Coleman, 1979). The large dispersed illite particles form seals with pores of a larger average size, which thus leads to a greater permeability (Lado et al., 2007). The HCl and HC_s of the Ca-illite seals were higher than those of the Na-illite seals, but the differences were not statistically significant (Table 2). The comparable HC_s of the Na- and Ca-illitic seals was probably a result of both homoionic illitic clays being dispersed in DW and neither were flocculated.

As noted for the montmorillonite seals, the addition of PAM increased the HC for Na-illite but not for Ca-illite (Fig. 3); however, this phenomenon was much greater in the case of Na-illite (Table 2). Different PAM responses to Na- and Ca-saturated clays are also indicated by the significant interactions between the exchangeable cations and clays (Table 1). The higher HC of the Na-illite seal in the PAM treatment compared with that of Na-montmorillonite is explained by the fact that PAM causes the flocculation of the suspended particles. For both the Na-illite and the Na-montmorillonite, the clay particles were fully dispersed because of their high flocculation value (45 and 12 mmol_c L⁻¹, respectively). As stated above, however, the dispersed illite particles are larger than those of Na-montmorillonite, thus on flocculation the illite particles form a more open structure with relatively large pores that can support a much higher HC (Fig. 3) than that obtained for the Na-montmorillonite system (Fig. 2).

Table 2. Initial and apparent steady-state hydraulic conductivities and hydraulic resistance at the apparent steady-state hydraulic conductivity (HR_{ss}) for different clay types and exchangeable cation and polyacrylamide (PAM) treatments.

| Treatment | Hydraulic conductivity | | HR _{ss} † |
|--------------------|---|------------------------------------|--------------------|
| | Without PAM | With PAM (20 kg ha ⁻¹) | |
| | mm h ⁻¹ | | |
| | <u>Initial hydraulic conductivity</u> | | |
| Soil only‡ | 5.69 ABCD§ | 5.87 ABC | |
| Na-montmorillonite | 2.78 F | 5.07 ABCDE | 346.10 a¶ |
| Ca-montmorillonite | 3.56 DEF | 4.37 CDEF | 45.90 b |
| Na-illite | 3.37 EF | 7.01 AB | 7.06 b |
| Ca-illite | 4.25 CDEF | 4.88 BCDEF | 29.50 b |
| Na-kaolinite | 4.44 CDEF | 7.26 A | 1.19 b |
| Ca-kaolinite | 4.31 CDEF | 4.94 BCDEF | 2.52 b |
| | <u>Apparent steady-state hydraulic conductivity</u> | | |
| Soil only | 3.75 A | 3.62 A | |
| Na-montmorillonite | 0.09 E | 0.12 E | |
| Ca-montmorillonite | 0.62 DE | 1.00 CDE | |
| Na-illite | 1.87 BC | 3.00 A | |
| Ca-illite | 1.31 CD | 0.87 CDE | |
| Na-kaolinite | 3.31 A | 3.37 A | |
| Ca-kaolinite | 3.50 A | 2.81 AB | |

† Average values for both with and without PAM.

‡ Soil without depositional seal at the surface.

§ Numbers followed by the same uppercase letters do not differ significantly at P > 0.005.

¶ Numbers followed by the same lowercase letters do not differ significantly at P > 0.005.

Kaolinite Seals

The Na- and Ca-kaolinite suspensions reduced HC in the soil columns, but this reduction did not increase with time as it did with the other clays (Fig. 4). The HCl, HC_s, and HR_{ss} of the Na- and Ca-kaolinite seals were similar and at the initial stages of leaching (fewer than four pore volumes) were only slightly below those of the base soil (Table 2). There were no significant differences in the HC and the HR_{ss} between Na- and Ca-kaolinite. Our suspensions had a pH of 6.5, so the charge on the edges of kaolinite particles was positive (Schofield and Samson, 1954; Van Olphen, 1977), and the kaolinite particles would tend to assume an edge-to-face association for both cations that, on flocculation, would form particles having an open structure and high permeability. The large size of the kaolinite clay particles suspended in DW is unaffected by the saturation cation (Lado et al., 2007), which explains the similar HC curves of the Na- and Ca-kaolinitic seals. This also explains the higher HC curves and HC_s values of the kaolinite seals compared with those of the montmorillonitic and illitic seals (Fig. 2–4, Table 2).

The effect of PAM on HC for kaolinite was similar to that for illite. The Na-kaolinite seals had higher HC (Fig. 4) and significantly higher HCl with PAM. After seven to eight pore volumes, however, the Na-kaolinite seals with PAM had the same HC as the untreated seals. The Ca-kaolinite seals did not have a significant change in HC due to the PAM, but the slight initial increase followed by a slight decrease was also evident as it was for illite.

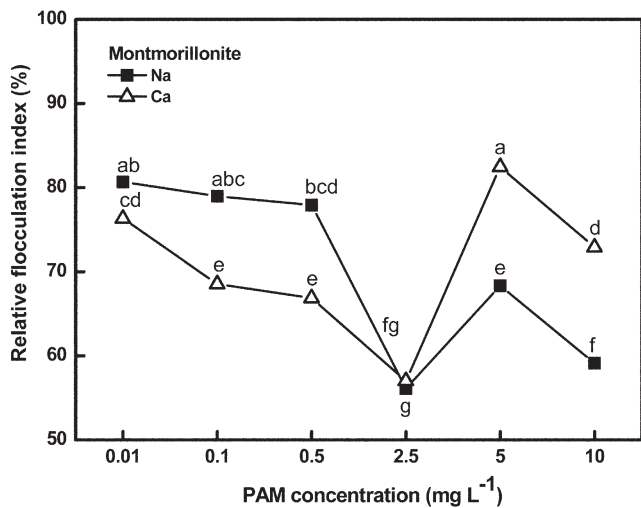


Fig. 5. Relative flocculation index (RFI) for Ca- and Na-montmorillonite suspensions as a function of polyacrylamide (PAM) concentration in the suspension. Plotted data points with the same lowercase letters are not significantly different at $P < 0.05$.

Polyacrylamide and Clay Flocculation

The RFI represents the degree of flocculation of the systems or, alternatively, serves as an indication of the amount of the small particles that are left in suspension and penetrate the base soil, clogging the water-conducting pores and decreasing the HC. Similar to the HCl and HC_{ss} data, RFI was significantly affected by the clay mineralogy, the type of exchangeable cation, and the addition of PAM, and all interactions were significant (Table 1).

The addition of PAM to the montmorillonite suspension yielded RFI values < 100 , suggesting that PAM enhanced clay flocculation (Fig. 5). In general, PAM was more effective in flocculating Ca-montmorillonite than Na-montmorillonite at low PAM concentrations, while the opposite was true for the higher PAM concentrations. The optimal concentration for both montmorillonites was 2.5 mg L^{-1} , similar to the optimal concentrations found for whole soils (McLaughlin

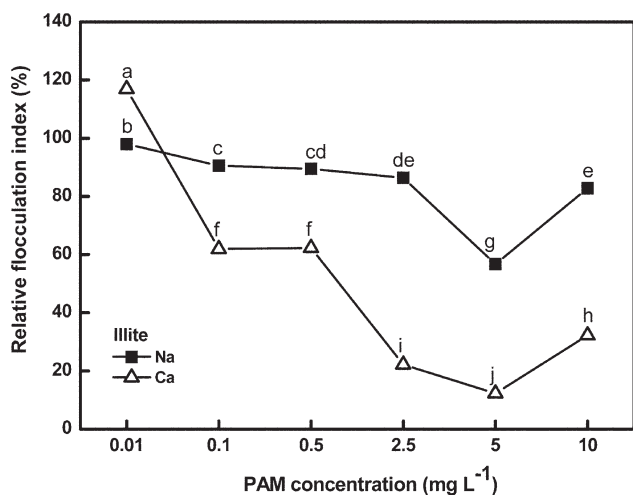


Fig. 6. Relative flocculation index (RFI) for Ca- and Na-illite suspensions as a function of polyacrylamide (PAM) concentration in the suspension. Plotted data points with the same lowercase letters are not significantly different at $P < 0.05$.

and Bartholomew, 2007). Relating this to the HC tests, the PAM concentration was highest in the beginning, and the Na-montmorillonite had a higher HCl with PAM. With more leaching and Na-montmorillonite deposition on the PAM grains at the soil surface, the concentration of dissolved PAM at the soil surface decreased and PAM was no longer effective in flocculation (Fig. 2).

Increasing the PAM concentration in the illite suspensions resulted, generally, in lower RFI values, i.e., greater clay flocculation, with this phenomenon being more pronounced in the Ca-illite than in the Na-illite (Fig. 6). The higher efficiency of PAM in flocculating Ca-illite than Na-illite suspensions suggests that cation bridging was the main mechanism bonding the anionic PAM and negatively charged illite clay particles. The effects of PAM on enhancing clay flocculation, however, could not explain its effect on the HC of the illitic depositional seals, as in the presence of PAM the HC of the Na-illite seal was higher than that of the Ca-illite seal (Fig. 3). The specific effect of PAM on the HC of Na-illite is explained by the effect of PAM on the floc density of Na-illite. Whereas the floc density of Ca-illite treated with PAM remained high (=low HC) and was not affected by the PAM treatments, the floc density of Na-illite decreased on the addition of PAM and the HC of the Na-illite seal increased (Fig. 3). This point is further discussed below.

When PAM was added to kaolinite suspensions, it served, at low PAM concentration, as a flocculant (RFI < 100) for both saturating ions (Fig. 7). At high PAM concentrations ($\geq 5 \text{ mg L}^{-1}$) it became a dispersant, similar to previously reported results (McLaughlin and Bartholomew, 2007). At high PAM concentrations, negatively charged PAM is adsorbed on the positively charged edge surfaces of the kaolinite particles, thus enhancing repulsion among the suspended negatively charged kaolinite particles (Gregory, 1989). In our study, PAM spread at the soil surface was effective in flocculating the Na-kaolinite particles during the initial stages of leaching and the HCl of the Na-kaolinite depositional seal was high (Fig. 4). With further leaching of the silt loam with the Na-kaolinite suspension, however, the concen-

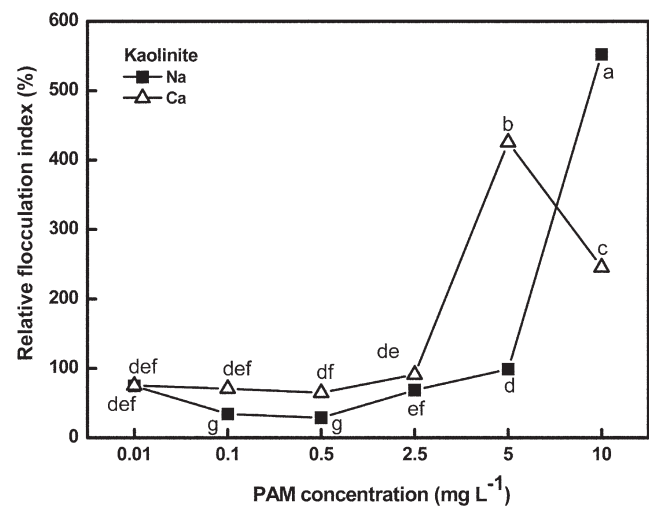


Fig. 7. Relative flocculation index (RFI) for Ca- and Na-kaolinite suspensions as a function of polyacrylamide (PAM) concentration in the suspension. Plotted data points with the same lowercase letters are not significantly different at $P < 0.05$.

tration of PAM at the soil surface decreased and the HC of the seal dropped to that of the control (Fig. 4).

Unlike the case for illite, PAM was, in general, more effective in flocculating the Na-kaolinite than the Ca-kaolinite (Fig. 7); this observation explains the higher HC curve for the Na-kaolinite seal treated with PAM than for the Ca-kaolinite seal treated with PAM (Fig. 4).

The greater impact of PAM in flocculating Na-kaolinite suspensions having pH 6.5 compared with the Ca-kaolinite suspensions having pH 5.7 (Fig. 7) was somewhat surprising because anionic PAM has been reported to be a more effective flocculant under acidic conditions and of Ca clays than of Na clays (Laird, 1997; Deng et al., 2006). For the particular case of kaolinite, Laird (1997) also reported that under acidic conditions, anionic PAM had a similar effect on the flocculation of Ca- and Na-kaolinite. The lower efficiency of PAM in flocculating Ca-kaolinite compared with Na-kaolinite, as in our study, can be attributed to the interactions between the Ca^{2+} ions and the PAM. The hydrolyzed divalent Ca^{2+} ions influence the behavior of the anionic polymer by adsorbing on the COO^- functional group of PAM to form $-(\text{COO})_2\text{Ca}$. The Ca^{2+} ion is the predominant ion at pH 6, with low concentrations of CaOH (Li and Somasundran, 1992). Calcium hydroxide may also adsorb on $-\text{COO}$ functional groups to form $-\text{COOCa}(\text{OH})$. As a result, the functional groups on the anionic PAM decrease, leading to decreased repulsive forces between these groups, adversely affecting the flocculation process (Peng and Di, 1994). The decreased flocculation in the presence of Ca^{2+} ions can also be explained by the cross linking of chains of organic polymer by the multivalent ions, leading to the loss of extendibility and the formation of curled PAM. The precipitation of hydroxyl complexes of Ca^{2+} , due to their lower solubility product at the interface than bulk solution, on the kaolinite surface can also be an important factor (Peng and Di, 1994).

Floc Density

The FD data are a measure of the degree of how dense or open the structure of the flocs formed is. Knowledge of the FD could possibly assist in understanding the changes that occurred in the HC of the depositional seal following the imposed treatment. Considering only the effect of PAM on floc density, it is expected that when PAM shows no effect on FD, there would be no effect of PAM on the HC of the seal. Conversely, when PAM decreases or increases FD, the HC of the seal is expected to increase or decrease, respectively. It should be remembered, however, that in the PAM treatments, the PAM grains at the soil surface might not reach the top of the depositional seal during prolonged leaching and the effect of spreading dry PAM at the soil surface on HC_{ss} could diminish.

The results of the FD tests (Table 3) revealed that similar FD values were obtained in the presence or absence of PAM for Ca-montmorillonite, Ca-kaolinite, Na-montmorillonite, and Na-kaolinite. This similarity in the FD data was in agreement

Table 3. Effects of clay mineralogy (montmorillonite, illite, or kaolinite), type of exchangeable cation (Ca or Na), and polyacrylamide (PAM) addition on floc density calculated from the difference between the initial weight of clay used (5 g) and the weight of clay in the decanted suspension (see Eq. [2]) (analytical method) or based on the weight of and volume occupied by the flocculated clay in Imhoff cones (cone method).

| Clay mineralogy | Exchangeable cation | Floc density | | |
|--------------------|---------------------|--------------------------|--------------|--------------|
| | | Without PAM (analytical) | With PAM | |
| | | | Cone | Analytical |
| Mg m ⁻³ | | | | |
| Montmorillonite | Na | NF† | NF | NF |
| | Ca | 0.28 (0.017)‡ | 0.23 (0.007) | 0.26 (0.015) |
| Illite | Na | 1.30 (0.016) | 0.30 (0.007) | 0.31 (0.009) |
| | Ca | 0.71 (0.005) | 1.07 (0.016) | 1.09 (0.005) |
| Kaolinite | Na | 0.07 (0.008) | 0.06 (0.006) | 0.06 (0.001) |
| | Ca | 0.27 (0.008) | 0.23 (0.008) | 0.24 (0.004) |

† NF = no settleable flocs formed.

‡ Numbers in parentheses indicate one standard deviation.

with the HC_{ss} data for the two clay types and exchangeable cations, where the HC_{ss} values in the presence and absence of PAM for each exchangeable cation and clay type were comparable (Table 2). The HC_i values were higher, however, in the presence of PAM for both Na-montmorillonite and Na-kaolinite compared with the no-PAM treatment (Table 2), but the FD was not changed in either case (Table 3). These discrepancies suggest that the HC of the depositional seal and the effects of PAM are not solely affected by the density of the seal formed but also by other factors such as the size and shape of the particles, their association and orientation in solution, and the fact that in the HC studies, depletion of PAM from the soil surface and its masking by the constant supply and deposition of sediments at the soil surface took place.

The addition of PAM decreased the FD of Na-illite and increased the FD of Ca-illite (Table 3). The decrease in the FD of the Na-illite in the presence of PAM was accompanied by a significant increase in both the HC_i and HC_{ss} of the Na-illite depositional seal (Table 2). In the case of Ca-illite, the increase in the FD following the addition of PAM had no significant effect on the HC of the Ca-illite seal, although the HC was lower (Table 2).

CONCLUSIONS

Our observations indicated that the effects of PAM addition on the HC and flocculation of depositional seals depended on both clay mineralogy and the type of exchangeable cation. Generally, in the absence of PAM, the HC of the Na-saturated depositional seals was lower than the HC of the Ca-saturated seals. This effect was more pronounced in seals made of montmorillonite than in illite or kaolinite depositional seals. The addition of PAM generally increased the HC of depositional seals formed by Na clays but it was not as effective in increasing the HC of Ca clays because, in the latter system, the clays were already in a more flocculated state. The impact of PAM on the HC of the depositional seals could be ascribed partially to the effects of PAM on the degree of clay flocculation and floc density, but clearly other factors were involved.

The initial improvement in the HC in the presence of PAM was often reduced by the deposition of more sediment. Hence, for cases of irrigation with runoff water that contains suspended sediments that might be deposited on the soil

surface, a constant supply of PAM to the soil surface is required to ensure that the beneficial impact of PAM on maintaining permeable depositional seals is a long-lasting one.

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