

# Aggregate Stability as Affected by Polyacrylamide Molecular Weight, Soil Texture, and Water Quality

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The favorable effects of the environmentally friendly, nontoxic, anionic polyacrylamide (PAM) as a soil conditioner have long been established. Some uncertainties exist, however, regarding the effects of PAM molecular weight (MW) on its performance as a soil amendment and its ability to penetrate into aggregates and stabilize interior surfaces. We studied the effects of two anionic polymers, a high-MW ( $12 \times 10^6$  Da) and a medium-MW ( $2 \times 10^5$  Da) PAM, using deionized water (electrical conductivity of  $0.004 \text{ dS m}^{-1}$ ) or a  $15 \text{ mmol L}^{-1}$  gypsum solution, on the stability of aggregates from four smectitic soils varying in clay content. Penetration of PAM into the aggregates was estimated from treating 0.5- to 1.0- and 1.0- to 2.0-mm aggregates with PAM and thereafter comparing the stability of the small aggregates to that of the large aggregates after the latter had been crushed and sieved to 0.5- to 1.0-mm size. The stability ratio (SR) ranged from 0.090 to 0.900 and tended to (i) increase with the increase in soil clay content, (ii) maintain, in the absence of PAM, a greater level with electrolyte solution than deionized water, and (iii) be greater for the PAM-treated aggregates than the control. In the finer textured soils, the SR of the initially small aggregates was generally greater than that of the initially large aggregates, indicating that most of the PAM was adsorbed on the exterior surfaces and only a small fraction of the PAM added, if any, entered into pores. A significant interaction among the treatments tested (PAM MW, aggregate size, and solution ionic strength), with respect to their effect on the SR, was identified. Consequently, neither of the two PAM polymers tested could have been singled out as preferable.

Abbreviations: DW, deionized water; GS, gypsum solution; MC, moisture content; MW, molecular weight; PAM, polyacrylamide; SR, stability ratio; VDP, volume of drainable pores.

Sustainable development and use of soil resources requires maintaining soil structure and reducing or eliminating the discharge of sediment and pollutants by runoff and erosion. The favorable effects of the environmentally friendly, nontoxic, anionic polyacrylamide (PAM) as a soil conditioner have recently been reviewed by Sojka et al. (2006). The positive effects of PAM are related to (i) preserving or increasing soil aggregation and pore continuity (Ben-Hur and Keren, 1997; Green et al., 2004; Ajwa and Trout, 2006), (ii) stabilizing the soil surface structure against shear-inducing detachment (Lentz and Sojka, 1994), (iii) increasing water infiltration and decreasing soil surface sealing (Levy et al., 1992; Shainberg et al., 1992), (iv) controlling runoff generation and soil erosion (Smith et al., 1990; Bjerneberg and Aase, 2000), (v) decreasing the settling time of particles that become suspended in runoff to aid in their deposition (Lentz and Sojka, 1994), and (vi) improving runoff water quality (Lentz et al., 1998; Sojka and Entry, 2000). These potential benefits from using PAM for soil aggregate or structural stability are influenced through complex relations among polymer properties (e.g., molecular weight [MW], charge type, and density), soil texture and structure, soil salinity, and clay mineralogy (e.g., Ben-Hur et al., 1992; Letey, 1994; Levy and Agassi, 1995; Laird, 1997; Miller et al., 1998; Levy and Miller, 1999; Green et al., 2000, 2004).

The effects of PAM as a soil conditioner could be influenced by the concentration and composition of the soil solution. The presence of salts in the soil solution enhanced the

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**Table 1. Selected properties of the four soils studied.**

Soil Type	Site	Particle-size distribution			CEC†	ESP‡	CaCO <sub>3</sub>	OM§
		Sand	Silt	Clay				
Loam	Nevatim	413	362	225	17.68	2.10	182.4	12.2
Sandy clay	Hafetz Haim	465	154	381	34.76	1.63	96.2	11.0
Clay-Y	Yagur	145	342	513	57.43	1.64	202.0	17.6
Clay-E	Eilon	137	213	650	64.90	1.12	4.6	18.2

† CEC = cation exchange capacity.

‡ ESP = exchangeable sodium percentage.

§ OM = organic matter.

favorable effect of PAM on infiltration (Shainberg et al., 1990) and hydraulic conductivity (El-Morsy et al., 1991). In the presence of electrolytes, the negative charge and the thickness of the diffuse double layer at the clay and polymer surfaces was suppressed, resulting in decreased repulsion forces and greater adsorption of soil particles to an anionic polymer (Letey, 1994; Shainberg and Levy, 1994). Thus, treatment of a soil with PAM together with a source of electrolytes, such as gypsum, was found to be very effective in controlling seal formation and runoff, because it slows both the physical disintegration of surface aggregates and the chemical dispersion of the soil clays (Levin et al., 1991; Shainberg et al., 1990; Tang et al., 2006).

When the soil is leached with a PAM solution, the presence of PAM increases the viscosity of the solution and leads to a reduction in soil hydraulic conductivity (Malik and Letey, 1992). In the presence of electrolytes, the adverse effects of PAM are alleviated, especially when the electrolytes contain Ca salts (Ajwa and Trout, 2006). It has been further suggested that in the presence of electrolytes, the PAM molecules coil and form short chains that are less effective in clogging the soil pores and reducing its permeability (Laird, 1997; Lentz, 2003; Yu et al., 2003; Ajwa and Trout, 2006). On the other hand, coiling of the PAM molecules in the presence of electrolytes in the soil solution may have an adverse effect on the soil stabilization efficiency of the PAM, since the “grappling distance” of the coiled molecules is substantially shorter compared with conditions where the molecules assume a stretched configuration.

Some uncertainty exists regarding the issue of whether PAM penetrates into aggregates or whether it adsorbs on the aggregates' exterior surfaces, and thus stabilizes only these exterior surfaces. Malik and Letey (1991) studied adsorption of high-MW anionic PAM (10<sup>7</sup> Da) by soil, soil clay, and washed quartz. Adsorption of PAM on soils and washed quartz was similar and three orders of magnitude lower than that on soil clay. They concluded that PAM adsorption by soils is mostly on exterior surfaces, and that PAM did not penetrate into aggregates. Conversely, the studies of Shaviv et al. (1987) for low-MW PAM and those of Miller et al. (1998) and Levy and Miller (1999) for high-MW PAM have shown that the PAM penetrated into pores within aggregates. Lu and Wu (2003) suggested that the depth of PAM penetration depends on PAM properties, the method of application, and the properties of the soil and water used. Levy and Miller (1999) emphasized the aspect of scale: when high-MW PAM is used, pores in small-size aggregates (<1 mm) are narrow and may not allow the large molecules of PAM to penetrate into the aggregates, while the opposite is true for large aggregates having more macroporosity and interaggregate porosity.

The effects of PAM MW on its performance as a soil amendment also deserve some attention. The MW of commercially available PAM ranges from a few thousand daltons to 20 × 10<sup>6</sup> Da (Barvenik, 1994). A PAM with high MW has longer molecules than a low-MW PAM, and is therefore considered a more efficient flocculent of colloidal systems (Theng, 1982). This efficiency of the high-MW PAM is related to the large “grappling distance” of its long molecules, which can facilitate the

formation of interparticle bridging (Theng, 1982). Similarly, Heller and Keren (2002), who studied the rheological behavior of a Na-montmorillonite suspension, reported that the higher the MW of PAM, the more effective its ability to stabilize flocs of clay in a free electrolyte clay suspension. It can be envisaged, however, that PAM of low to moderate MW will be more effective than PAM of high MW in penetrating into aggregates and contributing to their stabilization.

Contrary to the studies on clay materials, investigations of the response of soils to application of PAM with different MWs has yielded inconsistent results. Levy and Agassi (1995) studied the effects of 2 × 10<sup>5</sup> and 2 × 10<sup>7</sup> Da anionic PAMs on infiltration rate and erosion in three soils of different textures. In coarse- and medium-textured soils, high-MW PAM was more effective than low-MW PAM in maintaining a high infiltration rate. In the fine-textured soil, the effect of both polymers on infiltration was comparable. Furthermore, both polymers had similar effects on reducing erosion in the three soils (Levy and Agassi, 1995). Green et al. (2000) also noted a considerable interaction between soil type and the MW of PAM regarding its effect on the soil infiltration rate. They showed that MW played a significant role in determining the effectiveness of PAM in the stabilization of coarse-textured soils, but not of fine-textured ones (Green et al., 2000). In a later study, Green et al. (2004) observed that PAM formulas with MWs in the range of 6 to 18 × 10<sup>6</sup> Da had comparably favorable effects on enhancing the aggregate stability of soils with different textures. Conversely, for the aggregate slaking test, the effects of PAM were soil dependent, with only the low-MW PAM being effective in reducing aggregate slaking in an unstable silt loam soil (Green et al., 2004).

We hypothesized that (i) the effects of PAM on soil structural stability may depend on the ability of PAM to penetrate into aggregates and thus stabilize both exterior and interior aggregate surfaces or interaggregate porosity (i.e., macroporosity), and (ii) penetration of PAM into aggregates depends on PAM MW and solution ionic strength. Our objective was, therefore, to examine the impact of two PAM polymers having different MWs on the stability of two size classes of aggregates from four smectitic soils varying in clay content at solutions of different ionic strengths.

## MATERIALS AND METHODS

### Soils

Samples of four smectitic calcareous soils (Banin and Amiel, 1970), representing the main arable soils in Israel, were collected from the cultivated layer (0–250 mm) and used for this study: a loam (Calcic Haploxeralf)

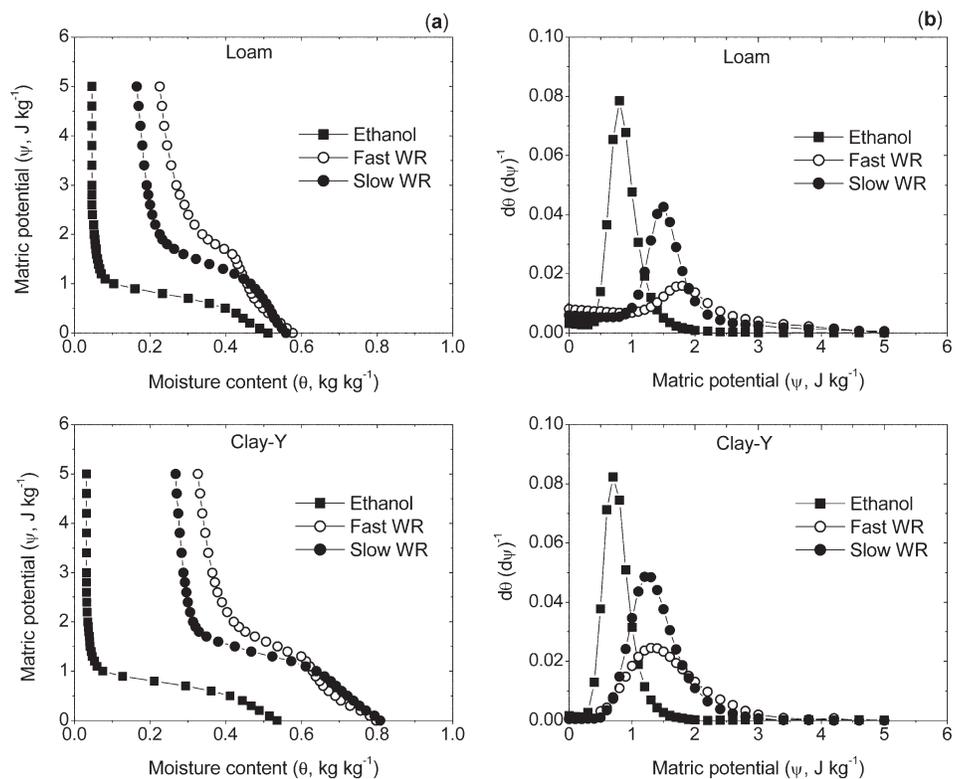
from Be'er Sheva Valley; a dark brown sandy clay (Chromic Haploxerert) from Hafetz Haim, in the Pleshet Plains; and two dark brown clays (Typic Haploxererts) from Yagur, in the Zevulun Valley (clay-Y), and Eilon, Western Galilee (clay-E). Selected physical and chemical properties of the soils are presented in Table 1. The samples were characterized for particle size distribution using the hydrometer method (Gee and Bauder, 1986), cation exchange capacity by NaOAc (Rhoades, 1982), exchangeable Na by  $\text{NH}_4\text{OAc}$  (Thomas, 1982),  $\text{CaCO}_3$  content using the volumetric calcimeter method (Nelson, 1982), and organic matter content by wet combustion (Nelson and Somers, 1982).

## Polymers

Two types of anionic PAM were studied. One PAM was a high-MW ( $12 \times 10^6$  Da) and 15% hydrolysis polymer, designated PAM(H), with a trade name of A110. The second PAM was a medium-MW ( $2 \times 10^5$  Da) and 10% hydrolysis polymer, designated PAM(M), with a trade name of Cyanamer p-26. Both polymers were provided by Cytec Industries BV, Rotterdam, the Netherlands. Polymer solutions ( $200 \text{ mg L}^{-1}$ ) were prepared with tap water [electrical conductivity  $\sim 0.9 \text{ dS m}^{-1}$ , sodium adsorption ratio of  $2 (\text{mmol}_c \text{ L}^{-1})^{0.5}$ , and pH of 6.7] under constant stirring and slow addition of polymer granules over 4 h. Polymer solutions were prepared with tap water rather than deionized water to improve the dissolution of the polymers and minimize the impact of the dissolved polymer on the viscosity of the solution (Barvenik, 1994). We expected that the use of a less viscous solution would reduce the undesired effect of solution viscosity on the degree of PAM penetration into intraaggregate porosity.

## Aggregate Preparation

The soil samples taken from the field were air dried, crushed, and sieved to 1 to 2 and 0.5 to 1 mm. We developed a procedure that ensured that (i) aggregates would not slake during wetting with the polymer solution, (ii) each individual aggregate would come in contact with the polymer solution, and (iii) the polymer in the solution would have the opportunity to penetrate into the aggregates. The following procedure was used. Plastic boxes (25 by 30 cm) were filled with a very coarse sand to form a 15-mm-thick layer that was then covered with a high-porosity (40–60- $\mu\text{m}$ ) filter paper. Aggregates from a given soil and size were gently spread on the filter paper to form a monolayer of aggregates. The aggregates were saturated at a rate of  $2 \text{ mm h}^{-1}$  from below with tap water or PAM solution, using a peristaltic pump, and were then kept in their respective solution for 24 h to reach equilibrium. The boxes were covered with plastic lids to eliminate possible evaporation. After 24 h, the solutions from the boxes were drained and the aggregates were left to dry in an oven at  $40^\circ\text{C}$  for 24 h. The small aggregates (0.5–1 mm) were sieved after drying to eliminate the broken ones. The bigger aggregates (1–2 mm) were sieved and



**Fig. 1. (a) Moisture release and (b) specific water capacity curves for the loam and clay-Y soils (0.5–1.0 mm aggregates) for fast and slow wetting rates (WR) with deionized water. The curve for ethanol represents data for both fast and slow wetting.**

crushed to a size of 0.5 to 1 mm. Finally, the polymer concentration in the solution before and after saturating the aggregates was checked. The analysis by a total C analyzer showed no considerable decrease in the polymer concentration, indicating no shortage of polymer for adsorption by the aggregates.

## Aggregate Stability Determination Theory

Soil structural stability was characterized by determining aggregate stability with the modified version of Levy and Mamedov (2002) to the High Energy Moisture Characteristics (HEMC) method. The HEMC method has been found to be a sensitive and useful method for determining the aggregate stability of arid- and humid-zone soils having a wide range of stability levels (Pierson and Mulla, 1989; Crescimano and Provenzano, 1999; Levy and Miller, 1997; Levy and Mamedov, 2002; Levy et al., 2003; Norton et al., 2006).

In the HEMC method, aggregates are wetted either slowly or rapidly in a controlled manner, and a moisture content (MC) curve at high energies (i.e., energies up to 500 mm  $\text{H}_2\text{O}$  tension) is performed. An index of aggregate stability is obtained by quantifying differences in MC curves for fast and slow wetting (Fig. 1a). For a given wetting rate, a structural index is defined as the ratio of the volume of drainable pores (VDP) to modal suction (Collis-George and Figueroa, 1984). Modal suction corresponds to matric potential ( $\psi$ ,  $\text{J kg}^{-1}$ ) at the peak of the specific water capacity curve (where  $\theta$  is the water content ( $\text{kg kg}^{-1}$ )) (Fig. 1b). The VDP is defined as the integral of the area under the specific water capacity curve and above its baseline (Fig. 1b) and thus is expressed in units of water content ( $\text{kg kg}^{-1}$ ). The ratio of the structural index obtained from fast wetting to the

structural index obtained from slow wetting is termed the stability ratio (SR). In general, the SR is used to compare the stability of aggregates on a relative scale of zero to one ( $0 < SR < 1$ ). Unity SR indicates stable aggregates that resisted slaking by fast wetting. A value of zero SR indicates that fast wetting destroyed the aggregates to the extent that all pores that drain at the matric range applied no longer exist. The use of other indices, however, to describe the stability of aggregates when using the HEMC method is also possible (Crescimano and Provenzano, 1999).

## Procedure

Fifteen grams of the oven-dried PAM-treated or untreated 0.5- to 1.0-mm aggregates were placed in a 60-mm i.d. funnel with a fritted disk to form a 5-mm-thick bed. The fritted disk had a nominal maximum pore size of 20 to 40  $\mu\text{m}$ . The fritted disk was saturated before placing aggregates in the funnel. The funnel was connected from its bottom via tubing to a peristaltic pump, which was then used to wet (full saturation) the aggregates in the funnel either rapidly ( $100 \text{ mm h}^{-1}$ ) or slowly ( $2 \text{ mm h}^{-1}$ ). Deionized water (DW, electrical conductivity of  $0.004 \text{ dS m}^{-1}$ ) or a solution containing  $2.5 \text{ g L}^{-1}$  gypsum (GS,  $15 \text{ mmol L}^{-1}$ ) was used for fast wetting of the control (untreated) and PAM-treated aggregates in the funnel. Ethanol was used (slow wetting) for the control aggregates as a reference for any given treatment (see below). Le Bissonnais (1996) also used ethanol as part of a series of treatments used to characterize aggregate stability. It has been pointed out by Le Bissonnais (1996) that the use of a nonpolar liquid such as ethanol for wetting the soil before wetting with water, for the elimination of aggregate slaking by the water, was suggested already by Henin et al. (1958).

A MC curve, at a matric potential range of 0 to  $-5.0 \text{ J kg}^{-1}$ , was obtained using a hanging water column, whereby the height of the meniscus in the pipette was decreased in increments of 0.1 to  $0.2 \text{ J kg}^{-1}$ , thereby increasing the suction applied. The volume of water that drained from the aggregates at each matric potential was recorded after a 2-min equilibrium period, and the corresponding water content of the aggregates was calculated. Preliminary studies showed that, under our experimental conditions, no additional change in the volume of drainage was noted at equilibrium times  $>2 \text{ min}$ . Each treatment was duplicated. The coefficient of variation between replicates of water content ( $\theta$ ,  $\text{kg kg}^{-1}$ ) was  $<6\%$ .

## Data Analysis

To accurately calculate the VDP and modal suction, modeling of MC curves was performed with the following seven-parameter modified van Genuchten model (Pierson and Mulla, 1989):

$$\theta = (\theta_s - \theta_r) \left[ 1 + (\alpha\psi)^n \right]^{1/n-1} + A\psi^2 + B\psi + C \quad [1]$$

where  $\theta_s$  and  $\theta_r$  are pseudo saturated and residual gravimetric water contents, respectively;  $\alpha$  and  $n$  control the location and steepness, respectively, of the S-shaped inflection of the MC curve; and  $A$ ,  $B$ , and  $C$  are the quadratic terms added by Pierson and Mulla (1989) to improve fitting of the model to the MC curve. The specific water capacity curve ( $d\theta/d\psi$ ), needed for obtaining the value of modal suction, was computed by differentiating Eq. [1] with respect to matric potential, and had the explicit form

$$\begin{aligned} (d\theta/d\psi) = & (\theta_s - \theta_r) \left[ 1 + (\alpha\psi)^n \right]^{1/n-1} \\ & (1/n-1)(\alpha\psi)^n \frac{n}{\psi \left[ 1 + (\alpha\psi)^n \right]} \\ & + 2A\psi + B \end{aligned} \quad [2]$$

The VDP was calculated by subtracting the terms for pore shrinkage ( $2A\psi + B$ ) from Eq. [2] and analytically integrating the remainder of that equation.

We deviated from the usual procedure used to determine the SR (e.g., Pierson and Mulla, 1989; Levy and Miller, 1997; Levy and Mamedov, 2002), and calculated the SR as the ratio of the structural index for any given treatment obtained by fast wetting with DW or GS to the structural index obtained with ethanol (slow wetting) for the same soil. Other researchers have also used wetting by ethanol in their aggregate stability studies for the purpose of avoiding the breakdown of the aggregates during the wetting process (e.g., Le Bissonnais, 1996; Lado et al., 2004; Annabi et al., 2007). Furthermore, we observed no notable differences between fast and slow wetting on the MC curves of the samples for wetting with ethanol. Thus, use of the structural index of ethanol as a reference allowed us to compare the effects of treatments on slaking (or pore size distribution) and aggregate stability of all soils in the range of 0 to 1.

## Statistical Analysis

The aggregate stability study tested four main treatments, four soil types, two levels of solution ionic strength, two aggregate sizes, and three PAM levels [control, PAM(H), and PAM(M)]. A full factorial design was used for this study of 48 treatments ( $4 \times 2 \times 2 \times 3$ ), each in two replicates. A multifactor ANOVA procedure (SAS Institute, 1995) was used to compare the effects of the four main treatments and their interactions on aggregate stability. When significant interactions ( $P < 0.05$ ) were found, treatment mean comparisons were made using the Tukey-Kramer honestly significant difference test at a significance level of 0.05 (SAS Institute, 1995).

## RESULTS AND DISCUSSION

### Characteristics of the Water Retention Curves

The water retention curves (i.e., the matric potential vs. the specific water capacity [ $d\theta/d\psi$ ] curves) for the loam and clay-Y soils wetted with DW or ethanol (fast and slow) are presented in Fig. 1; for ethanol, only one curve is presented as no differences in the curves for slow and fast wetting were observed. When DW was used, the differences between the fast- and slow-wetted curves was ascribed to aggregate slaking that itself was attributed to entrapped air, hydration of the exchangeable cations and clay surfaces of the soil particles, and differential swelling (Le Bissonnais, 1996). The hydration of exchangeable cations and clay surfaces, measured in kilojoules per gram of soil (Keren and Shainberg, 1975), weakens the bonds between soil colloids. In the case of ethanol, because of its relatively low dielectric constant ( $\epsilon = 25.3$ ) compared with water ( $\epsilon = 80.1$ ), no hydration was expected. The similarity in the fast and slow wetting curves for ethanol (Fig. 1) indicated that, in the absence of hydration, also no slaking took place. We postulate that, under conditions of no hydration, the soil aggregates remain strong. Thus, the aggregates can overcome the pressure built by entrapped air during wetting, and air can escape easily from the soil pores during wetting as the size of the pores is no longer reduced by the hydrated exchangeable cations and clay surface.

Although soil texture differed among the soils tested, they all exhibited similar water retention curves when wetted with ethanol (see example in Fig. 1 for data from the loam and clay-Y soils). For all the soils, the mean VDP was  $0.412 \pm 0.011 \text{ kg kg}^{-1}$  and the mean modal suction was  $0.7 \pm 0.015 \text{ J kg}^{-1}$ . We used low levels of matric potential (0–50 cm) to drain the aggregates. Under these conditions, it was mostly the interaggregate porosity that was being drained. Ethanol,

being a nonpolar liquid, did not hydrate the soil and therefore filled mainly the interaggregate porosity. Consequently, when no hydration was involved, the fact that the aggregates from the different soils all had the same size (0.5–1.0 mm), and thus similar interaggregate porosity, led to comparable characteristics of the water retention curves for the soils studied.

The water retention curves of some selected treatments for the loam and clay-Y soils are presented in Fig. 2. The use of PAM, GS, or both had considerable effects on the shape of the water retention curves. These observations suggested that the treatments studied impacted the sensitivity of the aggregates to slaking due to entrapped air or osmotic stress (low electrolyte concentration). To quantify the effects of the treatments, we opted to use the data obtained from the wetting with ethanol as a reference, and therefore calculated the SR of the aggregates as the ratio of the stability index for a given treatment to the stability index obtained from the wetting by ethanol.

### Drainable Porosity

A quantitative measure of the impact of the treatments on the structural stability and the resistance of aggregates to slaking can be obtained from the VDP data (i.e., the volume of pores that could not hold water at the suction range applied) for the various soils (Fig. 3). Results of a multifactor ANOVA test showed that the main treatments as well as their interactions, generally, had a significant effect on VDP (Table 2). Because soil treatment accounted for >75% of the variance (Table 2), however, we repeated the ANOVA test for each soil separately (Table 3), where the existence of a significant interaction among the main treatments was again noted.

The VDP data extended across a wide range, from 0.090 to 0.595 kg kg<sup>-1</sup> (Fig. 3), suggesting that the treatments tested had a substantial impact on the stability of the aggregates. In general, VDP tended to increase with the increase in soil clay content; in the loam, VDP was

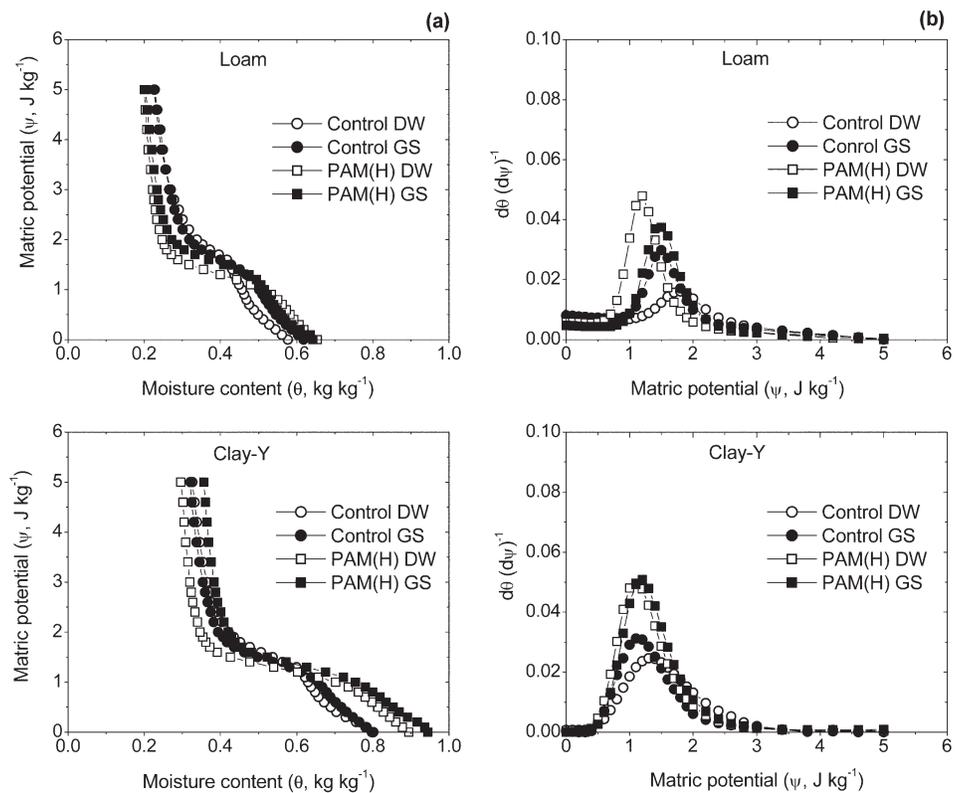


Fig. 2. (a) Moisture release and (b) specific water capacity curves for loam and clay-Y soils (control and treated with high-molecular-weight polyacrylamide, PAM(H), 0.5–1.0-mm aggregates) for fast wetting with deionized water (DW) and gypsum solution (GS).

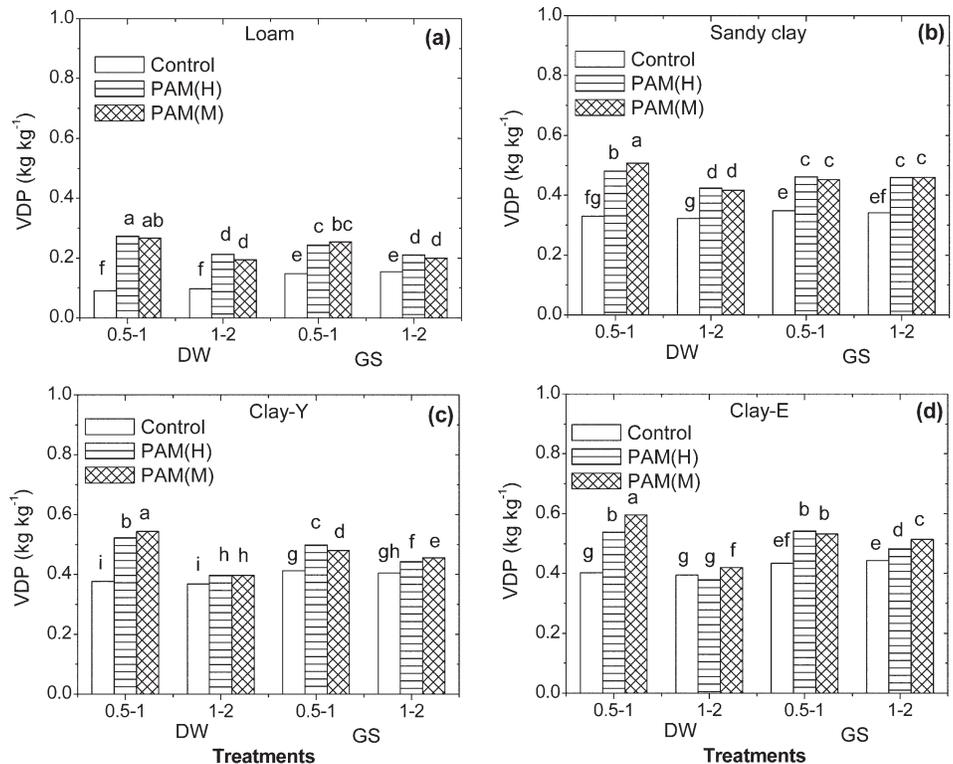


Fig. 3. Volume of drainable porosity (VDP) as a function of polyacrylamide (PAM) molecular weight for 0.5- to 1.0- and 1.0- to 2.0-mm aggregate size and either deionized water (DW) or gypsum solution (GS). For a given soil, columns labeled with same letter are not significantly different at the  $P < 0.05$  level. PAM(H) = high-molecular-weight PAM; PAM(M) = moderate-molecular-weight PAM.

**Table 2. Significance levels for treatment (soil type, water quality, polyacrylamide [PAM] type, and aggregate size) effects on the volume of drainable pores (VDP) and the stability ratio (SR).**

Source	df	VDP			SR		
		Sum of squares	F ratio	P > F	Sum of squares	F ratio	P > F
Soil	3	1.152	8339.82	***	3.077	3089.66	***
Water†	1	0.010	223.04	***	0.020	60.28	***
PAM‡	2	0.003	20.96	***	0.826	1244.34	***
Aggregate size§	1	0.203	2201.30	***	0.136	409.87	***
Soil × water	3	0.010	37.47	***	0.001	0.93	NS
Soil × PAM	6	0.004	44.42	***	0.023	11.37	***
Soil × aggregate size	3	0.003	11.03	***	0.019	19.01	***
Water × PAM	2	0.054	1183.07	***	0.026	38.75	***
Water × aggregate size	1	0.007	54.24	***	0.048	143.71	***
PAM × aggregate size	2	0.022	484.14	***	0.067	100.84	***
Soil × water × PAM	6	0.002	16.26	***	0.018	9.10	***
Soil × water × aggregate size	3	0.025	271.69	***	0.007	7.08	**
Soil × PAM × aggregate size	6	0.005	16.46	***	0.010	5.02	**
Water × PAM × aggregate size	2	0.011	122.72	***	0.031	47.05	***
Soil × water × PAM × aggregate size	6	0.001	3.78	**	0.006	3.06	*
Model	47	1.514	699.51	***	4.314	276.53	***
Error	48	0.002			0.016		
Corrected total	95	1.516			4.330		

\* Significant at the 0.05 level; NS, not significant.

\*\* Significant at the 0.01 level.

\*\*\* Significant at the 0.001 level.

† Water quality (deionized water or gypsum solution).

‡ High or medium molecular weight.

§ Small or large initial aggregate size.

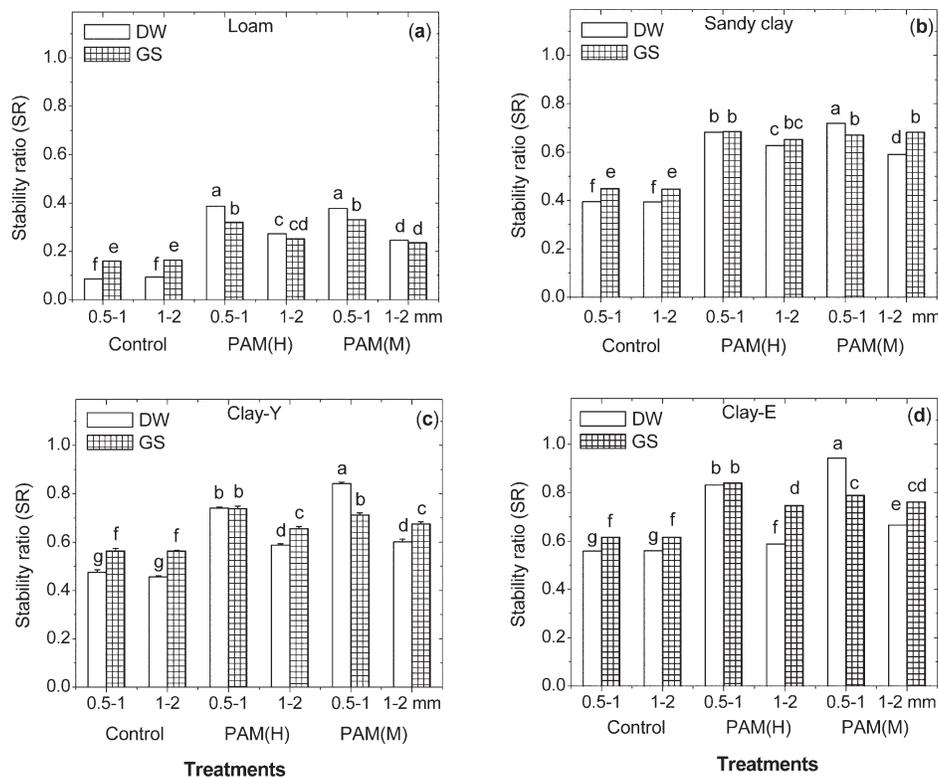
<0.3 kg kg<sup>-1</sup>, and increased to levels >0.5 kg kg<sup>-1</sup> in the clay soils (Fig. 3). Treating the aggregates with PAM, irrespective of its MW, resulted in aggregates with greater VDP levels than the untreated aggregates (Fig. 3). The difference in VDP between PAM-treated and control aggregates was, in general, more distinct in the initially small aggregates than the initially large ones. In addition, in the control aggregates, wetting with GS resulted in greater VDP than wetting with DW (Fig. 3).

Aggregate slaking generally results in the formation of a larger number of particles of smaller size than the original aggregates. This, in turn, causes the interparticle pore size distribution to shift toward a larger number of smaller pores and thus to a decrease in the VDP. Certain conditions enhance aggregate resistance to slaking, such as the presence of cementing or stabilizing agents, e.g., clay (Kemper and Koch, 1966) or PAM (Yu et al., 2003), and the suppression of differential swelling via the addition of electrolytes to the soil solution (e.g., GS treatment). Under these conditions, major changes in the original pore size distribution among the tested aggregates occurred, and hence high VDP levels were maintained.

### Stability Ratio

The SR data (Fig. 4) represent aggregate stability in relative terms, i.e., the sensitivity to slaking of aggregates from a given treatment relative to their sensitivity to slaking when wetted by ethanol. Similar to the results for the VDP data, results of a multifactor ANOVA test for the SR data showed that soil treatment accounted for >70% of the variance (Table 2). Thus, we repeated the ANOVA test for each soil separately and noted that, generally, the main treatments and their interactions had significant effects on the SR data (Table 4).

The SR data varied more than the VDP data, ranging from 0.090 to 0.900 (Fig. 4). Similar to the trends observed for the VDP, the SR tended to (i) increase with an increase in soil



**Fig. 4. Stability ratio of soils as a function of polyacrylamide (PAM) molecular weight [high molecular weight PAM(H) or moderate molecular weight PAM(M)], aggregate size (0.5- to 1.0- or 1.0- to 2.0-mm) and water quality (deionized water [DW] or gypsum solution [GS]). For a given soil, columns labeled with same letter are not significantly different at the  $P < 0.05$  level.**

clay content, (ii) maintain, in the absence of PAM, a greater level when GS was used than when DW was used, and (iii) be greater for the PAM-treated aggregates than the control aggregates. The latter observation was not trivial as it suggested that PAM enhanced the resistance of aggregates to slaking. Our finding disagreed with previously published data that suggested that PAM has only a negligible impact on aggregate slaking of stable soils (Green et al., 2004).

Detailed analysis of the combined impact of PAM MW, aggregate size, and water quality led to the division of soils into two groups with respect to their response to these treatments. The first group included the sandy clay and the two clay soils and the other included the loam.

### Sandy Clay and Clay Soils

For both types of PAMs, the SR of the initially small aggregates was, in general, greater than that of the initially large aggregates (Fig. 4). The lesser SR of the initially large aggregates was explained as follows. Some of the interior surfaces of the large aggregates have become external surfaces following the process of sieving and gentle crushing to a size of 0.5 to 1 mm. We suggest that, during the stage where the aggregates were saturated by a PAM solution, part of the PAM molecules penetrated to a certain depth into the pores within the aggregates (Lu and Wu, 2003), thus stabilizing interior pore surfaces of the aggregates only to a certain degree. Consequently, after sieving and crushing, the exterior surfaces of the aggregates contained a mixture of surfaces. One part consisted of surfaces that were exposed to PAM and were thus stabilized; the other part consisted of formerly interior surfaces that mainly were not stabilized by the PAM and thus exhibited lower resistance to slaking. Therefore, the overall stability of the initially large aggregates was less than that of the initially small aggregates, where all the external surfaces were stabilized by the PAM.

Based on the difference in the SR between the two groups, we conclude that (i) to enhance aggregates' resistance to slaking, it is enough to stabilize the exterior surfaces of the aggregates with PAM, and (ii) most of the PAM added to the aggregates was adsorbed on the exterior surfaces of the aggregates and only a small fraction of the PAM added, if any, entered into pores within the aggregates. The latter conclusion was consistent with the findings of Malik and Letey (1991), who also studied small aggregates. Evidently, pores in small-size aggregates are narrow and may not allow significant penetration of the large molecules of PAM into the aggregates; conversely, it has been suggested that, in large aggregates, the large molecules of PAM may penetrate into the aggregates (Levy and Miller, 1999).

In the PAM(H)-treated aggregates, water quality had no effect on the SR of the initially small aggregates; conversely, the initially large aggregates' SR was greater when wetted with GS than with DW (Fig. 4). The inconsistent impact of water quality in the two groups of aggregates was related to the aforemen-

**Table 3. Significance levels for treatment (water quality, polyacrylamide [PAM] type, and aggregate size) effects on the volume of drainable pores for each soil.**

Source	df	Sum of squares	F ratio	P > F
<u>Loam</u>				
Water†	1	0.0035	53.30	***
PAM‡	2	0.0628	481.22	***
Aggregate size§	1	0.0036	27.44	**
Water × PAM	2	0.0072	110.97	***
Water × aggregate size	1	0.0022	33.47	***
PAM × aggregate size	2	0.0052	39.70	***
Water × PAM × aggregate size	2	0.0011	8.38	**
Model	11	0.0856	119.20	***
Error	12	0.0008		
Corrected total	23	0.0864		
<u>Sandy clay</u>				
Water	1	0.0003	10.77	**
PAM	2	0.0795	1356.64	***
Aggregate size	1	0.0005	9.15	**
Water × PAM	2	0.0041	139.36	***
Water × aggregate size	1	0.0040	135.82	***
PAM × aggregate size	2	0.0012	21.01	***
Water × PAM × aggregate size	2	0.0025	42.03	***
Model	11	0.0921	285.78	***
Error	12	0.0004		
Corrected total	23	0.0924		
<u>Clay-Y</u>				
Water	1	0.0013	33.80	***
PAM	2	0.0314	406.90	***
Aggregate size	1	0.0015	19.81	***
Water × PAM	2	0.0226	585.94	***
Water × aggregate size	1	0.0060	156.59	***
PAM × aggregate size	2	0.0086	111.04	***
Water × PAM × aggregate size	2	0.0037	48.41	***
Model	11	0.0753	177.15	***
Error	12	0.0005		
Corrected total	23	0.0757		
<u>Clay-E</u>				
Water	1	0.0081	158.17	***
PAM	2	0.0394	385.80	***
Aggregate size	1	0.0015	14.59	**
Water × PAM	2	0.0280	549.35	***
Water × aggregate size	1	0.0123	241.78	***
PAM × aggregate size	2	0.0146	142.92	***
Water × PAM × aggregate size	2	0.0051	49.53	***
Model	11	0.1089	194.09	***
Error	12	0.0006		
Corrected total	23	0.1095		

\*\* Significant at the 0.01 level.

\*\*\* Significant at the 0.001 level.

† Water quality (deionized water or gypsum solution).

‡ High or medium molecular weight.

§ Small or large initial aggregate size.

tioned limited ability of the PAM molecules to penetrate into the soil aggregates and stabilize interior surfaces. In the case of the initially small aggregates, treating the exterior surfaces of the aggregates with PAM was sufficient to maintain the stability of the aggregates and the use of a saline solution had no advantage over the use of DW with respect to aggregate stability. In the initially large aggregates, however, where PAM-treated and fresh untreated surfaces were exposed to the wetting solution,

**Table 4. Significance levels for treatment (water quality†, polyacrylamide [PAM] type‡, and aggregate size) effects on the stability ratio for each soil.**

Source	df	Sum of squares	F ratio	P > F
<u>Loam</u>				
Water	1	0.002	10.35	**
PAM	2	0.166	417.91	***
Aggregate size§	1	0.027	137.72	***
Water × PAM	2	0.009	23.84	***
Water × aggregate size	1	0.006	29.99	***
PAM × aggregate size	2	0.016	41.19	***
Water × PAM × aggregate size	2	0.003	8.42	**
Model	11	0.230	105.53	***
Error	12	0.002		
Corrected total	23	0.233		
<u>Sandy clay</u>				
Water	1	0.005	16.29	**
PAM	2	0.315	488.26	***
Aggregate size	1	0.007	22.05	***
Water × PAM	2	0.002	2.75	NS
Water × aggregate size	1	0.005	13.99	**
PAM × aggregate size	2	0.003	5.40	*
Water × PAM × aggregate size	2	0.006	8.82	**
Model	11	0.343	96.62	***
Error	12	0.004		
Corrected total	23	0.346		
<u>Clay-Y</u>				
Water	1	0.007	30.93	***
PAM	2	0.176	392.41	***
Aggregate size	1	0.047	210.35	***
Water × PAM	2	0.016	34.57	***
Water × aggregate size	1	0.014	62.94	***
PAM × aggregate size	2	0.019	43.24	***
Water × PAM × aggregate size	2	0.009	20.39	***
Model	11	0.288	116.86	***
Error	12	0.003		
Corrected total	23	0.291		
<u>Clay-E</u>				
Water	1	0.007	11.50	**
PAM	2	0.192	164.79	***
Aggregate size	1	0.073	125.93	***
Water × PAM	2	0.017	14.68	***
Water × aggregate size	1	0.030	51.79	***
PAM × aggregate size	2	0.038	32.37	***
Water × PAM × aggregate size	2	0.019	16.43	***
Model	11	0.376	58.70	***
Error	12	0.007		
Corrected total	23	0.383		

\* Significant at the 0.05 level; NS, not significant.

\*\* Significant at the 0.01 level.

\*\*\* Significant at the 0.001 level.

† Water quality (deionized water or gypsum solution).

‡ High or medium molecular weight.

§ Small or large initial aggregate size.

the presence of electrolytes in the GS that suppress differential swelling contributed to the resistance of the aggregates to slaking and thus yielded greater SR values in comparison to aggregates wetted by DW.

In the PAM(M)-treated aggregates, the effect of water quality depended on the initial size of the aggregates. In the initially large aggregates, as noted for the PAM(H) treatment and for similar reasons, the use of GS resulted in a greater SR than the use of DW. For the initially small aggregates, the opposite was noted (Fig. 4), which was ascribed to the difference in the configuration of the PAM molecules in the two water qualities (DW and GS). In the presence of electrolytes (GS), the PAM molecules apparently tend to coil (Laird, 1997; Ajwa and Trout, 2006), thus the “grappling distance” of the coiled molecules is shorter than that of uncoiled molecules. Hence, although the use of GS reduced differential swelling, it did not enable the PAM(M), because of the coiling of its already relatively short molecules, to exhibit its full potential as a conditioner. Consequently, the SR of the aggregates in DW, where the PAM molecules could assume a stretched configuration, was greater.

The two PAMs studied had, in general, comparable SRs (for a given initial aggregate size) when GS was used (Fig. 4). As mentioned above, in the presence of GS the PAM molecules tend to coil. We postulate that when coiled, the differences in the length of the molecules arising from the differences in the MW between the two PAM polymers was reduced to such a degree that both PAM polymers had a similar impact on the stability of similar-size aggregates. When DW was used, the effect of PAM MW depended on the initial aggregate size. For the initially small aggregates, PAM(M) had a more favorable effect on the SR than PAM(H) (Fig. 4). This observation was in agreement with the findings of Green et al. (2004) for a silt loam. Furthermore, we suggest that, in comparison to the PAM(H), probably more of the PAM(M) was able to penetrate into the aggregates, and thus improve their overall stability. In the initially large aggregates, the effect of PAM MW differed among the three soils (Fig. 4). In general, however, the PAM(H) was more effective in the soil with relatively low clay content (sandy clay), while the PAM(M) was more effective in stabilizing the soil with the highest clay content (Clay-E). Green et al. (2000) also noted that different soils responded in dissimilar ways to the MW and charge density of PAM and therefore no specific PAM could have been singled out as preferable among the PAMs tested.

### Loam

Unlike the sandy clay and the two clay soils, where PAM MW had a significant effect on the SR, in the loam, the two PAM treatments studied had, in general, comparable SR values for a given aggregate size (Fig. 4). This observation further illustrates the intricate relation between PAM MW and soil type with respect to the efficiency of PAM as a stabilizing agent.

The effects of water quality on the SR of the loam aggregates were opposite to those noted in the other three soils. In the initially small aggregates, the use of DW in the loam resulted in a significantly greater SR than the use of GS, irrespective of PAM MW; in the other three soils, this observation was noted only with

the PAM(M) (Fig. 4). Evidently the importance of the PAM molecules assuming a stretched configuration (as explained above) was essential in stabilizing the aggregates of the loam soil, not only in the PAM with medium MW, but also in the PAM with the high MW. In the initially large aggregates, water quality had no effect on the SR of the loam, whereas in the other three soils the GS yielded greater SR values than DW (Fig. 4). We postulate that the contribution of differential swelling to aggregate slaking in PAM-treated aggregates was more important in the fine-textured soils than in the loam. Therefore, in the loam, the use of the GS had no advantage over the use of DW in determining aggregate stability.

## CONCLUSIONS

Aggregate stability, estimated from the sensitivity of the aggregates to slaking, was found to depend on the combined effects of PAM MW, soil solution ionic strength, and aggregate size. The results indicated that, to enhance aggregates' resistance to slaking, it is enough to stabilize the exterior surfaces of the aggregates with PAM. Because most of the PAM added to the aggregates was adsorbed on the exterior surfaces of the aggregates, the small fraction of the PAM that entered into the aggregates' pores, had no significant impact on aggregate stability. Treating aggregates with PAM, irrespective of its MW, improved their stability in comparison to that of untreated aggregates. No specific PAM could have been singled out as preferable between the two PAM polymers tested, as the effects of the PAM varied among the soils tested and depended on initial aggregate size and solution ionic strength.

Our results support the use of PAM as an amendment for stabilizing soil aggregates, which, in turn, could assist in the control of seal formation, runoff, and erosion. The choice of PAM to be used as a soil amendment, however, needs to be made in accordance with the soil to be treated and the specific conditions prevailing in the field. Further studies are needed to evaluate the role of PAM MW in stabilizing soil aggregates under prolonged aging duration and cycles of wetting and drying.

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