# Use of Synthetic Polymers and Biopolymers for Soil Stabilization in Agricultural, Construction, and Military Applications

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**Abstract:** Three relatively new applications for controlling wind and water erosion using polyacrylamide copolymers are described that take advantage of their ability to stabilize and add structure to soil. In the first application, low concentrations of anionic, high purity polyacrylamide (PAM) eliminates sediment in runoff water by more than 90% when added to irrigation water at 10 ppm, or at a rate of 1 to 2 kg $ha^{-1}$ per irrigation. Lab-furrow tests were utilized to characterize the role of molecular weight, charge, and ion concentrations in applying PAM during irrigation. In the second application, PAM is applied at construction sites and road cuts at rates of 22.5 kg $ha^{-2}$ (tenfold higher rates than in irrigation control) resulting in reduction in sediment runoff by 60–85% during (simulated) heavy rains. Finally, a formulation of PAM mixed with aluminum chlorohydrate and cross-linked poly(acrylic acid) superabsorbent at a ratio of (6:1:1) has been applied to create helicopter landing pads that minimize dust clouds during helicopter operation. This formulation was specifically developed to minimize dust clouds during landing of helicopters in fine, arid soils such as those potentially encountered in the Middle East. A biodegradable alternative to PAM, acid-hydrolyzed cellulose microfibrils, was tested in lab-scale furrows and was less effective than PAM at similar concentrations, but show promises. Microfibrils reduce sediment run-off in lab-furrow tests by 88% when applied at eight- to tenfold the concentration of PAM.

**DOI:** 10.1061/(ASCE)0899-1561(2007)19:1(58)

**CE Database subject headings:** Erosion; Runoff; Polymers; Soil stabilization.

## Introduction

The use of polyacrylamide (or PAM) as a soil-stabilizing additive has expanded significantly in the past decade with particular focus in this report on (1) agricultural use to control soil erosion during irrigation (Lentz et al. 1992; Lentz and Sojka 1994; Paganyas 1975; Wallace 1997; Flanagan 1997; Anonymous 1995); (2) reduction of wind and soil erosion at construction sites and road cuts (Roa-Espinosa et al. 2000); and (3) rapid formation of helicopter landing pads to minimize dust clouds during helicopter landings, particularly for military operations. Polyacrylamide, or PAM, loosely refers to the class of polyacrylamide homopolymers, and their acrylamide/acrylic acid copolymers (see Fig. 1). PAM sold commercially for wind or water erosion control is typically an anionic copolymer with roughly 15–40% of the acrylamide chain segments replaced by an acrylic acid group. Thus, commercial PAM used for soil stabilization is a polyelectrolytic random copolymer, potentially surrounded by oppositely charged salts to counter anionic charges. Molecular weights of PAM used for these applications range from 3 to 25 million, with the more common commercial products in the range of 12–20 million.

### *PAM Erosion Control during Irrigation*

Polyacrylamide (PAM) has long been recognized as a viable soil conditioner because it stabilizes soil surface structure and pore continuity (DeBoodt 1990; Malik and Letey 1991). The agricultural use of PAM has grown rapidly since 1995 with the commercial introduction of adding the conditioner to irrigation water, rather than the soil. Lentz and Sojka (1994) reported reduction in soil runoff by up to 97%, along with improved water infiltration (Mitchell 1986; Sojka and Lentz 1996), by adding high molecular weight anionic PAM to irrigation water at very low concentration (at 2–10 g $m^{-3}$, or 2–10 ppm) during the first several hours of irrigation. By adding PAM to the irrigation water, soil structure is improved in the all-important 1–5 mm thick layer at the soil/water interface of the 25–30% of field surface contacted by flow-

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Note. Associate Editor: Hilary I. Inyang. Discussion open until June 1, 2007. Separate discussions must be submitted for individual papers. To extend the closing date by one month, a written request must be filed with the ASCE Managing Editor. The manuscript for this paper was submitted for review and possible publication on February 11, 2005; approved on July 29, 2005. This paper is part of the ***Journal of Materials in Civil Engineering***, Vol. 19, No. 1, January 1, 2007. ©ASCE, ISSN 0899-1561/2007/1-58–66/$25.00.

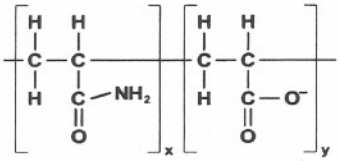


**Fig. 1.** PAM: polyacrylamide and poly(acrylic acid) random copolymer

ing water. PAM has since been identified as an environmentally safe and highly effective erosion preventing and infiltration-enhancing polymer, and is applied on over 1.1 million acres per year of irrigated cropland.

### Erosion Control during Construction

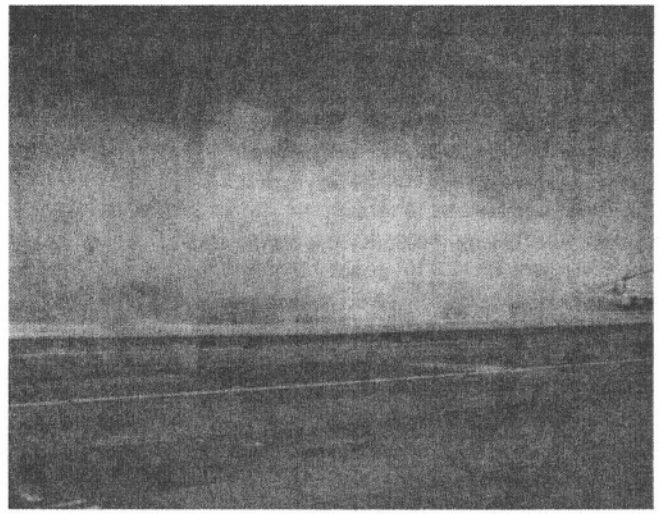
Sediment runoff is the biggest pollutant by volume in the state of Wisconsin (Roa-Espinosa 1996). Runoff from increasingly urbanized areas is a major problem when large areas of soil are exposed to the erosive action of rainfall and concentrated flow. Inadequate erosion control at construction sites results in increased sedimentation on streets and neighboring developments, increased suspended solids in lakes and rivers, and loss of integrity of building sites. With increasing legislation and litigation, contractors are facing increasing fines and actions against sediment runoff from construction sites. Application of PAM soil stabilizers presents a potential solution.

Roa-Espinosa et al. (2000) reported that, based on a three-year study of construction sites using PAM for controlling soil loss, PAM provided a 60–97% reduction in runoff-sediment for periods of roughly one month between applications. In this report, we will expand upon this particular study to provide improved strategies for application of PAM at construction sites to decrease sediment loss.

### PAM Use in Helicopter Landing Pads

Dust clouds, commonly referred to as "brown-outs" by the aviation community, are a constant hindrance to helicopter operations. Problems are especially acute during military operations, when landing pads have not always been predesignated, and often must be hastily prepared. As can be seen in Fig. 2(a), dust can completely obliterate vision, fouling helicopter moving parts and ventilation systems, and result in unhealthy operating conditions near the landing sites. Dust clouds vary depending on the soil type, the type of helicopter, wind velocity, and the helicopter's approach to the landing area, but are especially problematic in sandy soils with >10% fine particles.

Extensive testing (Roa-Espinosa and Mikel 2004) occurred at the Marine Corps Air Ground Combat Center (MCAGCC) in 29 Palms, Calif. This base was chosen because of the similar soil types in the Mojave Desert to soil types in Afghanistan, Iraq, and Kuwait (UNEP World Soils Map). After significant testing of off-the-shelf commercial PAM products as outlined in Table 1, it was concluded that a single, as-received product was inadequate for military helicopter operations. An array of products was tested using eight plots that were $45 \times 45$ m in dimension. These were compared against a control plot, with success determined by combining: (1) the amount of dust collected at various distances (10, 20, and 40 m) from the center landing mark; (2) subjective analysis of digital photos and video footage during helicopter landing;



(a)

(b)

**Fig. 2.** Brown outs: helicopter landing in arid conditions (a) before; (b) after application of Tri-PAM mixture

(3) pilot and crew comments on the visibility during landing and take off; and (4) the amount of dust collected from the crew's static night goggle material.

The PAM mix that performed best based on these criteria (Roa-Espinosa and Mikel 2004) was a fine-grained 35% anionic PAM/acrylic acid copolymer with a molecular weight above 20 million. The higher the molecular weight, the better the PAM efficacy. This high molecular weight PAM was combined with aluminum chlorohydrate and superabsorbent cross-linked PAM/acrylic acid copolymer (mixed at a ratio of 6:1:1, respectively), a mixture called "Tri-PAM." Tri-PAM was applied dry at a rate of 65 g $m^{-2}$, and then stabilized by applying roughly 8 L of water per $m^2$. After 15 min, the pad was ready for use.

Fig. 2(b) depicts a helicopter landing on a Tri-PAM-treated landing pad, with significantly better visibility and ultimately a significantly safer take-off/landing than the untreated pad [Fig. 2(a)]. A follow-up application of emulsified PAM (0.05%) in water every month was used to reseal the surface and increase the life of the landing pad. After final testing at MCAGCC, an urgent need to use this newfound technology became evident in Operation Iraqi Freedom. In July 2003, Combat Service Support repre-

**Table 1.** Summary of the Soil Amendment Products Tested and Their Potential Combinations for Dust Reduction during Helicopter Operation

| Product | Solubility | Method of application | Binding of sand | Binding of fines | Overall performance |
|---|---|---|---|---|---|
| Anionic PAM (Soilnet 1000) 35% acrylic acid, molecular weight=18–20 $\times 10^6$ g/mol | High | Dry | High | High | High |
| Anionic PAM (Floerger 934) 34% acrylic acid, molecular weight=24 $\times 10^6$ g/mol | High | Dry | High | High | High |
| Anionic PAM (Floerger 90035 K) 35% acrylic acid, molecular weight=12 $\times 10^6$ g/mol | Medium | Dry | High | Low | Low |
| Anionic PAM (Cytec 835) 32% acrylic acid, molecular weight=15 $\times 10^6$ g/mol | None | Dry | High | Low | Medium |
| Anionic PAM emulsion (Cytec A1820), molecular weight ~10 $\times 10^6$ g/mol M | Low | Wet | High | Medium | Low |
| Cationic PAM (alcostant) | High | Wet | Low | Medium | Medium |
| Superabsorbent: crosslinked PAM/polyacrylic acid copolymer (Stockhausen FLAVORPAC) | None | Dry | High | Low | Medium |
| Aluminum chlorohydrate (REACH 501) | High | Dry/wet | Low | High | High |

sentative from the Marine Corps Warfighting Laboratory deployed with a team from Marine Wing Support Squadron 273 to use the results of this collaborative effort to create a series of landing sites in Kuwait and Iraq.

Tri-PAM solution is relatively economical. The average price for products for one 50 × 50 m landing zone is about $400–$500, with relatively little material required compared to full construction of a landing pad. For example, during Operation Iraqi Freedom, two 463 L pallets of material were capable of treating over eight acres of soil.

The purpose of this report is to discuss some recent commercial applications of PAM as a water/soil additive for controlling wind and water erosion. Specifically, we will outline particular formulations and application details that optimize PAM-use during these applications. Then, we will describe various lab-results to elucidate some mechanisms that are important during these field applications. These include the size and shape of the polymer, its charge distribution, and its interaction with ions during application. In particular, lab-scale furrow tests will be used to convey the effect of PAM molecular weight and ion addition on erosion control. Finally, we will discuss the potential for applying biopolymers as biodegradable alternatives to PAM. Since PAM is not a biodegradable polymer, and not suitable for organic farming techniques, "green" alternatives to PAM are needed.

## Materials and Methods

Polyacrylamides from a variety of sources were used to establish parameters important for soil stabilization. All of the PAM samples were random copolymers of acrylamide and acrylic acid (Fig. 1), varying in molecular weight, charge content (acrylic acid concentration), and relative solubility in water. Cytec Industries of Stamford, Conn., provided a series of samples with the trademark, Magnifloc, and product Codes 835A, 836A, 837A, 846A, 905N, 442C, 492C, and 494C. Samples were also provided by Allied Colloids, Suffolk, Va., and trademarked Percol (product Codes 338, E24, and LT25). Additional PAM samples ranging in molecular weight from 40,000 to 15 million were obtained from Soilnet (Madison, Wis.), Stockhausen GMBH (Germany), and SNF Floerger (SNF Canada, Toronto) as noted in the text. Superabsorbing polymers consisting of crosslinked poly(acrylic acid) gels were also tested, and were obtained from Stockhausen GMBH (Germany), brand name FLAVOR-PAC. Molecular weight and charge data for all polymers were generally provided by the manufacturers.

### Construction Site Tests

Small test plots (1 × 1 m) at a construction site in Dane County, Wis. were used to test the effect of different PAM and PAM-mulch formulations on reducing sediment runoff. PAM solution (Cytec Magnifloc 836A) at a concentration of 0.045% was applied using a garden sprinkler at a rate of 22.5 kg $ha^{-1}$, while dry PAM (22.5 kg $ha^{-1}$) was applied with a typical garden fertilizer spreader. A rainfall simulator, which produced 6.4 cm/h, was applied for 10 min, and runoff from each plot was collected into a tank for 40–50 min. Runoff samples were extracted at 10 min intervals by diverting runoff into a collection container during each replication to determine sediment yield. Samples were dried at 110°C for 24 h and weighed to determine an average sediment load for each trial.

### Irrigation Model Furrows

For modeling agricultural use of PAM during erosion, control laboratory-scale furrows were created as outlined previously (Orts et al. 2000). Soils were dried, sieved and remoisturized to 18% (w/w) water content, and then formed into miniature furrows roughly 1/100th the size of a full furrow. Furrows were created by cutting a v-shaped wedge-cut 2.5 cm wide and 2.5 cm deep into a 1-m-long polystyrene foam slab. This foam slab was rested within a frame with adjustable angles (2–45°). For all experiments, the angle was set at angle of 5°. Moist soil (500 g) was packed flat into the v-shaped cuts into a 1 m long bar, and then a narrow furrow with dimensions 0.6 × 0.6 cm was pressed lengthwise down the center of the packed soil to create a mini-furrow. Test solutions were pumped down the furrow at flow rates of 7 mL $min^{-1}$ using a peristaltic pump. Water was collected at the lower end of the furrow and tested for solids contents by measuring turbidity using a Shimadzu UV-Vis UV1601 spectrophotometer, and correlating turbidity with those from a set of preweighed soil dispersions. The relative suspended solids content was determined for at least five replicate samples at each condition. Two types of soil were tested in the lab-furrow. The first soil was a Zacharias gravelly clay loam soil obtained from Patterson,

Calif., a northern California farming community 90 miles south of Sacramento. This soil was chosen because it is typical of California's Northern Central Valley (Michael McElhiney, USDA Natural Resources Conservation Service, personal communication 1998). It has a very low ion concentration, with an average electrical conductivity of $<0.05$ $dSm^{-1}$. The second soil sample was from the USDA-ARS Northwest Irrigation and Soils Research Laboratory at Kimberly, Id. It is of particular interest because it has been well characterized in many PAM field studies (Lentz and Sojka 1994). The Idaho soil is highly erodible Portneuf silt loam (coarse-silty, mixed, mesic, Durixerollic Calciorthid), with an average electrical conductivity of 0.5 $dSm^{-1}$ and a sodium adsorption ratio (SAR) of 0.6 (Carter et al. 1973).

### Cellulose Microfibrils

The microfibrils used in this study were derived from softwood dissolving pulp (kindly provided by Rayonier Corp.), cotton (Whatman filter paper #4), and bacterial cellulose from the food source, nata de coco. Microfibril isolation followed the method of Revol et al. [(1992), "Preparation and application of ordered cellulose microfibril suspensions," US Patent 5,629,055 (1995)] and Dong et al. (1998) as modified by Orts et al. (1998). Cellulose sources were ground in a Wiley mill to pass through a 20 mesh. Individual crystallites were isolated by hydrolysis with the following conditions: cellulose concentration of 10% (w/w) in 60% sulfuric acid at 46°C for 75 min. Hydrolysis was completed by adding fivefold excess water, isolating the microfibrils by centrifugation, and repeating this rinsing step until the pH of the suspension was above 5.0. Under these conditions, the crystallites obtain a charged outer surface by the formation of sulfate esters on the exposed, outer anhydroglucan residues (Revol et al. 1995). Charge coverage is estimated at 0.2 negative ester groups per $nm^2$. The procedure used here produces crystallites 0.2–0.5 microns in length (Orts et al. 1998).

### Small Angle X-Ray Scattering, SAXS, Measurements

The size and shape of PAM molecules in water was estimated using small angle X-ray scattering (SAXS) data obtained from a Bruker-AXS Nanostar small angle scattering diffractometer. This system uses an HR-PHK pinhole rotating anode SAXS camera with point source focus of 0.3 mm × 0.3 mm, and Cu-$K\alpha$ filtered radiation at 45 kV/90 mA. The beam was attenuated via a pair of cross-coupled Göbel Mirrors and pinholes of 750/400/1000 μm at distances from the source of 200/925/482 mm, respectively. Data was collected using a Bruker AXS HI-STAR two-dimensional (2D) position sensitive detector, and radially averaged over the scattering vector $Q=4\pi \sin\theta/\lambda$, where $\theta$=scattering angle, and $\lambda$=wavelength. Determining the size and shape of the PAM molecule in water is hampered by the fact that SAXS data does not provide a direct measurement of average size and shape. Rather, there is an inverse-Fourier transform relationship between the scattering data and the structural information, which is described mathematically as a "pair distance distribution function," $p(r)$. Data was analyzed (as will be described more fully below in the "Result and Discussion" section) using both Bruker commercial software (SAXS for Windows NT and fitting software developed in-house by Jan Skov Pedersen. The $p(r)$ function was calculated based on an iterative modeling procedure. A model $p(r)$ function was used to generate the "best-fit" scattering data. Linear regression analysis was used to fit this model scattering data with the measured scattering curves.

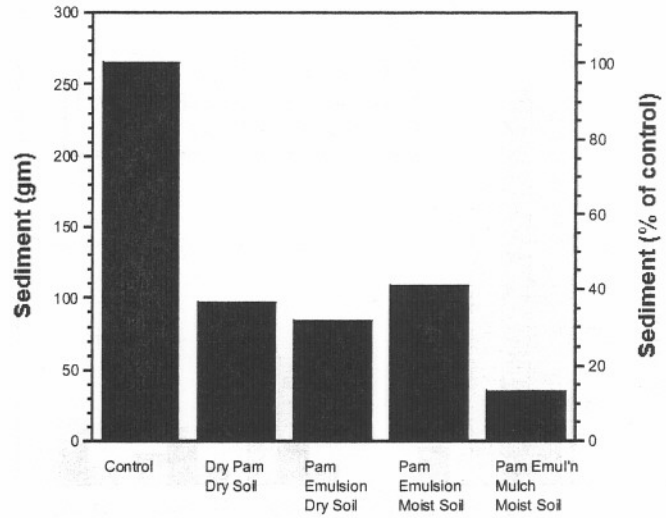



**Fig. 3.** Sediment data from runoff at construction-site plots under simulated rainfall, treated with different PAM treatments, as noted

## Results and Discussions

### Erosion Control during Construction

Test plots (1 m × 1 m) on a construction site with a 10% slope were used to assess different PAM and PAM-mulch formulations for minimization of sediment in runoff water. The results of this study are summarized in Fig. 3. The application of PAM on the soil surface significantly reduced the amount of sediment collected from the runoff. It is noteworthy that the amount of runoff water was statistically the same for all plots, implying that PAM did not stop runoff, just the amount of sediment in the runoff. When a covering of mulch/seeding followed application of PAM solution, sediment reduction was 87% (see the $y$-axis on the right) compared to the control (no PAM/dry soil). Regardless of the application method, PAM was effective in reducing sediment yield by at least 60% in the test plots. Roa-Espinosa (1997) has reported previously that application of PAM on a monthly basis will maintain more than 70% sediment reduction. The ease of application, low maintenance, and relatively low cost associated with PAM make it a practical solution to reduce sediment runoff at construction sites. This practice has been put into use throughout Wisconsin, especially by contractors who may face liability for sediment runoff (Roa-Espinosa 2000).

### PAM Erosion Control during Irrigation and Molecular Weight Effects

The agricultural use of PAM has grown rapidly since 1995 because of the commercial introduction of adding the conditioner to irrigation water, rather than the soil. Lentz and Sojka (1994) reported both reduced soil losses of up to 97% and improved water infiltration by adding high molecular weight anionic PAM (2 ppm) to irrigation water at very low concentration during the initial hours of irrigation. However, not all PAM was equally effective. It is to be shown that the molecular weight of PAM is an important factor in its application in the helicopter landing pad formulations (described in Table 1) as it was in field studies by Lentz and Sojka (1994).

Fig. 4 outlines the effectiveness of PAM in reducing soil runoff as a function of molecular weight, MW. Results of the

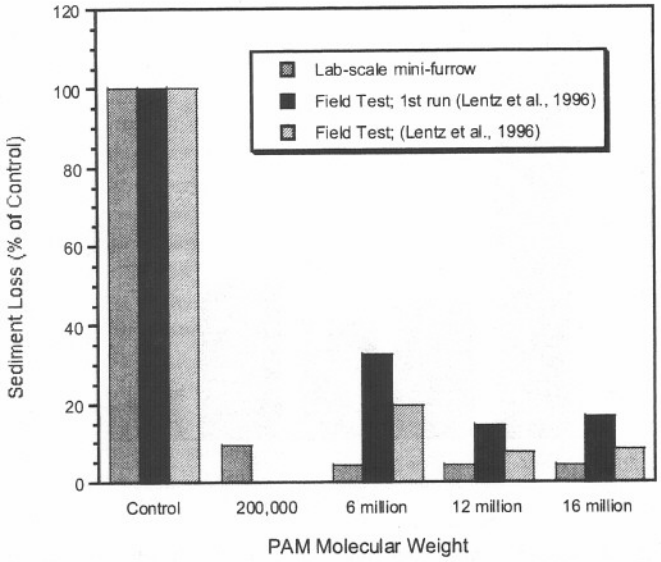



**Fig. 4.** Effect of PAM molecular weight on sediment in runoff (compared to sediment levels in controls with no PAM added) for both field tests (Lentz and Sojka 1994) and laboratory-scale furrow results

from lab-scale mini-furrow tests are compared with field tests reported elsewhere by Lentz and Sojka (1994). Sediment levels in the runoff water are reported based on a comparison between a polymer-treated furrow with that from a control furrow (no added polymer). Trends in Fig. 4 show that sediment reduction for furrows with added anionic PAM (all at roughly 18% charge density) increases with increasing MW up to at least 200 K. Above MW of roughly six million, there is little significant improvement in sediment reduction in the runoff. However, the reduction in sediments for the lab-scale furrow experiments are higher than for any reported field test. Applied studies, such as the field tests (Lentz and Sojka 1994) and the helicopter landing pad studies (Roa-Espinosaand and Merkel 2004) support the general guideline that the MW be above 12 million for commercial PAM soil stabilization.

### *Salt Effects*

The effectiveness of PAM varies with the type of soil, as well as with the type and concentration of dissolved salts (ions) in the water. The results in Fig. 5(a) were derived using highly calcareous soil from the Central Valley of Northern Calif. This particular soil has a pH of 8.4, and a low concentration of soluble, exchangeable ions, such as calcium. This soil was chosen because it did not interact well with PAM, especially using the relatively clean, ion-free water found in Northern California.

In lab-scale furrow experiments, PAM concentration was held constant at 10 mg $L^{-1}$ (10 ppm), [the concentration recommended in USDA-NRCS Conservation Standard (Anonymous 1995)], while the concentration of added salt levels was varied. The trends in Fig. 5(a) show a significant decrease in sediment levels as ion concentration increases for all of the added salts studied (calcium nitrate, calcium chloride, magnesium sulfate, and sodium chloride). In fact, for this particular soil, PAM is completely ineffective without the addition of salts. The addition of all salts up to 2 mM concentration reduces sediment levels, but calcium nitrate was the most effective. A reduction in sediment levels of 92% relative to control was achieved by adding 2 mM calcium

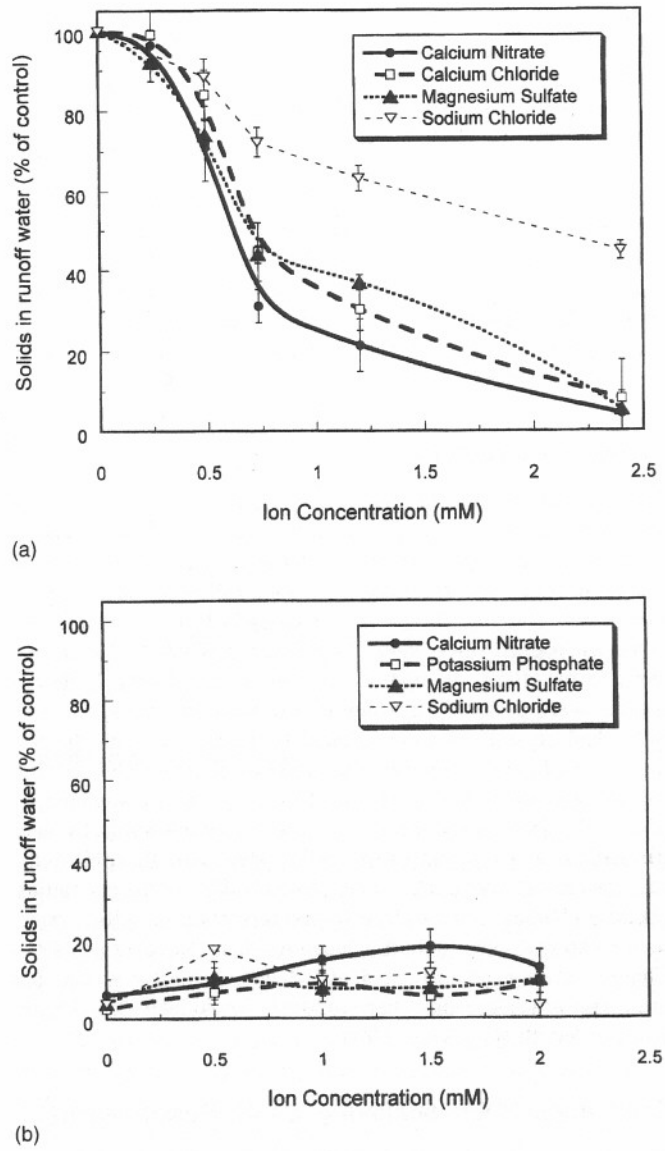



**Fig. 5.** Effect of added salt to PAM solutions (10 mg $L^{-1}$) during lab-scale furrow irrigation experiments using (a) highly calcareous soil from the Central Valley of Northern Calif., pH=8.4, low calcium; (b) highly erodible Portneuf silt loam (coarse-silty, mixed, mesic, Durixerollic Calciorthid), with high calcium levels

nitrate. The divalent salts were significantly more effective than monovalent sodium, as shown by the NaCl curve in Fig. 5(a).

Although the results in Fig. 5(a) are not universal, they document sediment reduction for one set of conditions related to specific soil type, water composition, and PAM properties. To contrast these results, a soil from Kimberly, Id. was tested under similar lab-furrow conditions. This soil is a highly erodible Portneuf silt loam (coarse-silty, mixed, mesic, Durixerollic Calciorthid), with an average electrical conductivity of 0.5 $dSm^{-1}$ and a sodium adsorption ratio (SAR) of 0.6 (Carter et al. 1973). Thus, it already has high levels of ions. Results in Fig. 5(b) are in direct contrast to those outlined in Fig. 5(a). For the Idaho Portneuf silt loam, no addition of salt was required for PAM solutions (at 10 mg $L^{-1}$) to reduce sediment runoff by up to 94%. Furthermore, salts made no significant improvement to PAM efficacy, and may have even hindered its effectiveness.

These results complement the report of Lu et al. (2002), a

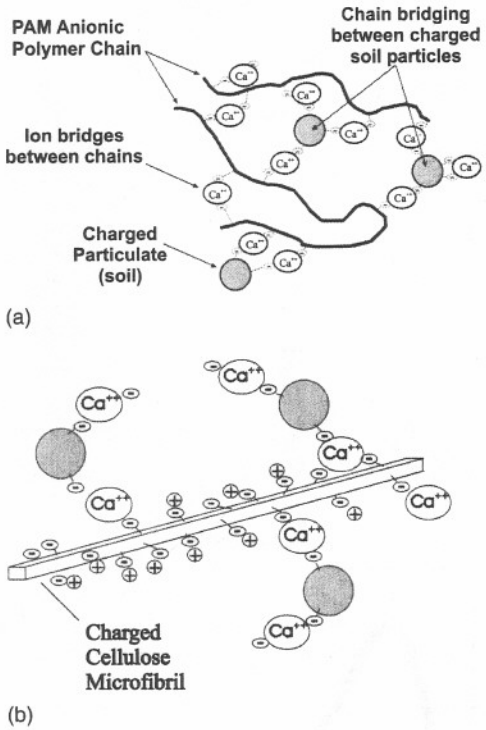



**Fig. 7.** Schematic depiction of (a) anionic PAM; (b) charged cellulose microfibrils interacting with charged soil particles in the presence of calcium

result is that the scattering information from this sample is beyond the resolution of the SAXS equipment used in this study, which is roughly 500 Å. Thus a featureless pair distance distribution function implies that the PAM chains at low calcium concentration in water are larger than 500 Å. This is not surprising, considering that Muller et al. (1979) showed by light scattering and intrinsic viscosity measurements that the radius of gyration for high molecular weight anionic PAM ranged from 950 to 1300 Å. It also been established (Muller et al. 1979) that the radius of gyration of these anionic polymers becomes smaller with increasing salt addition, especially for the addition of divalent calcium. Muller et al. (1979) used light scattering to show a four- to fivefold decrease in polymer size as a result of calcium addition. The ten fold variation in chain size implied by the results here, though is even larger than that seen by Muller et al. (1979), and must be explored more fully using a small angle scattering system that covers the full size range of interest. Also worthy of future study is the hint that the chain my form an elongated structure in the presence of calcium.

It has been hypothesized that high molecular weight PAM works most effectively in binding soil because its large size allows it to span between a greater number of soil particles. A puzzling result, then is coupling the two observations that the ability of anionic PAM to control erosion is increased as calcium is added, yet the apparent polymer chain size is smaller. Clearly, polymer size is not the only mechanistic factor that is important, and other binding mechanisms must be considered.

Anionic PAM interacts with soil potentially via three potential mechanisms: (1) coloumbic charge interactions; (2) hydrogen bonding; and (3) van der Waals interactions. The latter two mechanisms are clearly important, but are difficult to measure. For a polyelectrolyte polymer with up to 35% acrylic acid active sites, charge interactions are clearly a dominate determinant of interaction with soil. Fig. 7(a) is a schematic diagram of the role of charges in interacting with soil particles. Charge bridging between soil particles, which are often anionic, and PAM via divalent cations, such as calcium, explains the role of calcium and magnesium in improving the efficacy of PAM. The fact that PAM needs to "bridge" between different soil particles explains the relative effectiveness of high MW polymers. The presence of high sodium in the soil further complicates discussions of mechanisms. It is well known (Frenkel et al. 1978) that sodium has the opposite effect of salinity on soils. The primary physical processes associated with high sodium concentrations are soil dispersion and clay platelet and aggregate swelling.

## Environmental Impact of PAM—Alternatives to PAM

One overriding environmental impact of PAM is reduced erosion-induced sediment runoff. However, this very positive environmental impact is accompanied by several concerns, many of which have been addressed in the literature (Barvenik 1994; Barvenik et al. 1996; Shanker and Seth 1986; Shanker et al. 1990). The main environmental concerns in PAM-use are: (1) the unknown effect of long-term accumulation of this nondegradable, synthetic polymer in the soil; (2) questions regarding the formation of potentially toxic substituents during its degradation; and (3) concerns regarding the purity of PAM due to the toxicity of the acrylamide monomer (Barvenik 1994).

Since PAM degrades slowly, the long-term effects on organisms must be considered. One must note, though, that PAM has been used in wastewater treatment for decades, with little evidence that it is detrimental to organisms during release (Hamilton et al. 1994; Lande et al. 1979). Low levels of PAM are acceptable in potable water and in animal feeds. Degradation of PAM incorporated into soil has been estimated at about 10% per year (Barvenik et al. 1996), although application of PAM near the soil surface is thought to accelerate degradation via various pathways, including UV photosensitive chain scission (Barvenik 1994), deamination (Kay-Shoemake et al. 1998a,b,c), and shear-induced chain scission (Lande et al. 1979).

With a PAM degradation rate of ~10%, the amount of PAM accumulation for the uses described in this paper should not be considered significant, considering the low application rates (only kg/ha). For example, in field studies of furrow erosion, Sojka and Lentz (1996) showed that only 1–3% of applied PAM leaves fields in runoff, and that this is quickly adsorbed by entrained sediment or ditch surfaces. Barvenik (1994) noted that anionic PAM is safe for aquatic organisms at surprisingly high concentrations, with $LC_{50} > 10$ times the inflow dosage rates. Water impurities further buffer environmental effects by quickly deactivating dissolved PAM.

Polymer purity is important since the acrylamide monomer is very toxic. Manufacturers have dealt with this issue by maintaining very strict purity standards. Monomer content in the final product is often reported as less than 0.05%. Maintaining this level of purity likely adds to the cost of PAM. Two factors contribute to minimizing the toxic risk of acrylamide. First, the acrylamide monomer forms highly reactive free radicals. Thus, within minutes, it is likely to react with other entities and form less-toxic conjugates. More importantly, the monomer in its free-radical form is not likely to accumulate. Secondly, increasing data on the biological degradation of PAM by typical soil bacterial show that the observed route of degradation does not lead to the monomer (Kay-Shoemake 1998a,b,c), rather soil bacteria generally remove

the nitrogen source from the polymer via deamination. Bologna et al. (1999) showed that AMD is not absorbed by plant tissues, and apparently breaks down rapidly even when injected into living plant tissue.

The positive environmental effect of PAM is its proven effectiveness at reducing erosion-induced sediment loss by more than 90%, thus preventing sediment runoff. PAM keeps pesticides, herbicides and even construction waste at the field or construction site, preventing them from entering our riparian waterways. For example, PAM prevents yearly topsoil runoff of up to 15.8 t $ha^{-1}$ (Lenz and Sojka 1994) and at least three times that as on-field erosion. In addition to preventing herbicide and pesticide loss, PAM was recently shown to sequester biological and chemical contaminants of runoff, providing significant potential for reduced spread of phytopathogens, animal coliforms, and other toxic organisms (Entry and Sojka 2000, 2003; Entry et al. 2002, 2003).

PAM is not biodegradable and would not be allowed during organic farming operations. There is increasing incentive to develop biodegradable, renewable PAM alternatives that will reduce wind and water erosion and be suitable for organic farming operations. We have screened over 100 biopolymers for their sorptive behavior with soil and their ability to control water-induced erosion (Orts et al. 2000). These include chitin, chitosan, substituted starches (ether and ester linked starches), substituted cellulosics (cellulose xanthate, cationic cellulose, hydroxymethycellulose, etc.), and cheese whey. Many of these show an affinity to soil, but are not likely to compete with PAM on a cost per treatment basis. Several biopolymers however continue to hold promise. These include chitosan, starch xanthate, cellulose xanthate, and several specific polysaccharides.

In this study, cellulose microfibrils are highlighted as a potential PAM alternative. Cellulose microfibrils are charged nanoscale crystallites isolated from cellulose sources by acid hydrolysis (i.e., heating in 60% sulfuric acid at 60°C). Typical cellulose microfibrils are long crystalline "needles" ranging in size from 10 to 20 nm in width, with an average length of 100 to 400 nm (Dong et al. 1998; Orts et al. 1998). As a result of the acid hydrolysis, acidic sulfate ester groups are formed on the microfibril surface, creating an anionic surface.

Sources of cellulose microfibrils are widely diverse, and potentially providing a wide range of potential nanoparticle properties. Sources include wood, straw, bacteria, and sea animals. Fig. 8 shows the effect of increasing microfibril concentration for three different microfibril sources—cotton, softwood, and bacterial cellulose. All three cellulosic samples reduce sediment runoff with little significant difference between sources. The size of agriculturally based fibers and microfibrils reportedly vary depending on the isolation procedure and cellulose source (Dong et al. 1998). For example, preliminary unpublished data from our group suggests that rice straw microfibrils are ~20 to 25% shorter than cotton. More work will determine if these sources differences will matter for soil stabilization.

Compared to PAM, however, significantly higher concentrations of 60–80 $gL^{-1}$ were required to match the efficacy of PAM. This represents an eight- to tenfold higher concentration. More research is needed to determine the costs of processing these microfibrils to see if such a high concentration means huge cost differences. Also, further work will determine if particular microfibril sources exhibit any advantages, comparing the effect of fiber source on surface properties, length, and their ability to interact within polymer matrices.

Especially interesting is the mechanistic implications of the efficacy of these microfibrils. Potentially they can interact with soil using the same mechanisms as PAM (see Fig. 7). Their charged surface allows coulombic interaction with charged soil particles. Cellulose is rich in hydroxyl groups, so microfibrils can readily form hydrogen bonds. Finally, microfibrils are relatively large, spanning 100 to 400 nm, and could thus span between different soil particles.

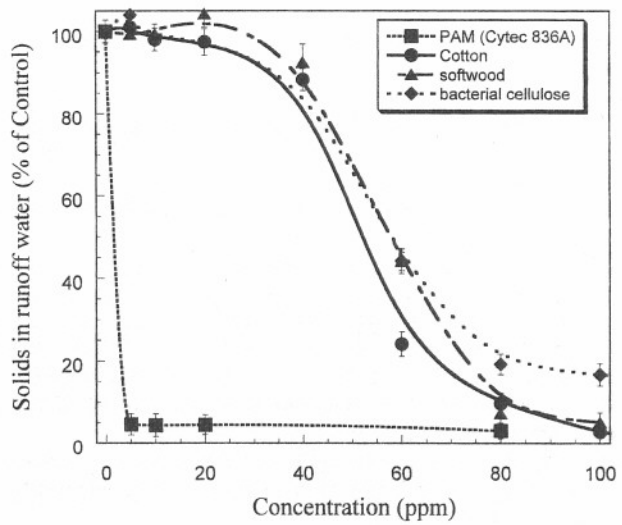



**Fig. 8.** Lab-scale furrow results showing the effect of additive concentration on soil sedimentation from erosion using three different sources of charged cellulose microfibrils; cotton (●), softwood (▲), and bacterial cellulose (♦) compared with PAM (■)

## Concluding Remarks

PAM has been applied to more than half a million ha of irrigated land in the United States for erosion control and runoff protection. The practice is spreading rapidly in the United States and worldwide, especially Australia. Construction applications of PAM will continue to grow, especially if contractors face fines for sediment pollution. Military applications of PAM may not be obvious to the general public, but could result in a significant number of critically important soil stabilization applications, such as rapid deployment of helicopter landing pads. The increasing market pull of organic farming techniques is a strong reason to explore alternatives to PAM, since PAM cannot be used during organic farmering. Biopolymer alternatives to PAM, which generally degrade more rapidly, would likely have marketing advantages due to the public *perception* of the relative safety of natural compounds. Interest in development of biopolymer alternatives for PAM may increase due to economic drivers. If the price of natural gas, the feedstock for acrylamide production, continues to climb, the industry may seek alternative polymers. For a more complete history of PAM, a bibliography of new PAM uses, and user technical information see ⟨http://kimberly.ars.usda.gov/pampage.shtml⟩.

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