POLYACRYLAMIDE IN AGRICULTURE AND ENVIRONMENTAL LAND MANAGEMENT

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I. Early Uses of Soil Conditioners
II. Major Conditioner Types
III. Synthetic Conditioner Uses and Application Strategies
IV. Overview of Current PAM Use
V. PAM Defined and Described
VI. PAM Properties Affecting Efficacy
VII. Early Contributions
VIII. Surface Irrigation
IX. Sprinkler Irrigation
X. Infiltration
XI. PAM Safety, Field Retention, and Environmental Impacts
XII. PAM Effect on Organisms in Runoff and Soil
XIII. PAM Degradation
XIV. PAM and Ca
XV. PAM for Construction Sites and Other Disturbed Lands
XVI. Canal and Pond Sealing
XVII. Biopolymers
XVIII. Conclusions
References

Anionic polyacrylamide (PAM) has been sold since 1995 to reduce irrigation-induced erosion and enhance infiltration. Its soil stabilizing and flocculating properties improve runoff water quality by reducing sediments, N, dissolved reactive phosphorus (DRP) and total P, chemical oxygen demand (COD), pesticides, weed seeds, and microorganisms in runoff. PAM used for erosion control is a large (12–15 Mg mol^{-1}) water-soluble (non-cross-linked) anionic molecule, containing <0.05% acrylamide monomer. In a series of field studies, PAM eliminated 80–99% (94% avg.) of sediment in runoff from furrow irrigation, with a 15–50% infiltration increase compared to controls on medium to fine-textured soils. Similar but less dramatic results occur with sprinkler irrigation. In sandy soils infiltration is often unchanged

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by PAM or can be slightly reduced. Typical seasonal application totals in furrow irrigation vary from 3 to 7 kg ha^{-1}. Research has shown little or no consistent adverse effect on soil microbial populations. Some evidence exists for PAM-related yield increases where infiltration was crop-limiting, especially in field portions having irregular slopes, where erosion prevention eliminated deep furrow cutting that deprives shallow roots of adequate water delivery. Modified water management with PAM shows great promise for water conservation. High effectiveness and low cost of PAM for erosion control and infiltration management, coupled with easier implementation than traditional conservation measures, has resulted in rapid adoption. About 800,000 ha of US irrigated land use PAM for erosion and/or infiltration management. In recent years, PAM has been deployed for uses beyond agricultural erosion control, including construction site erosion control, use in storm water runoff ponds to accelerate water clarification, soil stabilization and dust prevention in helicopter-landing zones, and various other high-traffic military situations. Among the newest topics being researched is the use of PAM to reduce ditch, canal, and pond seepage, using specific application protocols that take advantage of its increase of water viscosity at higher concentrations.

I. EARLY USES OF SOIL CONDITIONERS

Understanding the current success of and growing attention to polyacrylamide (PAM) and related synthetic and biopolymers for land care uses and environmental protection is easier if seen in the context of soil conditioner technology development. Animal and green manures, peat, crop residues, organic composts, lime, and various other materials have been used as soil conditioners for thousands of years. Conditioner identification, technology, and use have been largely a marriage of convenience between agriculture's need for chemical and physical maintenance or improvement of the soil, and for disposal or management of waste materials from the full range of human activities. Over time, the spectrum of materials used as soil conditioners has expanded to include composted manures, sawdust, or other milling residues as well as other organic industrial wastes such as food, textile, and paper processing wastes. Mineral materials such as rock phosphates, gypsum, coal dust, rock flour, and sand have also been used.

The terminology and concept of soil amendments and conditioners have become associated primarily with physical conditioning. Chemical conditioning for provision of plant nutrients to soil is largely ascribed to materials termed fertilizers. Clearly, however, there is overlap. Lime, for example, neutralizes acid, affecting pH, some structural phenomena such as aggregation, and fertility by affecting ion balances and reducing rooting impairment from acid soil conditions. Coal can provide humic acids which stimulate stabilization of soil organic fractions (Dzhanpelsov *et al.*, 1984). Many fertilizers directly and indirectly affect soil physical properties and many conditioners directly and indirectly affect soil fertility. The overlap occurs because of the intimate association of soil physicochemical processes and their linkage to soil-supported biotic processes, cycles, and functions. The designation of fertilizer versus conditioner tends to be based on the dominant effect. Categories are often assigned by law, based on the chemical analysis and/or the proof of claims for the materials. The development of soil conditioner technology has been comprehensively reviewed (De Boodt, 1975, 1990, 1992; Gardner, 1972; Stewart, 1975; Wallace, 1995, 1997, 1998a,b; Wallace and Terry, 1998; Wallace and Wallace, 1995).

II. MAJOR CONDITIONER TYPES

There are three major classes of soil conditioners: natural organic materials, inorganic or mineral materials, and synthetic materials consisting primarily of chemical polymers and surfactants. Organic conditioners have typically been used to increase infiltration and retention, promote aggregation, provide substrate for micro- and mesobiological activity, improve aeration, reduce soil strength, and resist compaction, crusting, and surface sealing. Effects, such as increased infiltration and water retention, are often evident immediately on soil incorporation, whereas other effects, such as aggregation, depend on chemical and biological processes occurring over weeks or months.

Mineral conditioners can modify chemical or physical processes. Lime, for example, raises soil pH. Gypsum or lime is often used to increase soil base saturation or reduce soil exchangeable sodium percentage (ESP) of retained cations. Both are good Ca sources that increase flocculation of primary particles and stabilize aggregates and other structural features and reduce dispersion and seal formation. In saline soils, especially if irrigation water contains significant amounts of Na, Ca sources are used to reduce water sodium adsorption ratio (SAR) and soil ESP. Mineral conditioners are especially important for management of arid or tropical soils where high temperatures promote rapid biooxidation of incorporated organic material. Oxides of iron have been used to promote aggregation in low organic matter soils (Rhoton *et al.*, 2002; Schahabi and Schwertmann, 1970; Vampati and Loeppert, 1986). Ferric hydrides are common water-treatment and industrial process waste products.

The third category of conditioner includes synthetic materials designed to produce specific physical and chemical interactions in soils. These are usually highly effective materials that produce physical effects with very small amounts of material added. The mode of action of these materials can be targeted to a particular physical process or property of soil. The two most common classes of synthetic amendments are surfactants and flocculants. Surfactants affect the surface tension of water and are most commonly used to enhance the wetting and infiltration of treated soils. Flocculants are materials that enhance the cohesive attraction among dispersed fine particulates. In aqueous media this leads to formation of loose aggregates known as flocs that achieve sufficient size and weight to settle out of suspension, leading to clarification of the suspension. When applied to consolidated soil these materials tend to enhance existing structural stability and, in the presence of flowing fluids, increase shear strength and reduce detachment. Most synthetic conditioners achieve their desired effects at applications of 100 kg ha^{-1} or less, compared to tonnes per hectare, as is the case for most organic or mineral conditioners. Some synthetic conditioners can have substantial effects on soil processes at kilogram per hectare rates or less, depending on application protocols.

III. SYNTHETIC CONDITIONER USES AND APPLICATION STRATEGIES

Soil conditioner use is limited by economics, often related more to transportation and application costs of bulky materials than to material price. Thus, organic and mineral soil conditioner use in production agriculture has been largely limited to a few highly efficacious materials such as lime, gypsum, and manure. High-value nursery operations, cash crops, turf, and landscape applications are less constrained by costs. Organic and mineral conditioners are used more often if available gratis as a means of by-product disposal from industrial processes, or if farms are located near sources, lowering transport cost. Synthetic conditioners, despite higher efficacy per unit of material, have seen limited use because of higher material cost, offsetting savings from lower application rates and transportation costs.

Cost is also related to the strategies of use and application. Until the 1990s the strategy for conditioner use was to change the overall physical and/or chemical makeup of a significant portion of the soil profile. This might mean attempting to condition a tillage slice, typically to a depth of 10–15 cm or even to a typical rooting depth of 30–45 cm. To modify such a depth of soil usually demands application of large amounts of conditioner. This strategy is inexorably linked to the cost considerations of material amount, bulk, and transportation, as well as application equipment, convenience, time, and labor. The advent of chemical polymer conditioners changed the logistics of this strategy because of the high efficacy of these conditioners. However, the strategy remained expensive because of the high cost of polymer conditioners, especially in the early decades of polymer conditioner development.

During World War II water-soluble polymers were used to stabilize soils for road and runway construction (Wilson and Crisp, 1975). Experimentation with these conditioners for agricultural applications began following World War II. Minsk *et al.* (1949) patented an industrial process for polymerizing acrylamide (AMD) molecules which made synthesis of a wide variety of water-soluble polymer compounds economical for industrial and environmental uses. Since the 1950s soil scientists have explored using synthetic polymeric conditioners to alter physical and, in some cases, chemical and biological soil properties for improved agricultural performance (Allison, 1952; Bear, 1952; Chemical and Engineering News, 1951; Fuller and Gairaud, 1954; Hedrick and Mowry, 1952; Martin, 1953; Martin *et al.*, 1952; Quastel, 1953, 1954; Ruehrwein and Ward, 1952; Sherwood and Engibous, 1953; Weeks and Colter, 1952). Wallace (1995) cited 16 reports of water-soluble polymer soil conditioners by 1952, and 99 reports by 1955.

Water-soluble polymeric conditioners improved soil physical properties, thereby improving root penetration, infiltration, aeration, erosion resistance, and drainage. These physical improvements usually increased rooting volume and plant interception of nutrients and water, indirectly improving plant nutrition. The main strategy for water-soluble polymeric soil conditioner use from the 1950s until the 1990s was application of sufficient conditioner material to physically modify soil properties to the depth of tillage. This mode of treatment usually entails multiple application operations, either as bulk solid materials or as sprayed liquids, solutions, or slurries at cumulative rates of 100 kg ha^{-1} or more. Tillage is usually required following each application to incorporate material to a desired depth. Because the mass of soil to 150-mm depth is typically 2 million kg ha^{-1}, it requires tonnes of organic or mineral amendments per hectare and hundreds of kilogram per hectare of water-soluble polymeric amendments to alter physical and chemical properties in the entire mass of soil to the tillage or rooting depth. The most commonly used water-soluble synthetic soil-conditioning polymers since the 1950s included: hydrolyzed polyacrylonitrile (HPAN), isobutylene maleic acid (IBM), PAM, polyvinyl alcohol (PVA), sodium polyacrylate (SPA), and vinylacetate maleic acid (VAMA). Commercial formulations of these compounds often combined polymers and extenders or solubility enhancing agents.

The most commercially successful water-soluble soil-conditioning polymer marketed before the 1990s was the powdered Monsanto product "Krilium" (Nelson, 1998; Quastel, 1953). It combined VAMA with a clay extender to improve application uniformity. Krilium and similar products typically cost \$4–5 kg^{-1} in the 1950s. The material cost and application amount limited use mainly to high-value crops and specialized uses. After initial enthusiasm for these conditioners, most products were withdrawn from the agricultural market because of lack of demand.

There has also been interest in super water-absorbent polymers for use in soils (Akhter *et al.*, 2004; Al-Darby, 1996; Al-Omran and Al-Harbi, 1998; Austin and Bondari, 1992; Baasiri *et al.*, 1986; Blodgett *et al.*, 1993; Boatright *et al.*, 1997; Bres and Weston 1993; Callaghan *et al.*, 1988; Choudhary *et al.*, 1995; Danneels and Van Cotthem, 1994; El-Hady *et al.*, 1981; Falatah and Al-Omran, 1995; Fonteno and Bilderback, 1993; Green *et al.*, 2004; Hemyari and Nofziger, 1981; Ingram and Yeager, 1987; Johnson, 1984; Katchalsky *et al.*, 1952; Miller, 1979; Orzolek, 1993; Rigas *et al.*, 1999; Sabrah, 1994; Sivapalan, 2006; Taylor and Halfacre, 1986; Tripepi *et al.*, 1991; Tu *et al.*, 1985; Wang and Boogher, 1987; Wofford, 1991; Woodhouse and Johnson, 1991). These are not water-soluble polymers, but rather are strongly hydrophilic gel-forming compounds that absorb up to 2000 times their weight in water. Cross-linked PAMs (gel-forming PAMs) and hydrolyzed starch-polyacrylonitrile graft polymers (H-SPANs), patented by the USDA in 1975 using the product name "Super Slurper," are the most common water-absorbent polymers used as soil conditioners. These compounds are also the water-absorbent polymers commonly used in such familiar products as disposable diapers. As soil conditioners, they improve the water retention of sandy soils, or around seeds, or roots of transplants or seedlings in situations where prolonged or untimely drought can occur, especially at planting. Spot placement of gel polymers can enhance emergence and seedling establishment without having to irrigate the entire soil profile. It should be noted that a perception exists that these gel polymers conserve water. But their mode of action is not one of water conservation but rather one of water storage enhancement. Optimal plant water requirements remain governed by principles of evapotranspiration. The polymers do not reduce the water demand or use, but can buffer the root zone against water loss in soils with low water retention properties (Letey *et al.*, 1992). Despite the potential benefits if properly used, costs are usually too high to modify an entire field's soil profile or its tillage zone or rooting depth, even at a cost of only \$2–3 kg^{-1}. Thus their use is typically restricted to high-value nursery or horticultural situations to reduce irrigation frequency, or lessen stress between irrigations, particularly where plant or crop quality and value are impaired by stress.

Since the 1980s and early 1990s polymer purity and molecular size have increased, greatly improving the efficacy, safety, and affordability of environmental polymers. These changes, coupled with new application strategies that only target critical portions of the soil for treatment, and that do not require expensive application protocols, have renewed interest in polymers for a growing number of agricultural and environmental uses. The best example of this progress is PAM use for erosion control and infiltration management in irrigated agriculture. Although less extensively researched, PAM use is also increasing rapidly for construction site and road cut erosion protection, for ditch and canal sealing against seepage loss, and for dust suppression in military encampments, helicopter-landing areas, and roadways.

IV. OVERVIEW OF CURRENT PAM USE

Many field trials from the 1950s to the present investigated polymer amendment effects on crop response and soil structural and hydraulic properties; these have been summarized in several reviews and monographs (Bouranis, 1998; Bouranis *et al.*, 1995; De Boodt, 1990, 1992, 1993; Levy and Ben-Hur, 1998; Polyakova, 1976, 1978; Seybold, 1994; Stewart, 1975; Terry and Nelson, 1986; Wallace, 1998a,b; Wallace and Terry, 1998; Wallace and Wallace, 1986a,b, 1995). In the 1980s and 1990s there were many laboratory column and mini-tray studies that investigated polymer effects on soil structure, infiltration, hydraulic conductivity, and related phenomena, often focusing on surface sealing, runoff, and soil aggregate dispersion. With time, research on soil-conditioning polymers focused on fewer polymers. Most polymer soil amendment research involved PAM, polysaccharides, or other biopolymer surrogates of PAM. Often the biopolymer surrogates of PAM have been grafted copolymers of PAM, developed in efforts to lower cost, to use other raw materials, and/or to achieve faster decomposition. There have also been a few reports of effective use of poly(diallyldimethylammonium chloride) (poly-DADMAC) polymers for erosion control and improvement of soil physical properties (Bernas *et al.*, 1995).

The insight that reenergized research interest in PAM for large-scale agricultural and environmental applications was its ability to prevent erosion when applied with surface irrigation water in very small amounts (1–2 kg ha^{-1} per treated irrigation). This occurred at the same time that environmental concern about the impacts of sediment-laden runoff from agriculture was emerging world wide as a major issue. Isolated reports hinted that very small amounts of PAM in irrigation water, flowing over soil in irrigation furrows, virtually eliminated detachment and transport of soil particles (Mitchell, 1986; Paganyas, 1975; Paganyas *et al.*, 1972). Paganyas *et al.* (1972) and Paganyas (1975) did not adequately identify the polymer used, referring to it as a "K" compound; however, the observations of reduced erosion in furrow runoff at low per hectare polymer application rates are probably the first in the literature. Mitchell (1986) gave only anecdotal observations of erosion control and concentrated on infiltration effects. Most of the literature of the 1990s to the present, which used PAM concentrations of 10 ppm or less in the water for erosion control, also reported infiltration increases on medium to fine-textured soils. The concentration dependence of this phenomenon has become better understood in recent years and will be discussed more fully later in this chapter.

Because of the ease of adapting PAM to furrow irrigation, that sector of irrigation received the most attention during the 1990s. Research showing efficacy of PAM to reduce erosion, limit surface sealing, and improve infiltration with sprinkler irrigation, however, was also being reported (Ben-Hur *et al.*, 1990) and has added to the momentum of this technology, although it was less recognized initially. The use of PAM for surface irrigation and sprinkler irrigation will be presented separately in this chapter.

The first research reporting a potentially practical and economical PAM-based field approach to reducing furrow irrigation-induced erosion was presented by Lentz *et al.* (1992). Related reports followed over the next several years (Ben-Hur *et al.*, 1992a; Gal *et al.*, 1992; Lentz and Sojka, 1994, 1996a,b,c, 2000; Lentz *et al.*, 2000; Levy *et al.*, 1995; Sojka and Lentz, 1994, 1996a,b,c, 1997; Sojka *et al.*, 1998a,b; Trout *et al.*, 1995). The success of this new research came from the realization that a better way to prevent furrow irrigation-induced erosion is to use the water to deliver the soil conditioner rather than modifying the soil to the depth of tillage. This delivery mode applies only minute amounts of PAM to a small fraction of the soil surface affecting the interaction of the flowing water with the rest of the soil profile. Irrigation, in general, is well suited to this mode of application, and it is especially suited to furrow irrigation. In this mode of application, only 1–2 kg ha^{-1} of PAM per treated irrigation were needed to halt an average of 94% of erosion from irrigation furrows (Lentz and Sojka, 1994). The soil treated in the irrigation furrow comprises only about 25% of the field surface area to a depth of a few millimeters. Inflows only need to be dosed as water crosses the field (the water advance). PAM application is halted at the initiation of runoff.

To ensure environmental safety, this application method was developed around the use of a food-grade class of PAM. These PAMs are anionic. They have a typical charge density of 18%, although the charge density can vary from only a few percent to 50% or more. The PAMs used for erosion control are regarded as moderately large molecules, having over 150,000-chained monomer segments per molecule, resulting in typical molecular weights of 12–15 Mg mol^{-1}. The molecules are manufactured to a high purity, and are the same PAMs used for a variety of food-processing uses and for drinking water treatment, with residual AMD monomer contents of <0.05%. The low AMD content and anionic nature of the molecule ensures safety for humans handling the PAM and for aquatic species, if any PAM is lost in runoff to surface waters. However, the anionic charge imparts the need for bridging cations in the solvating water to link the anionic polymer to the predominately anionic mineral and organic particulate surfaces. Waters and soils containing dissolved Ca enable better PAM efficacy than low-electrolyte (pure) water, and efficacy is best when there is little or no Na present. The small hydrated radius of divalent Ca helps shrink the electrical double layer surrounding charged particles, promoting flocculation. The monovalent Na ion, by contrast, has a large hydrated radius that interferes with the flocculation process by preventing attracted surfaces from migrating close enough to one another to form floccules.

PAM is so effective at stabilizing surface structure, even at these small application amounts, that, in most medium to fine-textured soils, infiltration is increased compared to nontreated water (Flanagan *et al.*, 1997a; Lentz and Sojka, 1994; Lentz *et al.*, 1992; Sojka *et al.*, 1998a,b; Trout *et al.*, 1995). Water without PAM, flowing over a soil surface, tends to disrupt aggregates and disperse them in the flow. As water containing the dispersed fines infiltrates, the fines are drawn into or over the pores, which plugs the pores and induces surface sealing. The effect is intensified if water arrives at the soil surface via water droplets from sprinklers or rain, which have additional kinetic energy that adds to the disruption and dispersion of encountered aggregates. While initial uses of irrigation-applied PAM were focused mainly on erosion control, farmers are often equally or more interested in using PAM for infiltration improvement where their particular soils or production systems are prone to slow infiltration. As technological barriers to PAM use in sprinkler irrigation are overcome, its growth in that segment of agriculture may be driven by efforts to improve the uniformity and rate of infiltration (Aase *et al.*, 1998; Bjorneberg and Aase, 2000; Bjorneberg *et al.*, 2000a,b). When runoff occurs, water redistribution results in inadequate wetting of the centers of raised beds and ponding in low areas of the field. The ponding can induce poor aeration and disease problems and/or the leaching of nutrients or agrochemicals. With proper application strategies, PAM can be used to both increase infiltration and improve infiltration uniformity. With PAM in the water, soil structure is stabilized and surface sealing is reduced; water droplets enter the ground where they land rather than causing surface seals that induce runoff and, hence, redistribution of water.

PAM use with irrigation for erosion control benefits water quality in a number of ways. By preventing erosion, it also reduces desorption opportunity for sorbed nutrients and pesticides, and limits dissolution of soil organic matter in runoff that elevates dissolved organic carbon (DOC) and biological oxygen demand (BOD) (Agassi *et al.*, 1995; Bjorneberg *et al.*, 2000b; Lentz *et al.*, 1998, 2001a,b). PAM-treated irrigation water has also proven highly effective at reducing movement off site of soilborne microorganisms and weed seed, greatly reducing the likelihood of downstream inoculation and, ultimately, reducing the need for pesticides (Entry and Sojka, 2000; Entry *et al.*, 2002; Sojka and Entry, 2000; Sojka *et al.*, 2000).

Because PAM increases the viscosity of water flowing through soil pores (Letey, 1996; Malik and Letey, 1992), the effects of PAM on infiltration are a balance of seal prevention (allowing greater infiltration) and increased viscosity (slowing the passage of water). Experiments are underway to use the viscosity effects together with other application and management strategies for canal and pond sealing, for improved infiltration uniformity along long irrigation furrows, and for better water retention in coarse-textured soils where infiltration is not a problem but poor water-holding capacity and leaching are problems. The ability to use PAM to selectively increase infiltration or to reduce it is application and management dependent and is discussed in greater detail later in the chapter.

Information on PAM use for erosion and pollution prevention and for better irrigation water management can be found at <http://sand.NWISRL.ars.usda.gov/pampage.shtml>.

V. PAM DEFINED AND DESCRIBED

The word *polyacrylamide* and the acronym "*PAM*" are generic chemistry terms, referring to a broad class of compounds. There are hundreds of specific PAM formulations. They vary in polymer chain length and number and kinds of functional group substitutions as well as molecular conformation, the most important conformation variation being linear or cross-linked conformation. Cross-linked PAMs are water absorbent but are not water soluble. Water-soluble PAMs have little if any cross-linking and the molecules, when dissolved in water, are nominally "linear," although they may be coiled or curled to varying degree due to either substitutions along the chain or as a result of electrolytes in the solvating water. In PAMs used for erosion control and infiltration management, the PAM homopolymer is copolymerized. Some of the spliced chain segments replace PAM amide functional groups with groups containing Na ions or protons that freely dissociate in water, providing negative charge sites along the polymer chain (Fig. 1). Typically one in five chain segments provide a charged site in this manner.

Barvenik (1994) described the common synthesis pathways for nonionic, cationic, and anionic PAM formulations. So-called nonionic PAMs are actually slightly anionic homopolymeric formulations due to slight (1–2%) hydrolysis of some of the AMD units during manufacture (Halverson and Panzer, 1980). Cationic and anionic PAMs are produced by one of a variety of postpolymerization reaction sequences beginning with the AMD homopolymer or via copolymerization of AMD and a suitable cationic or anionic comonomer (Mortimer, 1991). Cationic PAMs are commonly produced via two general processes. One is copolymerization with

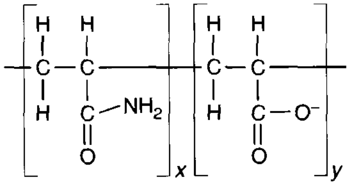

Figure 1 Polyacrylamide polymer structure unit (Sojka *et al.*, 2005).

acryloyloxyethyl-trimethyl ammonium chloride or any of several other cationic comonomers, resulting in relatively random distribution of cationic units along the polymer (Lipp and Kozakiewicz, 1991). Another method subjects the AMD homopolymer to further reaction yielding a tertiary amine, which is then reacted with a quaternizing agent. This latter method is referred to as the Mannich pathway (Lipp and Kozakiewicz, 1991).

Anionic PAMs are preferred for environmental applications because of their extremely low aquatic toxicity compared to nonionic or cationic forms. Anionic PAMs can also be produced by several reaction pathways. One pathway involves hydrolysis of nonionic PAM with a strong base. Using this pathway, the charge density is controlled by the quantity of base used. This pathway produces a copolymer of AMD and a salt of acrylic acid. The distribution of the anionic and nonionic units is controlled by varying the hydrolysis conditions (Lipp and Kozakiewicz, 1991). An alternative method produces anionic PAMs by hydrolysis of polyacrylonitrile (Halverson and Panzer, 1980). Common commercial anionic PAM formulations are produced by copolymerization of AMD and acrylic acid or one of its salts (Mortimer, 1991). The pH and ionic constituents of the formulation determine if the acrylic acid units are present as carboxylate ion or are paired with a counterion, which can be H^+, NH^+, or Na^+.

When anionic PAMs are dissolved in water and applied to the soil, the system pH controls the ionization. Above pH 6, the acrylic acid units tend to be anionic. Below pH 4, the anionic sites tend to be protonated, reducing the effective molecular charge (Halverson and Panzer, 1980). Anionic PAMs with sulfonic acid groups that hold their charge at lower pH are better suited for acid environments (Halverson and Panzer, 1980; Mortimer, 1991).

Natural gas has been the cheap abundant raw material from which the chemical building blocks used in PAM synthesis are derived. However, current supplies and economics may not reflect the future. The gradual increase in the cost of natural gas since 2000 has resulted in about a 30% increase in wholesale prices of PAM in that 6-year period. Work using chitin and starch to develop new copolymers of PAM or biopolymer surrogates that perform comparable to PAM has proven promising, although results are yet to match those achievable currently with PAMs (Orts *et al.*, 1999, 2000, 2001). Potential use of these materials for synthesis of effective flocculants and soil stabilizers carries the added benefit of using agricultural or other organic waste streams to produce value-added products.

PAM formulations for irrigated agriculture are water-soluble (linear, not gel-forming, not cross-linked, not super water absorbent) anionic polymers. They have typical molecular weights of 12–15 Mg mol^{-1} (over 150,000 monomer units per molecule). These PAMs are "off the shelf" industrial flocculant polymers that are used extensively to accelerate separation of solids from aqueous suspensions. Lists of common industrial and food-processing uses of anionic PAMs have been presented by Wallace *et al.* (1986b) and Barvenik (1994). Some of the most important uses include sewage sludge dewatering, drilling muds, mine slurry conditioning and mineral separation processes, paper manufacture, clarification of refined sugar, fruit juices and drinking water, thickening agents in animal feed preparations, antiscaling water treatment in steam processes in contact with processed foods, and as a coating on paper used for food packaging.

The surface chemistry of soils and the large physical-chemical domain of PAM macromolecules make them useful compounds for management of soil processes governed by flocculation, aggregation, and structure stabilization. In water with sufficient electrolytes, coulombic and van der Waals forces attract soil particles to anionic PAM (Orts *et al.*, 1999, 2000). These surface attractions stabilize structure by enhancing particle cohesion, thus increasing resistance to shear-induced detachment and transport in runoff. The few particles that do detach are quickly flocculated by PAM, settling them out of the transport stream. Minute amounts of Ca^{2+} in the water shrink the electrical double layer surrounding soil particles and bridge the anionic surfaces of soil particles and anionic PAM molecules, enabling flocculation (Wallace and Wallace, 1996).

Malik *et al.* (1991b) found that PAM applied via infiltrating water is irreversibly adsorbed in the top few millimeters of soil once dry. Lu and Wu (2003a) reported that PAM penetrated into organic matter-free soil 20–30 mm. PAM delivery via furrow streams is very efficient because it needs to only stabilize the thin veneer of soil directly active in the erosion process. In furrow irrigation PAM treats only about 25% of the field surface area to a 10- to 20-mm depth, requiring only 1–2 kg ha^{-1} of PAM per irrigation.

VI. PAM PROPERTIES AFFECTING EFFICACY

Both molecular properties and product formulation or preparation can influence how easily PAMs are handled and applied, as well as their behavior during or following application (Callebaut *et al.*, 1979). Barvenik (1994) noted that the most common commercial forms of PAM are as aqueous solutions, emulsions, and dry forms. Pure aqueous solutions of PAM become highly viscous at concentrations largely dependent on molecular weight. Lower molecular weight PAMs (30,000 g mol^{-1}) remain fluid even at 50% concentrations. However, the anionic PAMs commonly used for erosion control, infiltration management, and aggregate stabilization in soil since the early 1990s usually have molecular weights ranging from 12 to 15 Mg mol^{-1} and some products are available near 20 Mg mol^{-1}. At these high molecular weights, aqueous solutions of 1–2% are too viscous for practical use in liquid injection systems or spray applicators. The viscosity can be reduced if high concentrations of salts are added to the solutions; however, the salts can either be problematic in and of themselves in the application environment or can influence the resulting conformation of the deployed molecule on dilution. In addition, there is the practical consideration of shipping weight and volume, and thus cost, associated with distributing PAMs for use as low-concentration aqueous solutions.

For industrial applications where liquid injection is desirable, inverse emulsion formulations are useful. These formulations consist of aqueous droplets containing polymer suspended in a petroleum distillate or other appropriate oil or lipid matrix; the polymer is stabilized by inclusion of a surfactant (Barvenik, 1994; Buchholz, 1992; Lipp and Kozakiewicz, 1991), while in the formulated emulsion the PAM concentration can be as high as 50% on a weight basis. On injection to an aqueous environment under the proper mixing regime, the carrier quickly disperses and the PAM is released for dissolution. This process is accelerated by the action of the surfactant. Injection of the emulsion must be into a rapidly flowing stream of water with enough turbulence to rapidly disperse and mix the emulsion into the water stream, and with a sufficiently high flow rate to instantly dilute the PAM to low concentration. This prevents the rapid attainment of the high-viscosity characteristic of high-concentration aqueous PAM solutions. If adequate turbulence and flow are not provided, the partially hydrated PAM can form gel-like ultrahigh viscous bodies that resemble latex rubber or soft plastic. Once in this configuration further PAM dissolution becomes dependent on water contact with the PAM in the viscous mass. Since the surface area available for further dissolution under these conditions is greatly restricted, the masses become stable semipermanent features in the aqueous environment and can cause severe problems with pumping equipment, injectors, piping, and spray nozzles. Protocols have been suggested for agricultural settings to avoid these problems (Sojka *et al.*, 1998c), and emulsions have been utilized to a limited degree for injection of PAM in center pivots. The difficulty of maintaining adequate control in agricultural settings, however, has largely resulted in the abandoning of the use of emulsions for PAM application in irrigation.

There is increased interest in local preparation of aqueous PAM solutions of a few percent concentration utilizing various fertilizer salts or Ca salts to reduce the viscosity. These solutions are injectable in irrigation systems without the drawbacks of emulsions. The approach is targeted primarily at use of PAM in sprinkler irrigation systems. While this approach avoids the clogging possibility of emulsions, it carries the drawback of preparation and handling of greater solution volumes. By far the greatest on-farm use of PAM to date focuses on the use of dry granular PAM products that are either directly applied to irrigation furrows before the inflow or that are metered at head ditches with adequate turbulence and distance allotted to dissolve the PAM prior to water flowing onto the field. These approaches will be described in greater detail later in the chapter.

A variety of PAM molecular properties and environmental properties interact to affect PAM efficacy. These interactions can be significant given the range of PAM use in the environment and the number of environmental and application factors that can vary. PAM uses in the environment include, but are not limited to, flocculation of suspended solids, soil stabilization, and infiltration enhancement. Soil stabilization helps resist erosion, and the suspended solids can be mineral, organic, or biotic material. Reduction of turbidity and mixing reduces opportunities for desorption of pesticides and nutrients or other soluble organics. PAM can be directly applied through irrigation water or indirectly on activation by water (irrigation or rain) when applied initially as dry powder or granules to the soil surface. Advances in theoretical chemistry have aided in the continued improvement of PAM performance through design of molecular conformations optimally suited to given industrial and environmental applications (Bicerano, 1994; Bouranis, 1998; Bouranis *et al.*, 1995; Chamberlain and Cole, 1996). A good deal of information on the effects of coagulants and flocculants comes from the wastewater treatment literature, although often from polymers and compounds other than PAM, or in the case of PAM, often from cationic or nonionic formulations. Nonetheless, many of the general principles are worth noting as a framework for understanding the behavior of anionic high molecular weight PAMs, the dominant class of polymers for erosion control and infiltration management in agriculture.

At cool temperatures from 6 to 29 °C, flocculation for a variety of inorganic and polymer compounds tended to be slower and flocs tend to be smaller than at higher temperatures (Fitzpatrick *et al.*, 2004; Hanson and Cleasby, 1990). Furthermore, floc strength seems to vary with the shear conditions of the flow media in which flocs are formed. The larger flocs formed at higher temperatures are more easily disrupted and less capable of reformation than flocs formed at lower temperatures (Fitzpatrick *et al.*, 2004; Yeung and Pelton, 1996; Yeung *et al.*, 1997).

The mechanisms by which flocculation of suspended sediments takes place in the presence of polyelectrolytes was studied by Ruehrwein and Ward (1952) who associated this effect with stabilization of soil and resistance to dispersion. Ben-Hur and Letey (1989) and Ben-Hur *et al.* (1989) attributed this effect as the mechanism that reduced particle dispersion when sprinkler irrigating with PAM, which in turn reduced surface sealing and slowed the reduction of infiltration rate. The adsorption of polymers from aqueous media onto mineral surfaces has been reviewed several times (Greenland, 1963, 1972; Harris *et al.*, 1966; Theng, 1979, 1982) and has been the object of numerous investigations (Ben-Hur *et al.*, 1992a,b; Gu and Doner, 1993; Haschke *et al.*, 2002; Lakatos *et al.*, 1981; Letey, 1994; Lu and Wu, 2003a; Lu *et al.*, 2002a; Lurie and Rebhun, 1997; Malik and Letey, 1991; Mukhopadhyay *et al.*, 1994).

PAM conformation, charge type, and charge density influence their efficacy for soil stabilization. Malik and Letey (1991) reasoned that longer, less-coiled PAM molecules would be more strongly adsorbed to mineral surfaces. Michaels and Morelos (1955) reported that 20% hydrolysis of PAM provided the greatest degree of chain extension, facilitating adsorption. As PAM is drawn to mineral particle surfaces, surface-adsorbed water is driven away because of the stronger attraction for the polymer (Parfitt and Greenland, 1970). Nonionic PAMs are attracted to solids mainly through H bonding of hydroxyl groups on the polymer attracted to oxygen atoms on the silicate mineral surfaces or via other charge-dipole or dipole-dipole interactions. Theng (1982) noted that cationic PAMs are adsorbed through the interaction of cationic sites on the polymer and negative charge sites on clay particles. Adsorption of anionic PAMs to mineral surfaces, which carry predominately negative charges, is aided by an abundance of Ca^{2+} in the aqueous system. The opposite occurs for cationic polymers, whose adsorption to anionic mineral surfaces is interfered with by an abundance of electrolytes in the suspending water (Shainberg and Levy, 1994). Aly and Letey (1988) found that adsorption of anionic PAMs and polysaccharides in water of electrical conductivity (EC) 0.7 dS m^{-1} was greater than for water of EC 0.05 dS m^{-1}.

Entropy change as water is displaced is an important actuating force in bringing about adsorption of negative and nonionic polymers to negatively charged clay surfaces (Lyklema and Fleer, 1987; Theng, 1982). In the case of nonionic polymers, the entropy change increases with polymer molecular weight. Malik and Letey (1991) found that, in general, the molecular size and conformation of polymers affect adsorption with increasing molecular size and increasing chain extension leading to increasing adsorption. They also concluded that adsorbed polymers do not penetrate soil aggregates, but only coat and stabilize their surfaces. Ben-Hur *et al.* (1992b) found that adsorption of PAMs onto illite and montmorillonite clays was generally in the order cationic > nonionic > anionic regardless of the electrolyte content of the solvating water. Water that was more saline and sodic reduced adsorption of cationic and nonionic PAMs but increased adsorption of anionic PAMs. Janczuk *et al.* (1991) noted that PAMs affected the surface free energy and, therefore, the wettability of soil. Wallace *et al.* (1986c) reported on the effects of PAM on soil water relationships.

Malik and Letey (1991) and Nadler and Letey (1989) used tritium-labeled polymers to determine sorption isotherms of several types of polyanions on Arlington sandy loam (coarse-loamy, mixed, thermic Haplic Durixeralfs). They interpreted their results as showing that polymer sorption was restricted to the external surfaces of soil aggregates. A similar conclusion was arrived at by El-Hardy and Abd El-Hardy (1989) who saw only limited intrusion of high molecular weight PAMs into soil aggregates. Aly and Letey (1988) showed that the water quality of the solvating water used to apply the polymers also greatly influenced the degree of adsorption. Nadler *et al.* (1992) found that once adsorbed and dried there was subsequently little desorption of anionic PAM from soil. Lu *et al.* (2002a) found that PAM sorption isotherms on soil materials could be described well by the Langmuir equation and that soil texture, organic mater content, and dissolved salts all influenced the extent of PAM sorption. Soils with high clay or silt content and low organic matter content had high sorptive affinity of anionic PAM and sorption increased as total dissolved salts increased with divalent cations 28 times as effective in enhancing sorption as monovalent cations. Cation enhancement of sorption was more effective in fine-textured soils than in coarse-textured soils and presence of greater amounts of organic matter tended to interfere with PAM sorption.

Adsorption of PAM on soil and clay mineral surfaces has been demonstrated to be rapid and irreversible in several studies although the degree of adsorption is dependent on PAM conformation, soil or mineral properties, and soil solution characteristics (Hollander *et al.*, 1981; Nabzar *et al.*, 1984, 1988; Nadler *et al.*, 1992; Pradip and Fuerstnau, 1980; Tanaka *et al.*, 1990). Because of its high affinity for clay mineral surfaces in soil, PAM becomes concentrated in the upper portions of soil profiles to which it is applied in irrigation water. PAM remained stable at the original application depth even 10 months after application and with 720 mm of additional water application (Nadler *et al.*, 1994). The length of the polymer chain and large number of adsorption sites along the molecule contribute to PAM's adsorption strength. Desorption is difficult because some adsorption sites are nearly always attached to the adsorption surface, preventing removal of the molecule (Nadler and Letey, 1989). Because of the demonstrated high sorptive ability and low mobility (Malik and Letey, 1991; Malik *et al.*, 1991b), PAM is generally regarded as incapable of penetrating soil more than a few centimeters from the soil surface. This assumption is probably restricted to high molecular weight PAMs. Shaviv *et al.* (1987a,b) demonstrated that low molecular weight PAM (<75,000 g mol^{-1}) could move to about the same depth as the wetting front. The molecular gyration radius of low to moderate molecular weight PAMs (Muller *et al.*, 1979) is compatible with soil micropore size. This, considered in light of the relatively slow sorption kinetics of the large PAM molecule (Lu *et al.*, 2002a), has led to recognition that the depth of PAM penetration depends on PAM properties, application method, and the soil and water properties present in the application scenario (Lu and Wu, 2003a). Using anionic PAMs of 10–15 Mg mol^{-1}, Lu and Wu (2003a) found that PAM penetration depth was about one-eighth to one-half of the water penetration depth, with a particularly high PAM retention in the top few centimeters of the soil. The PAM retained in the top 0–2 mm of soil ranged from 16% to 95% of the total applied. PAM retention was greater at shallow depths when solution contact with the soil was favored by pore arrangement, contact time, and drier soil conditions on addition of PAM solutions.

Variations in PAM molecular properties and solution concentrations affect PAM interaction with mineral surfaces influencing the efficacy of PAM for erosion control and infiltration management when applied in the field. Lentz and Sojka (1996c) and Lentz *et al.* (1993, 2000) reported the effects of PAM charge type, charge density, and molecular weight on infiltration and control of furrow irrigation-induced erosion for Portneuf silt loam (Durinodic Xeric Haplocalcids) in Idaho production-scale fields treated with 10 mg liter^{-1} PAM during water advance in the furrow, followed by untreated water for an approximate PAM application of 1 kg ha^{-1}. Anionic and nonionic PAMs were twice as effective as cationic PAMs for controlling sediment loss in new furrows, with erosion control in the order anionic > nonionic > cationic. Erosion control efficacy increased with charge density from 8 to 19 to 35 mol% and with increasing molecular weight over the range of 4–17 Mg mol^{-1}. However, infiltration increased 14–19% when PAM molecular weight fell from 17 to 4 Mg mol^{-1}, and generally medium and high charge density anionic and nonionic PAM increased infiltration more effectively than cationic PAMs. Nonionic PAMs produced the greatest season-long infiltration gains compared to nontreated furrows (5% increase). Charged PAMs produced greater infiltration increases in the early season on newly formed furrows, but decreased infiltration on repeatedly irrigated furrows late in the season. Green *et al.* (2000) spray-applied 288 mg liter^{-1} PAM solutions to soils in small trays at an equivalent rate of 20 kg ha^{-1}, allowing them to air dry for 24 h before sprinkling them at 68 mm h^{-1} for 1 h. They obtained mixed results for PAM charge densities and molecular weights, which they attributed to specific soil interactions. They concluded that charge density was the main factor affecting infiltration, with a charge density of 30% optimal for the clay soil in their tests. On the sandy soil, however, molecular weight was the main factor affecting infiltration with

12 Mg mol^{-1} optimal. Their results were somewhat similar to an earlier study with anionic PAMs (Levy and Agassi, 1995) using similar application rates sprinkled at 48 mm h^{-1}. In rainfall simulator studies on mine soils, Vacher *et al.* (2003) saw improved erosion control with higher molecular weight formulations, but no differences in infiltration. PAM performance in their study was enhanced on soils with higher clay contents.

Levy and Agassi (1995) also noted the importance of viscosity in explaining the effects of PAMs applied to soil surfaces for infiltration and erosion control. This aspect of PAM performance in soil was explained earlier by Malik and Letey (1992) and again by Letey (1996). In essence, the infiltration of PAM solutions is affected by the increase in solution viscosity as concentration increases. As noted by Muller *et al.* (1979), the rotation radius of PAMs is affected by their molecular size and conformation. As concentration increases this affects the rate that viscosity increases. Molecular rotation is more constrained in smaller pores and, when polymers become attached to surfaces on the interior of pores, fluid movement in narrow pores is further restricted. This property of PAM and other large organic molecules was described by Malik and Letey (1992) and Letey (1996) as "pore size-dependent apparent viscosity."

Using a Cannon-Fenske style viscometer, Bjorneberg (1998) looked at PAM solution kinematic viscosity for performance in bulk flow situations and in pumping equipment and piping. The PAM evaluated was anionic with a molecular weight of 12–15 Mg mol^{-1}. PAM solution viscosity was not significantly affected below 400 ppm and had only minor temperature effects over the range of 10–40 °C. In large diameter vessels and for pump performance, Bjorneberg (1998) found that PAM solutions above 400 ppm performed as a non-Newtonian solution, meaning that viscosity changed with flow conditions. He also noted that large PAM molecules are subject to significant molecular shear when recirculated through pumping equipment (a common practice in agricultural solution tanks), resulting in loss of as much as half the kinematic viscosity with as little as five passes through a pump. This means that applying PAM as a liquid via standard agricultural mixing protocols can easily change PAM molecular conformation, reducing the average polymer chain length before PAM reaches the intended application target.

MacWilliams (1978) and Tolstikh *et al.* (1992) associated a decrease in chain length or molecular weight with high-speed agitation of PAM solutions or disruption via exposure to ultrasonic energy. High molecular weight PAM formulations are much more susceptible to shear. When exposed to a shear environment, high molecular weight formulations typically see an initial steep decline in viscosity which plateaus as the smaller remaining molecules flow around the source of shear more easily. Nagashiro *et al.* (1975) saw viscosity drop quickly as molecular weight fell from 5 to 3 Mg mol^{-1}. PAM solutions or PAM applied to targets can also experience gradual

(e. g., weeks) reduction of molecular weight due to environmental exposure, particularly UV light, or through gradual unfolding of the macromolecule (Molyneux, 1983).

As noted in the preceding paragraphs, viscosity can affect efficacy both for erosion control and infiltration management, as well as depth of PAM penetration into the soil. Ben-Hur and Keren (1997), using a rotary viscometer, found that a 10–15 Mg mol^{-1} PAM formulation produced a rapid increase in viscosity beginning at a solution concentration of about 2 g liter^{-1}, whereas two other formulations with molecular weights of 0.1–0.2 and 0.2–2.0 Mg mol^{-1} required about 50 and 4 g liter^{-1}, respectively, before rapid viscosity increases began occurring. The combination of the findings from Malik and Letey (1992), Letey (1996), Ben-Hur and Keren (1997), and Bjorneberg (1998) provides a theoretical starting point for one of the newer PAM uses, canal sealing, which will be described later in the chapter.

PAM solutions usually promote flocculation of suspended solids at low concentrations but can have the opposite effects at higher concentrations, where the large physical domain of the macromolecules themselves interfere with flocculation and actually stabilize dispersed suspensions as viscosity increases. The concentration at which the effects reverse depends on several factors including molecular weight, charge and conformation of the molecule, size and chemistry of the dispersed solids, and chemistry of the water, particularly EC and SAR (Sato and Ruch, 1980). Experience on highly calcareous silt loam soils of the Pacific Northwest suggests that for use of anionic PAMs of 12–15 Mg mol^{-1} with 18% charge density, applied in irrigation water, the concentration at which PAM ceases to aid flocculation and begins to act as a dispersant is in the range of 50–60 ppm, and the reversal occurs at even lower concentrations as soil SAR increases (Lentz, 2003). The actual value could be greater or lower, depending especially on EC and SAR of the irrigation water and pH and organic matter content of the soil. The role of Ca^{2+} in efficacy of anionic PAMs in general, and for flocculation in particular, is discussed in greater detail in a later section.

VII. EARLY CONTRIBUTIONS

The reduction of erosion and management of infiltration through improved uses of synthetic- and bio-polymers has been identified by Natural Resource Conservation Service (NRCS) as one of the most dramatically effective, agriculturally significant, and environmentally important advances in irrigated soil conservation management (Thomas Spofford, NRCS National Irrigation Engineer, personal communication). Practical application of the same technology in rainfed agriculture has been more difficult to achieve and less progress has been made. The advances in the irrigated sector from the late 1980s to the present have come about from the individual and collaborative efforts of several research groups worldwide. It is difficult to identify a single beginning for the acceleration in this field of research. We have attempted to cover the most noteworthy contributions.

Several lines of investigation developed more or less naturally. Rainfed agriculture and irrigated agriculture pursued PAM use more or less independently. While some research focused more on erosion control than infiltration, and vice versa, it was soon apparent that the phenomena were interconnected. Furthermore, it eventually became clear that PAM could be used to selectively increase or decrease infiltration to meet spatial and temporal needs of a given situation. In irrigated agriculture, researchers found that furrow, sprinkler, drip, and flood irrigation each has specific and unique considerations that affect how PAM technology needs to be deployed for those settings.

Of necessity, we have segregated this topic into subsections. However, the reader should be aware of the arbitrariness of the separation. Research on PAM underscores how potently the properties of water affect all soil processes. PAM is one of the few tools in soil management that does its work, in great respect, by changing the effective properties of water and how water interacts with the soil. Changes in PAM conformation, charge, charge density, molecular weight, concentration, product formulation, application amount, flow properties of the water, mineral ion composition of the water and soil, soil mineralogy, soil texture, and soil antecedent water content all affect the extent and "direction" of PAM effects. Scientists seeking expertise in PAM technology for soil management and environmental protection must be aware of the many and sometimes seemingly contradictory nuances that result from the various combinations of these factors.

Weeks and Colter (1952) and Bodman *et al.* (1958) recognized the potential for polymeric soil conditioners to reduce erosion and increase infiltration. Their obstacle was inability to identify an economical and practical application strategy. Investigations of a newer strategy of PAM and other polymer use, where the polymers were either only surface applied and/or applied via irrigation water began in the 1970s and early 1980s. Paganyas *et al.* (1972) and Paganyas (1975) treated only the surface of the soil with solutions of polymers prior to irrigation rather than attempting to modify the entire soil profile. Treating only the furrow bottoms in a light preirrigation with 15–20 kg ha^{-1} polymer per irrigation, Paganyas (1975) found that soil was stabilized against erosion, reducing losses about 90% across polymer treatments. Net infiltration increased and the infiltrated water moved farther laterally. Aggregate stability of the treated furrows greatly increased and losses of N and P in runoff were greatly reduced. These findings were confirmed and quantified in greater detail with specifically identified PAM formulations in later work in Kimberly, Idaho before researchers were fully aware of the earlier Soviet experiments. The Soviet work did not specify the polymers they used, referring only to them as a series of "K" compounds. However, the description of the K compounds suggests they were PAMs or closely related polymers.

Wallace and Wallace (1986a,b) noted the potential for use of very small application amounts of soil conditioners, especially PAM, to control erosion but reported only sparse observations. They also noted the potential for application of water-soluble polymer conditioners via irrigation (Wallace and Wallace, 1987). Mitchell (1986) applied PAM in furrow irrigation water to alter the infiltration rate and noted, but did not quantify, a marked reduction in runoff turbidity.

Work by Helalia and Letey (1988a,b) and Wood and Oster (1985) showed in rainfall simulator studies that soil dispersion was reduced and infiltration increased when PAM and other polymers were added to the water at rates as low as 10 ppm. This observation was bolstered by later studies (Ben-Hur *et al.*, 1989; Helalia and Letey, 1989) in which aggregate stability was increased by low-rate polymer additions to the water. Aly and Letey (1990) established that the direction and degree of these effects was dependent on matching polymer and soil properties. Reduced dispersion, stabilization of aggregates, and increased infiltration are all factors that tend to reduce the potential for erosion.

VIII. SURFACE IRRIGATION

Water-soluble anionic PAM was identified in the 1990s as a highly effective erosion-preventing and infiltration-enhancing polymer, when applied in furrow irrigation water at concentrations of 1–10 ppm for applications of 1–2 kg ha^{-1} per treated irrigation (Lentz and Sojka, 1994; Lentz *et al.*, 1992; McCutchan *et al.*, 1993; Sojka and Lentz, 1997; Sojka *et al.*, 1998a,b; Trout *et al.*, 1995; Yonts *et al.*, 2000). PAM achieves these results when applied to soil via the irrigation water at such low concentrations by stabilizing soil surface structure and pore continuity. Stabilized surface structure resists the shear forces of flowing water, thereby preventing detachment, transport, and dispersion of soil particles, thus eliminating detached solids for dispersal in flowing water that enter and block pores as water infiltrates downstream. In 1995 the US NRCS published an interim PAM-use conservation practice standard which was revised in 2001 (Anonymous, 1995, 2001; NRCS, 2001). The standard gives considerations and methodologies for PAM use. PAMs were first widely commercialized for erosion control in the United States in 1995. By 1999 about 400,000 ha were

PAM-treated in the United States. The current estimate is about 1 million ha. The US market is expected to continue to grow as water quality improvements are mandated by State and Federal legislation and court action because PAM use is one of the most effective, economical, and easily implemented technologies available that can achieve required water quality improvements. Overseas use of PAM for erosion control and infiltration management is also growing rapidly.

PAM, used following NRCS guidelines (Anonymous, 1995, 2001), reduced sediment in runoff 94% in 3 years of furrow irrigation studies in Idaho (Lentz and Sojka, 1994). The 1995 NRCS standard called for dissolving 10-ppm PAM in furrow inflow water as it first crosses a field (water advance-typically the first 10–25% of an irrigation duration). PAM dosing is halted when runoff begins. The PAM applied during advance generally prevents erosion throughout a 24-h irrigation. Application amounts under the NRCS standard usually work out to 1–2 kg ha^{-1}.

PAM treatment is recommended whenever soil is disturbed (loose and highly erodible) before an irrigation. Following initial PAM treatment, erosion in later irrigations can usually be controlled with only 1- to 5-ppm PAM if the soil was not disturbed between irrigations. Without reapplication of PAM, erosion control on reirrigation of previously treated furrows typically drops by nearly half (Lentz and Sojka, 1994; Lentz *et al.*, 1992).

Furrow irrigators often use a simple application strategy which they call the "patch method." This involves spreading dry PAM granules onto the furrow bottom of the first 1- to 2-m below the inflow point. The 2001 revision of the NRCS PAM standard recognized the patch method as an acceptable alternative to dosing furrow inflows with PAM predissolved in the irrigation water. The patch application method has become the most common mode of application for most furrow-irrigated situations. In the patch method, the amount of PAM granules can be accurately determined on an area-equivalent basis-furrow spacing × length at a 1 kg ha^{-1} field application rate. Typical patch doses are 15–30 g per furrow (approximately half ounce to an ounce or teaspoon to tablespoon amounts). Several simple application devices are commercially available to lay down measured PAM granule doses on furrow bottoms near inflow points prior to irrigation.

When water flows over a "patch" of dry granules, a thin slimy mat forms that slowly dissolves during the course of the irrigation. Erosion and infiltration effects of the patch method are comparable to dosing the inflow at 10 ppm (Sojka *et al.*, 1998b, 2003). Erosion control in subsequent nontreated irrigations is often better with patch application than where the initial PAM application was dissolved in the inflowing water supply. This is because bits of the patch are often still intact at the end of the initially treated irrigation, providing small amounts of PAM in later irrigations. Advantages and disadvantages of each application method depend on field conditions and system requirements (Sojka *et al.*, 1998c). The patch method works well in most circumstances, but is less reliable on steep slopes (Lentz *et al.*, 2003). Similarly, farmers have experienced problems with the patch if inflow rates are very high. These conditions can cause breakup and transport of the patch down the furrow, or burying of the patch by the sediment scoured at or near the inflow point. PAM predissolved in the advancing inflow performs more reliably at high water flow rates or on steep slopes. However, when soil is damp (from dew, or a light rainfall, or canopy shading) the patch method or use of a continuous low dosage seems to control erosion more reliably than the predissolved dosing only during advancing inflow; the reason for this is not fully understood. A possible explanation is that the initial surface soil wetness interferes with PAM adsorption (Lu and Wu, 2003a). Wetter soil also infiltrates less PAM-bearing water. Thus, delivering a constant small dose of PAM may compensate for weaker initial stabilization of soil surfaces already damp prior to irrigation.

In the US Pacific Northwest, farmers usually treat irrigation water with PAM only during the irrigation events that they perceive carry a high-erosion risk, or as required by conservation programs such as the Environmental Quality Incentives Program (EQIP). Farmers typically use 3–5 kg ha^{-1} of PAM during an irrigation season depending on field conditions and crop, which dictate the number of cultivations and irrigations. Thus, although research has shown that 94% seasonal erosion control is achievable, results from commercial farming situations are more commonly in the range of 80% because usually fewer irrigations are treated (Clair Prestwich, NRCS Water and Climate Center, Portland, OR, personal communication).

Much has been learned about controlling erosion and infiltration with PAM in furrow irrigation since the reports in the early 1990s. Trout *et al.* (1995) noted that there was a relationship between the effectiveness of erosion reduction and the resulting infiltration during an irrigation event (Fig. 2). Most of the erosion and depositional seal formation that drives this relationship occurs within the first minutes or hours of an irrigation set. Much of the efficacy of PAM in controlling furrow erosion and the related enhancing of infiltration is because, when properly applied, the initial detachment, aggregate dispersion, transport, and resulting deposition do not occur. This is because the furrow is immediately stabilized as water advances, delivering PAM simultaneously. Sojka *et al.* (1998b) suggested that a shallow subsurface impermeable layer (e.g., in a wheel track furrow) could also strongly affect infiltration and erosion relationships.

Lentz and Sojka (1999, 2000) noted the importance of achieving full dissolution of PAM when employing the strategy of predissolving PAM to a desired concentration prior to delivering the water to the furrow. They also noted the relative effectiveness of several dosing strategies. For freshly formed furrows, effectiveness of applying PAM at a uniformly dosed inflow

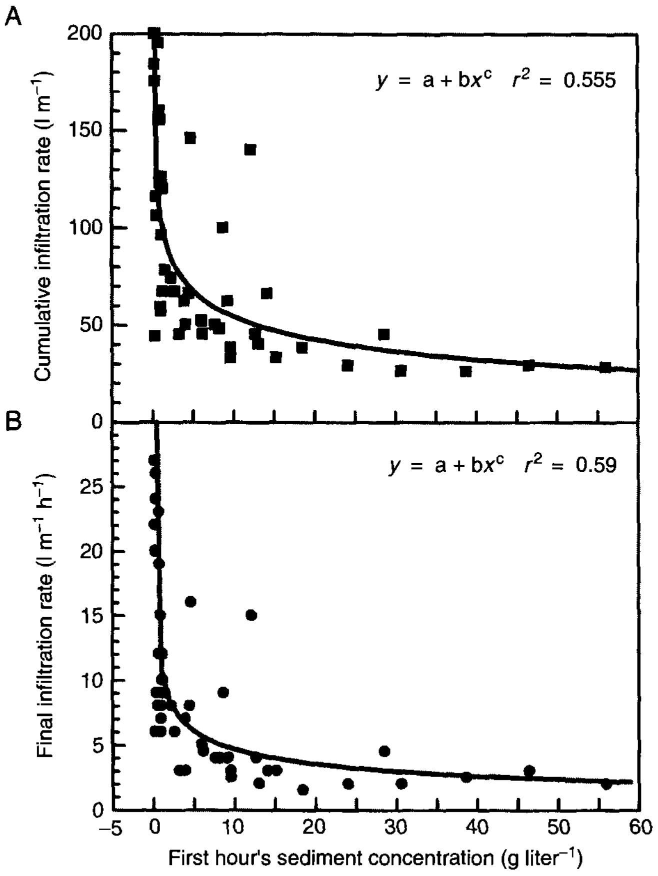

Figure 2 (A) Effect of sediment concentration in furrow water on cumulative infiltration into a Portneuf silt loam as measured for 8 h using a recirculating infiltrometer. (B) Effect of the first hour's sediment concentration on final (8 h) infiltration rate into a Portneuf silt loam, measured using a recirculating infiltrometer (Sojka *et al.*, 1998a).

concentration varied with inflow rate, PAM concentration, duration of furrow exposure, and amount of PAM applied. Erosion control with PAM on 1–2% slopes was similar for three application methods: (1) the NRCS 10 ppm standard, (2) application of 5 ppm during advance, followed by 5–10 min of 5-ppm reapplication every few hours, or (3) continuous application of 1–2 ppm. Constant application of 0.25 ppm controlled erosion about one-third less effectively. McCutchan *et al.* (1993) described a PAM-dosing strategy using predissolved stock solutions metered into furrow flows to achieve a constant 2.5-ppm PAM concentration. This proved highly effective at reducing sediment loss in runoff and was comparable to the third treatment described by Lentz and Sojka (1999, 2000). One disadvantage of maintaining a constant dose in this concentration range is the use of two to three times the total PAM per hectare in a typical 24-h irrigation set (vs 10 ppm dosing of the advance only) and some increased risk of eventual PAM loss in the runoff water.

Sojka and Lentz (1997) discussed general technical and practical considerations for controlling erosion in furrow irrigation with PAM. Among these was the importance of assuring that the first water to flow down the furrow already contains PAM. Adding PAM to an established flow reduces turbidity and erosion, but can be less durable and usually loses the infiltration-enhancing effect because PAM stabilizes the soil surface structure it encounters, but cannot create structure (other than the formation of flocs as PAM clarifies initially turbid water).

A common erosion control practice in some regions is placement of straw in irrigation furrows. Although highly effective at controlling erosion and increasing infiltration, the presence of straw in furrows often creates other problems. Straw can migrate downslope, leading to damming of the furrow and washing of water into adjacent furrows. This in turn damages the planted beds and results in some furrows being under-irrigated below the washout and others being over-irrigated. Shock and Shock (1998) and Lentz and Bjorneberg (2001, 2003) examined the relative effectiveness of straw and PAM as erosion prevention methods for furrow irrigation. Shock and Shock (1998) saw similar effectiveness of straw mulching and PAM use for both erosion control and infiltration, with slight advantages in their trials for straw mulching. They also reported a cost advantage for straw mulching at \$140 ha^{-1} versus \$169 ha^{-1} for PAM. Water and PAM application anomalies between treatments and costing assumptions, however, prompt some questions regarding the final analysis. PAM application was varied among irrigations resulting in erratic PAM performance, and irrigation duration was longer for PAM treatments than straw treatments. PAM cost was put at \$9.90 kg^{-1} (for a seasonal material total cost of \$106 ha^{-1}) with an additional estimate of \$55 ha^{-1} for delivery and mixing services. Competitive PAM prices currently remain well below this in most markets, and most farmers use application technologies that carry little or no delivery, preparation, or direct application cost. Furthermore, fuel costs for straw application since the study was published have doubled. Aside from the monetary aspects, a major barrier to adoption of straw mulching remains the intrusion of the practice itself (an inconvenient additional operation at a busy time of the year) and complaint by many farmers that bringing straw from other fields risks introducing weeds, in addition to frequent problems associated with straw migration and furrow damming.

Lentz and Bjorneberg (2001, 2003) evaluated the relative effectiveness of two straw rates and PAM plus the two straw rates compared to untreated furrows. Treatment effects varied among irrigations, particularly whether irrigating freshly irrigated furrows or reirrigating undisturbed furrows. In general, PAM in combination with straw gave erosion control of nearly 100% versus about 80% for straw alone and slightly added to the infiltration increase of straw alone. The effects of all treatments, and particularly the PAM enhancement, were greater in the early irrigations or when soil was disturbed. Two noteworthy observations in this study were reduction of residue migration down furrow and (because sediment moved less in the presence of PAM) the reduced tendency for transported soil to form dams when encountering clumps of transported straw. Straw remained better-anchored to the furrow, and what little sediment did move along the furrow passed under or through the anchored straw because straw accumulations were less restrictive at any one point along the furrow (Fig. 3). These two effects together prevented PAM plus straw furrows from overflowing into

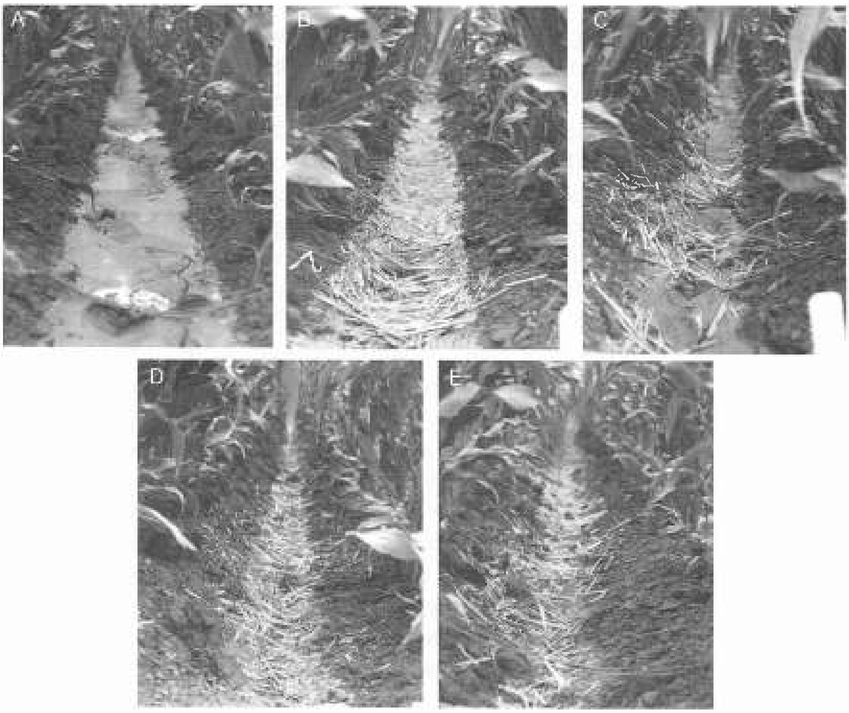

Figure 3 View upstream from the outflow end of furrows showing characteristic amounts of sediment and straw residue transported from upstream reaches and deposited there for control (A), low straw (B), high straw (C), PAM treated with low straw (D), and PAM treated with high straw (E). Photos were taken after the first irrigation (Lentz and Bjorneberg, 2003). (See Color Insert.)

adjacent furrows. Somewhat similar results were reported by King *et al.* (1996). This observation is encouraging since farmer reluctance to adopt reduced tillage in furrow-irrigated agriculture is due largely to residue migration, furrow damming, and downstream irrigation uniformity problems. Leib *et al.* (2005) found reduction in sediment loss with PAM-treated furrow irrigation, but reported the need to combine the practice with grassed return flow ditches to achieve desired return flow standards for the lower Yakima River Basin of Washington.

Some farmers were reluctant to adopt PAM for erosion control because of concerns over increased advance time. Sojka *et al.* (1998b) examined the effects of high (45 liter min^{-1}) and low (23 liter min^{-1}) furrow inflow rates and wheel track or nonwheeled furrows on erosion control, advance time, and infiltration. The application of PAM at 23 liter min^{-1} increased advance time 33% and reduced runoff soil loss 88% compared to controls. PAM applied at 45 liter min^{-1} reduced advance time 8% and soil loss 75% compared with controls irrigated at 23 liter min^{-1}, whereas untreated 45 liter min^{-1} inflows cut advance time 42% but raised soil loss 158%. PAM reduced erosion in all furrows, but in wheel track furrows had no effect on advance time and little infiltration effect after two or three irrigations. The authors also noted that the soil in treated furrows saw a 2-year mean increase of 23% in water-stable aggregates and that the soil on the furrow bottom had soil strength reduced from 1.7 to 1.1 MPa. This study showed that the potent erosion-reducing ability of PAM could allow farmers to use higher inflow rates and still greatly reduce erosion. At the same time infiltration opportunity time difference from the upper to lower end of the field was greatly reduced, allowing for improved infiltration uniformity in the field. In this study "cut back" irrigation was used, whereby inflows from all treatments were reduced to a low flow-sustaining rate of 19 liter min^{-1} once runoff began.

Another irrigation practice often used to reduce advance time is surge irrigation, sometimes called interrupted flow irrigation. The advantage of surge irrigation is that an intentional depositional seal is laid down in the furrow during the first surge of water across the field, and the brief interruption of flow stabilizes the seal through matric potential effects (Kemper *et al.*, 1988; Trout, 1991). The high flow rate used to form the initial depositional seal, however, is often at the expense of excessive erosion in the upper reaches of the furrow. Sirjacobs *et al.* (2000) studied the effects of combining PAM treatments with flow interruption on 0.5-m long × 0.05-m wide × 0.12-m deep miniflumes on a silt loam Alfisol and a clay Vertisol. They found that PAM reduced soil loss in all instances, but that changes in infiltration rate varied with the soil, irrigation, and PAM treatment. PAM reduced infiltration rate in the Alfisol and increased it in the Vertisol. In the Alfisol, interrupted flow with PAM reduced infiltration rate by 37% versus 18%

without PAM. In the Vertisol, PAM had no effect and interrupted flow had only slight effects. They explained the reduced infiltration rate with PAM in the interrupted flow treatment as due to pore blocking by the PAM, leading to greater suction and compaction of the soil surface. Because surge irrigation is a process very much dependent on large-scale field dynamics (differing effects in the upper scoured area of the field vs lower depositional areas), and since clay cracking effects cannot be well represented spatially in such small flumes, it is not certain how well these results reflect actual field irrigation.

Kornecki *et al.* (2005) used PAM applied to sugarcane field "quarter drains" in Louisiana to control erosion and transport of sediments to riparian waters following heavy rainfall. Water entering the quarter drains from sugarcane fields is somewhat like the inflow of water into furrows in furrow-irrigated fields, except the quarter drains would be wet by the time runoff began entering them. They spray-applied PAM at 18 kg ha^{-1} following formation of the quarter drains and monitored erosion over the course of six rainfall events totaling 368 mm. The treatment was highly successful, reducing erosion by 88% in the first three rainfall events (161 mm cumulative total) and by 76% for the six events. Significant advantage was also seen in elimination of the need to reshape the drains following severe rainfall events. Similarly, Peterson *et al.* (2003) looked at the effects of PAM treatment on erosion in concentrated flow channels prior to vegetation. PAM-treated channels had 93–98% reduction in erosion compared to untreated channels. Channel incision depth with PAM treatment was not significantly different from controls but incision width was significantly greater, and the rate of headcut movement varied from less than 0.6 m h^{-1} in PAM-treated channels to over 17.8 m h^{-1} in the controls. Research showing the prevegetative stabilization of concentrated flow areas with PAM is further encouragement to research showing that PAM stabilization of soil can enhance grass emergence (Rubio *et al.*, 1989, 1990, 1992). Sojka *et al.* (2003) showed that loss of weed seed from irrigated furrows was greatly reduced by PAM use; this is a further indication that PAM can benefit seed retention during the establishment phase of hydroseeded surface drainage control features. Others have shown increased emergence of fragile seedlings where PAM has been applied to reduce crusting effects (Chan and Sivapalan, 1996; Helalia and Letey, 1989).

IX. SPRINKLER IRRIGATION

Although the interest in PAM use for furrow irrigation has been phenomenal and dominated the initial technology development and practice adoption, there is as much and perhaps more interest in developing the technology for use in sprinkler irrigation. Farmers who irrigate with sprinklers are familiar with concepts of chemigation and generally have greater expectations for precision application of inputs, including water application. Because PAM reduces structural degradation caused by droplet impact, potential exists for reduced depositional sealing, with less runoff or runon, and hence more uniform infiltration. There is also the potential for improved stand establishment through reduction in crusting and reduced ponding.

Runoff and erosion increase with increasing water drop energy. PAM, however, limits aggregate disruption caused by water drop impacts. Smith *et al.* (1990) and Levin *et al.* (1991) reported that the relative effect of PAM on aggregate stability increased with increasing kinetic energy of the water drops. This may be related to the finding that only the outer surfaces of aggregates are stabilized by PAM treatment due to the relatively shallow penetration of the macromolecule (Ben-Hur and Keren, 1997; Malik and Letey, 1991). Thus, the value of PAM for erosion control in sprinkler irrigation is greater in systems that have high application rates, which typically means larger droplet sizes and greater droplet energy.

Very few papers have been published that report results of PAM application through the sprinkler system itself, especially in field scale studies. Most reports involve pretreatment of soil with PAM sprays or powders, and in this respect are closely related to rainfall simulator work targeted to rainfed situations. Shainberg *et al.* (1990, 1992) applied three rates of PAM on dry soil in a small-tray laboratory study prior to sprinkling in a rainfall simulator and reported that 20 kg ha^{-1} PAM best maintained high-infiltration rates. Smith *et al.* (1990) and Levin *et al.* (1991), in similar studies, found that 20 kg ha^{-1} of PAM increased infiltration and greatly reduced runoff and erosion. Peterson *et al.* (2001, 2002) also found in small-tray studies that PAM sprayed on soil prior to simulated rainfall reduced runoff and erosion. Cochrane *et al.* (2005) using a rainfall simulator on steep (8–12% slopes) coarse-textured tropical Alfisols found an average of 90% erosion reduction and 35% runoff reduction using a series of PAM-based soil amendment treatments in which PAM was sprayed before rainfall at 20 kg ha^{-1}. Kim *et al.* (2001) spray-applied PAM at 20 or 40 kg ha^{-1}on plots in vegetable fields in Korea which were then watered at 80 mm h^{-1} with a rainfall simulator three times for 30 min each at different times in the season. PAM reduced runoff and erosion significantly during the growing season but was no longer effective after harvest, probably as a result of soil disturbance during harvest.

Ben-Hur *et al.* (1989) concluded from a small-tray laboratory study that applying 5 kg ha^{-1} PAM with simulated irrigation water was more effective in maintaining high infiltration rates than was spraying the polymer on the dry soil surface prior to simulated irrigation. Levy *et al.* (1992) found that applying PAM at 10 mg $liter^{-1}$ to irrigation water in a small-tray laboratory study gave optimal effect on final infiltration rate and cumulative infiltration as well as on reducing erosion. Flanagan *et al.* (1997a,b) applied 10 mg liter^{-1} of PAM to tap water in simulated rainfall studies and found increased water infiltration, which they attributed to reduced surface sealing in the PAM treatment. They reported increased sediment concentrations from the PAM-treated runs compared to controls, but it was not clear how total sediment loss (concentration times runoff volume) was affected.

Surface sealing, crusting, runoff, and erosion have been reduced in field plot studies by spraying PAM on dry soil prior to sprinkler irrigation (Ben-Hur, 1994; Levy *et al.*, 1991; Zhang and Miller, 1996; Zhang *et al.*, 1998). Levy *et al.* (1991) and Ben-Hur (1994) reported the effects of 20 kg ha^{-1} of PAM spray-applied to small field plots that were subsequently irrigated with a moving sprinkler irrigation system. They saw reduced runoff, reduced erosion, and increased soil water profile uniformity. Effects were greatest on bare soil and greatly diminished after three or four irrigations. Stern *et al.* (1991, 1992) sprayed dry soil with 20 kg ha^{-1} PAM before sprinkler irrigation and saw increased wheat (*Triticum aestivum* L.) yields where PAM had been applied. They attributed the yield increases to improved water distribution and increased irrigation water use efficiency. Ben-Hur (2001) reported results from a field study with 3 × 20 m^2 treatment plots and 3.5 m^2 runoff plots on which a series of emitters and PAM application rates were compared. The PAM used was a relatively low molecular weight nonionic formulation. In that experiment PAM improved infiltration and reduced runoff and erosion with increased efficacy for application rates up to 10 kg ha^{-1}, but showed no effect on potato (*Solanum tuberosum* L.) yield. As in other studies, as the season progressed, the effectiveness of the initial PAM application declined.

While pretreating soil with PAM solutions or powder mixtures can be effective for erosion control and runoff reduction, they are not always easily executed on a field scale or production agricultural basis because of the bulk and viscosity of solutions and the difficulty of routinely achieving even surface distribution of granular- or powder-based PAM amendments. Sprinkler irrigation, particularly center-pivot irrigation, has the potential to overcome these obstacles through chemigation. Ben-Hur *et al.* (1989) found that the equivalent of 5 kg PAM ha^{-1} applied via water during rainfall simulations on small trays of soil prevented crust formation better than spraying the same amount of PAM on the soil surface. Flanagan *et al.* (1997a) reported that applying PAM at 10 ppm with simulated rainfall increased final infiltration rate compared to the untreated control, whereas 20 kg PAM ha^{-1} applied directly to the soil did not. Levy *et al.* (1992) applied 3, 6, or 12 kg PAM ha^{-1} with irrigation water for three consecutive irrigations on small trays. PAM increased final infiltration rate during treated irrigations, but final infiltration rates decreased to control values after irrigating twice more with only water.

A series of experiments (Aase *et al.*, 1998; Bjorneberg and Aase, 2000; Bjorneberg *et al.*, 2000a,b) were conducted in Kimberly, Idaho in a sprinkler irrigation simulator using soil boxes 1.5-m long × 1.2-m wide × 0.2-m deep on a 6.5% slope. The soil used was a Rad silt loam (Durinodic Xeric Haplocambid). In these experiments PAM was injected in the irrigation water using application scenarios that center-pivot farmers already familiar with chemigation procedures had indicated might be reasonable for use in commercial operations.

In the initial study, PAM rates of 2–4 kg ha^{-1} applied only on the initial irrigation reduced runoff 70% and soil loss 75% compared to controls (Aase *et al.*, 1998). By the third irrigation runoff reduction in the PAM treatments was only 20% and soil loss reduction 40%, indicating that, as has been seen in other studies, gradual effects of droplet impacts began disrupting surface structure and forming a seal. The gradual seal formation in PAM treatments was dependent on PAM application protocol. The presence of seals was determined through measurement of infiltration under 40 and 100 mm of tension. When the total PAM application was applied in the first 8 of 20 mm sprinkled water, seal differences were detectable when measured following the third irrigation. However, if the same amount of PAM was applied at greater dilution in the full 20 mm of sprinkled water, there was no longer a detectable seal difference between PAM treatments and controls. This indicated that treatment effects on runoff and erosion were predominately in the initial irrigation but did not persist in subsequent irrigations. Using the 8-mm PAM application protocol, the infiltration under 40-mm tension increased from 14 mm h^{-1} on the check treatment to 29 mm h^{-1} for the 4 kg ha^{-1} application rate and increased from 9 to 17 mm h^{-1} under 100-mm tension, when measured following the third 20-mm irrigation. Flanagan *et al.* (1997a,b) reported increased infiltration when rainfall simulator water contained 10-ppm PAM; they also attributed this to reduced surface sealing although direct measurements of seal properties were not made to verify the inference.

The role of PAM in stabilizing surface structure and seal prevention was further verified by Aase *et al.* (1998). Aggregate stability measurements across treatments showed a statistically significant 23% increase in aggregate stability with PAM treatment in the initial irrigation, but no statistical difference in aggregate stability in the third irrigation. Ben-Hur and Keren (1997), Levin *et al.* (1991), Aase *et al.* (1998), and Smith *et al.* (1990) all reported improved aggregate stability from sprinkler-applied PAM, leading to decreased runoff and erosion.

Although soil loss reductions in the Aase *et al.* (1998) sprinkler experiment were slightly less than is achievable for PAM use in furrow irrigation, it should be noted that properly engineered and managed sprinkler irrigation is already an effective erosion-limiting practice compared to most types of surface irrigation, and a 75% reduction of soil loss in this instance represents a conservation gain beyond that already expected from a sprinkler system. The results also underscore the observations that effectiveness of sprinkler-applied PAM is more variable than for furrow irrigation because of application strategies and system variables that affect water drop energy, the rate of water and PAM delivery, and possible application-timing scenarios (Aase *et al.*, 1998; Levin *et al.*, 1991; Smith *et al.*, 1990).

In a second experiment, Bjorneberg and Aase (2000) noted that greater erosion control was achieved by applying PAM over several sprinkler irrigations rather than applying all the PAM in the initial irrigation. Water was applied at 80 mm h^{-1} for 10 min (13-mm application) for four irrigations. PAM was either applied at 3 kg ha^{-1} in the irrigation water once in the first irrigation or at 1 kg ha^{-1} in each of the first three irrigations. Both PAM treatment scenarios were followed by a fourth nontreated 13-mm irrigation and were compared with controls of four nontreated 13-mm irrigations. All PAM treatments significantly reduced runoff and erosion compared to the controls for all four irrigations. The multiple PAM treatment, however, reduced runoff 30% more than the single application during the last two irrigations. The single PAM application reduced cumulative soil loss 60% compared to the control, whereas the multiple PAM application reduced cumulative soil loss 80% compared to the control. Splitting the PAM application increased both the effectiveness and the duration of the erosion-reducing and infiltration-enhancing effect. At the end of the irrigation series, the percentages of stable aggregates of the single and multiple PAM application treatments were 80% and 85%, respectively, compared to 66% in the controls. A column study by Gardiner and Sun (2002) saw similar results for splitting PAM applications.

A third study (Bjorneberg *et al.*, 2000a,b) evaluated the relative effectiveness of PAM and straw cover compared to untreated bare soil for erosion control with sprinkler irrigation. Where 4 kg ha^{-1} PAM was applied via sprinkler irrigation only in the first of three 20-mm irrigations (80 mm h^{-1} rate at 25 J kg^{-1}), a 30% straw cover treatment matched PAM treatment erosion and runoff effects. A 70% straw cover treatment had slightly greater erosion reduction and infiltration increase. Erosion, runoff, and P loss were controlled as well or slightly better than any separate PAM or straw treatment if PAM and straw were combined. If PAM application was split among irrigations, erosion and infiltration effects of PAM were much more persistent compared to a single application in the first irrigation.

In summary, PAM effects under sprinkler irrigation can be more transitory and less predictable than under furrow irrigation, depending on application amounts and protocols. Slightly higher seasonal field application totals for efficacy may be required in sprinkler application of PAM compared to furrow application in some cases. Sprinklers must stabilize two to three times more surface area than furrow streams, especially early in the season, and must also protect against water drop energy effects. Despite higher rates and technical challenges for provision of user-friendly PAM formulations allowing controlled injection, farmers with problems such as damping off or N loss, stemming from sprinkler infiltration nonuniformity, leading to runoff or runon, have begun to apply PAM with sprinklers. These problems are common on variable or steep slopes or in high-application areas at outer reaches of center pivots. Because of the larger scale necessary to run reasonable agronomic comparisons of PAM treatments under center pivots and other forms of production sprinkler irrigation, where PAM is injected via the system, some uncertainty remains as to seasonal costs and benefits for specific crops. This is particularly true given differences in season length and canopy effects.

Many farmers have noted that, with PAM use, yield often improves from zero or near-zero on upslope field areas or in areas with localized steep slopes, to near-normal yields when using PAM in either furrow- or sprinkler-irrigated systems. This is because in steep areas untreated water runs off so readily that insufficient infiltration occurs to allow plant growth and production (Shock *et al.*, 1988). This kind of production result and anecdotal observation is difficult to quantify systematically in normal field plot studies but is a very real effect that often greatly outweighs the more moderate effects reported from controlled studies in uniform experimental plots. A farmer invests inputs in these field areas, but receives no return from them. When PAM allows infiltration to occur in these areas the effect on farmer economic return can be substantial. The more extensive the occurrence of such areas in a farmer's field the greater the benefit from PAM use.

X. INFILTRATION

As noted in the prior section on erosion, many papers reporting erosion control with PAM application also reported increases in infiltration. We focus here on papers that were seminal in this area, that produced specific new insights on the infiltration process as affected by PAM application, or that were from field scale studies, which may provide better insight to real world deployment of the technology.

The papers that first investigated infiltration effects in which PAM application was through the irrigation system were Paganyas *et al.* (1972), Paganyas (1975), and Mitchell (1986). The reports by Paganyas and coworkers covered a range of application concentrations and amounts, and as stated previously, may have been a polymer other than PAM. Nonetheless, they provided coarse estimates of runoff reduction and infiltration increases, as well as yield improvement of several crops. Mitchell reported an initial increase in infiltration with PAM treatment which did not persist to the end of an irrigation. The PAM rates used were 6.6, 13.3, and 32.2 kg ha^{-1} applied as liquid concentrations of 25, 50, and 150 mg $liter^{-1}$ in irrigation flows. Mitchell estimated the material application rates were three times the calculated per hectare calculations since application was only in the actual furrow, and nonfurrow areas were not treated. PAM applied as an evenly dispersed powder at 42 kg ha^{-1} had no effect on infiltration. Mitchell speculated that the swell of wet subsoil overrode any PAM infiltration-enhancing properties.

Shainberg and Levy (1994) provided an excellent review of the concept of hydraulic conductivity-reducing surface seals, their role governing infiltration, and the history of polymer amendment of seals (particularly with PAMs or polysaccharides) through the late 1980s. Cultivated soils are structurally unstable and form a seal at the soil surface when exposed to rain or flowing water. The formation of a seal limits the water infiltration rate and influences runoff and erosion. A seal is a thin layer of oriented soil particles with low porosity, often high in clay, located at the soil's surface. Numerous early papers reported increased infiltration with dilute or low-rate PAM application to the soil surface, whether applied as a pretreatment dusting, low-volume aqueous spray, or in the irrigation water, or simulated rain water (Agassi and Ben-Hur, 1992; Agassi *et al.*, 1981; Ben-Hur and Letey, 1989; Ben-Hur *et al.*, 1989; Bryan, 1992; Fox and Bryan, 1992; Gabriels, 1990; Gabriels *et al.*, 1973; Helalia and Letey, 1988a,b; Levin *et al.*, 1991; Levy *et al.*, 1992; Shainberg *et al.*, 1990; Shaviv *et al.*, 1986, 1987; Smith *et al.*, 1990; Wallace and Wallace, 1986a,b). Soluble PAM was identified as a highly effective erosion-preventing and infiltration-enhancing polymer when applied in irrigation water at the rate of 1–10 ppm (Lentz and Sojka, 1994). PAM achieves this result by stabilizing soil surface structure and pore continuity against the effects of rapid wetting and flow shear that otherwise promoted detachment and transport of soil, leading to erosion and formation of infiltration-reducing seals.

As noted in much of the literature already reviewed in this chapter, very low application rates or dilute solutions of PAM stabilize soil surface structure, preventing or limiting formation of surface seals that reduce surface hydraulic conductivity. On irrigation or rainfall, this phenomenon results in better maintenance of initial infiltration rates compared to untreated soils (often reported as "increased" infiltration). The effect is concentration and application rate dependent. It is also affected by soil properties, including the structural condition of the soil at the time PAM is applied as well as being affected by PAM formulation, molecular configuration, concentration, and application methodology (Lentz, 2003; Sojka *et al.*, 1998a). The upper limit of "low application rate" and "dilute" cannot be precisely set; however, there is a large body of literature that reports infiltration increases for PAM concentrations in irrigation water of 20 ppm or less. Similarly, where PAM is applied other than through irrigation water, PAM application rates associated with infiltration increases are usually 20 kg ha^{-1} or less. The choice of these limits is supported by recent research (Lentz, 2003).

PAM maintains higher infiltration rates in treated soils primarily by stabilizing soil structure, preventing the breakdown of soil aggregates, and reducing dispersion of waterborne soil particles, leading to formation of infiltration-inhibiting surface seals. If the soil structure has already been destroyed or if the soil is sandy (thus composed mainly of primary particles and lacks soil structure resulting from the aggregation of fines), PAM treatment may reduce rather than increase infiltration. Since soil structure degradation has little influence on sealing under these conditions, PAM's tendency to increase viscosity of the infiltrating water becomes the dominant phenomenon. Increasing soil solution viscosity results in reduced infiltration (Malik and Letey, 1992). Lentz (2003) demonstrated that when 1- to 20-ppm PAM was dissolved in the first irrigation water applied to structured soils containing dispersible fines, it increased infiltration rates relative to untreated soils but at higher concentrations it decreased infiltration. Whereas, if the soils were pretreated with PAM solutions and allowed to dry before irrigation, PAM treatment did not inhibit infiltration into silt loam soils until the PAM concentration in the pretreatment solutions exceeded 500 ppm.

Furrow irrigation stream advance is usually slower when using PAM for erosion control, especially for the first irrigation on newly formed or cultivated furrows (Lentz *et al.*, 1992; Sojka *et al.*, 1998a,b; Trout *et al.*, 1995). Advance rate depends on inflow rate, slope, and infiltration rate. Advance of PAM-treated furrows slows because of the effect of PAM on soil structure, which in turn affects infiltration rate. Surface seals form on untreated furrow bottoms due to the destruction of soil aggregates with rapid wetting, and the detachment, transport, and redeposition of fine sediments in the furrow stream. This seal formation process blocks most of the pores at the soil surface, reducing the infiltration rate. For equal inflows, net infiltration on freshly formed PAM-treated furrows in silt loam soils is typically 15% more, compared to untreated water. Net infiltration usually increases more with PAM-treated irrigation on finer textured soils because the relative effects of sealing are greater with a greater abundance of clay available for dispersion, transport, and redeposition into pores. Pore continuity is maintained when aggregates are stabilized by PAM. Ross *et al.* (1996) and Sojka *et al.* (1998a) reported that infiltration at 40-mm tension varied among irrigations over the range 12.9–31.8 mm h^{-1} for controls and 26.7–52.2 mm h^{-1} for PAM-treated furrows, and that infiltration at 100-mm tension varied from 12.3 to 29.1 mm h^{-1} for controls and 22.3 to 42.4 mm h^{-1} for PAM-treated furrows.

PAM infiltration effects are a balance between prevention of surface sealing and apparent viscosity increases in soil pores. Bjorneberg (1998) reported that in tube diameters >10 mm, PAM solution effects on viscosity are negligible at 15 and 30 °C. Macropore viscosity rose sharply only after PAM exceeded 400 ppm. In small soil pores, "apparent viscosity" increases greatly, however, even at the dilute PAM concentrations used for erosion control (Malik and Letey, 1992). The more significant effect in medium to fine-textured soils is the maintenance of pore continuity achieved by aggregate stabilization and prevention of surface sealing. In coarse-textured soils (sands), where little pore continuity enhancement is achieved with PAM, there have been reports of no infiltration effect or even slight infiltration decreases, particularly at concentrations above 20 ppm (Sojka *et al.*, 1998a; Trout and Ajwa, 2001).

For furrows formed on wheel tracks, the increase of infiltration often seen with PAM did not last as long as on nontrafficked furrows (Sojka *et al.*, 1998b). They postulated that in wheel trafficked furrows reduced surface sealing with PAM improves infiltration only until repeated wetting and drying begins to disrupt subsurface aggregates and/or deliver enough surface-derived fines to seal the few remaining subsurface pores that are already partially reduced by compaction. On further consideration, it may have been that the repeated PAM applications in undisturbed wheel track furrows, which had greater pore restrictions to begin with due to compaction, eventually had some pore blockage from the PAM itself.

Gardiner and Sun (2002) used PAM rates of 0, 10, 25, and 40 ppm in deionized tap water or in water from a municipal wastewater treatment facility in a column study that tracked saturated hydraulic conductivity for a single PAM application over seven irrigations versus alternate PAM no-PAM irrigations. In all single-application PAM treatments, soil hydraulic conductivity was increased for the initial 2–3 weeks of column irrigation but fell to control values thereafter, whereas treating with PAM in alternate irrigations maintained higher hydraulic conductivities throughout the study, regardless of water quality. Gardner and Sun (2002) noted the reduction of infiltration rate at higher PAM concentrations and expressed concern over the cumulative effect of high application rates on long-term infiltration rate and hydraulic conductivity.

Trout and Ajwa (2001) saw an absence of response or minor reductions in infiltration rate with PAM use in a 2-year furrow irrigation study on a Hanford sandy loam (Typic Durixeralf), a coarse-textured San Joaquin Valley soil. Their conclusion was that if there is not an abundance of disruptable aggregates in a soil, then the balance of PAM effects shifts to greater expression of the "apparent viscosity" effect proposed by Malik and Letey (1992) and Letey (1996). Falatah *et al.* (1999) also saw reduced infiltration with use of PAM on a 90% sand soil in Saudi Arabia, which related to increased PAM concentration and measurements of PAM viscosity.

Because PAM prevents erosion of furrow bottoms and sealing of the wetted perimeter, lateral water movement increases about 25% in silt loam soils compared to nontreated furrows (Lentz and Sojka, 1994; Lentz *et al.*, 1992). This increased lateral movement of water results from several factors. One reason is simply because the furrow is not eroding, thus the water level in the furrow maintains a higher elevation. To the extent that the wetting pattern has shoulders, these shoulders are nearer the soil surface. The pores along the side of the furrow (upper portions of the wetted perimeter) are stabilized, just as the pores at the bottom of the furrow, thus the restriction to water movement along potential gradients in the lateral direction are less if PAM is present to preserve pore continuity. Also, to the extent that apparent viscosity is a factor in PAM movement through soil pores, the downward movement of water may be slightly more impeded, again, tending to broaden the shoulders of the wetting pattern. Increased lateral wetting can be a significant water-conserving effect for early irrigations, where the intent is only to germinate seeds or to provide water to seedlings that are still evapotranspiring smaller daily amounts of water. Since most farmers only irrigate alternate furrows, the early irrigations need only apply enough water for the wetting front to reach seeds or seedling roots; they do not need to thoroughly wet the entire rooting depth or wet beyond the row middle for water storage. These goals are achieved with less total water per hectare if lateral movement of water is favored.

Falatah *et al.* (1999) used concentrations of 10–50 ppm of three different water-soluble PAMs. They saw decreased depth of wetting and greater lateral movement of water that corresponded to the increases in concentration and resultant viscosity changes of the polymers they tested. The calcareous soil (Typic Torripsamment) contained 90% sand, 5% silt, and 5% clay. The effects also occurred with decreases in infiltration rate in the PAM-treated soils. The authors concluded that the PAMs could help prevent deep percolation losses in this sandy soil, but were concerned that the reduced infiltration reduced the usefulness of water-soluble PAMs for water conservation. However, in other areas of the world, this specific pairing of properties has been interpreted as a way in sandy soils (where infiltration rate is rarely a problem) to slow the loss of water, making it and the nutrients carried in the water available for a longer time by the crop root system (Shane Phillips, Adelaide University, Australia, personal communication). In Australia, water-soluble PAMs are being marketed for use in center pivots on coarse sands as a water and nutrient conservation tool. Levy and Rapp (1999) reported that water-soluble PAM, applied to the surface of a silt loam soil, reduced the loss of water during the drying process.

With further verification this could be an important new direction for PAM research in coarse-textured soils and other water-limiting situations.

PAM use in both furrow and sprinkler irrigation increased infiltration and reduced erosion in Portugal (Bjorneberg *et al.*, 2003; Santos and Serralheiro, 2000; Santos *et al.*, 2003). Furrow infiltration was characterized in 100-m furrows with recirculating infiltrometers, double-ring infiltrometers for saturated infiltration, as well as tension infiltrometers. Net infiltration improved 20% and 14% for continuous application of 1 and 10 ppm advance-only application. Tension infiltration of controls was 19.4 and 15.8 mm min^{-1} for 40- and 100-mm tension values, respectively, compared to 36.6 and 30.1 mm min^{-1} for the continuous 1-ppm PAM treatment and 28.0 and 20.2 mm min^{-1} for the 10-ppm advance-only treatment. Double-ring infiltration rates were 53% greater than controls on the final irrigation with the continuous 1-ppm PAM treatment and 60% greater with the advance-only treatment. Surface hydraulic conductivities of the control treatment were 14.4, 8.8, and 11.8 cm h^{-1} for 0-, 40-, and 100-mm tension values, respectively, compared to 67.5, 24.1, and 42.4 cm h^{-1} for the continuous 1-ppm PAM treatment and 52.4, 15.3, and 32.4 cm h^{-1} for the 10-ppm PAM at advance-only treatment.

PAM's erosion prevention properties can permit farmers who furrow irrigate to improve field infiltration uniformity through altered inflow management. This can be done by increasing inflow rates two- to threefolds (compared to normal practices), thereby reducing infiltration opportunity time differences between inflow and outflow ends of furrows (Sojka and Lentz, 1997; Sojka *et al.*, 1998b). When runoff begins, the higher initial inflow must be reduced to a flow rate that just sustains the furrow stream at the outflow end of the field. Initial field observations suggest that coupling PAM with surge flow irrigation can be a beneficial practice (Bjorneberg and Sojka, unpublished data). With PAM in the water, there is still enough reconsolidation of the furrow surface for surges to accelerate advance. However, the upper-field scouring associated with doubled flows (as is common when surge valves are used) does not occur.

It is generally accepted that lower molecular weight polymers (0.1–5.0 Mg mol^{-1}) can be more effective at stabilizing infiltration than higher molecular weight polymers because they penetrate soil pores more readily and provide structural stabilization to a greater depth, better preserving soil hydraulic properties. However, lower molecular weight polymers are usually less effective for erosion control. Thus the choice of polymer can be a compromise dependent on which management factor is of greater concern. Because anionic PAMs of 12–15 Mg mol^{-1} have so many safety and efficacy attributes favoring them for multiple environmental uses, this class of PAMs has become the standard and the center of discussion for PAM use in erosion and infiltration control since the early 1990s.

As noted in the opening discussion about infiltration, PAM's effect on structure stabilization is a key element in surface seal prevention and increasing infiltration. However, it should be emphasized that PAM does not improve soil structure. It merely stabilizes the existing structure it encounters during application. Several researchers have noted that application of PAM for erosion control works best when applied to soil with newly prepared, aggregated soil surfaces (Cook and Nelson, 1986; Lentz and Sojka, 1994; Shaviv *et al.*, 1987a,b; Sojka and Lentz, 1997). In this manner the PAM applied stabilizes structure that is both conducive to infiltration and preserves surface roughness to resist shear in the presence of flowing water. Sojka *et al.* (1998b) found increased aggregate stability within the entire wetted perimeter of PAM-treated irrigation furrows in all PAM treatments, which also had increased infiltration and reduced erosion.

Several papers have been published indicating that PAM adsorption is relatively shallow in soil and that perhaps only the outsides of aggregates adsorb PAM, so that the applied PAM does not reach aggregate interiors (Malik and Letey, 1991; Malik *et al.*, 1991b; Nadler and Letey, 1989; Nadler *et al.*, 1994, 1996). Work by Miller *et al.* (1998) and Levy and Miller (1999) indicate, however, that this may not be universally the case. Their work with Worsham sandy loam (Typic Ochraquults) and Cecil sandy clay (Typic Hapludults), soils with predominately 1:1 clay minerals, concluded that PAM penetrated and stabilized the interiors of even relatively large aggregates (6–8 mm) and increased the percentage of large stable aggregates. They concluded that PAM was a more effective structure stabilizer in light- to medium-textured soils, where the addition of 10–20 kg ha^{-1} tripled the fraction of water-stable aggregates. As with many other aspects of PAM performance, the evidence suggests that PAM properties and solution concentrations may interact differently with varying soil properties, affecting the degree of PAM penetration into aggregates.

Although many papers have reported that PAM application "prevents" seal formation, it is probably more accurate to state that PAM "changes" seal formation. Extensive work from Kimberly, Idaho, applying PAM through both furrow- and sprinkler-irrigated systems, has repeatedly noted that soil surface structure changes with irrigation, both with and without the application of PAM in the irrigation water. Surface seals form in both cases. The difference is that in the PAM-treated systems, the seals formed are typically more porous and thinner than the seals formed by untreated water (Fig. 4). Soil in PAM-treated furrows is held in place against shear forces of flowing water by the thin web of polymer that coats particle surfaces at the soil water interface, maintaining better pore continuity to the soil below (Fig. 5). Finally, although we state rather unequivocally that PAM does not create structure, but rather it only stabilizes the structure it encounters on application, there is a minor exception. PAM does create

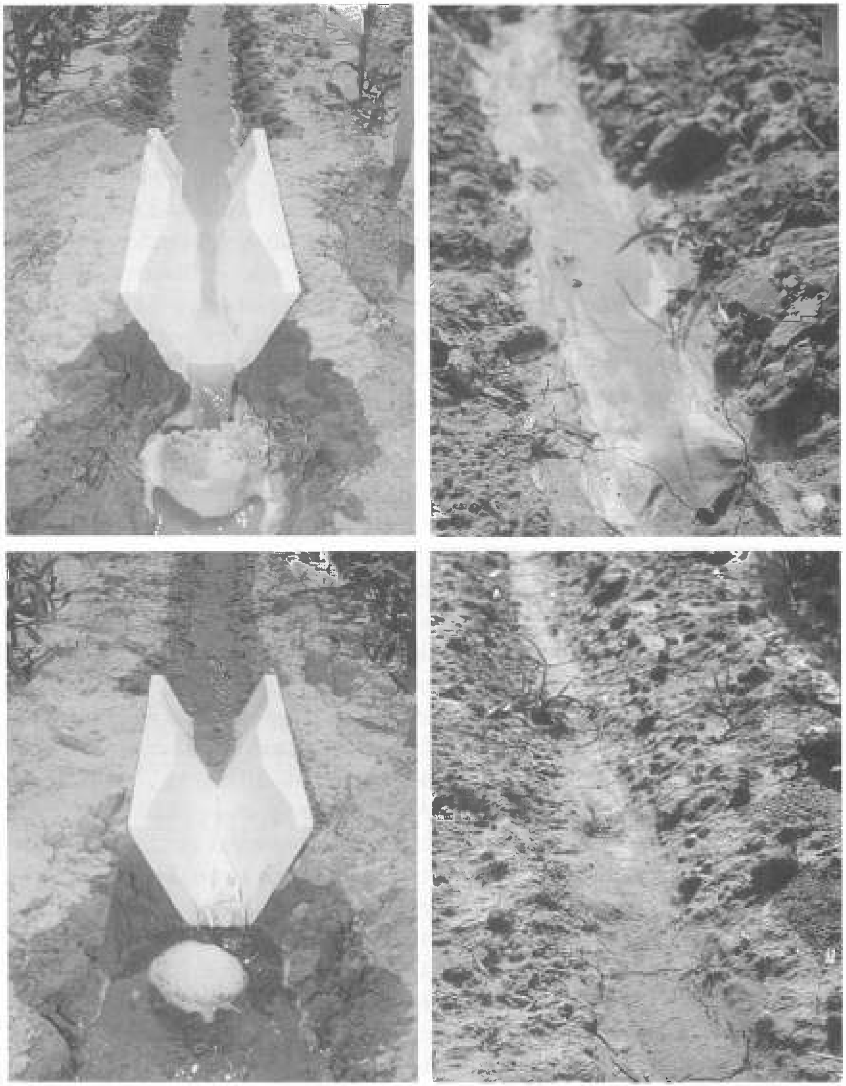

Figure 4 Effects of furrow irrigation water treatment on soil surface structure in a Portneuf silt loam soil. Top left: Turbid water carrying sediment flowing in an untreated furrow. Top right: Slick impervious surface seal left after flow ceases in untreated control furrows. Bottom left: Clear sediment free water flowing in a PAM-treated furrow. Bottom right: Rough porous surface left after flow ceases in a PAM-treated furrow. (See Color Insert.)

structure to the extent that, in turbid water, it creates floccules which settle out of suspension onto the furrow's (or other water body's) soil surface. These floccules tend to be loose open structures that do not restrict water

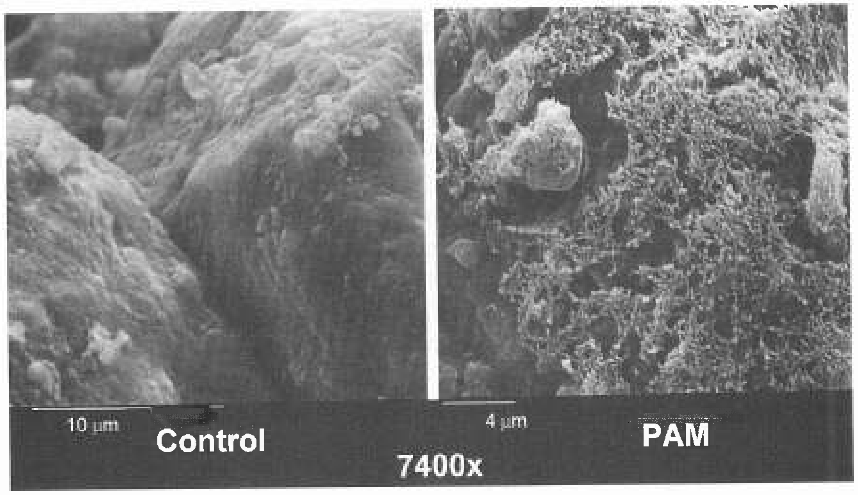

Figure 5 Scanning electron micrographs of untreated soil particles (left) and PAM-treated soil particles (right) showing strandlike PAM filaments coating and binding soil particles (Sojka *et al.*, 2005).

entry, and which do not seal surfaces in the manner of dispersed clays or other unconsolidated fines.

XI. PAM SAFETY, FIELD RETENTION, AND ENVIRONMENTAL IMPACTS

At this time PAM is not regulated under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), however, it is regarded as a macropollutant with low toxicity and side effects. As noted earlier, PAM has been used for many decades ubiquitously in a number of food, environmental, and other sensitive applications, often involving significant disposal or release to the environment. Some safety and environmental cautions are warranted, but the low toxicity of PAMs in general, especially large molecular weight anionic PAMs, means that if used according to prescribed guidelines risks to human and environmental health are small. The greatest concern surrounding PAM use is generally a concern stemming not from PAM itself, but rather from the presence of unreacted residual AMD as a product contaminant.

AMD is a neurotoxin and a suspected carcinogen in humans and animals (Garland and Patterson, 1967; WHO, 1985). It has not been shown to cause mutations in bacteria but has been shown to cause chromosome damage to mammalian cells *in vitro* and *in vivo* (Bull *et al.*, 1984; Shiraishi, 1978; WHO, 1985). AMD is readily absorbed by ingestion, inhalation, or dermal contact and is then moved freely through body fluids. Unlike PAM, AMD can cross membrane barriers. However, AMD is also easily metabolized and is largely excreted as metabolites in urine and bile, although fecal excretion is minimal in hours to a few days (Miller *et al.*, 1982). AMD exposures have resulted in isolated human fatalities and temporary injury or impairment with ingestion or extensive exposure to concentrations of over 400-ppm AMD (Garland and Patterson, 1967; Igisu *et al.*, 1975). However, the exposure levels required to cause neurotoxic or carcinogenic effects in humans are several orders of magnitude above those conceivable from exposures resulting from current environmental applications. National Institute of Occupational Safety and Health (NIOSH) guidelines recommended an exposure limit 0.03 mg m^{-3} which is equivalent to 0.004 mg $kg^{-1}day^{-1}$ for an 8-h work day (NIOSH, 1992), and for a 100-kg human that would equal 0.4-mg AMD, which is 80% of the allowable unreacted AMD in a kilogram of the anionic PAMs used for erosion control.

PAM's potent efficacy for reducing runoff and erosion from treatment sites translates into substantial additional benefits off site as well. Irrigation runoff ultimately reaches riparian waters in most instances. These waters are important ecologically, as drinking water sources and for recreational use, with potential for human exposure to or ingestion of contaminants. A substantial body of research documents water quality benefits of PAM use beyond reduction of runoff sediment per se. Among the components of water quality impairment that PAM use significantly mitigates are sediment, BOD, mineral nutrients, pesticides, weed seed, and pathogenic microorganisms. Furthermore, rigorous tests of PAM concentration downstream from PAM application sites have shown that, properly applied, PAM poses no serious risk of PAM loss. Where minor PAM losses occur, its strong surface attractive properties result in rapid PAM removal from water bodies through adsorption and flocculation of suspended solids within a few hundred meters of transport from an application site (Lentz *et al.*, 2002). In most instances, the latter aspect is actually a continuation of PAM's water quality improvement benefit occurring downstream when small losses from the application site occur.

An important environmental and applicator safety consideration is the need to use PAMs that contain <0.05% AMD. AMD is a neurotoxin, but PAMs below these AMD contents are safe, when used as directed at low concentrations. In soil, PAM degrades at rates of at least 10% per year as a result of physical, chemical, biological, and photochemical processes and reactions (Azzam *et al.*, 1983). Because PAM is highly susceptible to UV degradation, its breakdown rate when applied at the soil surface for erosion control may be faster than the 10% per year reported rate, which was for biological degradation of PAM mixed into a large soil volume. Possible indirect evidence of the accelerated breakdown of surface-applied PAM is the gradual loss of treatment effectiveness between irrigations on furrows receiving no additional PAM (Lentz *et al.*, 1992). PAM does not revert to AMD on degradation (MacWilliams, 1978). Furthermore, AMD is easily metabolized by microorganisms in soil and biologically active waters, with a half-life in tens of hours (Lande *et al.*, 1979; Shanker *et al.*, 1990). Bologna *et al.* (1999) and Barvenik *et al.* (1996) showed that AMD is not absorbed by plant tissues and apparently breaks down rapidly when exposed to living plant tissue.

While anionic PAMs are safe if used as directed, prolonged overexposure can result in skin irritation and inflammation of mucus membranes. Users should read label cautions and take reasonable care not to breathe PAM dust and to avoid exposure to eyes and other mucus membranes. Another caution is that PAM spills become very slippery if wet. PAM application onto roadways should be avoided, and PAM spills should be thoroughly cleaned with a dry absorbent and removed before attempting to wash down with water. Practical user considerations are numerous. Labels, website information, and available extension information should be consulted before embarking on large-scale use of PAM.

Used at prescribed rates, anionic PAMs are environmentally safe. Although cationic and neutral PAMs have toxicities warranting caution or preclusion from sensitive environmental uses, NRCS specifies anionic PAMs for controlling irrigation-induced erosion. Negative impacts have not been documented for aquatic macrofauna, edaphic microorganisms, or crop species for the anionic PAMs used for erosion control when applied at recommended concentrations and rates.

Several studies examined the fate of PAM when applied to furrow irrigation inflows at 10 ppm during furrow advance. PAM was applied to inflowing irrigation water as an aqueous solution or granular material either by injection into a gated pipe (Lentz and Sojka, 1996a,b; Lentz *et al.*, 2002) or soil-lined water supply ditch (Stieber and Chapman-Supkis, 1996) at the head of the field. The researchers measured dissolved PAM flux in treated inflows, furrow streams, and in tailwater ditches and calculated cumulative PAM losses. They determined that PAM concentrations in furrow streams decreased to undetectable levels within 30 min of stopping PAM applications and, because of PAM's high affinity for suspended sediments and soil in waste ditch streams, only 1–5% of the PAM applied left fields in runoff. Furthermore, for those early season, highly erosive irrigations most commonly treated with polymers, any PAM leaving the field in waste ditches only traveled 100–500 m before being completely adsorbed on sediments in the flow or onto ditch surfaces (Lentz *et al.*, 2002). Ferguson (1997) reported on a watershed scale test of PAM, where over 1600 ha were irrigated using

PAM-treated water for a 2-week period. On any given day, about half of the 40 farms in the study were contributing runoff to the watershed's drainage, which collected in Conway Gulch, a tributary of the Boise River. Waste water from the fields and the drain was analyzed for P, sediment, and PAM. About half of the water in the drain was field runoff. PAM was not found detrimental to the drain's water quality and was detected in drain water samples only twice (<0.8 ppm) during monitoring. PAM was found to be an effective sediment control practice that was well adopted by farmers and did not negatively impact the drain.

PAM water quality protection begins with the choice of an appropriate PAM formulation and product. Barvenik (1994) and Deskin (1996) summarized the safety considerations for use of PAMs in environmentally sensitive applications and as impacts human safety for exposure during material handling. Their summaries note that the broad class of PAM chemicals in general exhibit a low order of toxicity to mammals, with high acute LD_{50} by oral and dermal routes (>5 g kg^{-1}). They noted there were no significant adverse effects in chronic oral toxicity studies, no compound-related reproductive lesions in a three-generation study in rats, and only slight dermal and ocular irritation at high doses (Stephens, 1991). Human epidemiologic studies saw no association between unintentional occupational exposure to PAMs and tumors, which support the findings from chronic animal studies. Furthermore, the molecular size of these PAMs is too large to allow absorption via the gastrointestinal tract since the dimensions of the macromolecules preclude movement across biological membranes (Stephens, 1991).

While nonionic and especially cationic PAM formulations pose some risk to aquatic organisms at low concentration (Biesinger and Stokes, 1986; Hamilton *et al.*, 1994), the anionic formulations do not. Environmental toxicities of PAM and AMD have been published in a number of reports (King and Noss, 1989; Krautter *et al.*, 1986; McCollister *et al.*, 1964, 1965; Petersen *et al.*, 1987; Shanker and Seth, 1986; Walker, 1991). Cationic PAMs have LC_{50} values of 0.3–10 ppm. Cationic PAMs bind to sites rich in hemoglobin such as fish gills, posing a barrier to oxygen diffusion rather than causing a systemic toxicity. However, the class of anionic PAMs specified by NRCS for use in soil erosion and infiltration management shows no measurable toxicity at concentrations up to 100 pm (i.e., $LC_{50} > 100$ ppm in deionized water).

It is well established that values of PAM toxicity determined in deionized water indicate lower LC_{50} values than actually occur in natural waters because of the interferences of suspended sediments, humic substances, and other dissolved organic compounds normally present in natural waters (Buchholz, 1992; Goodrich *et al.*, 1991; Hall and Mirenda, 1991). Dissolved humic substances have been shown to raise LC_{50} measurements for test organisms by an order of magnitude for as little as 5 ppm (Goodrich *et al.*, 1991) and as much as two orders of magnitude for 60 ppm (Hall and Mirenda, 1991). Carey *et al.* (1987) and Biesinger *et al.* (1976) showed that the addition of organic C and bentonite clay also reduced polymer toxicity to test species.

It should also be noted that the absence of a measurable LC_{50} for PAM at 100 ppm represents an order of magnitude safety margin for the highest concentration of PAM present during initial application on agricultural fields (10 ppm) following the NRCS application standard (most aquatic organisms carried in irrigation water onto a cropped field will not survive regardless of PAM concentration). Furthermore, since only 1–5% of applied PAM leaves field application sites, and is only active for a few 100 m from field tail ditches (Lentz *et al.*, 2002), there are an additional two to three orders of magnitude concentration protection even if field runoff were to flow directly into a riparian body.

Just as for human exposure, concern regarding the aquatic environment is not simply for PAM exposure but also for the more toxic AMD monomer, which is present in very small quantities in PAM formulations. US Environmental Protection Agency (USEPA, 1994) reported AMD LC_{50} values for several aquatic species. The 24-, 48-, and 96-h flow-through LC_{50} values for harlequin fish (*Rasbora heteromorpha*) were 460, 250, and 130 ppm, respectively. The 24- and 96-h static LC_{50} values for goldfish (*Carassius auratus*) were 460 and 160 ppm, respectively. The 7-day LC_{50} value for guppy (*Poecilia reticulata*) was 35 ppm. The 24-h LC_{50} for water flea (*Daphnia magna*) was 230 ppm. These concentrations and exposure values are all several orders of magnitude above any conceivable exposure scenarios to AMD derived from PAM application for erosion of infiltration management, and probably for any other responsible and affordable agricultural or environmental use of PAM.

PAM used for erosion control has been shown in numerous studies to benefit runoff water quality not only by limiting the loss of sediment itself, but also nutrients carried on and released from eroded sediment. Lentz *et al.* (1996b) reported results from a study that applied 0.25–0.50 ppm of a nonionic PAM to furrow inflows during a single 24-h irrigation. Runoff samples taken at 4 and 9 h were analyzed for P and showed little effect of PAM treatment on *ortho*-P but about a 25% reduction in total P. Lentz *et al.* (1998) compared treating furrow advance flow (only) with 10-ppm PAM or continuously treating with 1-ppm PAM throughout the irrigation. Significant water quality improvement compared to controls was seen in both cases. Sediment was reduced 89% and 92%, respectively, for 1 ppm continuous and 10 ppm advance dosing. Dissolved reactive phosphorus (DRP) and total P concentrations in control tailwaters were five to seven times that of PAM treatments and chemical oxygen demand (COD similar to BOD) of controls were four times those measured in the PAM treatments. Results in several reports from Kimberly, Idaho have confirmed the ability of PAM used in irrigation water to reduce the nutrient enrichment and general cation concentration of runoff water (Bjorneberg *et al.*, 2000b; Entry and Sojka, 2003; Lentz *et al.*, 2001a; Sojka *et al.*, 2005). Vanotti *et al.* (1996) showed that PAM was also highly effective at removing solids and nutrients from swine wastewaters.

A common practice in many furrow-irrigated areas where erosion is a problem is the use of settling ponds to remove sediment, nutrients, and other agrochemicals from tailwater. In the Lower Boise River Pollution Trading Project in southwest Idaho, the question arose whether PAM use and settling ponds gave an additive effect on tailwater quality protection. Bjorneberg and Lentz (2005) found that in 3 years of study either PAM use or sediment ponds reduced sediment 86% and total P loss 66% but the combined effect of PAM and sediment pond treatments reduced mass transport of sediment 95–99% and total P 86–98%. Neither PAM nor settling ponds had any appreciable effect on DRP retention.

The Imperial Valley of California is one of the most intensively farmed and economically important surface irrigated areas in the United States. In recent years, public concern has mounted for the impacts of return flows on algae growth and eutrophication in the Salton Sea. Goodson *et al.* (2006) conducted a series of tests using continuous application of 1-, 5-, or 10-ppm PAM to irrigation water. The 1-ppm PAM treatment reduced turbidity 74% and total suspended solids 82%. The loss of particulate borne P was reduced 48% but there was no reduction in the soluble fraction. The higher PAM applications improved both suspended solid retention and particulate borne P retention but resulted in some measurable PAM loss, which was seen as an unnecessary risk for the relatively small gains and the significant increased costs of dosing.

Public concerns for water quality are probably more emphatic regarding pesticides than any other component of water pollution. When detached sediments are transported in runoff, their agitation and mixing while flowing in the runoff stream increases the potential for desorption of nutrients and pesticides. Reducing erosion helps prevent contamination of receiving waters with pesticides much as it helps prevent nutrient enrichment.

Agassi *et al.* (1995) used miniature furrows in the laboratory to study the loss of the nonionic herbicide napropamide from Hanford sandy loam soil (Typic Xerorthent) in runoff. Irrigation flow rates were controlled among treatments and were either distilled or treated with 10-ppm anionic PAM. Napropamide loss varied in direct proportion to sediment loss regardless of water treatment. Agassi *et al.* (1995) expressed caution in extrapolating the minifurrow results to field results, noting that in field situations, most of the water running along a furrow infiltrates to irrigate the field, and deposition of some of the fines occurs before loss in the tailwater. Thus, the proportional relationship between sediment loss and napropamide loss in the minifurrow might not be the same relationship that occurs in an actual field. Nonetheless, the study pointed toward the potential for PAM to help with pesticide sequestration.

Singh *et al.* (1996) conducted a field study on a Capay clay soil (Typic Haploxererts) to study the effects of PAM-treated furrow irrigation on loss of the miticide Kelthane. Kelthane is regarded as slightly water soluble with a high soil sorption affinity. The two irrigation treatments were a control and dosing with at 10-ppm anionic PAM. PAM greatly reduced sediment loss and increased infiltration, with amounts varying with sampling times and irrigation dates. Kelthane loss was proportional to sediment loss. In two posttreatment irrigations, Kelthane loss was double in the untreated controls compared to the furrows that had only residual PAM effects.

Several studies in Idaho have shown reductions in pesticides in PAM-treated runoff. PAM-treated furrow irrigation runoff was compared to controls for all forms of N, total and *ortho*-P, and the pesticides terbufos, cycloate, EPTC, bromoxinil, chlorpyrifos, oxyfluorfen, trifluralin, and pendimethalin in two production sugarbeet fields and one onion field (Bahr and Steiber, 1996; Bahr *et al.*, 1996). PAM was predissolved at 10 ppm in the inflow and applied only during inflow advance across the field. The PAM treatment reduced sediment losses up to 99% and N and P concentrations were reduced up to 86% and 79%, respectively. For sites where pesticides were detected in control runoff, PAM treatment greatly reduced the pesticide losses. Pesticide reductions were more variable than the nutrient reductions, and were related both to compound attributes and pesticide application protocols and timing. Nonetheless, the effectiveness of PAM in reducing the losses was substantial.

Watwood and Kay-Shoemake (2000) investigated the impact of PAM on the sorptive dynamics and degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) and atrazine in soils where PAM had been used for erosion control for 5 years. In their study sorption of atrazine and 2,4-D in soil was unaffected by PAM treatment, as was atrazine desorption. However, 2,4-D desorbed slightly faster in PAM-treated soil. Decarboxylation of the 2,4-D carbolic acid side chain was significantly reduced in the PAM-treated soil. Degradation of atrazine to CO_2 or bound residue components was also reduced in PAM-treated soils. The authors concluded that the modifications in fate of these two pesticides were not "dramatic" and that the interpretation could be seen as positive from a herbicide efficacy perspective, but drew attention to an aspect of PAM–herbicide interaction that might warrant further research over a broad spectrum of additional herbicides.

There has been great concern in Australia over runoff containing residues of the pesticide endosulfan. A series of on-farm and laboratory studies were conducted in the late 1990s to determine the relative effectiveness of conservation tillage practices and use of PAM for erosion control and prevention of endosulfan contamination of runoff (Hugo *et al.*, 2000; Waters *et al.*, 1999a,b). In surface irrigated situations PAM treatment was equally effective as conservation tillage for controlling soil loss and endosulfan loss in runoff, on the order of 70%. Part of the benefit in both instances was recognized to be the infiltration enhancement of either practice. Where fields were subject to intermittent rainfall, residual PAM effects (from the PAM applied during irrigation) did not always withstand the additional erosive force of raindrop impact. PAM was recognized as a potent tool for irrigated control of erosion control with a need recognized for either a combination approach or further research to improve the PAM methodology for better performance in intermittent rain situations. Oliver and Kookana (2006a,b) investigated the effect of using PAM-treated irrigation water in the Ord River irrigated region of Australia on pesticide losses. PAM reduced the loss of endosulfan, chlorothalonil, and bupirimate 54%, 49%, and 38%, respectively. The bupirimate loss was not statistically significant at the 5% level. Endosulfan and chlorothalonil are relatively insoluble whereas bupirimate is more soluble. The reduced effectiveness for PAM at reducing soluble pollutants is not uncommon.

Lu *et al.* (2002b,c) studied the effects of anionic and cationic PAM on picloram and napropamide sorption and anionic PAM effects on sorption and desorption of metolachlor, atrazine, 2,4-D, and picloram. The authors concluded that, as might be expected, the charge make up of the polymers and the pesticides influenced the degree to which affinity for sorption to soil was affected. However, the degree of change in sorption was very minor and was mitigated by the presence of salts in soil and by the increased infiltration and reduced loss of sediment that occurred with PAM treatment. In view of the small amounts of polymers added to soil and the far greater impact on soil loss, the authors did not identify use of PAM as contributing meaningfully to field loss of pesticides.

By far the most significant environmental effect of PAM use for erosion reduction is its improvement of surface water quality. This is achieved through reduction of sediment and nutrient losses, and decrease of organic and agrochemical contaminants released from sediment in runoff.

XII. PAM EFFECT ON ORGANISMS IN RUNOFF AND SOIL

As human population and the numbers of animals reared to feed the human population continue to increase, land disposal of animal and human wastes is becoming more widespread. This trend is also encouraged by the interest in some sectors for organically produced crops. When runoff occurs from fields amended with animal manures or municipal waste there is a significantly increased risk of pathogen contamination of receiving waters. Even in the general context of agricultural production, the movement of soilborne disease organisms in runoff is an important vector for the spread of crop diseases. PAM has proven to be as effective at sequestering microorganisms in runoff as it is in sequestering sediment.

Broad categories of microorganisms carried across and among furrow-irrigated fields by furrow streams, runoff, and return flows are reduced by PAM in irrigation water (Entry and Sojka, 1999; Sojka and Entry, 1999, 2000). Similar reductions occur for weed seed in runoff (Sojka *et al.*, 2003). These findings point to potential improved management that may ultimately reduce pesticide use.

Sojka and Entry (2000) examined runoff from furrow-irrigated plots fed by a storage reservoir that frequently experienced algal blooms when the runoff-enriched water warmed in summer months. Plots were either controls or treated with PAM patch application in the first meters of the furrow. Samples taken 40-m down furrow from the PAM patch on three dates at three different flow rates saw significant reduction in numbers of algae, numbers of active and total bacteria, active and total fungal length, and total bacterial and fungal biomass compared to the control treatment (Entry and Sojka, 2000; Entry *et al.*, 2003). Reductions varied with flow rate, furrow-sampling position, and organism and ranged from 0% to 20% for total bacteria sampled 1 m below the patch at the lowest flow rate to 100% removal of active and total fungi at the 40-m sampling point and greatest flow rate. Higher flow rates and greater flow distance generally favored organism removal indicating that mixing and opportunity for exposure to PAM and furrow adsorption sites favored organism removal. Common removal rates for all organisms, flow rates, and sampling positions ranged from 50% to 90%. The results have immediate implications for phytosanitation and soilborne phytopathogen epidemiology. There are additional implications that can be extrapolated from the finding. If disease spread is reduced, then pesticide use can likely be reduced as well.

The Sojka and Entry (2000) findings prompted immediate follow-up to determine the potential for reducing migration of coliform bacteria from furrow-irrigated fields with recent manure application. Entry and Sojka (2000, 2001) found that after water flowed over three manure sources and then PAM, PAM + $Al_2(SO_4)_3$, or PAM + CaO in furrows, total coliform bacteria, fecal coliform bacteria, and fecal streptococci were reduced up to 99.9% in water flowing 1- and 27-m downstream of the treatments compared to the control treatment. A similar study conducted in Australia confirmed the organism sequestration, findings but underscored the need for adequate exposure to PAM in the furrow system for optimal performance

(Entry *et al.*, 2003). For grassed systems, where the manure source at the head of the furrow was the only dosing point for organisms and PAM, 100 m of uncontaminated grassed furrow below the dosing point was as effective at removing coliform organisms as PAM (Spackman *et al.*, 2003). The latter study suggests that if coliform losses are a problem in runoff from heavily stocked pastures, the PAM application would likely be more effective in the lower reaches of the pasture.

As with microorganisms, the spread of weed seeds in fields can also occur in furrow irrigation. Where runoff is collected for reuse, the water can be a potent vector for inoculation of other fields. Sojka *et al.* (2003) conducted a 2-year furrow-irrigated field experiment that compared the effects of predissolved or patch-applied PAM on weed seed loss and weed growth dynamics in a corn (*Zea mays* L.) crop. As in previous studies erosion was greatly reduced and infiltration was increased with PAM use. PAM also reduced runoff loss of weed seeds 62–90%, including barnyard grass (*Echinochloa crus-galli*), kochia (*Kochia scoparia* L. Schrad.), redroot pigweed (*Amaranthus retroflexus* L.), common lambsquarters (*Chenopodium album* L.), and hairy nightshade (*Solanum sarrachoides* L. Sendtner). Where PAM was used, the reduction in furrow erosion slightly favored the establishment of in-furrow weed emergence, although weed vigor was greatly reduced by the herbicides. Nonetheless, the result suggested the need for greater attention to weed control at lay-by when using PAM for erosion control in furrow irrigation, since the scouring of emerging weed seedlings, which normally occurs in eroding furrows, is prevented with PAM. The results were also seen as evidence that PAM used for erosion control as an additive to hydromulching can be expected to favor seed retention and seedling establishment. Corn yield was slightly increased in 1 year of the study with PAM use, which the authors attributed to the increased infiltration with PAM.

Reports on the effects of PAM on bacterial biomass in soils and waters have been mixed and sometimes conflicting (Kay-Shoemake *et al.*, 1998a,b; Mourato and Gehr, 1983; Nadler and Steinberger, 1993; Steinberger and West, 1991; Steinberger *et al.*, 1993). Larger populations of culturable heterotrophic bacteria were found by Kay-Shoemake *et al.* (1998a) in PAM-treated soils planted to potatoes, but not if planted to beans. These observations and other from studies showing either increased or decreased bacterial numbers for PAM-treated soils suggest that the effects are site, season, and cultural practice specific and may interact with other important variables such as nutrient levels, crop cover type, or herbicide regimes. Bacterial enrichment cultures, derived from PAM-treated field soils, were capable of growth with PAM as a sole N source but not sole C source, whereas AMD served as either a sole N or C source for bacterial growth (Kay-Shoemake *et al.*, 1998b). Work by Grula *et al.* (1994) showed that PAMs are an N source for bacteria and stimulate the growth of a number of *Pseudomonas* sp.;

only cationic formulations were toxic to the organisms they cultured using PAM concentrations under 0.2%.

Kay-Shoemake *et al.* (1998a,c) described a unique PAM-specific amidase that is apparently induced by PAM in soils. It breaks amide linkages found in PAM, releasing N_4^+ which is rapidly assimilated by bacteria during growth. In laboratory incubations, 20% of the N in the added PAM was removed within 120 h (Kay-Shoemake *et al.*, 1998b). PAM-specific amidase activity was documented in laboratory cultures and in field soil samples following exposure to PAM (Kay-Shoemake *et al.*, 1998b). The enzyme seems to have a broad substrate range and exhibits activity against formamide and propionamide, but does not impact degradation rates of carbaryl, diphenamid, or naphthalene acetamide in PAM-treated soils (Kay-Shoemake *et al.*, 2000a,b). Intra- and extracellular activities were noted, and production and secretion of the enzyme seemed dependent on C availability, as cells cannot derive C rapidly enough from PAM as the sole C source to sustain cultures.

Nitrification of added urea appeared somewhat accelerated (approximately 10% over 2 weeks) in PAM-treated microcosm soils (Kay-Shoemake *et al.*, 2000b), but no other significant impacts of PAM application on fertilizer fate were noted. Sorptive dynamics of the common pesticides, 2,4-D and atrazine, were not dramatically altered by PAM treatment of field soil samples, but some slight changes in desorption and degradation rates were reported (Watwood and Kay-Shoemake, 2000). Kay-Shoemake and Watwood (1996) and Kay-Shoemake *et al.* (1998a,b, 2000a) reported that although PAM additions to field soils correlate with detectable changes in microbial C utilization, the effects are masked by the influences of other field variables such as crop cover type or nutrient status.

Sojka *et al.* (2006) reported the effects of ultrahigh PAM application rates to irrigated soils. Over a 6-year period 1000 kg ha^{-1} $year^{-1}$ of a commercial anionic PAM product was added to the soil. New plots were established each year to give a range of 0–6 years for effects to materialize and allowing a sixfold range of high application rates for analysis. Analysis at the end of the study concentrated on plots receiving either 2691 or 5382 kg active ingredient PAM ha^{-1}. Active bacterial, fungal, and microbial biomass were not consistently affected by high PAM additions; effects were moderate (considering the massive PAM rates) and were driven more by date of sampling effects than by PAM treatment effects. In June and August, active bacterial biomass in soil was 20–30% greater in the control treatment than where soil was treated with 2691 or 5382 kg PAM ha^{-1}, but there were no significant differences in July (Table I). There were no differences in soil active bacterial biomass between the 2691 or 5382 kg PAM ha^{-1} treatments regardless of sampling time. Control treatment active fungal biomass was 30–50% greater than soil treated with 2691 or 5382 kg PAM ha^{-1} in June and July, but not in August. There was no difference in soil active fungal biomass between the

Table I
Active Bacterial, Fungal, and Microbial Biomass in Soils Treated with 2691 and 5382 kg Active Ingredients (a.i.) PAM ha^{-1} (Adapted from Sojka *et al.*, 2006)

Month	Treatment	ABB mg C g^{-1} soil	AFB	AMB
June	Control	9.04 a	10.16 a	19.21 a
	2691 kg PAM ha^{-1}	7.20 b	6.77 b	13.97 b
	5382 kg PAM ha^{-1}	7.32 b	7.24 b	14.56 ab
July	Control	5.31 b	10.64 a	15.95 a
	2691 kg PAM ha^{-1}	4.86 b	6.64 b	11.51 b
	5382 kg PAM ha^{-1}	5.39 b	5.32 b	10.71 b
Aug	Control	9.13 a	6.28 b	15.42 a
	2691 kg PAM ha^{-1}	7.20 b	6.93 b	12.54 b
	5382 kg PAM ha^{-1}	6.33 b	4.70 b	11.03 b

ABB, active bacterial biomass; AFB, active fungal biomass; AMB, active microbial biomass. In each column values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$; $n = 27$).

2691 or 5382 kg PAM ha^{-1} on any sampling date. Active microbial biomass in soil was 27–48% greater in the control treatment than soil treated with 2691 or 5382 kg PAM ha^{-1} except in June for the 5382 kg PAM ha^{-1} treatment. Nutritional characteristic analysis using Biolog GN plates suggested a separation of the nonamended control soils from the high PAM treatment for the June sampling, but not for July or August. Whole-soil fatty acid profiles showed no change in the soil microbial community due to any PAM application rate on any sampling date. In contrast, both the fatty acid and Biolog analyses indicated that the microbial communities present at the June sampling (in all plots) were different from those sampled in July and August, both taxonomically and metabolically independent of PAM treatment.

The Sojka *et al.* (2006) study was important because despite large cumulative additions of PAM over a 6-year period, there was little effect on soil microbial biomass or metabolic potential as measured by gram-negative Biolog microtiter plates or whole-soil fatty acid methyl ester (FAME). Although measurable, the effects on soil microbial population size were inconsistent and moderate, considering the massive PAM amounts added. Their results from massive PAM application rates and prolonged exposure times suggest that concerns about effects of PAM on soil microorganism population size and function, applied at more typical 5–10 kg ha^{-1} year^{-1} application rates, are not warranted. To the extent they saw soil microbial biomass shifts, interpretation, especially in light of earlier literature, suggests this could be due to N enrichment resulting from the PAM addition rather than a direct effect of the PAM polymer chemistry itself. This has been seen in other studies where high soil N concentration reduced microbial biomass and mineralization of cellulose, lignin, and herbicides (Entry, 1999, 2000;

Entry and Backman, 1995; Entry *et al.*, 1993). Thus if large amounts of PAM are applied to soil, it is reasonable to expect the additional N contained in PAM may slightly reduce microbial biomass. In addition to the N enrichment from the amide groups in PAM, some commercial formulations also contain a few percent additional N, commonly as urea, to promote dissolution on hydration. Environmentally, the small shifts in soil microbial biomass and metabolic potential in the Sojka *et al.* (2006) study were insignificant when weighed against the significant erosion prevention and runoff water quality protection afforded by the use of 5–15 kg PAM ha^{-1} per season in normal PAM use scenarios, compared to the 2691 and 5382 kg PAM ha^{-1} applied in their study. In order to apply the amounts of PAM added in their study, even assuming no PAM degradation annually, farmers would need to apply 15-kg active ingredient PAM ha^{-1} for 180 years to accumulate 2691 kg ha^{-1} and 360 years to accumulate 5382 kg ha^{-1}. In a separate study, Spackman *et al.* (2003) reported that PAM applied at 16 kg ha^{-1} active ingredient did not affect survival of total bacteria or coliform bacteria in soil.

Wallace *et al.* (1986b) also reported on the effects of ultrahigh rates of PAM application to soil in a small pot study in the greenhouse. They compared the effect of adding 1% and 5% by weight of anionic PAM to soils with controls. Additional details of the PAM formulation were not given. The 1% PAM rate increased vegetative growth of wheat (*T. aestivum* L., cv. INIA66R) and tomato (*Lycopersicon esculentum* Mill., cv. Tropic). The 5% rate produced growth results equivalent to controls. Increased Na concentrations in plant tissues were attributed to Na associated with the PAM formulation used. Other minor reductions in mineral nutrients occurred, but were regarded as largely inconsequential in view of the vegetative yields and because of the exceedingly high PAM application rates.

The overwhelming interest in PAM use on farm fields is for erosion control and/or infiltration management. However, the increase of interest in PAM in the last decade has prompted exploration of other novel uses of PAM. In a completely different strategy for PAM use, Entry *et al.* (2000, 2005) found that PAM could be used in mixtures with wood chips or other organic materials to provide a protective physical barrier to verticillium wilt infection for potato seed pieces. In this case PAM, enriched with beneficial organisms, forms the immediate seed environment, making competition and infection from the disease organisms more difficult.

XIII. PAM DEGRADATION

Very few experiments have been conducted to quantify PAM degradation, especially for PAM applied to soil. Significant problems surround the ability to remove PAM from soil once applied. The use of radiolabeled PAM would provide the best option for studying PAM decomposition; however, the difficulty and cost of labeling the appropriate C bond to follow chain fragmentation are significant. These difficulties increase when attempting to label the large molecules in current use. Thus what is known about PAM degradation is drawn from sparse reports, often using smaller molecular weight PAMs, radiolabeling of the molecule's H atoms, or from indirect measurements of decomposition.

PAM degradation occurs slowly in soils as a result of several processes including chemical, photo, biological, and even mechanical processes (such as tillage abrasion, freezing and thawing, and so on) because of the enormous molecular size. Abiotic processes break the polymer molecule into progressively shorter segments over time (Hayashi *et al.*, 1993). When polymer segments are 6 or 7 monomer units long, they are consumed by soil microorganisms (Hayashi *et al.*, 1993). Both temperature and soil salt content are thought to influence degradation processes (Tolstikh *et al.*, 1992; Wallace *et al.*, 1986b). Azzam *et al.* (1983) estimated these rates at around 10% per year, but it is not certain how well their experimental conditions reflect the common mode of PAM use where PAM is mainly added to the soil surface and exposed to far harsher environmental extremes, than when mixed into the soil volume. Soil microcosm studies examining biodegradation rates of cross-linked PAM copolymer indicate that polymer molecules may be mineralized at rates as high as 7% per 80 days (Stahl *et al.*, 2000). PAM cannot reasonably be expected to degrade in such a way as to release AMD because of the high-temperature requirement (MacWilliams, 1978). Johnson (1985) followed degradation of a cross-linked PAM over an extended period in sandy desert conditions and found no AMD degradation products.

Some controversy arose over reports by Smith *et al.* (1996, 1997) suggesting that PAM could degrade to AMD due to thermal and photolytic effects occurring in a natural environment in the presence of the herbicide glyphosate. Their paper reported a slow release of AMD over the course of a 6-week study, which they attributed to natural degradation of the PAM macromolecule to release AMD. They concluded that PAM degrades to AMD via a free radical process initiated by sunlight. In their study the PAM was added as an emulsion requiring inversion to dissolve into stock solutions and they reported that solutions were initially milky in appearance but became clear over the 6 weeks. A subsequent study by Ver Vers (1999) disputed the Smith *et al.* (1996, 1997) results, pointing to problems in proper dilution of the emulsions (possibly accounting for the initial milky appearance of solutions) and attributing the detection of small amounts of AMD over time to the gradual release of unreacted AMD contaminant from the incompletely dissolved emulsion. Ver Vers (1999) concluded that PAM does not degrade to AMD in the presence of glyphosate or sunlight or any combination of the two in a natural environment and that glyphosate influences the solubility of PAM requiring that added care must be used when combining the two.

Photodegradation of PAM has been described by Decker (1989). The C–C, C–H, and C–N bonds in PAM have bond strengths of 340, 420, and 414 kJ mol^{-1}, which can be cleaved by wavelengths of 325, 288, and 250 nm, respectively (Crosby, 1976). However, most of the UV radiation in sunlight at wavelengths below 300 nm is absorbed by atmospheric ozone before reaching the earth's surface (Diffey, 1991). A study by Caulfield *et al.* (2003a,b) reported that strong UV radiation at 254 nm released AMD from solutions of a nonionic water-soluble PAM. However, the release of AMD was generally <50 ppm repeat monomer units in the polymer. They also noted a drop in solution viscosity which indicated that the AMD released was the result of chain scission, not an "unzipping of the polymer chain." Their study reported that PAM was stable under fluorescent lights and did not release detectable amounts of AMD in hot aqueous solutions at 95°C. Suzuki *et al.* (1978, 1979) also reported a number of low molecular weight PAM decomposition products when degraded using ozone or strong UV irradiation in the presence of ozone, but AMD was not among them.

These results together with those of Ver Vers (1999) and MacWilliams (1978) indicate that there is no basis for assuming that PAM degrades to AMD in the natural environment. In soils acclimated to PAM amendment, it has been shown that microbes attack the amide functional group on the polymer, utilizing it as an N source without degradation of the molecule's C spine (Kay-Shoemake *et al.*, 1998a,b). Thus even if there existed a small probablility for the AMD production from polymer chain scission, it would decrease drastically with time. Other research shows that any AMD present in microbiologically active soil environments is rapidly metabolized as an N source by several soil microorganisms including *Nocardia rhodochrous*, *Bacillus sphaericus*, *Rhodococcus* sp., *Arthrobacter* sp., and *Pseudomonas putrefaciens* (Abdelmagid and Tabatabai, 1982; Arai *et al.*, 1981; Brown *et al.*, 1980; Croll *et al.*, 1974; Lande *et al.*, 1979; Shanker *et al.*, 1990; USEPA, 1985).

Wallace *et al.* (1986b) noted that the end products resulting from PAM decomposition would not be AMD, even if the first step of PAM decomposition yielded the monomer. AMD is rapidly decomposed to propionamide and propionic acid, and propionamide rapidly hydrolyzes to propionic acid as well. They noted that propionate is a fatty acid which is metabolized by plants (Mahler and Cordes, 1971). Propionates are the nontoxic mold inhibitors commonly used in the baking industry (Goodman and Gilman, 1965) and in perfume formulations (Morrison and Boyd, 1966). The ultimate breakdown products of AMD are CO_2, NH_3, and H_2O. Kay-Shoemake and Watwood (1996) and Kay-Shoemake *et al.* (1998a,b, 2000a) reported that biodegradation of anionic PAMs are likely limited to enzymatic hydrolysis and the release of NH_3. Hayashi *et al.* (1994) suggested that the simple compound polyacrylic acid might be another product of PAM degradation under some conditions, which can also be metabolized by microorganisms. Kay-Shoemake and Watwood (1996) and Alexander (1994) suggested that to the extent that PAM molecules remain intact in the soil, even if somewhat reduced in chain length they are likely incorporated into the soil organic fraction.

Degradation of the AMD is fairly rapid (Kay-Shoemake *et al.*, 1998a; Lande *et al.*, 1979; Shanker *et al.*, 1990). AMD was completely degraded within 5 days after applying 500 kg PAM kg^{-1} garden soil (Shanker *et al.*, 1990). Lande *et al.* (1979) applied 25 kg PAM kg^{-1} soil and reported that the half-life of AMD in agricultural soils was 18–45 h. Degradation may be slower in cooler more sterile waters, in sandy soils, or soils with low respiration rates because of temperature, soil water content, or other factors slowing microbial metabolism (Brown *et al.*, 1980, 1982; Conway *et al.*, 1979; Croll *et al.*, 1974; Davis *et al.*, 1976). Metcalf *et al.* (1973) and Neely *et al.* (1974) concluded that because of the ease with which AMD is metabolized by biological organisms and otherwise degraded, it is not likely that it can bioaccumulate to any extent in the food chain.

Reports by Tareke *et al.* (2002) and others (Ahn *et al.*, 2002; Andrzejewski *et al.*, 2004; Bacalski *et al.*, 2003; Konings *et al.*, 2003; Palevitz, 2002; Roach *et al.*, 2003; Rosen and Hellenas, 2002; Svensson *et al.*, 2003; Zyzak *et al.*, 2003) have drawn new attention to health concerns related to AMD. Their papers (and many others) reported the AMD content of a wide range of cooked, baked, and fried foods. The range of AMD found in all categories of food tested by Svensson *et al.* (2003) was from 25- to 2300-ppb AMD. Baked and deep fried starchy foods proved most problematic. The mean values for some popular food items were: potato chips (1360 ppb), French fries (540 ppb), bread crisps (300 ppb), cookies (300 ppb), tortilla chips (150 ppb), popcorn (500 ppb), and breakfast cereals (220 ppb). Various meat products ranged from 30 to 64 ppb. The Food and Agricultural Organization and World Health Organization concluded that food makes a significant contribution to total exposure of the general public to AMD, with average intake rates in the range of 0.3–0.8 μg of AMD intake per kilogram of body weight per day. AMD concentrations in these commonly eaten foods are 5–460 times greater than the maximum residual AMD concentrations expected in irrigation water treated with 10 ppm of the food-grade anionic PAM products containing no more than 0.05% AMD. Yet, no neurotoxic effects are expected from the AMD concentrations ingested in diets that include these foods. The ubiquitous human exposure to AMD from common food provides a quantitative contrast for considering risk from exposure to AMD from environmental uses of recommended PAM products at recommended application rates.

Very few studies have analyzed for fate of PAM applied in irrigation water or for other environmental uses. This is largely because PAM cannot be effectively desorbed (extracted) for analysis once it has been adsorbed on mineral or other solid surfaces. Lentz *et al.* (1996a) developed an indirect assay that measured light transmittance in a spectrophotometer as affected by flocculation and settling of a known concentration of kaolinitic clay. The technique showed sensitivity at or slightly below the range of 0.1 ppm. However, the technique was only applicable for PAM still in solution in irrigation water and required minor adjustments for salinity-wide variation in runoff water sediment content, possibly due to the influence of other dissolved organic materials. The method was a significant improvement over methods previously compiled (Daughton, 1988), both in sensitivity and because earlier methods required use of significant amounts of toxic reagents.

Several recent papers have explored other new techniques for PAM analysis and techniques for removal of PAM adsorbed to soil (Lu and Wu, 2001, 2002, 2003b; Lu *et al.*, 2003). These PAM analytical techniques use size exclusion chromatography. They can be slightly more sensitive than the earlier analytical techniques but require more sophisticated analytical capacity than the Lentz *et al.* (1996a) method. Although PAM can be removed from soil with vigorous chemical stripping, some questions remain about the thoroughness of the removal and the accuracy of the determination because of the effects on analyte molecular conformation and influence of other organics that might mask or otherwise interfere with determination of the analyte. Nonetheless, the contribution of new techniques for PAM analysis has greatly widened the scope of potential PAM fate studies. This potential has yet to be fully realized because of the considerable additional time and expense involved in making these analyses.

XIV. PAM AND Ca

Anionic PAMs bond to mineral surfaces only if there is sufficient electrolyte present to overcome the repulsion of the polymer anionic sites and mineral anionic sites to allow weaker van der Waals forces, H bonding, or dipole attractions to be effective; this effect is enhanced if polycations such as Ca^{2+} are present to "bridge" between the negative charge sites of the polymer and mineral surfaces (Laird, 1997; O'Gorman and Kitchener, 1974; Orts *et al.*, 2001; Pefferkorn, 1999; Theng, 1982; Wallace and Wallace, 1996).

El-Morsy *et al.* (1991a,b) noted that water quality interacted with PAM treatment, affecting clay migration and infiltration and that these effects were magnified with increased sodicity but moderated with increased salinity (EC). Lecourtier *et al.* (1990) found that a critical salt concentration exists for adsorption of anionic PAMs to overcome electrostatic repulsion from charged mineral surfaces. Anionic polymers may also adsorb to the broken edges of minerals, where positive charges from aluminum ions or other isomorphously substituted crystal lattice elements may be exposed (Greenland, 1972). Lurie and Rebhun (1997) noted that the adsorption phenomena of PAMs and other polymers with suspended organic solids and in waters with high concentration of dissolved organic compounds is a complex process that is impacted by molecular mass as well as charge and molecular conformation. Larger polymer chains behave differently than smaller polymer chains and the interaction can vary with the properties of the other dissolved organics in solution. For cationic PAMs Edwards *et al.* (1994) found that the ability of dissolved organic matter to interact with cationic polymers through precipitation increased with increasing molecular mass and decreasing anionic functional group content of the soluble organics. Haschke *et al.* (2002) measured the sorbtive strength of a single PAM molecule to a mica surface to be 200 pN.

H bonding (Kohl and Taylor, 1961; Nabzar *et al.*, 1984, 1988) and ligand exchange (Theng, 1982) are often sighted as primary bonding mechanisms. H bonding may occur between polymer amide groups and free hydroxyl groups of the adsorbent surface that are not already bonded with other close hydroxyls (Griot and Kitchener, 1965; Pefferkorn *et al.*, 1990). Theng (1982) suggested that ligand-exchange bonding results when the carboxylic group of the PAM enters the inner coordination layer of edge Al, thereby forming a coordination complex. However, both these sorption mechanisms are unlikely in the normal soil pH ranges of 5–9 because of electrostatic repulsion, which can only be overcome by presence of additional electrolytes in the soil solution (Lecourtier *et al.*, 1990). Rengasamy and Sumner (1998) presented the relative flocculation power of cations as $Na^+ = 1$, $K^+ = 1.8$, $Mg^{2+} = 27$, and $Ca^{2+} = 45$. Lu *et al.* (2002a) working with a range of soils, water qualities, and polymer concentrations found that on average divalent cations were 28 times more effective in enhancing PAM sorption than monovalent cations.

Wallace and Wallace (1996) and Orts *et al.* (2001) noted the need for Ca electrolytes in irrigation water when using anionic PAM for infiltration and erosion control. Ca has a double charge and small hydrated radius which favors flocculation. Na, on the other hand, has a large hydrated radius which generally prevents ion bridging, generally leading to dispersion rather than flocculation of solids. Lentz and Sojka (1996b) noted that when irrigation water SAR was increased from 0.7 to 9.0 $[\text{m mol}_c\ \text{liter}^{-1}]^{0.5}$ that PAM's infiltration enhancement over control water was greatly diminished. Water low in electrolytes or with high SAR can be amended relatively easily through addition of gypsum ($CaSo_4$) or $Ca(NO_3)_2$ fertilizer.

PAM has been used in conjunction with gypsum to accelerate leaching of sodic soils, by reducing surface sealing (Malik *et al.*, 1991a; Zahow and Amrhein, 1992). When surface seals are prevented and when near surface structure is stabilized infiltration and throughput of water are increased and the added Ca applied via gypsum is more effectively delivered to deeper in the profile. A similar response was noted for use of PAM with soybean in Australia (Sivapalan, 2003). Gypsum used with PAM aided soil management of soils irrigated with high Na waste water (Gardiner, 1996). Wallace *et al.* (2001) reported synergistic effects of gypsum and PAM in limiting erosion on southern Brazilian soils.

In rice (*Oryza sativa*) in Australia, water management involves balancing several considerations which often are in conflict with one another. Turbidity is a problem for rice establishment and early growth, but growers prefer to restrict infiltration to conserve water. Sivapalan (2005) found that with sodic waters used for rice irrigation on Vertisols in Australia, the dispersive action of Na could be overcome by adding gypsum to the inflows and following a split PAM application as proposed by Sojka and Surapaneni (2000). Yu *et al.* (2003) found that in small-tray studies that applying PAM alone at the surface of two coarse-textured soils reduced erosion from simulated rainfall but not runoff; adding gypsum alone decreased runoff but not erosion. However, spreading dry PAM at the equivalent of 20 kg ha^{-1} mixed with gypsum at 4 Mg ha^{-1} increased the final infiltration rate by a factor of 4 and reduced erosion 70% compared to controls.

XV. PAM FOR CONSTRUCTION SITES AND OTHER DISTURBED LANDS

Ironically, interest in the use of polymer soil amendments was first prompted by their use in road and runway construction during World War II (Wilson and Crisp, 1975). Interest spread rapidly to the agricultural sector from whence emanated the majority of soil-conditioning research on polymers and soil applications for most of the years since then. Polymers have, however, been used in construction for a variety of applications, including grouting, drilling muds, dust suppression, roadway stabilization, and a variety of other, largely high-rate applications, in much the original manner identified originally. PAM and other polymers were introduced as drilling mud additives in about 1949 and rapidly became an important tool in the drilling industry that has continued to the present (Barvenik, 1994; Scanley, 1959). DeBoot (1975) reported that during the construction of Belgium's superhighway system, in 1975, PAM was widely used to stabilize more than 3000 ha of exposed soil in road cuts.

More recently, however, the dramatic successes of low-rate PAM application strategies in irrigated agriculture and the improved efficacy of new higher molecular weight environmentally friendly anionic PAMs have spawned renewed interest in PAM for construction site and road cut protection at low rate of application, and hence at low cost. Traditional techniques involving rock, metal or plastic armoring, straw bales, fiber batting, filter fences, settling ponds, and so on commonly cost \$2000–\$10,000 ha^{-1} depending on site conditions and the requirements of applicable laws governing water quality protection in the particular state, county, or municipality.

Reduction of sediment from fiber mats, straw bales, and so on in well-designed sites can be as high as 80–90% on a mass basis (Barnett *et al.*, 1967; Benik *et al.*, 2003a,b; Grace, 1999; Jennings and Jarrett, 1985). Nonetheless, Minton and Benedict (1999) noted that the turbidity from these best management practices (BMPs) often still range in value from hundreds to even thousands of nephelometric turbidity units (NTUs). Turbidity is generally affected more by suspended clay-sized fractions than coarser particulates. Thus, for many soils runoff NTUs can remain high using conventional BMPs despite great reductions in sediment mass. Brown *et al.* (1981) showed that the sediment loss from holding ponds is almost entirely in the clay fraction, which carries most of the soil nutrient and chemical load responsible for surface water quality impairment. Depending on design adequacy and efficacy of individual or combinations of treatments, many traditional techniques are still incapable of meeting sediment retention requirements, which in recent years are commonly prescribed in terms of maximum NTU thresholds (Tobiason *et al.*, 2001). Turbidity is generally raised mostly as a result of clay-sized sediments in suspension, which traditional techniques are least effective at removing from runoff. PAM, on the other hand, is particularly effective at stabilizing soil against detachment and transport of fines as well as flocculating and removing fines from runoff, especially if a runoff pond can briefly provide quiescent storage. Even in the absence of retention ponds, flowing water, as the experiences with furrow irrigation have shown, can also be very effectively clarified, although in nonagricultural settings, limitations of flow volume, rate, and capacity can challenge dosing strategies. In performing economic assessments of the cost effectiveness of traditional versus PAM-based erosion control at construction sites, an additional factor is important to the analysis that does not come into play in agricultural scenarios. That factor is the magnitude of fines that are often incurred if the contractor fails to prevent runoff quality deterioration beyond prescribed limits (Tobiason *et al.*, 2001). A single failure at a development site in 1996 in Washington state resulted in a \$65,000 fine (Bremerton Sun, 1996). This factor has increased the interest in PAM use because of its ability to ensure against failure of traditional erosion protection techniques, which may be more effective against massive point failures, but which cannot adequately meet turbidity thresholds in and of themselves.

In their study, Tobiason *et al.* (2001) found that wet PAM applications of as little as 90 g ha^{-1} applied in a 10-ppm spray reduced runoff turbidity considerably for as long as 6 weeks. Optimal PAM application doses were 40–80 ppm. Dry granular applications were also effective but required 10 times the material to yield the same degree of effectiveness as spray-applied PAM. Their study used a cationic polymer from Calgon identified as Catfloc 2953 and was described as a polyaluminum chloride-based PAM. Tests of aquatic organism survival in treated runoff using daphnia in this series of studies showed no mortality under these conditions. The series of tests found turbidity reductions with PAM from 80% to 100% where influent turbidities were as high as 1000 NTUs or more, with all PAM-treated discharges meeting Washington's strict guidelines. The tests were conducted over a 5-month period with rainfall totally 1010 mm.

Roa-Espinosa (1996) and Roa-Espinosa *et al.* (1999) found that several different PAM formulations provided excellent efficacy for erosion control. In these experiments anionic formulations with 15% or greater charge density were generally among the most effective PAMs. Overall treatment strategies for the field tests were best when the PAM was mixed with grass seed and used, essentially, as a hydroseeding matrix. In these treatments, seed germination was improved because the PAM prevented seed from washing away and promoted better seedling emergence and sward establishment, an observation which was further substantiated in work by Sojka *et al.* (2003) who saw greater weed establishment in PAM-treated furrows.

Teo *et al.* (2001, 2006) compared a number of PAM formulations for use in reducing erosion in a variety of Hawaiian soil management situations, including from construction sites where sediment-laden runoff posed significant risks to reef flora and fauna. Their findings indicated that although there were occasional minor advantages of matching specific polymer formulations to specific soils, generally good performance was achieved with anionic PAMs of the type specified by the NRCS PAM standard (Anonymous, 2001). Flanagan *et al.* (2002a,b) reported good successes applying PAM for erosion control on steep slopes.

Soupir *et al.* (2004) investigated a number of PAM- and mulch-based treatments for erosion control on construction sites in Virginia. Her results parallel others in the literature including those of Roa-Espinosa *et al.* (1999) that optimal overall effectiveness is obtained by combining PAM with a mulch or hydroseeding mix. Another aspect of the study by Soupir *et al.* (2004) worth noting is the difficulty that can occur if the PAM application solution is too concentrated, resulting in restriction of infiltration, thereby generating more runoff and preventing maximum erosion control efficacy or stand establishment. This result is in line with the finding of Lentz (2003) and indicates that for best results, especially in hydroseeding a careful control of PAM concentration is important, as well as provision of enough total solution volume to assure some penetration of the PAM into the surface few millimeters of soil. Similar results were obtained in a study of PAM for erosion control on road cuts in North Carolina (Hayes *et al.*, 2005). Their study saw less than optimal PAM performance when applying PAM alone at concentrations of 76 and 468 ppm of product formulation (active ingredient concentrations not given). While PAM mixed with mulch saw sediment reductions of 95%, the high PAM concentration applications only showed 20–40% reductions. As noted by Lentz (2003), unless PAM in these high-concentration ranges are allowed to achieve complete dry-down before being irrigated or rained on, they will restrict infiltration. As noted earlier in the chapter, a significant body of literature has noted the desirability, when applying PAM in solution form, to hold concentrations below 20 ppm for optimal infiltration and erosion control in furrow irrigation; it could be that similar concentration-dependent effects influenced the outcomes of both the Soupir *et al.* (2004) and Hayes *et al.* (2005) studies.

Open pit and strip mining can pose significant environmental risks due to erosion and runoff. They can also pose significant challenges to revegetation because of poor infiltration and, when rainfall is seasonal, due to sheet erosion of seeded areas before stand establishment has had a chance to occur. Vacher *et al.* (2003) studied the use of PAM in large erosion plots using soil from three Australian mine sites. A range of PAM materials and application rates and strategies were studied in replicated tests under a rainfall simulator. Application rates of an anionic PAM meeting US NRCS recommendations (Anonymous, 2001) were applied at rates of 5, 10, 20, and 40 kg ha^{-1}. All materials were applied as liquid solutions diluted to allow application with hand sprayers, applying 57 liter m^{-2} total solution to rainfall plots and 25 liter m^{-2} to overland flow plots. In addition to PAM treatments, the study included a 2.75 t ha^{-1} barley straw plot and one straw plus PAM plot. Overland flow plots also applied 5 t ha^{-1} gypsum. Plots were allowed to dry 12 h before erosion and runoff tests were conducted. All PAM treatment infiltration rates were significantly improved compared to controls but did not match the straw or straw plus PAM treatment. Most PAM treatments significantly reduced erosion, with the numerically best treatment being the straw plus PAM treatment, statistically equal to the straw-only treatment. These two treatments typically performed five- to tenfold better than the PAM-only treatments for erosion control and about twofold better for infiltration improvement. In a side study, PAM performance was enhanced in some instances by adding small amounts of suspended clay material to the coarser textured soils. Higher molecular weight formulations outperformed lower molecular weight formulations for erosion control, but no differences were seen for infiltration.

Another important development in PAM use has been its deployment for dust control in helicopter-landing zones and high-traffic areas of military encampments (Mikel, 2003; Orts *et al.,* 2006; The Furrow, 2004). Again, this represents a full circle return to uses originally developed in the late 1930s and early 1940s. However, better PAM formulations and five decades of additional scientific insight and experience with application techniques have improved the effectiveness and longevity of application. Over two dozen military PAM application rigs have been deployed in Iraq and Afghanistan to improve the safety of landing zones and the hygiene and living conditions of bivouac areas and have been attributed with preventing costly dust-related helicopter repairs as well as preventing landing accidents that have often been fatal in the past. Use of PAM for wind erosion reduction in agricultural settings has not been thoroughly researched. A few studies (Armbrust, 1999; Armbrust and Dickerson, 1971; Armbrust and Lyles, 1975) demonstrated that PAM and other polymer materials can be effective at reducing detachment, but did not effectively resist the erosive effects of saltation from adjacent unprotected areas. Since few studies have been conducted to explore the range of new polymer materials and potential application strategies available with sprinklers and other forms of irrigation and so on, there may yet be room for optimism for development of polymers for economical wind erosion control for agriculture.

XVI. CANAL AND POND SEALING

Water conservation and efficient transfer of precious water resources in arid zones from water source to point of use via unlined canals is becoming increasingly important. Seepage losses from unlined canals can be significant, typically 20–30% of the volume conveyed (Tanji and Kielen, 2002). In a world with ever increasing water shortages and water demands, prevention of unwanted seepage loss could be of staggering importance. In many arid areas, seepage also results in the mobilization of Se from soils and underlying strata, which can accumulate in seeps and wetland areas. Excessive Se has proven to be toxic to waterfowl.

Conventional canal lining methods using concrete or various types of membranes can effectively reduce seepage losses but are costly. Development of lower cost seepage control technologies can increase benefit to cost ratios and may provide a better investment (Kahlown and Kemper, 2005). Polymer applications are being investigated as a potentially more cost effective means for controlling irrigation-related seepage losses. In the late 1950s, the US Bureau of Reclamation evaluated the use of a proprietary emulsion made with resinous polymers and diesel oil. When added to the irrigation water in canals the chemical penetrated the soil and altered its hygroscopic properties. The product reduced seepage losses in nonreplicated tests, but was toxic to fish (Cron, 1959). Better polymers have been developed since then, and greater sensitivity to and regulation of environmental effects have resulted in more sophisticated exploration of the potential for use of polymers as seepage-inhibiting sealants.

More recently, a demonstration project in Colorado evaluated two canal seepage control treatments (Valliant, 2000). In one treatement, water-soluble granular PAM (18 kg per season) was metered intermittently into canal water. In the second treatment, cross-linked PAM was applied to the canal perimeter (630 kg ha^{-1}) prior to filling the canal. The tests monitored the seepage and sediment effects of treating a number of canal lateral segments with granular anionic water-soluble PAM applied into flowing water in two 2.3-kg applications separated by an hour between each application. The treated canal lateral sections were 70 m in length. Depending on the individual canal segment and date, flows varied from approximately 10,000 to 40,000 liter min^{-1}. The cross-linked PAM treatement proved ineffective. However, seepage loss was reduced from 40% to 70% for the water-soluble PAM treatment, although results were variable. Sediment in the delivered water was also reduced with PAM application. Variations in results were attributed to flow rate, sediment load, and the peculiarities of the individual lateral segments monitored in each test. Strict replication is not possible in these kinds of experiments, however, the trends among the compared control and PAM-treated lateral segments were consistent.

Other demonstration projects are evaluating treatments that apply water-soluble PAM directly to the canal perimeter before water fills the canal in spring (Marc Catlin, personal communication, 2000). One of the interesting properties of PAM, noted earlier in this chapter (Lentz, 2003), is that although at low concentrations it can stabilize soil pores and enhance infiltration, at higher concentrations viscosity effects eventually reduce infiltration. Lentz (2003) conducted a systematic soil column and miniflume study that quantified the infiltration-inhibiting effect of water-soluble PAM treatments for different soils under ponded and flow conditions. Surface applications of 250- to 1000-ppm PAM solutions to silt loam and clay loam soil reduced water infiltration 50–90%. Lentz (2001) also evaluated cross-linked PAM treatments which amended a thin layer of soil with 5- to 10-g PAM hydrogel per kilogram soil. These treatments reduced effective conductivity of soils 87–94%. The seepage reduction was greatest in soils with balanced particle size distributions and least in soils with high sand fractions or higher clay and organic carbon contents. Preliminary field investigations have shown that these treatments effectively reduce seepage losses in irrigation ponds and canals (Lentz and Kincaid, 2004). With respect to water-soluble PAM treatments, it is uncertain whether the viscosity is the sole or primary mechanism responsible for seepage reduction. The PAM may decrease infiltration simply by increasing sediment deposition in conducting pores, or PAM's ability to attract suspended fines from flowing water may contribute to establishment of a thin sediment layer of low permeability along the channel bottom that is held in place by the PAM.

Because of their ability to restrict infiltration at sufficiently high concentration, either alone or in combination with clays, there has been interest in the use of PAM and other polymers for pond and landfill sealing since the 1970s. Use of cationic polymers in conjunction with bentonite clays were shown to help stabilize the desired low hydraulic conductivity of clay liners against fluctuations in water content and the adverse effects of leachate constituents from landfills, often lowering hydraulic conductivity more than an order of magnitude (Ashmawy *et al.*, 2002; Bart *et al.*, 1979; Elhajji *et al.*, 2001; Petrov *et al.*, 1997; Pezerat and Vallet, 1973; Shackleford *et al.*, 2000).

Experiments are continuing among United States Bureau of Reclamation (USBR), Agricultural Research Service (ARS), and Desert Research Institute (DRI) to quantify the magnitude of the PAM sealant effect, the influence of a variety of application strategies, the influence of site conditions and soil properties, its durability, and effects, if any, on introduction of AMD from product residual AMD. NRCS has issued an Interim Conservation Practice Standard (NRCS, 2005) to define the practice and provide guidelines during the time of further testing and development.

XVII. BIOPOLYMERS

Farmers, environmentalists, the polymer industry, and other industries producing recalcitrant organic waste streams have shown interest in the possible development of biopolymer surrogates of PAM for a variety of reasons. PAM is inexpensive because the raw material currently used most commonly to synthesize the molecular building blocks of PAM is natural gas. Natural gas prices have risen greatly in recent years, resulting in about a 30% increase in PAM wholesale costs since 2000. Because so many industrial and food-processing activities depend on PAM-like polymers there is interest in guaranteeing the future availability of suitable polymers. Development of biopolymers may help assure future availability of suitable polymers. A class of biopolymers commonly explored in soil-conditioning research has been polysaccharides (Ben-Hur and Letey, 1989; Fuller *et al.*, 1995; He and Horikawa, 1996;

Malik and Letey, 1991; Malik *et al.*, 1991b; Nadler *et al.*, 1992; Parfitt and Greenland, 1970; Singh *et al.*, 2000a,b; Wallace *et al.*, 1986a).

Also, there is a perception among some that biopolymers represent a more sustainable and environmentally friendly basis for industrial and environmental technology. Research is underway to develop biopolymers synthesized from organic by-products of crop agriculture and shell fish food processing. Biopolymers may be substitutes for PAM in uses where easier biodegradability is desired or where bio-based chemistry is seen as an environmental benefit (Orts *et al.*, 1999, 2000, 2001, 2002; Sojka *et al.*, 2005).

Orts and colleagues tested biopolymers for furrow irrigation erosion control and infiltration enhancement in laboratory soil bins and in field plots. They showed that biopolymers are feasible, although current compounds are less effective and more expensive than PAM. Figure 6 shows the relative efficacy of PAM surrogates based on starch xanthate and/or microfibril suspensions in laboratory tests. Degree of substitution (ds) is the number of hydroxyls per glucose molecule (maximum of 3) replaced with a xanthate (CS_2) group. While several biopolymers reduced erosion significantly compared to controls, PAM was still five to six times more effective at a much lower concentration. Similar results were obtained for field and laboratory tests of chitosan-based polymers, although they showed efficacy at much lower concentrations (Fig. 7). These data also show the difficulty of drawing conclusions solely based on laboraory results. Earlier studies with polysaccharides and cheese whey for erosion control in furrow irrigation were also promising, fueling optimism that commercially viable biopolymer compounds may eventually be developed (Brown *et al.*, 1998; Robbins and Lehrsch, 1997; Shainberg and Levy, 1994; Singh *et al.*, 2000a,b).

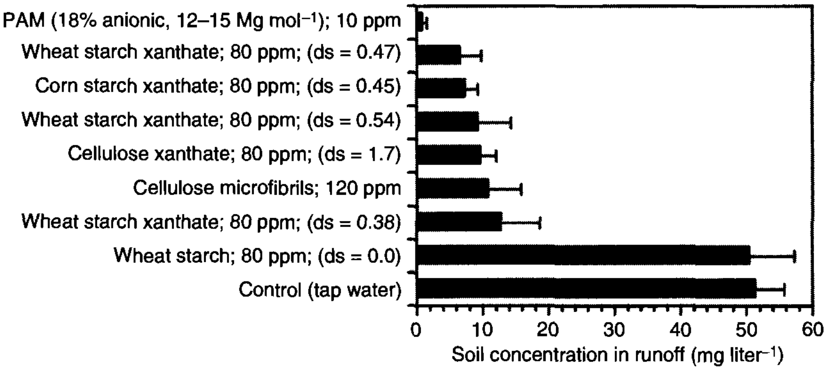

Figure 6 Relative efficacies of several biopolymer surrogates of PAM as determined from benchtop miniflume studies (Sojka *et al.*, 2005).

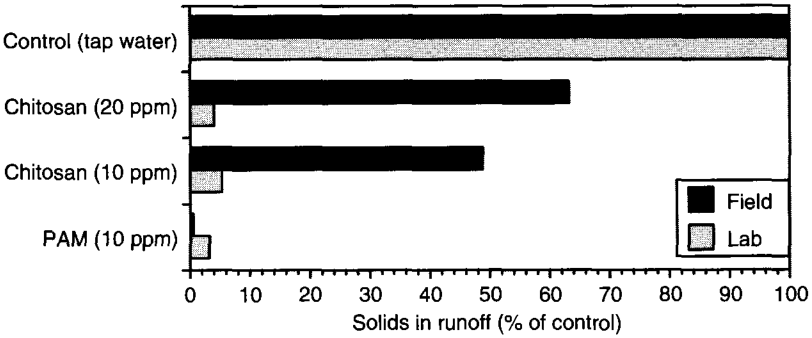

Figure 7 Degree of correspondence of benchtop miniflume results for actual field results using Portneuf silt loam soil in comparing a chitosan-based biopolymer with PAM (Sojka *et al.*, 2005).

XVIII. CONCLUSIONS

The advancement of PAM-based agricultural and environmental management technologies since the early 1990s has been rapid, dramatic, and expansive. PAM is an extraordinarily versatile polymer. The variety of its effects on the properties of water itself and the surface interactions of solids it sorbs with allow a wide range of potential management scenarios for the protection of the environment and the improved productivity of managed lands, especially in irrigated agriculture. The compound is very safe and very inexpensive in view of its remarkable potency to influence physicochemical processes. Coupled with the ingenuity and creativity of soil and water researchers, PAM, related synthetic polymers, and potential future biopolymers hold significant potential for affordable environmental protection and improved efficiencies and economies of environmental, agricultural, and industrial processes dependent on the management of soil structure, water behavior, and control of suspended solids.

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