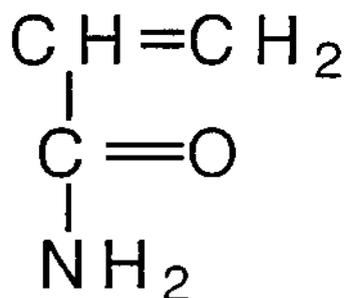


FATE OF ACRYLAMIDE MONOMER FOLLOWING APPLICATION OF POLYACRYLAMIDE TO CROPLAND

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Acrylamide (AMD) is the basic monomeric unit used in the production of a major class of water soluble polymers, generically termed polyacrylamides (PAMs). The structural formula of AMD is shown in Fig. 1.

FIG. 1.
Acrylamide (AMD).



MW = 71.08

Under the proper conditions and with suitable catalysts, AMD can polymerize with other molecules of AMD, or with other vinyl monomers to yield products with extremely high molecular weights. PAMs with molecular weights in excess of 10 million, i.e. with chain lengths of more than 105,000 monomeric units, are produced commercially. By utilizing the appropriate comonomers or by post-reaction with other reagents, these polymers may be cationic, nonionic, or in the case of those used to control soil erosion, anionic. The anionic reaction product of AMD and a salt of acrylic acid is shown in Fig. 2. The same chemical structure can also be produced by hydrolysis of the nonionic homopolymer of AMD or by hydrolysis of polyacrylonitrile.

Although anionic PAMs exhibit little toxicity to human and other mammalian systems, and aquatic animals, the toxicological effects of AMD monomer have been docu-

mented (Anon. 1991; Buchholz 1992; Health and Environ. Internat. 1990; Ohara, et al. 1985; Smith and Oehme 1991; Stephens 1991). These effects include neurotoxicity and animal carcinogenicity, which have resulted in stringent controls on handling of the monomer in manufacturing operations, labeling of products and residual AMD concentrations in commercial PAM products used for sensitive applications.

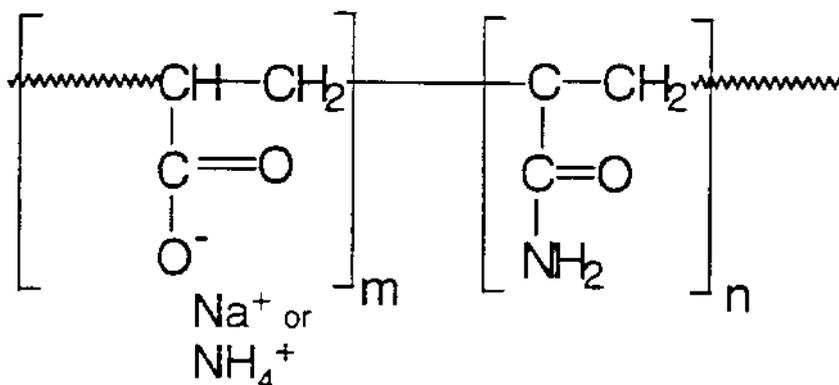
PAMs of various chemical types and molecular weights are employed in a wide variety of applications, including water and wastewater clarification, biosolids dewatering, paper making, scale control, mineral dispersion, food and animal feed processing, mineral and coal processing, petroleum production, water absorption, soil additives, cosmetics, friction reduction, viscosification, textile production, adhesives and laboratory applications (Barvenik 1994; Lipp and Kozakiewicz 1991; Mortimer 1991; Thomas and Wang 1985).

Of particular interest is the widespread usage of PAMs in potable water purification plants. PAMs func-

tion as aids in the process of flocculation of waterborne solids, and are useful for the removal of particulate contaminants including pathogenic microorganisms. When employed for the purification of potable water, PAMs are typically used in conjunction with coagulants such as aluminum and iron salts or low molecular weight cationic polymers, in gravity settling chambers, air flotation units and/or filters.

As potable water coagulant aids, PAMs are regulated by the U.S. EPA and agencies in several other countries. In the U.S., PAM products allowed for treatment of potable water may contain up to 0.05% residual AMD monomer. If a PAM product with 0.05% residual AMD monomer were used at the maximum recommended potable water dosage (1.0 ppm), the resultant maximum "at the tap" AMD concentration would be 0.5 ppb. Numerous commercial PAM products meet this residual AMD criterion, including anionic, nonionic and cationic PAMs in dry and inverse emulsion forms. The current regula-

FIG. 2. Anionic Polyacrylamide (PAM).



MW = 10-20 million

m + n = 140,000 - 280,000

tory standard for potable water treatment chemicals in the U.S. is "ANSI/NSF Standard 60, Drinking Water Treatment Chemicals - Health Effects". A variety of products manufactured by several companies are in the final stages of certification.

In addition, PAMs are commonly employed in the clarification of municipal and industrial wastewaters, and dewatering of wastewater sludges. For example, they can be used to aid in the economic removal of fine suspended solids from overloaded wastewater effluents, to settle bulking sludges within clarifiers in biological treatment plants, and to capture metallic hydroxides, thus preventing contamination of surface waters. Although most PAM products in the wastewater marketplace routinely contain no more than 0.1% AMD, apart from labeling requirements, there is no regulated limitation on the residual AMD concentration in the product. The PAM dosage is commonly of the order of 5-50 ppm for clarification of sewage. In wastewater clarification, PAM products are commonly used in one of the last unit processes before discharge to a receiving water. The resultant maximum AMD concentration in wastewater effluents discharging to public waterways is approximately 50 ppb.

Also, PAMs are allowed for use in several indirect food-contact and direct food additive applications, including preparation of food-contact paper, production of sugar and corn starch hydrolysate, preparation of animal feed additives, etc. These applications are regulated by the U.S. FDA (Title 21 of the Code of Federal Regulations) and comparable agencies overseas. In many of the specific FDA approvals there are limitations on the maximum level of residual AMD. For example, anionic PAMs containing up to 0.05% AMD are permitted for clarification of beet and cane sugar juice and liquor and corn starch hydrolysate (21 CFR, Section 173.5), and as a boiler water additive in the preparation of steam in contact with food (21 CFR, Section 173.310). Also, anionic PAMs containing up to 0.2% AMD may be used as components of paper and paperboard in contact with food (21 CFR, Section 176.110).

The PAMs used for soil erosion applications typically have residual AMD concentrations no more than 0.05%, in some cases significantly lower. In other words, the AMD concentrations in PAMs used for soil erosion control in agriculture are of the same level of purity re. residual AMD as U.S. "potable water grade" flocculants and products used in FDA sanctioned indirect and direct food applications. When used at the current recommended application rate of 10 ppm in irrigation water, the maximum AMD concentration in water would be 5 ppb.

The intention of this paper is to survey the literature relating to the fate of AMD monomer in the water/soil/plant system, and to briefly introduce recent studies on plant uptake of AMD.

PAM Degradation

PAMs are remarkably stable molecules. Under certain conditions they do participate in a number of chemical reactions which have been summarized in various review articles (*American Cyanamid 1970; Buchholz 1992; Lipp and Kozakiewicz 1991; MacWilliams 1973; Molyneux 1983; Mortimer 1991; Thomas and Wang 1985*). However, there is no evidence in the literature of regeneration of AMD monomer from the degradation of PAM by chemical or physical means. Regeneration of the double bond of AMD is not thermodynamically plausible. The polymerization is strongly exothermic, has a very rapid propagation rate, and proceeds essentially to completion. In modern manufacturing processes, the residual AMD monomer is below 0.1%, or lower in the case of PAMs used for agricultural soil erosion control. Thermal depolymerization does not occur; other reactions take place upon heating PAM, e.g. loss of ammonia from the amide group. Also, the closely related polymer, polyacrylic acid, will tend to decarboxylate upon heating rather than release free monomer (*Gurkaynak, et al. 1996*).

Probably the most notable chemical reaction of nonionic and anionic PAMs in aqueous solution is hydrolysis under acidic or basic conditions, leading to formation of ammonia and a strongly anionic PAM of essentially

the same molecular weight (*Lipp and Kozakiewicz 1991; MacWilliams 1973; Molyneux 1983; Thomas and Wang 1985*). The end product under extremely alkaline conditions would be a PAM with approximately 70 mole% anionicity. At neutral pH, high temperature would be required for the non-biological hydrolysis of PAMs. Other reactions have been described in the literature, including reaction with alcohols, aldehydes, amines, ammonia, chlorine and bisulfite. However if these agents are present, they would also react with any AMD monomer that may be present as residual from the manufacturing process, thus reducing the concentration of AMD.

In the presence of some strong oxidizing agents, such as persulfate or peroxide, permanganate, ozone, and/or radiation, it is possible to degrade the backbone of the PAM molecule; this may result in formation of gel or decrease in solution viscosity, depending on the polymer concentration (*Alexander and Charlesby 1957; Grollman and Schnabel 1982; Suzuki, et al. 1978*). Commonly, loss in viscosity is indicative of a decrease in the molecular weight. However, even under the extreme conditions of ozonation in the presence of intense ultraviolet irradiation, which yields a variety of low molecular weight end products, there was no evidence of AMD regeneration (*Suzuki, et al. 1979*).

PAM solutions will lose viscosity slowly over the timespan of days to weeks in the absence of agitation (shear). This has been interpreted in a number of ways, including disentanglement, disaggregation, change in molecular structure due to hydrogen bonds, breaking of weak links and/or slow chemical attack (*Kulicke and Klein 1977; Molyneux 1984; Narkis and Rebhun 1966; Shyluk and Stow 1969*).

In addition, high speed agitation or ultrasonics will lead to a more rapid loss in viscosity due to decrease in chain length or molecular weight (*MacWilliams 1973; Nagashiro, et al. 1975; Okkuama and Hirose 1963; Shyluk and Stow 1969; Thomas and Wang 1985; Tolstikh, et al. 1992*). This shear-induced viscosity loss occurs in the timespan of hours with

high molecular weight polymers. However, low molecular weight PAMs are much more resistant to the effect of shear. With high molecular weight polymers exposed to high shear conditions, the viscosity will decrease rapidly for a short time, then level off. In other words, once the molecular weight decreases somewhat, the molecules become more stable, presumably because the lower molecular weight fragments move more freely and do not entangle with each other. For example, in the high shear study by Nagashiro, et al. (1975), the viscosity stabilized once the molecular weight was decreased from about 5 million to 2.5-3 million. A PAM with a molecular weight of 2.5 million represents a chain length of 35,000 AMD monomer units.

Although PAMs are water soluble, they adsorb on solids by a number of mechanisms, including electrostatic attraction or charge neutralization, as well as bridging between adjacent particles due to their extremely large molecular dimensions, resulting in large aggregates or flocs (Mortimer 1991). Adsorption of polymer on solid surfaces has been demonstrated to be rapid and irreversible (Hollander, et al. 1981; Pradip et al. 1980; Tanaka, et al. 1990).

PAMs are considered to have molecular sizes too large to be transported across biological membranes (Stephens 1991), and the fact that they would tend to be adsorbed to soil aggregates makes such biological transport even less likely. Biodegradation of anionic PAMs may be limited to enzymatic hydrolysis and release of ammonia (Watwood and Kay-Shoemaker 1996). However, there is evidence in the literature that extremely low molecular weight polyacrylic acid, which may conceivably be fragments of PAM degradation under some conditions, can be metabolized by microorganisms (Hayashi, et al. 1994; Kawai 1993).

In the soil/water system, one can speculate that high molecular weight PAM, which is likely to be adsorbed to soil particles, might experience molecular weight loss due to tillage and other mechanical shear, as well as oxidative and/or photolytic attack. This may gradually yield very low molecular weight fragments that might be biologically degraded to

TABLE 1. Aquatic Toxicity of AMD Monomer (LC₅₀).

| | |
|-------------------|--------------|
| Goldfish: | 460, 140 ppm |
| Fathead Minnow: | 56, 120 ppm |
| Rainbow Trout: | 110 ppm |
| Bluegill Sunfish: | 100 ppm |
| Daphnia magna: | 160 ppm |
| Midge larvae | 410 ppm |

(Anon. 1991; Health and Environ. Internat. 1990)

CO₂ and H₂O. None of the above PAM degradation reactions yield acrylic acid or AMD monomer. Thus, the only likely source of AMD is the residual from the PAM manufacturing process.

AMD Mobility and Adsorption

AMD is highly water soluble (215.5 g/100 ml at 30°C), poorly adsorbed by solids and relatively insoluble in hydrophobic solvents (Anon. 1991; Haberman 1991; Health and Environ. Internat. 1990; Smith and Oehme 1991). The octanol/water partition coefficient (log Kow = -0.67) indicates low lipid solubility and little tendency toward bioaccumulation. Brown, et al. (1980a) found that AMD is not appreciably adsorbed by activated carbon, silica, clay minerals, peats, sediments and sludges. Employing thin layer chromatography with soil as the solid phase, Lande et al. (1979) found that AMD tends to be mobile in a soil/water system. It was quite mobile in all soils tested, ranging from 2.8 to 16% organic matter, especially in those with organic content less than 5%.

Although AMD is volatile, especially at high temperature, it exhibits low vapor pressures at temperatures <40 °C, therefore only a small portion is likely to transport from the soil/water system into the atmosphere (Anon. 1991; Haberman 1991; Health and Environ. Internat. 1990; Smith and Oehme 1991). The fraction that does migrate into the atmosphere would tend to adsorb from air to particulates, and therefore would be likely to transport back to the earth with rain. Also, in the atmosphere AMD reacts rapidly with photochemically produced hydroxyl radicals.

Thus, AMD delivered to the soil/water system by treatment with PAM, is likely to migrate largely with water unless it reacts to form other end products.

Aquatic Toxicity

Published acute toxicity information related to the effects of AMD monomer on aquatic organisms is summarized in Table 1. The LC₅₀ values for AMD for a variety of fish and invertebrates range from 56 to 410 ppm, i.e. four to five orders of magnitude higher than would result from current recommended application rates of PAM in agricultural irrigation water.

However, it is well known that cationic polyelectrolytes including PAMs can be toxic to fish and other aquatic animals when tested in the absence of solids and dissolved organics, resulting in low LC₅₀ values (Buchholz 1992; Goodrich, et al. 1991). The toxicity of cationic polymers does not result from residual monomer, but rather from mechanical suffocation caused by binding of the cationic polymer with anionic sites on fish gills. These polymers also have a high affinity for suspended solids and dissolved anionic solutes. In their normal usage for solids/liquid separation in wastewater treatment plants, the products are used in the presence of high suspended solids concentrations, and the polymer binds irreversibly and migrates with these biosolids rather than with the finished water. Also, Goodrich, et al. (1991) demonstrated that the LC₅₀ values for rainbow trout exposed to cationic polymers were increased by about an order of magnitude in the presence of as little as 5 ppm humic acid, commonly present in natural surface waters. Furthermore, cationic PAMs are not currently

recommended for control of agricultural soil erosion.

This toxic effect does not occur with anionic PAMs. Anionic PAMs exhibit high LC_{50} values (>100 ppm) vs. fish, i.e. low toxicity (Barvenik 1994). Data summarized by Buchholz (1992) indicates that some species of fish appear to be unaffected by anionic PAM at concentrations of 100 ppm in 90 day tests. However, minnows were killed by 2500 ppm solutions of anionic PAM due to the extreme viscosity of the fluid. This is more than two orders of magnitude higher than recommended for addition to irrigation water.

AMD Chemical Reactivity

The chemistry and high degree of reactivity of AMD has been extensively reviewed (American Cyanamid 1970; Anon. 1991; Haberman 1991; MacWilliams 1973; Ohara, et al. 1985; Smith and Oehme 1991; Thomas and Wang 1985). There are two reactive sites on the molecule (Fig. 1), the amide group and the double bond. The amide group readily hydrolyzes in the presence of base or acid to yield acrylic acid. The rate and degree of completion of this hydrolysis is dependent on the pH conditions and temperature. The hydrolysis rate is somewhat higher under basic than acidic conditions, and it is quite slow at pH close to neutral. Microbially produced amidase enzyme can accelerate the hydrolysis in the neutral pH region (Shanker, et al. 1990). In addition, under mild conditions in water solution the amide will react with various aldehydes.

AMD will polymerize with other molecules of AMD or other vinyl monomers, such as acrylic acid, in the presence of free radicals and the absence of oxygen. This nonreversible polymerization can yield polymers with molecular weights ranging from 10^3 to $>10^7$. In addition, under moderate pH and temperature conditions a variety of compounds will react with AMD at the double bond, to yield less toxic end products. These include ammonia, amines, alcohols, cellulose, starch, mercaptans, sulfite and bisulfite, sulfides, and strong oxidizing agents such as chlorine and hypochlorite, bromine, permanganate and ozone. It should be noted that

post-polymerization addition of sulfites or bisulfites is one of the common approaches toward reducing the level of residual AMD in commercial PAM products. Sulfites are also found in natural waters under moderately reducing conditions.

In the current study (discussed below; also see Table 3), AMD rapidly disappeared from aqueous extracts of plant tissues. It is not known whether this was due to hydrolysis mediated by plant or microbial amidase enzymes, or some combination of the other reactions mentioned above. However, AMD appears to be relatively stable in the time frame of weeks to months at neutral pH, in water and soil systems in the absence of microorganisms or enzymes (Brown, et al. 1982; Lande, et al. 1979; Shanker, et al. 1990).

AMD Uptake by Plants — Literature Background

Castle, et al. (1991) grew tomato plants hydroponically on commercial polyacrylamide gel bags, containing 0.018% AMD. AMD was not detectable in the tomato fruit. The limit of detection in tomato tissue of their gas chromatography-mass spectrometry (GC-MS) method was 1 ppb. The same method was used by Castle (1993), who found no evidence of AMD uptake by edible mushrooms grown in a casing mix containing polyacrylamide gel, with a detection limit of 0.5 ppb in the mushroom tissue. The polyacrylamide used by Castle (1993) contained 0.022%

AMD, which translated into 220 ppb in the mushroom casing medium.

On the other hand, Nishikawa, et al. (1983) demonstrated migration of AMD monomer into the roots (1.7 ppb) and stalks (41 ppb) of rice grown in a polyacrylamide hydroponics medium containing 50 ppm AMD (four orders of magnitude higher than would result from currently recommended practice for erosion control). The concentration in the rice tissue decreased by 10-100 fold in approximately five days. They observed no inhibition of the growth of the rice by 50 ppm AMD. However, Nishikawa, et al., also presented evidence of growth rate inhibition of Chinese cabbage by >5 ppm AMD (three orders of magnitude higher than currently recommended practice). Kuboi and Fujii (1984), also working with hydroponics media, demonstrated an EC_{50} for root elongation turnips of 220 ppm AMD.

AMD Uptake by Plants — Materials and Methods

A study was conducted at the USDA-ARS Laboratory in Kimberly, ID, employing commercial anionic PAM containing <0.025% AMD. The PAM was provided by CYTEC Industries, West Paterson, NJ. In 1994 irrigation water for potatoes and beans was treated with 10 ppm PAM. In 1995, in an effort to significantly increase the AMD exposure of the crops beyond levels reasonably used for soil erosion control in the agricultural sector, PAM was broadcast on

TABLE 2. PAM Applications in This Study.

| YEAR | CROP | NUMBER of TREATMENTS | TOTAL PAM APPLIED, kg/ha | MAX. AMD in TOP 6 in., ppb |
|------|-------------|----------------------|--------------------------|----------------------------|
| 1994 | potatoes | 15 | 19.9 | 5 |
| 1994 | beans | 5 | 7.4 | 2 |
| 1995 | potatoes | 10 + broadcast | 1140 | 312 |
| 1995 | beans | 10 + broadcast | 1140 | 312 |
| 1995 | sugar beets | 10 + broadcast | 1140 | 312 |
| 1995 | corn | 10 + broadcast | 1140 | 312 |

plots used for growing potatoes, beans, sugar beets and corn at a rate of 1000 kg/ha, then tilled into the soil. Irrigation water was also treated with 20 ppm PAM in the 1995 experiment. The treatment levels are summarized in Table 1. At the end of the normal growing season, the crops were harvested. The tissues were extracted with water, then analyzed by a procedure employing derivatization of AMD to 2-bromopropenamide, then analysis of ethyl acetate extracts with gas chromatography, employing an electron capture detector (*Hashimoto 1976; Andrawes, et al. 1987*). The standard curves in aqueous extracts of the plant tissue were linear in the range of 25-100 ppb ($R^2 = 0.967-0.993$) and the limit of detection was <10 ppb.

AMD Uptake by Plants — Study Results

AMD, if present, was below the limit of detection (<10 ppb) in all samples of plant tissues harvested in this study. Also, the lability of AMD in aqueous extracts of the crops was demonstrated. Concentrations of AMD in samples spiked with 50-500 ppb, decreased in the time span of minutes to hours. The effect was more dramatic in some plant extracts than in others (Table 2). This suggests that if any uptake occurs, the AMD is likely to rapidly convert to some other chemical species in the plant tissue. These results will be described in more detail in a subsequent publication.

AMD Biological Degradation

There have been several studies on the biodegradation of AMD in aqueous natural environments, including rivers, lakes, seawater, sewage effluents and aquatic sediments (*Brown, et al. 1980b, Croll, et al. 1974, Davis, et al. 1976, and others summarized in Health & Environ. Internat. 1990*). In general, the rates of biodegradation appear to be slow in oligotrophic water, and more rapid in eutrophic waters, sediments and sewage effluents. A lag period of hours to weeks, presumably allowing for enrichment of AMD decomposing bacteria or induction of enzymes in existing popu-

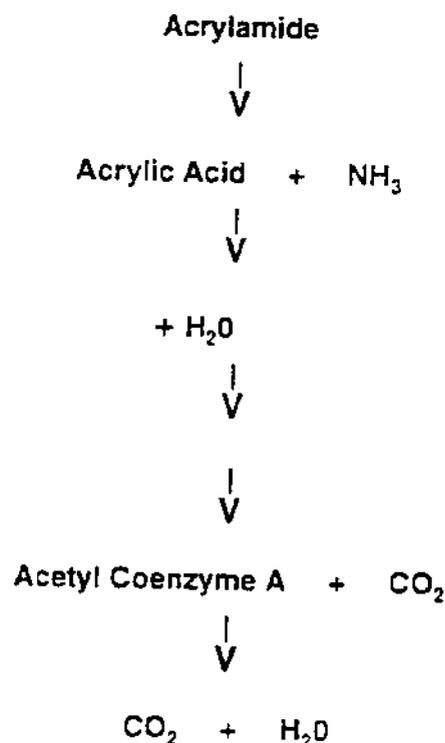
lations, has been commonly observed. The half-life for AMD appears to range from hours to weeks in waters acclimated to AMD. The rate of biodegradation in water is generally more rapid at temperatures ranging from 20-35°C than at temperatures below 10°C. Also, the rate is significantly higher in aerobic waters than under anaerobic conditions. Presumptive evidence that this degradation is biologically mediated has been provided by *Brown, et al. (1980b)*, who demonstrated that AMD disappearance from water is much slower in samples which have been sterilized by autoclaving.

Lande, et al. (1979) used a radiolabelling approach in their studies of AMD metabolism in soils. They added ^{14}C AMD (labelled in the 1-position, i.e. the carbonyl) to four different soils under aerobic and anaerobic conditions and monitored production of $^{14}\text{CO}_2$ with time. At dosing of 25 ppm under aerobic conditions at 22°C, they observed apparent AMD half-life ranging from 18 to 45 hr with no significant lag time. Note that *Shanker, et al. (1990)* (summarized below) demonstrated that the first step in AMD biodegradation may be hydrolysis to acrylic acid and ammonium, rather than decarboxylation. If

this is the case, a study in which $^{14}\text{CO}_2$ is monitored would result in an overestimate of the half-life of disappearance of AMD itself.

Lande, et al. also observed an apparent seasonal effect, i.e. a silt-loam collected in March at the time of spring thaw gave an AMD half-life 2.5 higher than a June sample from the same site. Temperature had a significant effect, with half-lives of 96, 18 and 9.6 hr at 10, 22 and 37°C respectively. As with the aquatic studies summarized above, the rate in autoclaved soil was much lower than in non-sterilized soil. In addition, *Lande, et al.* demonstrated an effect of AMD concentration on the half-life of decay to $^{14}\text{CO}_2$, i.e. much shorter half-life at 25 ppm than at 500 ppm. Note that currently recommended soil erosion control practice with PAM would result in AMD concentrations in soil several orders of magnitude lower yet. Under anaerobic conditions, the rate of $^{14}\text{CO}_2$ evolution was much lower than in the presence of oxygen. Using high performance liquid chromatography (HPLC) *Lande, et al.* were not able to detect ^{14}C -acrylic acid under aerobic or anaerobic conditions, suggesting that if it were an intermediate in AMD biodegradation in soil, it may be very tran-

FIG. 3. Postulated AMD Biodegradation Pathway (Abbreviated from *Shanker, et al. 1990*).



sitory or strongly adsorbed to some component of the soil system.

The fate of nitrogen from the AMD molecule has been examined by Abdelmagid and Tabatabai (1982). They incubated high levels of AMD (197 ppm) in five different soils and tracked the generation of inorganic nitrogen species. Ammonium accumulated in the soils under anaerobic conditions. In the presence of oxygen, ammonium was further oxidized to nitrite and nitrate, presumably mediated by nitrifying bacteria. Temperature had a significant effect on the rate of nitrogen mineralization in soil (rate at 30°C > 20°C > 10°C).

Shanker, et al. (1990) added 500 ppm AMD to a tropical garden soil and incubated at 30°C, analyzing for AMD and acrylic acid with an HPLC method. The AMD concentration was reduced to undetectable levels within five days, with no significant degradation in autoclaved controls. They were able to demonstrate acrylic acid as an intermediate, and ammonia and nitrate as products of nitrogen mineralization in this alkaline soil system. Nitrate production was inhibited by 2-chloro-6-trichloromethyl pyridine, a known inhibitor of nitrifying bacteria. They isolated a *Pseudomonas sp.* which was able to degrade AMD in culture media containing 4000 ppm of the monomer. The *Pseudomonas sp.* was capable of hydrolyzing AMD to acrylic acid and ammonia, and of utilizing AMD as sole source of carbon and nitrogen. They isolated an amidase enzyme from this culture which was active vs. AMD. A postulated pathway for the biodegradation of AMD is shown in Fig. 3.

Conclusion

PAMs added to irrigation water are effective for the control of agricultural soil erosion. Because the PAM molecule does not degrade to yield free AMD, residual monomer from the manufacturing process is the only environmental source in the soil/water system. The residual AMD content of PAMs used in agricultural soil erosion control is <0.05%. When PAM is used at the recommended application rate of 10 ppm in irrigation water, the maximum AMD concentration in the water would be 5

TABLE 3. Decay of Spiked AMD in Aqueous Crop Extracts.

| Beans Spiked | Blending time | | % Recovery | |
|-----------------|---------------|-----------|------------|------|
| | | | | |
| • 100 ppb: | | 10 sec | | 75 |
| | | 1 min | | 56 |
| | | 2 min | | 46 |
| | | 5 min | | 29 |
| | | 10 min | | 22 |
| Beans Spiked | | overnight | | 7 |
| • 500 ppb: | | | | |
| Beans Spiked | | | | |
| | • 100 ppb: | 1 min | | 93 |
| | | 5 min | | 77 |
| Corn Spiked | | | | |
| • 50 ppb: | | 10 sec | | 112 |
| | | 1 min | | 103 |
| | | 5 min | | 29 |
| Potatoes Spiked | | | Pulp | Skin |
| • 100 ppb: | | 5 min | 125 | 90 |
| | | 10 min | 81 | 85 |
| | | 20 min | 90 | 88 |

ppb. If applied at a rate of 1 kg of PAM/ha, ten times during the course of a growing season, and if the AMD were to be uniformly distributed in the top 15 cm of soil, the annual total applied AMD would amount to approximately 2.5 ppb in the soil.

However, although PAM is rapidly and irreversibly bound to soil particles in the process of flocculation, AMD is much more mobile. Very little adsorption of AMD to soil particles is likely to occur and AMD would tend to migrate with water.

AMD is not toxic to fish, aquatic invertebrates and crops at the usage concentrations. In fact, toxic effects in plants and aquatic animals have been demonstrated only at levels several orders of magnitude higher than realistically applied for the purpose of agricultural soil erosion control.

AMD is slowly chemically labile and highly biodegradable in soil and water. The less toxic compound acrylic acid has been demonstrated as an intermediate. The nitrogen has been shown to be released as ammonia by microbial amidase enzymes, followed by nitrification under aerobic soil conditions. Bacteria capable of using AMD as sole source of carbon and nitrogen and oxidizing the organic residue to CO₂ and H₂O have been isolated from soil.

Studies reported in the literature as well as the current work have demonstrated that AMD is not accumulated in crops, when applied at recommended dosages for erosion con-

trol. With the exception of one study with rice grown via hydroponics in the presence of very high AMD levels, there is no evidence of AMD uptake by crops. In the current study, PAM was applied to soil at rates two orders of magnitude higher than required for erosion control, with no AMD detectable in the crop tissues.

References

- Abdelmagid, H.M. and M.A. Tabatabai. 1982. Decomposition of acrylamide in soils. *J. Environ. Qual.* 11:701-704.
- Alexander, P. and A. Charlesby. 1957. Effect of X-rays and gamma rays on synthetic polymers in aqueous solution. *J. Polym. Sci.* 23:355-375.
- American Cyanamid Company. 1970. Chemistry of Acrylamide. Bulletin #PRC-109. 64 p.
- Andrawes, F., S. Greenhouse and D. Draney. 1987. Chemistry of acrylamide bromination for trace analysis by gas chromatography and gas chromatography-mass spectrometry. *J. Chromatogr.* 399:269-275.
- Anonymous. 1991. Chemical review: Acrylamide. *Dangerous Prop. Ind. Mater. Rep.* 11:2-18.
- Barvenik, F.W. 1994. Polyacrylamide characteristics related to soil applications. *Soil Sci.* 158:235-243.
- Brown, L., K.D.C. Bancroft and M.M. Rhead. 1980a. Laboratory studies on the adsorption of acrylamide monomer by sludge, sediments, clays.

peat and synthetic resin. *Water Res.* 14:779-781.

Brown, L., M.M. Rhead, K.D.C. Bancroft and N. Allen. 1980b. Model studies on the degradation of acrylamide monomer. *Water Res.* 14:775-778.

Brown, L., M.M. Rhead, D. Hill and K.D.C. Bancroft. 1982. Qualitative and quantitative studies on the in situ adsorption, degradation and toxicity of acrylamide by spiking of the waters of two sewage works and a river. *Water Res.* 16:579-591.

Buchholz, F.L. 1992. Polyacrylamides and poly(acrylic acids). p. 143-156 In: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A21. Ed. by B. Elvers, S. Hawkins and G. Schulz. VCH, Weinheim, Germany.

Castle, L. 1993. Determination of acrylamide monomer in mushrooms grown on polyacrylamide gel. *J. Agric. Food Chem.* 41:1261-1263.

Castle, L., M-J. Campos and J. Gilbert. 1991. Determination of acrylamide monomer in hydroponically grown tomato fruits by capillary gas chromatography-mass spectrometry. *J. Sci., Food Agric.* 54:549-555.

Croll, B.T., G.M. Arkeil and R.P.J. Hodge. 1974. Residues of acrylamide in water. *Water Res.* 8:989-993.

Davis, L.N., P.R. Durkin, P.H. Howard and J. Saxena. 1976. Investigation of selected potential environmental contaminants: Acrylamide. EPA-560/2-76-008. Washington, DC. 147p.

Grollmann, U. and W. Schnabel. 1982. Free radical-induced oxidative degradation of polyacrylamide in aqueous solution. *Polym. Degrad. and Stabil.* 4: 203-212.

Gurkaynak, A., F. Tubert, J. Yang, J. Matyas, J.L. Spencer and C.C. Gryte. 1996. High temperature degradation of polyacrylic acid in aqueous solution. *J. Polym. Sci. Part A: Polymer Chemistry*. 34:349-355.

Haberman, C.E. 1991. Acrylamide. p. 251-266 In: *Kirk-Othmer Encyclopedia of Chemical Technology*. 4th. Ed., Vol. 1. Ed. by J.L. Kroschwitz and M. Howe-Grant. Wiley, N.Y.

Hashimoto, A. 1976. Improved method for the determination of acrylamide monomer in water by means of gas-liquid chromatography

with an electron-capture detector. *Analyst* 101:932-938.

Hayashi, T. H. Nishimura, K. Sakano and Y. Tani. 1994. Microbial degradation of poly(sodium acrylate). *Biosci. Biotech. Biochem.* 58:444-446.

Health & Environment International, Ltd. 1990. *Comprehensive health and environmental monograph on acrylamide*, 79-06-1. Wilmington, DE. 62 p.

Hollander, A.F., P. Somasundaran and C.C. Gryte. 1981. Adsorption characteristics of polyacrylamide and sulfonate-containing polyacrylamide copolymers on kaolinite. *J. Appl. Polym. Sci.* 26: 2123-2138.

Kawai, F. 1993. Bacterial degradation of acrylic oligomers and polymers. *Appl. Microbiol. Biotech.* 39:382-385.

Kuboi, T. and K. Fujii. 1984. Toxicity of cationic polymer flocculants to higher plants. I. Seedling assay. *Soil Sci. Plant Nutr.* 30:311-320.

Kulicke, W.-M. and J. Klein. 1977. Zur Frage der Instabilität von Polyacrylamidlösungen. *Agnew. Makromol. Chem.* 69: 189-210.

Lande, S.S., S.J. Bosch and P.H. Howard. 1979. Degradation and leaching of acrylamide in soil. *J. Environ. Qual.* 8:133-137.

Lipp, D. and J. Kozakiewicz. 1991. Acrylamide polymers. p. 266-287 In: *Kirk-Othmer encyclopedia of chemical technology*, 4th. Ed., Vol. 1. Ed. by J.L. Kroschwitz and M. Howe-Grant. Wiley, N.Y.

MacWilliams, D.C. 1973. Acrylamide and other alpha, beta unsaturated amines. p. 1-197 In: *Functional Monomers; Their Preparation, Polymerization, and Application*. Vol. 1. Ed. by R.R. Yocum and E.B. Nyquist. Marcel Dekker, N.Y.

Molyneux, P. 1983. *Water-Soluble Synthetic Polymers: Properties and Behavior*. CRC Press, Boca Raton, FL. p. 75-117.

Mortimer, D.A. 1985. Synthetic polyelectrolytes - a review. *Polymer Internat.* 25:29-41.

Nagashiro, W., T. Tsunoda, M. Tanaka and M. Oikawa. 1975. Degradation of polyacrylamide molecules in aqueous solutions by high-speed stirring. *Bull. Chem. Soc. Japan.* 48: 2597-2598.

Narkis, N. and R. Rebhun. 1966. Ageing effects in measurements of polyacrylamide solution viscosities. *Polymer (London)* 7:507-512.

Nishikawa, J., T. Hara and Y. Sonoda. 1983. Absorption of acrylamide by plants. *Nippon Dojyou Hiryou Gaku Zasshi.* 54:55-57.

Ohara, T., T. Sato, N. Shimizu, G. Prescher, H. Schwind, O. Weiberg and K. Marten. 1985. Acrylic acid and derivatives. p. 161-176 In: *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A1. Ed. by W. Gerhartz, Y.S. Yamamoto, F.T. Campbell, R. Pfeferkorn and J.F. Rounsaville. VCH, Weinheim, Germany.

Okkuama, M. and T. Hirose. 1963. Mechanics of ultrasonic degradation of linear high polymer and ultrasonic cavitation. *J. Appl. Polym. Sci.* 7:591-602.

Pradip, Y.A.A. and D.W. Fuerstenau. 1980. The adsorption of polyacrylamide flocculants on apatites. *Coll. & Polym. Sci.* 258: 1343-1353.

Seybold, C.A. 1994. Polyacrylamide review: soil conditioning and environmental fate. *Commun. Soil Sci. Plant Anal.* 25:2171-2185.

Shanker, R., C. Ramakrishna and P.K. Seth. 1990. Microbial degradation of acrylamide monomer. *Arch. Microbiol.* 154:192-198.

Shyluk, W.P. and F.S. Stow, Jr. 1969. Aging and loss of flocculation activity of aqueous polyacrylamide solutions. *J. Appl. Polym. Sci.* 13: 1023-1036.

Smith, E.A. and F.W. Oehme. 1991. Acrylamide and polyacrylamide: A review of production, use, environmental fate and neurotoxicity. *Rev. Environ. Health.* 9:215-228.

Stephens, S.H. 1991. Final report on the safety assessment of polyacrylamide. *J. Am. Coll. Toxicol.* 10:193-202.

Suzuki, J., H. Harada and S. Suzuki. 1979. Ozone treatment of water-soluble polymers. V. Ultraviolet irradiation effects on the ozonation of polyacrylamide. *J. Appl. Polym. Sci.* 24: 999-1006.

Suzuki, J., S. Iizuka and S. Suzuki. 1978. Ozone treatment of water-soluble polymers. III. Ozone degradation of polyacrylamide in water. *J. Appl. Polym. Sci.* 22: 2109-2117.

Tanaka, J., L. Odberg, L. Wagberg and T. Lindstrom. 1990. Adsorption of cationic polyacrylamides onto monodisperse polystyrene latices and cellulose fiber: Effect of molecular weight and charge density of cationic polyacrylamides. *J. Coll. Interface Sci.* 134: 219-228.

Thomas, W.M. and D.W. Wang. 1985. Acrylamide polymers. p. 169-211 In: *Encyclopedia of Polymer Science and Engineering*. Vol. 1. Ed. by: H.F. Mark, N.M. Bikales, C.C. Overberger, G. Menges and J.K. Kroschwitz. Wiley, N.Y.

Tolstikh, L.I., N.I. Akimov, I.A. Golubeva and I.A. Shvetsov. 1992. Degradation and stabilization of polyacrylamide in polymer flooding conditions. *Internat. J. Polymeric Mater* 17:177-193.

Watwood, M.E. and J.L. Kay-Shoemake. 1996. The role of amidase in microbial utilization of PAM as an N-source. *Proc. Conference on Managing Irrigation-Induced Erosion and Infiltration with Polyacrylamide*. Twin Falls, Idaho, U.S.A., May 6-8, 1996.