Polymer Backgrounder: The Nature, Efficacy and Safety of Polymers for Erosion and Sediment Control

Prepared by Toronto and Region Conservation
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Sustainable Technologies Evaluation Program

Toronto and Region Conservation
for The Living City

THE SUSTAINABLE TECHNOLOGIES EVALUATION PROGRAM

The Sustainable Technologies Evaluation Program (STEP) is a multi-agency program, led by the Toronto and Region Conservation Authority (TRCA). The program helps to provide the data and analytical tools necessary to support broader implementation of sustainable technologies and practices within a Canadian context. The main program objectives are to:

• monitor and evaluate clean water, air and energy technologies;
• assess barriers and opportunities for implementing technologies;
• develop supporting tools, guidelines and policies; and
• promote broader use of effective technologies through research, education and advocacy.

Technologies evaluated under STEP are not limited to physical products or devices; they may also include preventative measures, alternative urban site designs, and other innovative practices that help create more sustainable and liveable communities.

NOTICE

PUBLICATION INFORMATION

FOREWARD

This backgrounder has been developed to provide introductory information and a summary of current literature on the use of polymers for construction site erosion and sediment control. It is intended for use as a reference document by persons involved in the design, application, inspection and maintenance of erosion and sediment control (ESC) measures that incorporate polymers. It provides a foundation of information on the safety and efficacy of using polymers on construction sites, but does not substitute for the need for ESC professionals to undertake practical training specific to the use and application of these products.

This document is intended to serve as a primer to the Anionic Polyacrylamide Application Guide for Urban Construction in Ontario (June 2013), which provides detailed guidance on the use of anionic polyacrylamide for erosion prevention, sediment control, and pond dredging on construction sites.

ACKNOWLEDGMENTS

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1.0 POLYMER BASICS

Polymers have been used for decades in a variety of industries, and have proven particularly effective for facilitating solid liquid separations during waste and drinking water treatment, and clarifying various types of effluents (Barvenik, 1994). Some of the main industries that use polymers in this capacity include pulp and paper manufacturing, mining, aquaculture and food processing. The use of polymers can improve the quality of industrial and agricultural effluents by removing suspended sediments as well as associated contaminants like nutrients (e.g. phosphorus) and metals. The polymers used in these applications promote the separation of solids through the processes of flocculation and/or coagulation.

During flocculation, the polymer adsorbs onto suspended particles and forms bridges between them, creating larger aggregate masses, or flocs (Figure 1.1). Coagulation differs from flocculation in that it involves charge balancing, and occurs when the coagulant polymer neutralizes the negatively charged particle surface (Laird, 1997). Once neutralized, the particles will no longer repel one another. This allows them to bind together to form larger flocs through particle collisions (Exall et al., 2008). Polymers that are coagulants tend to have a low molecular mass and high charge density, while polymers that are flocculants have a high molecular mass and low to moderate charge density (Exall et al., 2008). In water treatment, coagulants and flocculants are often used together – coagulants are used first to neutralize charges and flocculants are then added to cause the small neutralized particles to form large aggregates (Mason et al., 2005).
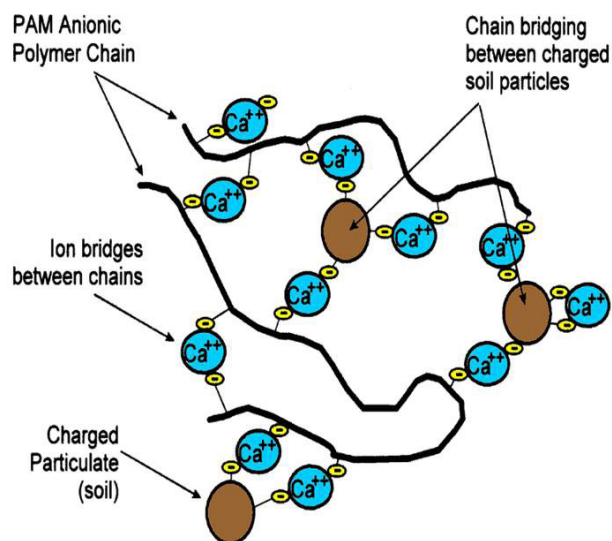

Figure 1.1: Interaction between a polymer (anionic polyacrylamide) and soil particles in the presence of calcium. Source: Orts et al., 2002.

For several years, polymer flocculants have been marketed as an effective means of managing sediment on construction sites. Although polymer-based water clarification is a technique that is well established in industrial applications, treatment of construction runoff is a newer and less established use of this technology. Today there are several products on the market that are intended to provide both erosion prevention and clarification of sediment laden runoff. Their effectiveness lies in their ability to enhance coagulation and/or flocculation of fine suspended sediment particles, allowing for more rapid settling in downstream detention practices. Once these larger flocculated particles have formed (Figure 1.2), they are also more readily removed through other means, such as filtration or sedimentation. As an erosion control, polymers are applied to bare soils, with or without ground covers, and function by causing soil particles to bind to one another, forming a surface resistant to erosive forces (Figure 1.3).

Figure 1.2 Water clarification with a polymer flocculant.

Figure 1.3: Soil surface treated with anionic PAM.

Some of the most common polymers currently marketed for construction sediment control applications – polyacrylamides and chitosan – are described in the following sections.

1.1 What are Polyacrylamides?

Polyacrylamides (PAMs) are a group of compounds formed by the polymerization of acrylamide and related monomers (Barvenik, 1994). The molecular structure of PAM is shown in Figure 1.4. They are synthetic polymers that can be manufactured to have different molecular weights, charge densities, molecular conformations and chemical reactivities by varying the reaction parameters and/or the relative quantities of reagents used. These variations can result in significant differences in polymer toxicity and the extent to which the PAM will bind to different types of particles.
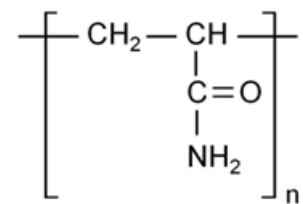
With respect to charge density, PAMs are classified as anionic (negatively charged), cationic (positively charged) and nonionic. Nonionic PAMs are very slightly anionic due to the nature of their manufacturing process. The charge density is often expressed in the literature as percent anionic or cationic, referring to the percentage of the monomers in the polymer chain that contain a charged functional group. The molecular conformation of a PAM can be linear or cross-linked, with only the linear molecule being water soluble (Sojka et al., 2007).

For decades water soluble anionic and cationic PAMs have been used to facilitate solid-liquid separations in wastewater and drinking water treatment, the pulp and paper industry, aquaculture, and many other industrial processes. The use of PAM in the treatment of turbid stormwater (during construction and post-development) is a newer and less common application that has recently begun to garner more attention. For applications in the natural environment, such as stormwater treatment applications, high molecular weight anionic PAM is preferred due to its lower toxicity to aquatic organisms compared to cationic PAM. Toxicity studies are addressed in Section 3.0.

Water soluble anionic PAM is also marketed for use as a tackifier in erosion control and pond demucking applications. As soil particles treated with PAM bind to one another they become more resistant to shear-induced detachment (Entry et al., 2002). As a result, high purity anionic PAM has become the most common synthetic polymer for reducing erosion caused by construction, and agricultural activities such as furrow irrigation (Sojka et al., 2005). Depending on the intended function, it can be applied directly to soil surfaces, added to water used for irrigation, or used as part of a seed mix, such as in hydroseeding (Figure 1.5). Treatment with PAM has been shown to reduce both water and

wind erosion, and in certain conditions, prevent surface sealing and maintain the soil's capacity to infiltrate water (Shainberg et al., 1990). In pond demucking, PAM helps to bind soil particles together and thereby facilitates the removal and transport of wet sediment, usually from the bottom of a pond. PAM is usually applied to wet sediment after water has been pumped out of the pond. Once PAM has reacted with the sediment, the pond can be excavated and the thickened sediment transported offsite.

For more detailed information on the history, nature, applications and performance of PAMs for management of environmental and agricultural lands, the extensive literature review completed by Sojka et al. (2007) should be referenced.

1.2 What is Chitosan?

Chitosan is a cationic linear polymer that is produced through the deacetylation of chitin, a natural polysaccharide found mainly in the exoskeletons of crustaceans and insects and the cell walls of certain fungi. The molecular structure of chitosan is shown in Figure 1.6.
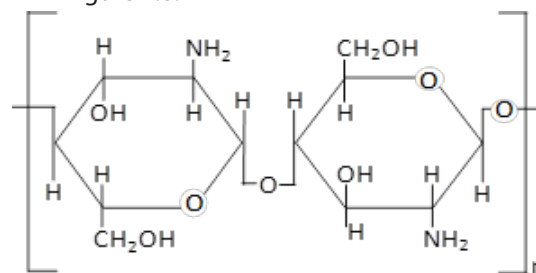
Figure 1.6: Chitosan molecule (n is the number of repeating units)

Chitin is abundant in nature, biodegradable, biocompatible and derived from renewable sources. In addition to its ability to flocculate suspended particles, it also has antimicrobial properties. These factors and other unique properties of chitin and chitosan make them valuable polymers with applications in a variety of industries, including biomedicine, pharmaceutical, food manufacturing, agriculture, cosmetics and toiletries manufacturing, and water treatment. Chitosan is widely used in the manufacture of many consumer products and is even marketed and sold today for as an ingestible dietary supplement to lower cholesterol and block fat absorption (Rinaudo, 2006). Like PAM, chitosan can be manufactured to have different characteristics, such as molecular weight and degree of deacetylation. Both will affect the way the final product behaves, including its toxicity (Kean and Thanou, 2010).

As a flocculant, chitosan has been widely used for the treatment of wastewater, drinking water, and various industrial effluents. The polymer has been used to aid in the removal of largely anionic waste solids as well as heavy metals, petroleum based substances and other contaminants from liquid effluents and wastewater (Dutta et al., 2004). As a stormwater treatment practice, chitosan

is often used with a sand filter in a process known as chitosan-enhanced sand filtration. In this process, the application of chitosan to sediment-laden water causes flocculation of suspended sediment, resulting in enhanced gravitational settling. The sand filter helps to remove flocculated particles that remain in suspension, and greatly minimizes the risk that residual chitosan will be released in the system effluent. If the system discharges to a water body that serves as aquatic habitat, effluent chitosan levels are often monitored with residual chitosan test kits.

2.0 POLYMER PERFORMANCE IN ESC

2.1 Erosion Control

The ability of polymers to stabilize soils and prevent erosion has made this technology a valuable tool in both the construction and agriculture industries. In agriculture, the use of anionic PAM in furrow irrigation is an application of great interest to the industry, and consequently the subject of much of the existing research on PAM for erosion control. In the early 2000's, PAM was being applied to approximately 400,000 irrigated hectares in the U.S. on an annual basis (Lentz et al., 2002). Research on the benefits of anionic PAM as an erosion control measure have focused primarily on prevention of soil loss and the transport of sediment, nutrients and other contaminants from the soil surface to receiving waterways.

Most of the studies in which anionic PAM was applied for preventing erosion demonstrated substantial reductions in levels of sediment, nutrients, and metals in runoff from treated areas. In two studies that specifically explored the efficacy of anionic PAM for construction site erosion control, soil losses were reduced by 83% (Roa-Espinoza et al, 2000 and Flanagan et al. 2002) and by as much as 93% when a PAM solution was applied to the soil surface with mulch (Roa-Espinoza et al, 2000). Factors impacting erosion control performance in the studies reviewed were slope, application method and rate, physical form of PAM used, soil texture, and overland flow rate.

Experiments by Hayes et al. (2005) yielded very different results when anionic PAM solutions were applied to moderate and steep slopes (20% and 50%) on a construction site. The anionic PAM products used in the study did not

Figure 2.1: Application of granular anionic PAM to a construction site soil stockpile

significantly reduce soil losses. The authors suggest that the application rates used in the study (10.5 kg/ha for Siltstop and 1.5kg/ha for Soilfix) are not sufficient to prevent erosion on steeper slopes.

 Anionic PAM is often used in conjunction with other ground covers on construction sites to enhance erosion control. McLaughlin and Brown (2006) evaluated the additional benefit of PAM applied with several erosion control practices including straw, straw erosion control blankets, bonded fiber matrices, and wood fibres. The experiments conducted, in which PAM was applied at a rate of 19 kg/ha to a 4% slope, determined that while all the other covers used resulted in reduced runoff volume, turbidity and soil loss, PAM used alone was only effective for turbidity reduction. The authors also tested the ability of PAM to improve vegetation establishment on bare soils and found that treatment with PAM resulted in a statistically significant increase in vegetative cover relative to a control (McLaughlin and Brown, 2006). Soupir et al. (2004) concluded similarly that PAM is most effective as an erosion control when it is applied with mulch or as part of a hydroseeding mix.

Cationic PAMs and chitosan are less popular choices for erosion control, although there is a growing interest in the use of chitosan for this application. Chitosan is often viewed as a more sustainable option because it is readily biodegradable and derived from natural by-products, whereas PAMs are synthetic and derived from products of oil refining.

Orts et al. (2000) evaluated and compared the performance of anionic PAM and several biopolymers, including chitosan, applied to agricultural irrigation furrows in both laboratory and field settings. It is important to note that the method of application and performance of polymers used for erosion control on a construction site can differ significantly from their application in agricultural irrigation furrows. Nevertheless, the experiment yields important information on the erosion control performance of chitosan relative to that of anionic PAM. Of eight products tested, anionic PAM was the most effective in reducing sediment content in runoff from laboratory-scale mini-furrows. While laboratory performance of chitosan was close to that of anionic PAM (both >85% sediment reduction), field results diverged substantially, with chitosan resulting in a sediment reduction of 51% compared to 99% for PAM. The authors suggest that the biopolymer could be more effective in preventing soil loss if its properties were optimized for the specific application.

2.2   Water Clarification

While there were few studies that specifically investigated polymer based water clarification of construction runoff, the Toronto and Region Conservation Authority carried out a field evaluation of anionic PAMs in 2010, and Benedict et al. (2004) studied both chitosan and cationic PAM in a construction setting.

During TRCA's field evaluation, anionic PAM based products were applied to reduce the turbidity of water being pumped out of a construction sediment control pond. Two applications were evaluated; in the first, PAM products were used in a roadside ditch (Figure 2.2) and in the second the product was

Figure 2.2: TRCA evaluation of anionic PAM for water clarification in a ditch

Figure 2.3: TRCA evaluation of an anionic PAM based clarification system using a mixing tank (right) and settling tank (left) installed in series.

Table 2.1: Summary of performance for all experiments

Experiment date	Application	Event Type	Average TSS concentration (mg/L)				Average % Reduction in TSS	
			Control influent	Control effluent	Polymer influent	Polymer effluent	Control	Polymer
Aug. 20	ditch	rainfall	78	73.7	115.3	106.5	5.4	7.7
Sept. 9	ditch	manual agitation	148	108	171	20.4	22.3	87.7
Dec. 2	tank	rainfall	TSS data not collected				-1.5 *	16.2 *
Dec. 4	tank	manual agitation	706	126	706	41.6	82.2	94.1

* No TSS data obtained for this experiment, number shown is percent difference in turbidity.

introduced via a mixing tank installed in series with a larger settling tank (Figure 2.3). For both applications, controls were also set up to allow for performance comparisons. Results are summarized in Table 2.1.

Despite a wide variation in performance among different experiments, the systems that employed the anionic PAM products were consistently more

Type of Treatment	Total volume treated (L)	Turbidity, untreated water (NTU)		Turbidity, treated water (NTU)	
		Range for indiv. samples	Range for median values	Range for indiv. samples	Range for median values
Polymer Clarification (cationic PAM)	219,837,789	7 – 22,000	117 – 14,000	<1 – 45	4 – 11
Chitosan-enhanced sand filtration	3,671,849	71 – 710	168	<1 - 4	2

effective at reducing total suspended solids (TSS) than the corresponding controls. The Aug. 20 ditch experiment was the only one for which the average effluent TSS concentration was higher for the polymer system. The poor performance of the polymer ditch during that experiment is largely attributable to poor orientation of the polymer product within the ditch – a problem that was corrected before the Sept. 9 experiment. The modest reduction in turbidity observed for both the polymer and control tanks on Dec. 2 (16.2% and -1.5%, respectively) is likely attributable to a finer influent particle size distribution compared to the Dec. 4 test. The naturally turbid runoff from the Dec. 2 rainfall event would be expected to contain finer particles than influent from Dec. 4, which was turbid as a result of manual agitation.

In Benedict et al. (2004) a liquid cationic PAM product (known as Catfloc 2953) was added to the construction stormwater through metered dosing in lined detention cells, while the chitosan in liquid form was mixed with water in a mixing chamber followed by a sand filter. A comparison of influent and effluent turbidities resulting from the use of both products is shown in Table 2.2.

Table 2.3: Summary of turbidity reductions reported in anionic and cationic PAM performance studies.

Study	Polymers tested	Study details	Turbidity reduction achieved
Wood et al., 2004	Cationic PAM	Treatment of stormwater in a clarifier with PAM and metal lamellar plates	52% (PAM alone) 83% (with plates)
Mason et al., 2005	Cationic PAM	Lab-scale study tested aluminum sulfate and PAMs (at different mixing speeds) to reduce turbidity and phosphorus loadings from tributaries to the Salton Sea.	>90% at 25 RPM ~65% at 300 RPM
	Anionic PAM		>90% at 25 RPM ~15% at 300 RPM
Iwinski and Snowdon, 2006	Anionic PAM	• Manufacturer study (Applied Polymer Systems Inc.) • Tested effectiveness of anionic PAM blocks used within a ditch-type system for clarification of water pumped from a construction sediment pond.	95 - 98%
Moran and Young, 2007	Anionic PAM	• Lab-scale study using jar tests • Turbid solutions created by adding kaolinite clay to water. • Measured effect of seven different doses of anionic PAM (0.5 - 32 ppm) on solutions of varying turbidity (150, 300 and 600 NTU).	~86 - 95%

Based on these results, the chitosan based system seems to have performed slightly better than the system using cationic PAM, although differences in system components make it difficult to isolate the specific effect of the polymers and conclusively state that one polymer is more effective than the other. Nevertheless, the study demonstrated that both systems performed well, resulting in effluent turbidity levels in line with state standards (i.e., Washington Administrative Code WAC 173-201A), which require that discharges to receiving waters not increase turbidity by more than 5 NTU for background levels up to 50 NTU, or by more than 10% when background is above 50 NTU (Benedict et al., 2004).

A study by Divakaran and Pillai (2002) applied chitosan for removal of silt in river water in India and also found that turbidity was significantly reduced. In the study, chitosan treatment without filtration resulted in reduction of turbidity levels to below 5 NTU for influent turbidities ranging from 10 to 160 NTU.

Additional studies evaluating the performance of anionic and cationic PAMs summarized by TRCA (2010) demonstrated that both are highly effective for clarification of turbid waters. Table 2.3 provides a summary of turbidity reductions reported in the studies reviewed. Cationic PAM was capable of yielding a total suspended solids (TSS) removal greater than 80% when used to treat stormwater in a clarifier with lamellar plates (Wood et al. 2004), and a turbidity reduction of at least 90% in a laboratory scale study of samples from the Salton Sea in California (Mason et al. 2005). Studies that assessed performance of anionic PAM found that it was also highly effective, resulting in turbidity reductions of 85% and greater (Mason et al., 2005; Moran and Young, 2007; Iwinski and Snowdon, 2006).

3.0 ENVIRONMENT AND HUMAN HEALTH

The toxicity of polymers used for onsite stormwater treatment and erosion control has been investigated in several studies, many of which have focused on potential impacts to aquatic invertebrates and fish. While some of these polymers have already been investigated as a means of establishing limits for use in food products and other consumer goods, the emphasis on examining aquatic toxicity has to do with determining whether the polymer compromises gill function, ion regulation and other activities such as breeding and feeding.

3.1 Polyacrylamides

Risks associated with the use of PAM for erosion and sediment control can be divided into the following main categories:

• Acute and chronic toxicity of unreacted PAM to terrestrial and aquatic biota
• Potential release of acrylamide monomer (a carcinogen and neurotoxin) to the environment-stripped areas left inactive for extended periods of time
• Physical impact of PAM deposited in receiving waters

While there have been numerous studies investigating the toxicities of various polymer products and the risks of acrylamide release associated with PAM, no studies have been encountered that specifically addressed the potential physical impact of polymer deposition in streams.

Another important consideration is the long-term sustainability of PAM production and use, given (i) its high stability and slow rate of degradation and (ii) its synthesis from a product derived from a non-renewable resource. Orts et al. (2000) explain that the stability of PAM, which degrades less than 10% per year, may result in accumulation in the natural environment in the long term. If allowed to accumulate, levels of PAM in the natural environment may reach levels substantially higher than those intended during its initial application.

Toxicity

Concerns regarding the toxicity of PAMs are largely focused on assessing potential impacts to aquatic life. With respect to toxicity to mammals, Stephens (1991) summarizes numerous experiments that investigated chronic and acute toxicity, dermal and ocular irritation, and reproductive effects of PAM on mammals (rats, dogs and rabbits). Findings showed that PAM exhibited little to no ill effect during all experiments carried out.

In the literature reviewed as part of the TRCA study (2010), cationic PAM was

consistently found to be more toxic to aquatic organisms than anionic PAM. This conclusion was reached in several studies comparing the toxicity of anionic and cationic PAMs (Biesinger and Stokes, 1986; de Rosemond and Liber, 2004; Liber et al., 2005). Anionic PAMs exhibited low to unobservable toxicity when tested on a variety of aquatic organisms, and LC-50 concentrations (the concentration of polymer that is lethal to 50% of the sample population) were sometimes two orders of magnitude higher than for cationic PAM. For example, Liber et al. (2005) found that for lake trout fry, anionic and cationic PAMs had 96 hour LC-50 values of 600mg/L and 2.08 mg/L, respectively. The concentrations at which anionic PAM was found to be toxic were often much higher than the suggested application/release rates of the PAM products. A summary of the studies reviewed on toxicity of anionic PAM to aquatic invertebrates and fish is provided in Tables 3.1 and 3.2.

Table 3.1: Summary of studies on toxicity of anionic PAM to aquatic invertebrates

Study	Form of anionic PAM	LC50 (mg/L)	Comments
Weston et al., 2009	granular	*Hyalella azteca:* >100 *Chironomus dilutus* : >100 *Ceriodaphia dubia* : 28.7	*H. azteca* and *C. dilutus* tested for 96 hrs, *C. dubia* for 6-8 days
	oil-based emulsion	*Hyalella azteca* : 0.8 and 2.1 *Chironomus dilutus* : 3.0 *Ceriodaphnia dubia* : 0.3	*H. azteca* and *C. dilutus* tested for 96 hrs, *C. dubia* for 6-8 days 2 different trials done for H. azteca
	water-based liquid	*Hyalella azteca* : >100 *Chironomus dilutus* : >100 *Ceriodaphnia dubia* : >100	*H. azteca* and *C. dilutus* tested for 96 hrs, *C. dubia* for 6-8 days
Hall and Mirenda, 1991	emulsion	*Daphnia pulex* 0.09 – 0.66	96 hr test, range of anionic PAM emulsions tested
de Rosemond and Liber, 2004	granular	*Ceriodaphnia dubia* : 218	48 hr test
Biesinger et al., 1976	granular	*Daphnia magna* : 345*, 17**	*48 hr test, **96 hr test
Biesinger and Stokes, 1986	granular	*Daphnia magna* : >100	48 hr test

Table 3.2: Summary of studies on toxicity of anionic PAM to fish

Study	Form of anionic PAM	LC50 (mg/L)	Comments
Weston et al., 2009	granular	*Pimephales promelas* : >100	Tested for 7 days
	oil-based emulsion	*Pimephales promelas* : 16.6	Tested for 7 days
	water-based liquid	*Pimephales promelas* : >100	Tested for 7 days
Hall and Mirenda, 1991	emulsions	*Pimephales promelas* : 21 - 85	96 hr test, range of products tested
Kobunshi Gyoshuzai Konwakai (1986)*	unknown	*Oncorhynchus mykiss* : 53.2 and 75.2	96 hr test, two different PAM products tested
Biesinger & Stokes, 1986	granular	*Pimephales promelas* : >100	48 hr test
Liber et al., 2005	granular	*Salvelinus namaycush* : >600	96 hr test

Some of the studies summarized found that toxicity of anionic PAM to certain species of invertebrates was higher than to fish (e.g. Weston et al., 2009; Hall and Mirenda, 1991). Aquatic invertebrates are a diverse group with a wide range of sensitivities to water quality conditions. The diversity of aquatic invertebrates as a group makes it difficult to draw conclusions about how different species will be impacted, however Hall and Mirenda (1991) did observe physical entrapment or clumping of the water flea Daphnia pulex during their toxicity study. The observation suggests that their very small size (< 2 mm) and the increase in water viscosity caused by high concentrations of PAM contributed to their higher mortality rate relative to the fathead minnow (Pimephales promelas).

Studies in which the form of anionic PAM product used was an emulsion generally resulted in a lower LC-50 concentration (i.e. higher toxicity) than studies in which water-based liquid or granular forms of anionic PAM were used (Weston et al., 2009; Hall and Mirenda, 1991; Applied Polymer Systems Inc., 2010). This may be a result of other components such as emulsifiers and surfactants that are used, for example, in the manufacture of oil-based PAM emulsions (Weston et al., 2009).

Recognizing the higher toxicity of cationic polymers, several studies (Biesinger and Stokes, 1986; Hall and Mirenda, 1991; Goodrich et al., 1991; Muir et al., 1997; Bullock et al., 2000) have also focused on understanding the mechanism by which these polymers result in increased fish mortality. While the literature suggests more than one potential mechanism, there is some agreement that (i) there is a potential attraction between negatively charged sites on fish gills and the cationic polymer and (ii) the impact of the cationic polymer on fish gills is the primary cause of mortality. Muir et al. (1997) found that the cationic polymer concentrates in gill tissue and not in other organs, suggesting that the polymer causes mortality by interfering with gill function and ion regulation.

Risks associated with acrylamide

One of the key concerns regarding the safety of PAM products is the potential release of its monomer acrylamide (AMD), which is considered by several authorities, including the U.S. Environmental Protection Agency, to be a likely human carcinogen and neurotoxin (U.S. EPA, 2010). All PAM products contain some level of residual AMD, but the amount of residual can vary substantially depending on what measures were taken during the manufacturing process to maximize the extent of polymerization. Research conducted on AMD risks associated with PAMs consider two potential methods by which AMD levels may be increased: (i) the use of PAM products that contain high levels of residual AMD and (ii) the release of AMD during the breakdown of the PAM molecule.

In Canada, the federal government regulates PAM-related AMD releases in the following ways (Environment Canada and Health Canada, 2009):

•   Natural health products containing PAM as a non-medicinal ingredient are subject to a 5 ppm AMD threshold.
•   Soil additives containing PAM must be registered as supplements under the Fertilizers Act, which requires disclosure of the percentage of

residual AMD in the product.

•   Voluntary health-based standards (adopted from National Sanitation Foundation Standard 60: Drinking Water Treatment Chemicals) limit the amount of AMD residual present in the finished drinking water to 0.5 ppb (0.5 µg/L for liquids).

Other jurisdictions have developed more stringent and application-specific limits for residual AMD in PAMs. Within the European Union, all PAMs are required to contain less than 0.1% residual AMD (European Chemicals Bureau, 2002), and more stringent thresholds are also set for specific PAM uses. In PAMs used to treat potable water, the U.S. EPA (2010) specifies that the amount of residual AMD must not exceed 0.05%, and the USDA Natural Resources Conservation Service (2002) applies the same threshold for anionic PAM used for erosion control in irrigated agriculture. Some agencies also set standards for levels of residual AMD remaining in drinking water that has been treated with PAM. The World Health Organization and European Union set this threshold at 1 µg/L, while the U.S. EPA specifies a lower threshold of 0.5 µg/L (Exon, 2006).

Several studies have also considered potential AMD release caused by degradation of PAM.   PAM is considered a highly stable polymer, known to degrade at a rate of only 10% per year (Orts et al., 2000). There is general consensus that the degradation of PAM to AMD is not a thermodynamically favourable reaction, and thus will not occur in the absence of certain catalysts. What remains uncertain is the stability of PAM under various temperature, chemical and irradiation conditions, and the extent to which its degradation in these conditions releases AMD. Studies investigating this issue have often applied conditions that are expected to be encountered in the environment in which the PAM is being used, such as UV or chlorine exposure for disinfection in water treatment facilities (e.g., Caulfield et al., 2003).

While some studies have demonstrated that degradation of PAMs are accelerated by exposure to UV irradiation and oxidants like chlorine and ozone, the literature appears to be divided on whether or not AMD is liberated in the process. Kay-Shoemake et al., (1998) and Vers (1999) both considered the effect of UV radiation on PAM and determined that the polymer did not degrade to AMD. The combined effect of exposure to ozone and intense UV radiation on PAM was tested by Suzuki et al. (1979, as cited in Barvenik et al., 1996), who also determined that AMD was not liberated despite the fact that the conditions did break the polymer chain. Contrary to these findings, Caulfield et al. (2003) found that UV exposure did cause AMD to be liberated. When they exposed PAM to UV radiation with a 254 nm wavelength (which is used in water disinfection), the average amount of AMD released over 10 days was 50 ppm (50 AMD monomers for every 1 million AMD monomers in the PAM chain). The authors noted that the polymerization method used affected stability due to slight variations in the orientation of bonds.

Barvenik et al. (1996) addressed the fate of AMD when applied to cropland and also considered levels resulting from various other applications. The authors state that a PAM product with 0.05% residual AMD monomer, applied at dosage of 1.0 ppm PAM, would result in a maximum "at the tap" AMD concentration of 0.5 ppb (or 0.5 µg/L) which would be in line with the U.S. EPA standard. One

of the study's key conclusions is that, while AMD is highly mobile and will not readily bind to soil particles, levels in runoff from PAM treated cropland would not be toxic to aquatic organisms or crops, given the AMD level in the PAM product was less than 0.05% and the product is applied at the recommended application rates. Further, Lentz et al. (2008) found that the potential for groundwater contamination by AMD was minimal in PAM treated furrow irrigated soils when AMD residual was 0.05% or less.

3.2 Chitosan

In chitosan based products, characteristics of the chitosan itself (e.g. molecular weight, degree of deacetylation) and other chemical additives in the final product can significantly affect toxicity. In particular, the studies reviewed demonstrated that a common preparation of chitosan solution – chitosan acetate – exhibited higher toxicity to the organisms tested in comparison to free chitosan. Chitosan acetate (chitosan dissolved in acetic acid) is used because the polymer is most soluble in a slightly acidic solution.

In toxicity tests carried out by Arai et al. (1968), mice fed 20 g/kg of free chitosan or chitosan formate (chitosan in formic acid) exhibited no toxic effects, while 40% of the mice died when fed the same quantity of chitosan acetate. Other studies in which free chitosan was fed to marine fish and rainbow trout also found that there were no toxic effects on the fish (Kono et al., 1987; Siwicki et al., 1994, as cited in Bullock et al., 2000).

In aquatic toxicity studies that specifically investigated the impact of chitosan acetate, the polymer exhibited high toxicity to rainbow trout, while acetic acid alone did not have toxic effects. Natural Site Solutions (2004) assessed effects on rainbow trout and determined that the 96 hour LC-50 concentrations were 1.7 mg/L and 6.4 mg/L for two different physical forms of chitosan acetate tested. Testing by Bullock et al. (2000) revealed that a dose as low as 0.075 mg/L resulted in mortality for 40% of the rainbow trout within 24 hours. During exposure to 0.75 mg/L, the mortality rate increased to 80% over 24 hours. Similar to studies of other cationic polymers, the authors of this study also determined that the mechanism of toxicity was related to damage of gill tissue. Valenzuela et al. (2003) carried out a more in depth investigation of the mechanism of toxicity of chitosan acetate by looking at hematological changes in the trout, and discovered that the respiratory stress chitosan induced in the fish caused death by hypoxia.

5.0 SUMMARY

Variations in polymer manufacturing processes can have a significant effect on their toxicity and performance. As an example, PAMs can be manufactured to have different molecular weights, charge densities, molecular conformations and chemical reactivities by varying the reaction parameters and/or the relative quantities of reagents used. These variations can result in significant differences in toxicity and the extent to which the PAM will bind certain types of particles. Chitosan can also be manufactured with different characteristics, such as molecular weight and degree of deacetylation. Both will affect the way the final product behaves, including its toxicity (Kean and Thanou, 2010).

Most studies investigating PAM as a construction site erosion control have demonstrated that it is effective in reducing levels of sediment, nutrients and metals in runoff from treated areas. In both Roa-Espinoza et al. (2000) and Flanagan et al. (2002), anionic PAM reduced soil losses by 83%. The polymer was often more effective when applied in conjunction with other ground covers, such as mulch or vegetation (McLaughlin and Brown, 2006; Soupir et al. 2004). Factors impacting erosion control performance in the studies reviewed were slope, application method and rate, physical form of PAM used, soil texture, and overland flow rate.

Both anionic and cationic PAMs and chitosan are effective in clarifying turbid waters. Both forms of PAM were capable of reducing turbidity by 85% and greater in the studies reviewed (Mason et al., 2005; Moran and Young, 2007; Iwinski and Snowdon, 2006; TRCA, 2004). Chitosan-enhanced sand filtration was demonstrated by Benedict et al. (2004) to reduce the turbidity of construction effluent by more than 94%.

The cationic polymers considered in this review displayed higher toxicity to aquatic organisms than anionic PAM. Several studies comparing toxicity of anionic and cationic PAMs have reached this same conclusion (Biesinger and Stokes, 1986; de Rosemond and Liber, 2004; Liber et al., 2005). Anionic PAMs exhibited low to unobservable toxicity to various organisms, and LC50 concentrations were sometimes two orders of magnitude higher than for cationic PAM. For example, Liber et al. (2005) found that for lake trout fry, anionic and cationic PAMs had 96 hour LC-50 values of 600mg/L and 2.08 mg/L, respectively. The concentrations at which anionic PAM was found to be toxic were often much higher than the suggested application/release rates of the PAM products. The cationic biopolymer chitosan acetate also exhibited

high toxicity, specifically to rainbow trout. In the two studies reviewed, the polymer was found to cause significant mortality of rainbow trout, even at low concentrations (Natural Site Solutions, 2004; Bullock et al., 2000).

The impact of cationic polymers on fish gills is believed to result in mortality. While the literature suggests more than one potential mechanism, there is some agreement that there is a potential attraction between negatively charged sites on fish gills and cationic polymers, and that the impact of the cationic polymer on fish gills is what results in mortality. Muir et al. (1997) investigated the mechanism of toxicity and found that cationic polymers tend to accumulate in fish gills, interfering with gill function and ion regulation.

Certain chemical compounds added during manufacturing of polymer based products can make the final product more toxic than the pure form of the polymer. For example, chitosan itself is considered non-toxic but has low water solubility. It is dissolved in acetic acid to form the water soluble chitosan acetate, which has been found to be toxic to rainbow trout (Natural Site Solutions, 2004; Bullock et al., 2000). Another example is the oil-based emulsion form of anionic PAM, which studies demonstrate is much more toxic than the powder form, mainly due to other components in the product, such as emulsifiers and surfactants (Weston et al., 2009).

Certain species of aquatic invertebrates are more sensitive than fish to anionic PAM. This was not observed for all aquatic invertebrates due to the great diversity within this group of organisms, which also increases uncertainty about how other invertebrates would respond. In Hall and Mirenda (1991) physical entrapment or clumping of the Daphnia pulex was observed during exposure to anionic PAM, suggesting the smaller size of aquatic invertebrates could partly explain why anionic PAM was more toxic to these species than to fish.

PAMs are highly stable and degradation to acrylamide monomer has only been observed in the presence of specific reaction catalysts. UV radiation applied to PAM alone and in the presence of iron was shown to result in the release of AMD from the breakdown of PAM in studies by Caulfield et al. (2003) and Woodrow and Miller (2007). In other studies, exposure of PAM to UV radiation did not liberate AMD (Kay-Shoemake et al., 1998; Vers, 1999). Given the conflicting information regarding the degradation of PAM to AMD, there appears to be a need for further research that specifically measures the extent of AMD liberation from PAM if it was present in a natural environment (e.g., stream, wetland).

Acrylamide is not expected to be released from anionic PAM at levels that are toxic to aquatic biota, if it is properly selected and applied. It is essential that the anionic PAM application rate and other application procedures are carried out in accordance with product manufacturer recommendations. Further, residual AMD levels should be below the thresholds set by the USDA and U.S. EPA (0.05%) to reduce risk of AMD release to the natural environment.

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