Super-absorbent water crystals – are they really so “super?”

What are hydrogels?

While gardeners may not be familiar with the term “hydrogel,” nearly everyone who has worried about watering their plants has heard about “watering crystals” or “water retention granules.” The ability of these synthetic polymers to absorb water and selectively bind to other substances has led to their use as soil stabilizers, water purifiers, juice clarifiers, animal feed thickeners, and in the processing of oil, pulp and paper, and fruits and vegetables. Moreover, they are widely used in cosmetics and other personal products, and have medical application in tissue augmentation (**see sidebar 1**). Although our main interest is in the effectiveness of garden-variety hydrogels, it is important to realize how widely these compounds are used in other contexts and to understand their positive – and negative – impacts.

There are two broad classes of polyacrylamide (PAM) hydrogels: soluble (linear) and insoluble (cross-linked). Linear PAM dissolves in water and has been successfully used in reducing irrigation-induced erosion in agricultural fields (**see sidebar 2**). Cross-linked PAM does not dissolve, but forms a gel when water is added and is often used in garden, landscape, and nursery situations as a way of retaining moisture. Insoluble PAM products are marketed as “superabsorbent gels” or “hydrating crystals.” Instead of dissolving, these gels absorb water, swelling to many times their original size. As they dry, water is slowly released to the soil. Popular with the nursery industry and homeowners alike, these latter compounds are the focus of this article.

How do hydrogels work?

In addition to their solubility, hydrogels are also defined by their overall chemical charge: they may be characterized by a negative (anionic), positive (cationic) or neutral charge. These charge classes are found in both linear and cross-linked PAM; the charge determines how they will react with soils and solutes. Briefly, clay components of soils have a negative charge; heavy metals have a positive charge, and other commonly found minerals in soils and water may possess either a positive or a negative charge, depending on the compound in question. Therefore, cationic PAMs (+) generally bind to clay components (-) and act as flocculants (congealers); anionic PAMs (-) cannot directly bind to clay (-) and may act as dispersants. However, anionic PAMs can bind to clay and other negatively charged particles in the presence of ionic bridges, such as calcium (Ca^{+2}) (Wallace and Wallace, 1996).

How polyacrylamide gels will act in any given situation can be hard to predict, as the chemical interactions between the gels, soil components, and dissolved substances are complex and occur simultaneously. Electrical charges, hydration levels, van der Waals forces, and hydrogen bonding all modify the affinity of the gel for other compounds. The polyacrylamide polymer contains a complex array of positively charged, negatively charged, and neutral chain segments, all with varying affinities for other molecules. The stronger the attraction between the gel and surrounding solutes and soil particles, the greater the ability of the gel to absorb water, create aggregates, and stabilize soil structure.

Unfortunately, on-the-ground conditions can prevent PAM hydrogels from functioning optimally. Fertilizers and other dissolved substances can interfere with hydrogel water-holding capacity. Hot, dry weather conditions can lead to increased degradation and decreased effectiveness of PAM hydrogels. And for every success story, one can find a situation where hydrogels have failed to function.

Hydrogel effects on plants:

The documented impacts of cross-linked PAM hydrogels on plant survival and establishment are variable. Some researchers report enhanced growth of crop and tree species. Presumably this enhancement is due to improved soil water conditions, though in some cases salt tolerance is also reported. This latter ability may be due to the ability of cross-linked gels to enhance calcium ion availability, reducing the amount of sodium uptake.

According to other researchers, however, PAM did not improve plant survival compared to control or other treatments, especially if performance was evaluated over time. In several cases, PAM-treated plants performed worse than the untreated controls. Moreover, excessive use of PAM can lead to nutrient deficiencies; phosphate and silicon were reduced in tomato and wheat, and this latter plant also suffered manganese and boron deficiencies when grown in under high PAM concentrations.

Why is there such high variability among research results? I believe the cause is both environmental and temporal. Many of the positive results are drawn from studies that are short-term and/or performed under controlled conditions; for instance, one study reports on tree survival only a few months after installation. As we already know, PAM gels lose their water-holding effectiveness over time, especially when exposed to high levels of UV, salts, and freeze-thaw cycles. Positive results in the short term may be perfectly valid for nursery plant production, where environmental conditions can be more tightly controlled, but they are not as applicable to landscapes. Indeed, it is under such conditions (e.g. revegetation of quarries and mines) over the long term that PAM gels perform most poorly.

Long-term effectiveness:

Although synthetically produced, polyacrylamides are organic chemicals that can be degraded by both living and non-living environmental factors. Exposure to ultraviolet radiation, chemical oxidizers, fertilizer salts, mechanical abrasion, and freeze-thaw events will degrade the polymer, breaking it up into smaller fragments. These smaller fragments do not have the same properties as the larger polymers, and thus the hydrogel's water-retaining capacity and other functions are reduced and ultimately lost. Gels that are applied to soil surfaces experience these environmental stresses most frequently and will degrade most rapidly, especially in soils with high levels of solar UV.

Even if gels are protected from environmental exposure they will still be broken down by decomposition. A number of naturally occurring soil microbes have been identified as active decomposers of both soluble and cross-linked polyacrylamide gels. Decomposers include bacterial species (*Bacillus sphaericus* and *Acinetobacter* spp.) and white rot fungi (*Dichomitus squalens, Phanerochaete chrysosporium*, and *Pleurotus ostreatus*). The fungal species solubilize the polymer, which is then susceptible to further degradation by many other soil microbes.

It's not surprising that polyacrylamide is rapidly broken down by decomposers; one study found the average size of the polymer to be less than 25% of the original in only 14 days of microbial action. These gels contain a significant amount of nitrogen, which is often a limiting nutrient in both aerobic and anaerobic environments.

In most outdoor applications, therefore, the functional life of polyacrylamides is short; this is borne out by a number of studies that have noted decreased efficacy of field-applied polyacrylamide gels over time. If gel activity is destroyed in as little as 18 months, there should be serious reservations about its use in long-term landscape applications.

Gel contamination and degradation:

As the name suggests, polyacrylamides consist of many linked acrylamide units (monomers). Acrylamide is a known neurotoxin in humans and is suspected to be carcinogenic as well. During the manufacture of PAM gels, residual acrylamide is present as a contaminant and strictly regulated in the United States to levels no more than 0.05% or 500 ppm for agricultural use. However, an international study recommended that polyacrylamide gels used in cosmetics contain a residual monomer level of only 0.1 to 0.5 ppm. Therefore, the PAM hydrogels manufactured for agricultural and garden use can contain much greater concentrations of toxic acrylamide than that found in personal products.

While new PAM hydrogels contain a higher initial level of acrylamide than older gels, there is bitter debate over whether the degradation of polyacrylamide gels provides a constant, significant source of environmental acrylamide. On one hand there are the researchers who claim that microbes quickly metabolize the nitrogen from the polymer, eliminating the possibility of acrylamide production (acrylamide contains nitrogen). Yet others have argued that degrading gels do produce measurable levels of acrylamide, especially when exposed to elevated temperatures or high levels of solar radiation. In any case, there is no question that PAM hydrogel degradation produces uncharacterized, variable polyacrylate units whose environmental and human impacts are unknown.

Hydrogels and human health:

There are two separate, but related, human health issues relevant to PAM hydrogels: risk of polyacrylamide exposure and risk of acrylamide exposure. The dangers from acrylamide exposure were briefly mentioned earlier and tend to be greatest for workers in occupations that routinely use polyacrylamide-based products such as grouts and wastewater flocculants. It is unlikely that the infrequent user of garden hydrogels will experience any significant exposure to acrylamide from this source.

The other health issue is that presented by exposure to the more or less intact polyacrylamide gel. Though PAM gels are much less toxic than acrylamide, chronic exposure can cause minor problems such as skin irritation and mucus membrane inflammation. More worrisome are recent reports of toxic effects of PAM both at the cellular and whole organism levels. An earlier article from 1992 reported on the accidental aspiration of polyacrylamide by a patient who subsequently died from lung injuries.

Finally, there is the issue of exposure to degrading PAM hydrogels, whose risks are entirely unknown. People most likely to be exposed to degradation products would be those involved in agricultural or nursery production where gels are commonly used and where environmental degradation would be most likely to occur. Compost piles containing potting mixes with hydrogels would also be a source of exposure.

Should you be concerned about your exposure to PAM hydrogels? This is where the big picture regarding hydrogel usage becomes important. Because these compounds are so ubiquitous, it's likely that most of us are exposed to a number of PAM gel sources every day. Studies that estimate lifetime risks of developing cancer usually focus on only one source of exposure, such as that from usage of personal care products that contain polyacrylamide. While these individual estimates are almost always very low, there have not been analyses to determine additive risks associated with exposure to multiple sources of polyacrylamide. The lack of scientific data makes it difficult to predict risks associated with exposure to polyacrylamide gels.

Hydrogels and environmental health:

As a neurotoxin and carcinogen, acrylamide is dangerous not only to humans but to other organisms as well; the evidence does not need to be repeated here. Of more concern for gardeners and landscapers is the impact of PAM hydrogels on other organisms in the environment.

Microbes do not appear to be negatively affected by PAM gels; indeed, we already know that gels are colonized and degraded by a number of naturally occurring bacteria and fungi. Toxicity information on terrestrial organisms (other than humans) exposed to PAM gels is nearly non-existent and therefore can't be addressed. Some inhabitants of aquatic systems, however, have been studied in relation to PAM gel toxicities and the news is not good.

There are few indications that anionic PAM gels, used appropriately, pose a significant health threat to aquatic organisms. Cationic and neutral PAMs, however, have greater toxicities and should not be used. The charged nature of cationic PAM hydrogel is attracted to hemoglobin in fish gills, where the gel binds and suffocates the fish. In addition to fish, a variety of algal and invertebrate species are also injured or killed when exposed to low levels of cationic PAMs. Since cationic PAMs may also contain higher levels of acrylamide monomer, many researchers recommend against any environmental use of cationic PAM hydrogels and in fact use of these compounds is illegal in a number of municipalities where aquatic contamination is likely.

Alternative products and strategies:

The recognized hazards associated with cationic PAM gels, as well as those associated with residual acrylamide, have spurred many researchers to develop alternatives for agricultural and landscape usage. These alternatives include resins, paper-making by-products, and a number of polysaccharides such as gums, starches, and gels. These alternatives are more environmentally sound, and in many cases are reportedly cheaper to use and functionally superior to polyacrylamide gels.

The best news for those of us managing a home garden or landscape is that simple changes in management practices are often superior to using polyacrylamide hydrogels. In several cases, alternative water management strategies had higher success rates than usage of PAM. These strategies were as simple as adding 2 liters of water when planting *Pinus patula* seedings, or providing wind protection to reduce water stress in musk melon. More commonly, mulches (especially organic) were rated superior to hydrogels in terms of erosion control, enhancing water infiltration and conservation, plant growth and establishment, and nutrient value.

Summary and recommendations:

Many of the products labeled “water gel crystals” and “poly-clear” are cationic PAM gels. Not only are they are more toxic to aquatic organisms and generally less effective than anionic gels in landscape situations, they can also contain higher levels of residual acrylamide. Even though these cationic gels are banned for many applications, they are still manufactured and sold in the United States, China, and other countries. <u>Cationic PAM hydrogels should not be used in gardens and landscapes.</u>

It is difficult to predict short-term effectiveness of anionic PAM hydrogels on plant survival and establishment, since the ability to absorb water is reduced by several environmental factors, especially salt, temperature extremes, ultraviolet radiation, and microbial activity. The functional lifespan of cross-linked PAM hydrogels used outdoors can be as short as 18 months and at best only a few years; they cannot be regarded as long-term solutions to landscape water needs.

As PAM gels degrade, they give rise to smaller, less functional polymers whose risk to people and ecosystems is unknown; they also produce some level of acrylamide, a known neurotoxin. Lack of documented information on the nature and toxicity of degraded PAM hydrogels makes it impossible to assess human or environmental health effects. People need to be aware of their total exposure to polyacrylamides from all sources, including occupational use, garden products and cosmetics.

There are a number of products and management practices that can reduce unnecessary usage of and exposure to polyacrylamide. In particular, cultural practices that conserve soil moisture are simple, inexpensive, safe, effective, and natural alternatives to PAM hydrogels.

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Sidebar 1: Polyacrylamides up close and very personal

People are exposed to polyacrylamides every day: over 100 formulations are used in cosmetics such as sunscreen, shampoo, soap, lotion, and shaving cream. They are used in such personal products as denture adhesives, contact lenses, diapers, and wound dressings. Now injectable polyacrylamide gels are becoming increasingly popular for use in plastic and reconstructive surgery, especially for facial and breast augmentation. Proponents of this application claim that the gels are non-toxic and stable. More recently, PAM hydrogels have been injected directly into the urethral wall to treat stress incontinence in women. The researchers state that polyacrylamide gel "seems to be a promising new bulking agent" in treating incontinence, despite the fact that 16 of the 17 patients in the study had negative health events (such as urinary tract infection) associated with the treatment.

Alarmingly, there have been dozens of studies reporting of hundreds of patients with complications resulting from polyacrylamide injection, including pain, hematoma, nodule formation, gel migration resulting in tissue asymmetry or deformation, inflammation, and even cancer. The recommended treatment for complications arising from injectable polyacrylamide gels is full removal of the gel and replacement with silicon.

Even the most fervent advocates of PAM gels for tissue augmentation acknowledge the existence of these adverse reactions, though they place blame on human error (i.e. contaminated gel, improper technique, poor hygiene) as the underlying cause. Other researchers blame the gel itself. Several researchers have noted that it may take several months to a few years for complications to arise; thus, the impact of injectable PAM gels must be studied over time. In fact, enough negative evidence now exists that usage of PAM hydrogels in tissue augmentation surgery is forbidden in Russia and Bulgaria, where they had been used since the early 1990's. Regardless of arguments regarding culpability, researchers are increasingly recommending against its use for facial tissue augmentation or tissues that have not been previously operated upon. Still others call for prohibiting its use in plastic surgery and searching for safer alternatives.

Sidebar 2: Hydrogel use for erosion control

Soluble polyacrylamide gels have been used for over a decade in reducing erosion and enhancing water infiltration of fine-textured agricultural soils. Unlike "water crystals" that retain their shape as they absorb water, soluble PAM dissolves in water, forming a thin slimy film that coats the soil surface. In irrigation furrows and other bare soils where irrigation can exacerbate erosion, this film protects the soil from washing away with irrigation flow and hydrates the surface so that irrigation water can more easily permeate.

Many studies have been conducted on a variety of soils in different environments show that agricultural PAMs are a viable (though short-term) solution to soil loss and degradation. Often their effectiveness can be enhanced by the addition of gypsum – a calcium source - especially in saline soils. Anionic soluble PAMs have generally been found to be more effective than cationic formulations in reducing soil erosion, which is fortunate considering the environmental toxicity of cationic gels.

Certain soils and environmental conditions are antagonistic to soluble PAM gel effectiveness. In general, soluble PAM gels do not work well on sandy soils, and can actually reduce infiltration, possibly due to pore blockage by the viscous gel. They may not work well on clay soils. Sodic soils decrease soluble PAM gel effectiveness since sodium prevents ion bridging and prevents soil aggregation. Neither do they perform well on slopes, often increasing runoff, and requiring either higher applications of gel or additional mulching materials to maintain effectiveness.

Usage of soluble PAM is acknowledged to be a short-term solution to erosion; for this reason its usage should not be extended to garden and landscape use. Mulches are demonstrably better in reducing erosion than bare soil and PAM hydrogel and provide other, additional benefits. Moreover, the soluble PAM hydrogels have no documented benefit to plant growth. Like many other agricultural production practices, soluble PAM usage does not translate well to home gardens and landscapes.

Soil scientists R.E. Sojka and R.D. Lentz have provided a concise and informative review of linear PAM applications in agriculture; it can be found at **http://polymersinc.com/polymers/pam2.htm**