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Polyacrylamide degradation and its implications in environmental systems

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High molecular weight (10^6 – 3×10^7 Da) polyacrylamide (PAM) is commonly used as a flocculant in water and wastewater treatment, as a soil conditioner, and as a viscosity modifier and friction reducer in both enhanced oil recovery and high volume hydraulic fracturing. These applications of PAM can result in significant environmental challenges, both in water management and in contamination of local water supplies after accidental spills. This paper provides a short review of current applications of high molecular weight PAM, including the potential for PAM degradation by chemical, mechanical, thermal, photolytic, and biological processes. Methods for treating wastewater containing partially degraded PAM are then discussed along with issues related to the potential toxicity and mobility of PAM in the environment after disposal or accidental release.

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INTRODUCTION

The term “polyacrylamide” is loosely used to describe any polymer with acrylamide present as one of the monomers.¹ More rigorously, its IUPAC nomenclature is poly (prop-2-enamide), which defines it as a water-soluble polymer formed by the polymerization of either acrylamide monomers or *N,N'*-methylenebis(acrylamide).^{2,3} Polyacrylamide with only acrylamide monomers is nonionic; other monomers such as acrylate or 2-acrylamido-2-methylpropane sulfonate (AMPS) can be copolymerized at various percentages to form anionic PAM;^{1,4} dimethyldiallylammonium, ethanaminium (*N,N,N*-trimethyl-2-((1-oxo-2-propenyl)oxy)), and 1,2-dimethyl-5-vinylpyridinium are common co-monomers for cationic PAM.⁵ Table 1 summarizes the structure and name of commonly used PAM and its co-polymers.

The molecular weight (MW) of commercial PAM ranges from 10^5 to $>10^7$ Da. High MW PAM ($>10^6$ Da) has a wider range of applications due to its high viscosity, drag reduction capabilities, and water retention characteristics.^{6–8} PAM is widely used in environmental systems including:

1. as a viscosity enhancer in enhanced oil recovery (EOR) and more recently as a friction reducer in high volume hydraulic fracturing (HVHF)^{1,4,9–15};
2. as a flocculant in water treatment and sludge dewatering^{13,16,17}; and
3. as a soil conditioning agent in agricultural applications^{18–20} and other land management practices.

The applications, properties, specific MWs, and concentration ranges of PAM are summarized in Table 2. The hydrolyzed form of polyacrylamide (HPAM), a co-polymer of acrylamide and acrylic acid, is the most widely used anionic PAM in oil and gas development as well as in soil conditioning.^{1,9,12,21} The most common commercial PAM formulation in the oil and gas industry is a water-in-oil emulsion, where the polymer is dissolved in the

aqueous phase which is encapsulated by a continuous oil phase stabilized by surfactants.¹

High MW PAM is widely applied in unconventional natural gas development as a “friction reducer” to minimize frictional losses during pumping.^{4,22–24} The drag reduction properties of PAM arise from polymer elongation, which dampens the quasi-streamwise vortices that are characteristic of turbulent flow.^{25–27} The drag reduction properties increase with increasing polymer MW due to the more pronounced stretching of the very long polymer chains.^{7,28} Anionic polyacrylamides perform better as drag reducers in a fresh water environment⁹; cationic PAM has shown enhanced performance at high salinity¹ due to the reduced electrostatic repulsion from electrolyte shielding present with anionic species.²⁹ We reviewed and summarized information from 750 fractured wells across six states from content available on FracFocus.org³⁰ (Table S1); 98% of the wells utilized PAM-based friction reducers with the majority of these using anionic forms of the polymer. It is estimated that fracturing jobs consume 0.2–6 tons of PAM per well,³⁰ corresponding to as much as 75,000 tons of PAM per year in the U.S. alone.

High MW anionic PAM is also the most commonly applied polymer in enhanced oil recovery applications; the use of surfactant-polymer flooding can increase oil recovery by 5–30%¹⁴ and in some cases by as much as 80%.³¹ The surfactant solution increases the mobility of trapped oil by lowering surface tension and increasing rock wettability while the polymer improves oil recovery based on the increased viscosity (5–30 cP³²). On average, effective polymer flooding requires 0.7–1.75 tons of polymer per ton of oil extracted¹⁴ at a concentration of 500–3000 mg/L³². Both HVHF and EOR processes produce a large quantity of wastewater containing residual PAM at a concentration that is as much as half of that in the injected fluid.³²

Synthetic polymer conditioners like PAM are more effective options than organic or inorganic conditioners in enhancing soil stability, infiltration rate, and erosion resistance. This requires the

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Table 1. Chemical structures of PAM and acrylamide co-polymers

| Category | Name | Structure |
|---------------|--|---|
| Non-ionic PAM | Polyacrylamide | $\left[\begin{array}{c} \text{H} \quad \text{H}_2 \\ \quad \\ \text{---C---C---} \\ \\ \text{C=O} \\ \\ \text{NH}_2 \end{array} \right]_n$ |
| Anionic PAM | Polyacrylamide-co-acrylic acid, hydrolyzed polyacrylamide | $\left[\begin{array}{c} \text{H} \quad \text{H}_2 \\ \quad \\ \text{---C---C---} \\ \\ \text{C=O} \\ \\ \text{O}^- \end{array} \right]_n \left[\begin{array}{c} \text{H} \quad \text{H}_2 \\ \quad \\ \text{---C---C---} \\ \\ \text{C=O} \\ \\ \text{NH}_2 \end{array} \right]_m$ |
| | Poly-acrylamido-2-methylpropane sulfonate | $\left[\begin{array}{c} \text{H}_2 \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \\ \text{C=O} \\ \\ \text{HN} \\ \\ \text{C} \\ / \quad \backslash \\ \text{H}_2\text{C} \quad \text{CH}_3 \\ \\ \text{SO}_3^- \end{array} \right]_n \left[\begin{array}{c} \text{H}_2 \quad \text{H} \\ \quad \\ \text{---C---C---} \\ \\ \text{C=O} \\ \\ \text{NH}_2 \end{array} \right]_m$ |
| Cationic PAM | Poly(acrylamide-co-diallyldimethylammonium)poly(AM-co-DADMAC) | $\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{---C---C---} \\ / \quad \backslash \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \quad \\ \text{H}_3\text{C} \quad \text{N}^+ \quad \text{CH}_3 \end{array} \right]_n \left[\begin{array}{c} \text{H} \quad \text{H}_2 \\ \quad \\ \text{---C---C---} \\ \\ \text{C=O} \\ \\ \text{H}_2\text{N} \end{array} \right]_m$ |
| | Poly(acrylamide-co- <i>N,N,N</i> -trimethyl-2-((1-oxo-2-propenyl)oxy)) | $\left[\begin{array}{c} \text{H} \quad \text{H}_2 \\ \quad \\ \text{---C---C---} \\ \\ \text{C=O} \\ \\ \text{O} \\ \\ \text{H}_2\text{C} \\ \\ \text{CH}_2 \\ \\ \text{N}^+ \\ / \quad \backslash \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array} \right]_n \left[\begin{array}{c} \text{H} \quad \text{H}_2 \\ \quad \\ \text{---C---C---} \\ \\ \text{C=O} \\ \\ \text{H}_2\text{N} \end{array} \right]_m$ |

application of 1–20 kg of polymer per hectare (ha),^{33,34} with typical MW of 1–20 × 10⁶ Da^{21,33,35} and concentrations less than 10 mg/L;³³ the high cost of PAM is a significant limitation to more widespread use. PAM is currently used as a soil conditioner on ~800,000 ha³³ of irrigation land in the U.S., corresponding to

900–18,000 tons of PAM per year. PAM binds with soil particles through electrostatic interactions forming aggregates that prevent irrigation-induced erosion and increase the hydraulic conductivity of the soil. Cationic PAM easily adsorbs onto negatively charged clays, while anionic PAM can bridge between clay surfaces via

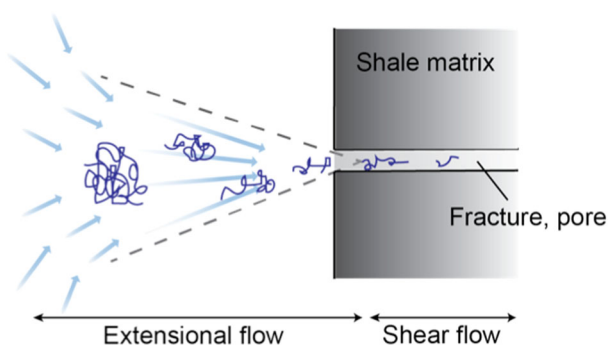


Fig. 1 Mechanical degradation of PAM under extensional flow field through narrow pores and fractures in shale formation

multivalent cations.³⁶ Adsorption is enhanced by ion-dipole interactions between the polymer C=O groups and clay exchangeable cations and by hydrogen bonding interactions.²¹ Anionic PAM is most commonly used in soil conditioning due to its low mobility in soil and the lower level of residual acrylamide monomer (<0.05%).^{21,35}

PAM is also widely used as a flocculant in drinking water treatment (at concentrations <1 mg/L).³⁷ PAM can create bridges between destabilized particles, forming micron-size aggregates with good settling properties.³⁸ Cationic, nonionic, and anionic PAM have all been studied for flocculation. The flocculation and adsorption capacity increase with increasing MW due to the greater number of binding sites.¹³ However, polymer molecules with a MW greater than around 18×10^6 Da are more likely to entangle, reducing interactions with small particles.²⁰ High salinity and low pH suppress electrostatic interactions, while increasing temperature (from 20 to 60 °C) enhances the adsorption of anionic PAM to clays due to the reduction in hydrogen bonds between PAM and water¹⁷ and the increased penetration of PAM into the internal clay structure.¹⁶

Although the PAM used in environmental systems has a very high MW, it is well known that PAM can undergo degradation by a variety of mechanisms, significantly increasing its mobility and potentially leading to the release of acrylamide monomer, a known toxin and potential carcinogen. This review examines the chemical, mechanical, thermal, photolytic, and biological degradation of PAM under a broad range of environmental conditions. We then consider available options for treating water/wastewater containing PAM, including biodegradation, oxidation, coagulation, and membrane filtration. We also examine the potential for acrylamide release into the environment.

POLYACRYLAMIDE DEGRADATION

The presence of degraded polyacrylamide could lead to a significant increase in mobility of the molecule in the environment due to the more hydrophilic nature of polyacrylamide with increased content of carboxylic groups after hydrolysis and degradation under various environmental conditions.^{33,39–42} This creates potential challenges for water supplies and wastewater treatment. The general mechanisms of PAM degradation have been reviewed by Caulfield et al.⁴³ and are summarized briefly in the following sections.

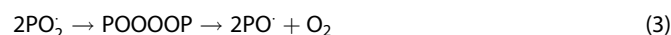
Degradation mechanisms

Mechanical degradation is mostly likely to occur in oil and gas processing due to the high shear and elongational rates under turbulent flow through the small pores and fractures within the porous media in these formations as shown schematically in Fig. 1^{44–52}. Chain rupture typically occurs at the entrance to narrow pores in the sandstone face where the elongational stress is

greatest,^{45,53,54} with the polymer chain mostly breaking near the mid-point.^{55,56} The pure shear flow through pores or fractures generally causes limited chain scission.⁵⁷ Model experiments showed that polymer degradation in a pure shear flow required more than a 100-fold greater shear rate for equivalent degradation than was observed for flow through a screen mesh where both elongational and shear flows are present.⁴⁵ Thus, limited mechanical degradation is expected during pumping of PAM through chokes, valves, and fractures where flow rates are low; degradation should be higher during flow through near-wellbore areas and perforations where velocities are much higher.^{58–60} Mechanical degradation of PAM is enhanced at high salinity due to changes in polymer rigidity as a result of polymer complexation with ions.⁶¹

Chemical degradation of PAM that leads to chain scission involves activation of the polymer by free radicals,^{42,62–66} most commonly hydroxyl radicals generated in the environment from the Fenton reaction,^{62,65} interactions between oxygen and dissolved Fe^{2+} ,^{41,42,62,67} or other transition metals, and sulfate radicals through persulfate activation.⁶⁶ Hydroxyl radicals can also be generated from ozone and UV treatment, which will be discussed in the section on photolytic degradation. Free radical induced chain scission has been shown to reduce the MW of PAM from 10^7 to 10^5 Da within 24 h upon exposure to iron-bearing shale (1.5 mg/L Fe^{2+}) at 80 °C.⁴² Incubation of 0.6% PAM with 30 mM potassium persulfate at 50 °C caused a 90% reduction in viscosity in 2 h.⁶⁸ In these studies, free radical chain scission reactions were also found to have a much higher rate under higher temperature conditions. Thermal degradation of polyacrylamide (in the absence of free radicals) does not cause substantial chain scission except at very high temperatures, on the order of 300 °C. Thermal decomposition is a result of inter- or intramolecular imidization of the amide groups, releasing ammonia and forming nitrile groups; as well as the breakage of imide/amide groups and backbone chain scission, generating both nitrogen and carbon dioxide.^{12,69–71} Thermal degradation is unlikely to occur in environmental applications, although temperature does play an important role in determining the rate of chemical and photolytic degradation.

As shown in Equation 1, free radicals attack the polymer backbone via hydrogen abstraction at both the secondary and tertiary carbons, as well as the primary amine, generating polymer radicals (P^\cdot) as shown in Fig. 2. These polymer radicals react with dissolved oxygen to form polymer peroxy radicals (PO_2^\cdot) at diffusion-controlled rates. Chain scission occurs by a bimolecular reaction between two polymer peroxy radicals, which then decompose to form polymer fragments (F_1^\cdot and F_2^\cdot in Equations 3 and 4).⁶⁴



Many previous studies have demonstrated the importance of dissolved oxygen and Fe^{2+} in the chemical degradation of PAM

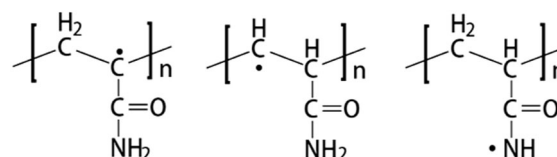


Fig. 2 Three possible forms of polymer radicals of polyacrylamide (adapted from ref.,⁶⁴ copyright 1982, with permission from Elsevier)

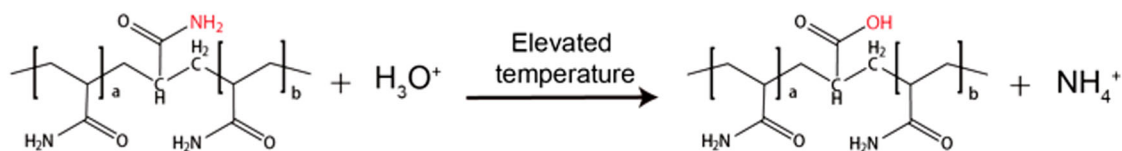
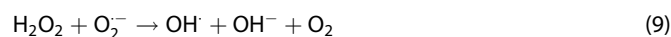


Fig. 3 Hydrolysis of PAM generating a carboxylic acid group and an ammonium ion under acidic conditions

under environmental conditions.^{40–42,62,64,67,72,73} In the absence of dissolved oxygen, polymer viscosity is stable at room temperature,⁶⁷ and may increase slightly due to crosslinking reactions.⁶⁴ Fe²⁺ can generate hydroxyl radicals by autoxidation under acidic conditions with hydrogen peroxide as an intermediate product.⁷⁴ Fe²⁺ can be released by oxidative dissolution of pyrite minerals or other iron-bearing clays, which simultaneously acidifies the fluid; this drop in pH is minimized in the presence of alkaline minerals such as calcite (typical in the Eagle Ford and Antrim shale plays).⁷⁵ Although deep subsurface conditions in EOR or HVHF are anoxic, the injected fluids will carry significant concentrations of oxygen into the formation. This oxygen can cause PAM degradation, although it can also react with pyrite and various hydrocarbons.^{67,76} Oxygen scavengers have been added to EOR fluids to improve fluid stability;^{41,67} this has not been discussed in HVHF applications. In addition, some EOR and HVHF operations utilize persulfate breaker to maximize the fluid return, which will cause accelerated chemical degradation of PAM through the formation of sulfate radicals.⁶⁶

In addition to chain scission, hydrolysis of the amide group leads to the generation of a carboxylic acid group and an ammonium ion (at low pH, see Fig. 3), or the conversion of the acrylamido-2-methylpropane sulfonic acid group (AMPS, Table 1) to a carboxylic acid and an ammonia-2-methyl propanesulfonic acid.⁷⁷ Hydrolysis of nonionic PAM in 0.3% NaCl initially causes an increase in viscosity due to the increase in negative charge, with a reduction in viscosity often seen at very high degrees of hydrolysis.⁷⁸ The rate of viscosity decrease during a 24 h incubation in 1 wt% HCl is greatest for PAM, followed by the AMPS co-polymer and then polyDADMAC.²⁹ The highly hydrolyzed PAM (>30% degree of hydrolysis) is prone to precipitation as a result of complexation with divalent cations^{39,78,79} or cross-linking with ferric iron.⁶⁷

Photolytic degradation of PAM in the presence of oxygen is similar to chemical degradation: light exposure generates free radicals (such as hydroxyl radicals) that yield carbon-centered polymer radicals leading to chain scission.^{43,80,81} Equations 5–9 illustrate the pathways of hydroxyl radical generation by photo-activation of catalyst such as TiO₂,^{81,82} the hydroxyl radicals generated then cause polymer chain scission based on Equations 1–4.



PAM is exposed to sunlight during soil conditioning, while UV is often used in disinfection of treated water. Model studies show significant photolytic degradation of PAM under illumination by a 125 W lamp with a photon flux of 5.4 μmol/s, reducing the MW from 1.6 × 10⁵ to 7 × 10⁴ Da; no degradation was observed using an 80 W lamp with photon flux of 3.5 μmol/s (365 nm) after 3 h. The presence of TiO₂ nanoparticles caused a further reduction in MW to 3 × 10⁴ Da.⁸¹ Photocatalytic degradation is also enhanced

in the presence of Fe³⁺ at low pH.^{83,84} The MW of PAM (15 mg/L concentration) was reduced from 2.4 × 10⁶ to 1.2 × 10⁶ Da during 3 h exposure to simulated sunlight (2 W/m² at 300 nm) in the presence of 2 mg/L ferric ion.⁸⁵

Biodegradation of PAM occurs as microorganisms utilize the amide group of the polymer as a nitrogen source and/or the carbon backbone as a carbon source.^{19,86} The amide group can be hydrolyzed by extracellular amidases, similar to the chemical hydrolysis discussed previously. For example, aliphatic amidase (cd07565) from *Pseudomonas putida* is expressed upon incubation in the presence of PAM, leading to 46% degradation of 1000 mg/L PAM after 7 days at 39 °C.⁸⁷ *Enterobacter aerogenes*, *Rhodococcus sp.*, *Helicobacter pylori*, *Bacillus sp.*, *Acinetobacter sp.*, *Azomonas sp.*, *Pseudomonas sp.*, *Chlostridium sp.*, and others also express PAM-induced amidases.^{19,43,88–90} It is much harder for microorganisms to utilize the carbon backbone of PAM as a sole carbon source due to the lack of appropriate enzymes.⁹¹ Wen et al.¹⁷ have reported that the *Bacillus* genus can grow on PAM, although the mechanism of backbone chain scission is unclear. Table S2 provides a summary of various bacterial species that are naturally occurring in sludge, soil, and wastewater that are known to degrade PAM. To the best of our knowledge, there have been no reports of detectable residual acrylamide release in aerobic culture media.^{91–93}

PAM used as a flocculant in water treatment or sludge dewatering is disposed in high-solid biogas digestors or landfills.⁹⁴ Although PAM is typically considered to be relatively recalcitrant to organic decomposition,⁹⁵ it can be degraded during anaerobic digestion. For example, anaerobes have been shown to hydrolyze PAM complexed with tyrosine-rich proteins.⁹⁶ A recent study found that cationic PAM can be converted to methane via methanogenesis, and it can be depolymerized generating acrylamide and acrylic acid. Acrylamide concentrations as high as 15 mg/L were identified in a 22-day digestion of sludge containing 12 g/kg total suspended solids (equivalent to 240 mg/L PAM).⁹⁷ Kinetic models of PAM biodegradation under both aerobic and anaerobic conditions have been developed and used to maximize the rate of PAM removal using biological degradation.⁹⁸

Degradation by-products from PAM have not been extensively studied. The mobility of PAM increases as the MW decreases; thus, small chain fragments are likely to be much more mobile than the high MW PAM used in fracking, enhanced oil recovery, and environmental applications.³³ In addition, hydrolyzed PAM will be more hydrophilic due to the presence of large numbers of carboxylic acid groups.

Acrylamide concentrations in commercial PAM products are typically less than 100–500 parts acrylamide per million repeat units (w/w) as regulated by the Food and Drug Administration (FDA), the U.S. Environmental Protection Agency (EPA), and the National Resources Conservation Services (NRCS).^{85,99–102} During flocculation, conformational changes in the polymer chain can release acrylamide that is initially entrapped within the chain.^{13,38,100} Therefore, PAM used as a flocculant in drinking water treatment is maintained at a concentration <1 mg/L, ensuring that the concentration of acrylamide monomer in the treated water is less than 0.5 ppb (w/v). The European Commission (EC) has a stricter limit of 0.1 ppb (w/v) acrylamide.¹⁰³ The toxicity and environmental fate of acrylamide is discussed in the Outlook section.

Chain scission of PAM by hydroxyl radicals could lead to the release of acrylamide monomer. Woodrow et al.⁸⁵ detected 3.5 ppb acrylamide (0.038% of the monomer units in the initial polymer) after 3 h exposure to simulated sunlight in the presence of 4.5 mg/L ferric ion. It was found that PAM solvated with Fe³⁺ generated ppb levels of acrylamide after exposure to sunlight under acidic conditions (pH 6). They concluded that release of acrylamide would be insignificant at low levels of iron (<0.02 mg/L) under alkaline (7.5–8.5) conditions. Other groups have found that acrylamide can be released from soil conditioners (70 parts per million repeat units) after exposure to natural sunlight over a 2–5 week long period.^{104,105} However, there are still many unresolved questions regarding the release of acrylamide after exposure to UV, with conflicting results reported in the published literature.^{68,85,93,105,106}

TREATMENT OF POLYACRYLAMIDE CONTAINING WASTEWATER

PAM, including degraded PAM molecules, can be present in wastewater generated from oil and gas operations, in runoff from agricultural lands, and in surface waters contaminated by accidental spills or wastewater leakage. While there are no treatment strategies that have been specifically developed for treating PAM/PAM residues, many of the existing water treatment processes should be effective for the removal and/or degradation of PAM.

Coagulation/flocculation utilizes aluminum or iron salts, often in combination with high MW polymers like PAM, to remove organic matter and suspended solids via charge neutralization, adsorption, complexation with metal ions, and sweeping.^{107,108} This process has also been applied for the treatment of oily wastewaters, sometimes in combination with membrane filtration.^{109–113} Zhang et al.⁹⁸ have shown that aluminum sulfate is able to remove 90% PAM from high salinity oilfield water at pH 5 with a dosage of 80 mg/L. During this process, PAM is removed in flocs and/or sludge, suggesting that coagulation/flocculation can also remove high MW PAM from produced and flowback water. Coagulation is likely to be less effective in removing lower MW degraded PAM, although this has not been studied in any detail. Additional studies are also needed to understand the effects of various produced water constituents on the removal of PAM and degraded PAM by coagulation.

Oxidation of PAM by peroxide, persulfate, ozone, hypochlorite, and permanganate all target the carbon backbone leading to chain scission.^{65,114–116} The resulting polymer fragments are likely to contain ketone, aldehyde, carboxylate, and carbonyl groups.¹¹⁷ Persulfate is the most commonly used oxidant in oilfield operations, reducing the viscosity and improving oil recovery.^{68,118} Persulfate can effectively degrade PAM at 82 °C after only 1 h at concentrations as low as 5 ppt,⁶⁶ leading to more than a 50% reduction in viscosity. High temperatures and persulfate concentrations both increase the rate of polymer degradation by increasing the concentration of sulfate radicals.

Fenton reactions are widely used in advanced oxidation processes to decompose hydrocarbons,⁶⁵ natural organic matter,¹¹⁹ and emerging contaminants.¹²⁰ In the Fenton reaction, hydroxyl radicals (*OH*) are generated via reaction between ferrous iron and hydrogen peroxide.^{62–64,121} The hydroxyl radicals generated via the Fenton reaction can degrade more than 90% of PAM with initial MW of 5.2×10^6 Da at a concentration of 5000 mg/L.⁶² Ramsden and McKay observed a 54% reduction of the initial MW after 1 h incubation of PAM with 1 mg/L of Fe²⁺ and H₂O₂; increasing the Fe²⁺ concentration to 50 mg/L caused a 93% reduction in MW.⁶² Studies of PAM degradation by the Fenton reaction alone did not detect any acrylamide monomer,⁶² although there is evidence for acrylamide release from combined UV/Fenton reactions.⁶⁵

Ozone is widely used as a disinfectant in water treatment.¹²² The ozone molecule is extremely unstable in the presence of UV, releasing oxygen and forming hydrogen peroxide after reaction with water.¹²³ Ozone degrades PAM via free radical induced chain scission as described previously.¹²³ Ozonation at a concentration of 3.0 mg/L (w/v) leads to an 80% reduction in the MW of PAM within 15 min at pH 3. Suzuki et al.¹¹⁷ also demonstrated that acrylamide monomer could be almost completely degraded after 30 min of exposure to ozone at pH 6.

Chlorine is the most widely used disinfectant in drinking water treatment. Chlorination was found to reduce the MW of nonionic PAM by 19% after 10 min at a chlorine concentration of 20 mg/L.¹¹⁴ In contrast, anionic PAM was largely unaffected by chlorine.¹¹⁶ Gas chromatography (GC) coupled with an electron capture detector (ECD) has shown that chlorination does not cause the release of acrylamide. The double bond in the acrylamide monomer present in the original polymer solution can react with chlorine to form -ClC-CO-^{114,116,124} and possibly chloroform, which is a health concern at concentrations >50 mg/L.¹²⁵ Solution pH dictates the speciation of chlorine with the highest removal of acrylamide observed at pH 6 and 10 when hypochlorous acid (HOCl) and hypochlorite (OCl⁻) are the dominant species, respectively.¹²⁶

Biological treatment in the form of membrane bioreactors,^{127,128} biologically active filtration,¹²⁹ or conventional activated sludge^{19,130} can effectively remove more than 90% of the organic matter in wastewater. However, relatively little is known about the effectiveness of these processes at removing PAM. Bao et al.¹²⁷ found that a membrane bioreactor removed no more than 40% of PAM after 7 days.¹²⁷ Previous studies suggest that *Bacillus flexus* can remove more than 75% of a 10⁷ Da PAM at 60 mg/L after incubation for 96 h,¹⁹ although only 20% removal was achieved in the first 24 h. Additional work will be needed to optimize the design of biological systems for the effective degradation of PAM.

Membrane processes such as microfiltration (MF) and ultrafiltration (UF) are commonly used in oilfield wastewater treatment to remove suspended solids, oilfield chemicals, and residual oil.¹³¹ Nanofiltration (NF), reverse osmosis (RO),¹³² forward osmosis (FO),¹³³ and membrane distillation (MD)¹³⁴ have all been examined for the removal of monovalent and divalent salts.¹³⁵ Membrane processes coupled with coagulation, acid hydrolysis, and biological processes have been shown to remove up to 95% of the residual PAM from oily wastewater.¹¹⁰ UF membranes can potentially remove lower MW PAM from HVHF wastewaters, while even smaller PAM fragments (<10³ Da) can be removed by NF and RO. Acrylamide monomer (71 Da) is likely to be only partially removed by RO, although high rates of removal should be possible using activated carbon and advanced oxidation.

The biggest challenge in applying membrane processes to produced waters generated from oil and gas processing is membrane fouling caused by the high concentrations and wide range of constituents present in these wastewaters.^{109,136,137} HPAM was found to be the dominant membrane foulant in EOR wastewater, responsible for 80% of the fouling followed by oil and suspended solids.¹³⁸ PAM rejection and fouling is typically increased at high salinity due to compaction of PAM on the membrane surface.^{139,140} High pH leads to the formation of molecular complexes and a corresponding increase in fouling.^{141,142} High polymer concentrations can be particularly problematic due to the formation of entanglements and micelles (at PAM concentrations above the critical micelle concentration or CMC).¹³⁹ Furthermore, residual PAM in EOR wastewater¹¹⁰ was found to stabilize oil–water emulsions, leading to increased fouling.^{143,144} Pretreatment strategies that remove PAM are likely to mitigate the degree of fouling during subsequent membrane processes. Future work is needed to identify optimal cleaning strategies for membranes fouled by PAM.

OUTLOOK

High MW PAM and its co-polymers are used extensively in oil and gas processing, water treatment, and agricultural applications. Oil and gas processes utilize PAM at much higher concentrations (500–3000 mg/L) than in water treatment and soil management (<10 mg/L). In addition, the former applications also impose a much higher mechanical stress and much harsher chemical/thermal conditions, both of which can lead to significant chemical and mechanical degradation of the PAM. In contrast, the very long time exposure of PAM in agricultural (and landfill) applications increases the likelihood and degree of both photolytic and biological degradation.

Although much is known about the factors controlling the rate and extent of PAM degradation, there are still significant unanswered questions, particularly in emerging applications like high volume hydraulic fracturing (HVHF). A significant level of mechanical degradation of PAM is inevitable in HVHF applications due to the high flow rates, pressures, and elongational stresses during fracturing operations. However, the magnitude of the shear and elongational stresses in different shale plays and under different fracturing conditions needs to be quantified, e.g., through the use of core-flooding tests on different shale samples. Several methods have been proposed for enhancing fluid stability by reducing PAM degradation in EOR applications, such as the utilization of oxygen scavengers and reducing agents, replacement of alloys in surface facilities to reduce iron dissolution, and selection/design of proper chokes and pumps;³² additional work will be required to determine how to most effectively apply these approaches in HVHF operations.

Degraded PAM can be discharged to the environment directly from agricultural runoff and in the discharge from water treatment facilities, both of which will be at very low concentrations (< ppm). In contrast, wastewaters generated from oilfields and fracturing sites contain a high concentration of PAM residues (10–1000 mg/L) that can be released via accidental spill and leakage. However, relatively little information is currently available regarding the detailed chemical characteristics of the degraded products produced by mechanical, chemical, and photolytic degradation of PAM. Analytical methods such as gel permeation chromatography (GPC) and viscosity measurements are most widely employed to quantify PAM degradation. Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance (NMR) have been used to identify specific functional groups; ketone, aldehyde, and carboxylic groups have all been reported in chemically, photolytically, and thermally degraded PAM. To the best of our knowledge, mechanically degraded PAM has not been chemically analyzed. Future studies using liquid/GC coupled with mass spectrometry could provide a more comprehensive analysis of the products present in degraded PAM under a variety of conditions. Moreover, the toxicity, transport, fate, and removal efficiency of degraded PAM needs to be re-examined in light of existing information on both PAM and the acrylamide monomer. The mobility of PAM in natural environments is limited due to its high MW and adsorption onto mineral surfaces. PAM is highly retained in porous media, such as soil, and it easily settles in water-beds.^{100,145} PAM is also too large to penetrate biological cell membranes.¹⁴⁶ However, smaller PAM with different functional groups could behave very differently.

Although PAM is relatively nontoxic to humans, animals, fish, or plants,^{6,33,65,147} the acrylamide monomer can be adsorbed via dermal exposure and inhalation, and it is a known neurotoxin and a potential carcinogen¹⁴⁸; it is immediately dangerous at concentrations of 0.06 mg/L and is lethal (LD50) at 150–200 mg/kg body weight.^{149–151} A 13-week exposure to acrylamide in drinking water at a concentration above 1 mg/kg/day leads to peripheral nerve alterations as observed under electron microscopy. Acrylamide at a dose of 20 mg/kg/day stimulated the

degeneration of peripheral nerves and the spinal cord of rats, although no obvious effects were found at doses less than 0.2 mg/kg/day.¹⁵² Acrylamide is highly soluble in water ($\log K_{ow} = -0.67$)¹⁵³ and is therefore highly mobile in the environment. Several studies support the hypothesis that naturally occurring microbes in soils, sediments, and water systems can degrade acrylamide to the nontoxic products ammonia and acrylic acid over periods of days to months.^{92,93,104,145,154,155} For example, Shanker et al.⁹² observed the complete disappearance of 500 mg/L of acrylamide (w/w of soil) within 5 days under aerobic conditions at 30 °C. In aquatic systems, complete degradation of acrylamide likely occurs within 2 weeks.^{92,156,157} However, in tap water, acrylamide can persist for more than 2 months.¹⁵⁸ Even if acrylamide is readily biodegradable in the environment, careful monitoring should be implemented to ensure that there are no dangerous releases of acrylamide from various applications.

The complexity of the produced and flowback waters generated in oil and gas processing creates major challenges for wastewater treatment; current industry practice makes extensive use of permanent storage in tanks or injection wells at a cost of ~0.03 \$/L.¹⁵⁹ The substantial demand for water to fracture wells has also led to the reuse of flowback water in subsequent fracking operations. Residual PAM has not been identified as a significant challenge for reuse, although the degraded polymer could lead to plugging of small fractures and formation pores which would reduce gas and oil permeability.^{160–162} A variety of treatment technologies are potentially available for removal/degradation of PAM, although the performance of these systems has yet to be evaluated, particularly for PAM fragments. Previous studies have shown high rates of PAM degradation by oxidation.^{65,163} Dai et al. showed that a hybrid treatment process combining hydrolysis-coagulation with a membrane bioreactor could reduce PAM concentrations by more than 95%.⁹⁶ It may also be possible to use chemical oxidation, such as the Fenton reaction, combined with coagulation. Membrane processes such as RO can provide treated water with a low TDS and TOC, although pretreatment costs, including those associated with the removal of PAM, are likely to be high. Detailed cost analyses will need to be performed to determine the most effective strategies for water treatment in these diverse applications, taking into account the nature of the feed and the concentration/properties of the degraded polyacrylamide.

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AUTHOR CONTRIBUTIONS

B.X., R.D.L., D.S., R.H., and T.P. performed the literature survey and prepared an initial draft of the manuscript. A.L.Z. and M.K. supervised the work and provided extensive contributions to the preparation of the final version of the manuscript.

ADDITIONAL INFORMATION

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