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Chemical and photolytic degradation of polyacrylamides used in potable water treatment

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Chemical and Photolytic Degradation of Polyacrylamides

Used in Potable Water Treatment

by

Peiyao Cheng

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
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LIST OF ABBREVIATIONS

Adam MeCl  Ethanaminium  
N,N,N-trimethyl-2-(1-oxo-2-propenyl)oxy, chloride  
AWWA  American Water Works Association  
ACM  Acrylamide  
CD  Charge Density  
CV  Crystal Violet  
DADMAC  Diallyl dimethyl ammonium chloride  
DBP  Disinfection by-products  
EAD  Electron Capture Detector  
EPA  Environmental Protection Agency  
Epi-DMA  Epichlorohydrin-dimethylamine  
GC  Gas Chromatography  
GH  Glyphosate-surfactant herbicide  
LD<sub>50</sub>  Lethal dose for half population studied  
MS  Mass Spectrometer  
M.W.  Molecular Weight  
MSDS  Material Safety Data Sheet  
NDMA  N-nitrosodimethylamine  
NOM  Natural Organic Matter  
PAM  Polyacrylamide  
PATA  Polyacrylamide thickening agent  
Py-GC  Pyrolysis Gas Chromatography  
Py-GC-MS  Pyrolysis-Gas Chromatography-Mass Spectrometry  
SEC  Size Exclusion Chromatography  
TOC  Total Organic Carbon  
UV  Ultra-violet  
WHO  World Health Organization
CHEMICAL AND PHOTO-DEGRADATION OF POLYACRYLAMIDES USED IN POTABLE WATER TREATMENT

PEIYAO CHENG

ABSTRACT

Polyacrylamides (PAMs) are a class of polymers formed from acrylamide alone or copolymerized with other monomers. PAMs have been used in drinking water treatment as flocculants or coagulants in the highest volume among all the polymer types. In potable water treatment processes, polyacrylamides are often exposed to oxidants (e.g. chlorine and permanganate) and UV irradiation from sunlight or artificial sources. The purpose of this study is to evaluate the possible degradation of PAMs caused by chemical oxidation and/or UV irradiation.

Three types of PAM products (nonionic, cationic and anionic) were studied under free chlorine and permanganate oxidation, UV irradiation, and their combined effects. It has been found that the cationic PAM was the most unstable polymer among the three types of polymer sample studies, however, only partial degradation was observed. Acrylamide residual in the cationic PAM C-3280 was higher than the U.S. guideline value, and exposure to either chlorine or permanganate resulted in decline of acrylamide level to some extent. UV irradiation did not cause reduction of total polymer
contents and acrylamide residuals, but did accelerate chemically induced degradation.

Exposure to chlorine or permanganate for one hour resulted in about 20-35% loss in flocculation performance for each polymer sample. Short time exposure (5 minutes) did not result in loss of flocculation performance for the nonionic and anionic PAMs. However, for the cationic PAM, even short time exposure to chlorine led to loss of flocculation performance of 25-35 %, which indicated that the cationic PAM was more susceptible to oxidation.
INTRODUCTION

Organic polymers have been used in drinking water treatment for more than 40 years. In 1967, the first completely synthetic organic polymer was accepted by the US Public Health Service for drinking water treatment (AWWA, 2001). After 15 years, it was estimated that more than half of the water treatment plants in the United States used one or more polymers to improve treatment efficiency (AWWA Coagulation and Filtration Committee, 1982). Although there are thousands of polymer products accepted by the EPA, it is believed that the number of compounds associated with those products is less than 20, among which polyacrylamide products are used in the greatest volume (Hanson et al., 1983; Mangravite, 1983).

Polyacrylamides (PAMs) are a family of polymers and copolymers which differ in product form, charge type, charge density, molecular weight, and other properties. They are generally prepared by polymerizing acrylamide (ACM) alone to form a nonionic polymer, with acrylic acid or acrylic acid salts to form an anionic polymer, or with a cationic monomer (e.g. DADMAC) to form a cationic polymer. Anionic PAMs can also be prepared by alkaline hydrolysis of nonionic PAM. The structures of PAM and some of its copolymers are shown in Figure 1.1 (adapted from Bolto, 1995).
PAMs have been used in a variety of applications, such as drinking water and wastewater coagulation/flocculation, soil conditioning, agriculture, oil recovery, and biomedical applications. This thesis focuses on their application in drinking water treatment.

In drinking water treatment, PAMs are usually added during coagulation or flocculation to destabilize particles and natural organic matter (NOM), and facilitate removal by sedimentation or filtration. Cationic PAMs are frequently used as primary coagulants to enhance the coagulation and deposition (or filtration) of negatively charged particles in natural water via
adsoption and surface charge neutralization (Letterman and Pero, 1990). Nonionic and anionic PAMs usually have higher molecular weight (or longer chains) than cationic PAMs. They are often added after coagulation to help bind the positively charged particles to form larger agglomerates through a mechanism called polymer bridging.

In potable water treatment, along with organic polyelectrolytes, a variety of chemicals are also used, including oxidants (i.e. chlorine, ozone, permanganate, and chlorine dioxide), lime, inorganic coagulants, fluoride, and corrosion inhibitors. In treatment of surface water, oxidants are often added before coagulation (called pre-oxidation) to treat reduced minerals and compounds associated with taste and odor (Levine et al., 2004). There is a concern that those residual oxidants might react with organic polyelectrolytes added for coagulation/flocculation, and that those reactions may adversely impact the performance of polymers, and produce precursors of disinfection by-products (DBPs) (Levine et al., 2004). In most circumstances, oxidants are added after water clarification for disinfection. An oxidant residual is usually maintained in finished water to control bacterial growth in distribution systems. If residual polymers exist, it is possible that reactions may occur with residual oxidants in water distribution system and possibly produce some toxic substances (i.e. acrylamide monomer) or disinfection byproducts.
This study was designed to provide an assessment of the changes of polyacrylamides and acrylamide monomers during water treatment, and the results from this study can provide scientific data that might be helpful in assessing the effectiveness of current policy related to the use of polyacrylamides.

The specific objectives of this study are:

1) Evaluate the chemical degradation of polyacrylamides caused by chlorine and permanganate, based on the reduction of oxidant residuals and possible changes of polyacrylamides (total organic carbon and UV spectra/absorbance) and their impurities (acrylamide residuals and inorganic nitrogen residuals);

2) Examine the photodegradation of polyacrylamides by exposure to artificial sunlight with UV spectrum, based on changes of total organic carbon, UV absorbance and acrylamide residuals, and also evaluate the impact of UV on the chlorine/permanganate oxidation of PAMs;

3) Assess the impact of oxidants (chlorine and permanganate) on the flocculation performance of polyacrylamides, based on the settling rates of kaolin slurry; and

4) Provide suggestions on selection and usage of polymers in potable water treatment.
BACKGROUND

This chapter reviews the characteristics of acrylamide and its polymers. The chapter presents a summary highlighting prior studies on photolytically and chemically induced polymer degradation, performance changes associated with polymer degradation, and chemical analysis of polyacrylamides (PAMs) and acrylamide (ACM) monomers. The last section reviews current regulations on PAM products.

1. Acrylamide and Polyacrylamides

Acrylamide is the main monomer of polyacrylamides. However, acrylamide and polyacrylamides have quite different properties. This section introduces the physical, chemical and biological characteristics of acrylamide and polyacrylamides, which are very important for understanding the degradation of polyacrylamides and their monomers.

1.1 Acrylamide

Acrylamide is a white odorless crystalline solid that is highly soluble in water and other polar solvents, such as acetone and acetonitrile. It contains two primary functional groups, an amide group and the vinyllic carbon-carbon double bond (Figure 2.1) (Caufield et al., 2002). Because of the electron deficient double bond, acrylamide is susceptible to a wide range
of reactions, such as nucleophilic additions, Diels-Alder, and radical reactions (MacWilliams, 1973).

\[ \text{CH}_2\text{CH} \]
\[ \hspace{1cm} \text{C}=\text{O} \]
\[ \hspace{1cm} \text{NH}_2 \]

**Figure 2.1 Structure of acrylamide (adapted from Caufield et al., 2002)**

Acrylamide can be acutely toxic. It is readily absorbed by ingestion and inhalation, and through the skin, and then, is widely distributed in body fluids (WHO, 1996). The oral LD\textsubscript{50} (lethal dose for half of the population) is 100-170 mg/kg body weight for mice and 120-250 mg/kg body weight for rats (Letterman and Pero, 1990). The dermal LD\textsubscript{50} in rats is 400 mg/kg body weight (WHO, 1996). Acrylamide is also a cumulative neurotoxin, which can result in nerve damage from chronic oral exposure in humans and animals, with effects such as numbness and weakness in hands and legs (U.S. EPA, 1999). Cancer risk has also been documented in human populations and also in studies conducted on rats. Thus, the U.S. Environmental Protection Agency (EPA) classified acrylamide as a B2, a probable human carcinogen (U.S. EPA, 1984 and 1993).

1.2 Polyacrylamides

Polyacrylamides are prepared through free radical polymerization of acrylamide using a variety of initiation systems (i.e. peroxides, persulfates, redox couples, and photochemical) in aqueous solution or dispersions.
(Caulfield et al., 2002). The physical properties of each polyacrylamide product are usually different. For example, the form of PAMs can be solid, emulsion, or solution, with molecular weight ranges from thousands to over million Dalton. Polyacrylamide is considered to be relatively nontoxic to humans, animals, fish, or plants (Seybold, 1994; WHO, 1985). The oral LD$_{50}$ is greater than 5000 mg/kg body weight for rats, and greater than 100 mg/kg for fishes (Material Safety Data Sheet in Appendix E).

While the acrylamide reaction is due to its electron deficient double bond, polyacrylamides are considered to be relatively inert due to the absence of a double bond which is removed by the polymerization process (MacWilliams, 1973). However, polyacrylamides are susceptible to a variety of degradation processes, depending on the nature of polymer, impurities present, and the conditions to which they are exposed. For example, the amide group in polyacrylamides can undergo hydrolysis and dehydration (Caulfield et al., 2002). Generally, degradation reactions are irreversible and alter the physical and chemical properties of the polymer. The degradation byproducts are also a concern because they may contribute to toxicity by releasing acrylamide monomers or forming disinfection byproducts (e.g. trihalomethanes) from chlorination.

2. Degradation of Polyacrylamides

There are five major degradation pathways for polyacrylamides: thermal, photolytic, biological, chemical, and mechanical degradation. The
mechanisms of these degradation pathways have been reviewed by Caulfield et al. (2002) and are summarized in Table 2.1. Chemical and photo- induced degradation are the focus of this thesis and are discussed here.

**Table 2.1 Degradation pathways of polyacrylamides (Caulfield et al., 2002)**

<table>
<thead>
<tr>
<th>Degradation Pathways</th>
<th>Thermal</th>
<th>Photolytic</th>
<th>Chemical</th>
<th>Biological</th>
<th>Mechanical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 200 °C: relatively stable</td>
<td>Bond scission from adsorption of UV irradiation</td>
<td>Acidic hydrolysis</td>
<td>Biological hydrolysis of amide group</td>
<td>Reduction in viscosity and performance from external stimuli (i.e. 200 °C to 300 °C: irreversible reaction of amide functional group)</td>
<td></td>
</tr>
<tr>
<td>200 °C to 300 °C: irreversible reaction of amide functional group</td>
<td>Addition of O₂ during UV irradiation (photooxidation)</td>
<td>Basic hydrolysis</td>
<td></td>
<td>high shear, direct mechanical load, agitation</td>
<td></td>
</tr>
<tr>
<td>Temp &gt; 300 °C: decomposition of amide, main chain scission, random bond scission</td>
<td></td>
<td>Chemically induced free radical degradation (i.e. H₂O₂, K₂S₂O₈)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.1 Chemical Degradation of Polyacrylamides

In water treatment, a variety of chemicals may be used in parallel with polyelectrolytes, including oxidants (i.e. chlorine, chloramines, ozone, permanganate, peroxide), coagulants (i.e. alum, ferric sulfate), chemicals to adjust pH (i.e. lime, caustic soda, soda ash, sulfuric acid), fluoride, and corrosion inhibitors. Those chemicals, especially oxidants, may react with polyelectrolyte residuals in water and result in their degradation. The pH
also influences the rate and extent of polymer degradation (Soponkanaporn and Gehr, 1989).

Under acidic or basic conditions, polyacrylamides are susceptible to hydrolysis. The acidic hydrolysis reaction (Figure 2.2) involves the nucleophilic addition of water to the protonated amide, followed by elimination of NH$_3$. The basic hydrolysis (Figure 2.3) involves nucleophilic addition of hydroxide to the amide carbonyl, followed by loss of NH$_2^-$ to form an acrylic acid residue, then a proton is removed by NH$_2^-$ from acrylic acid residue to form more stable carboxylate anion and ammonia (Caulfield et al., 2002). It is believed that only the amide group of PAMs is changed during acid or basic hydrolysis, while no reduction of the molecular weight has been observed.

![Figure 2.2 Acidic hydrolysis of polyacrylamide (adapted from Caulfield et al., 2002)](image)

![Figure 2.3 Alkaline hydrolysis of polyacrylamide (adapted from Caulfield et al., 2002)](image)
The degradation of polyacrylamides caused by chlorine and ozone has been studies extensively. A comparison of research findings is presented in Table 2.2.

Soponkanaporn and Gehr (1987) used size exclusion chromatography to investigate degradation of a cationic polyacrylamide by ozone. It was reported that molecular weights of the polymers decreased from about 6 million to less than 1 million after exposure to ozone for 10 minutes.

The degradation of a cationic PAM (1 to 100 mg/L) was further studied by exposure to both chlorine (20 mg/L) and ozone (3 mg/L) over pH levels ranging from 3 to 9 (Gehr and Soponkanaporn, 1990). Double-distilled water was used in all treatment tests. Chlorine and ozone oxidation both resulted in reduction of polymer molecular weight, without any significant loss of total organic carbon (TOC) and total nitrogen (TN). This result was confirmed by Levine et al. (2004) who studied the degradation of two polyacrylamides and found chlorine had minimal effect on the total organic carbon.

The production of toxic byproducts (i.e. acrylamide, chloroform) during polymer degradation has also become an additional but important concern. Studies have shown that acrylamide monomers were not generated during PAM degradation with both chlorine and ozone. In fact, oxidation resulted in reduction of the concentration of acrylamide residual (Gehr and Soponkanaporn, 1990). The result agrees with that of Mallevialle et al.
## Table 2.2 Degradation of polycrylamides upon exposure to chlorine or ozone

<table>
<thead>
<tr>
<th></th>
<th>Polymers</th>
<th>Oxidants</th>
<th>Parameters Monitored</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Type</td>
<td>Dose, mg/L</td>
<td>Oxidant Residual</td>
<td>Polymer M.W. Distribution</td>
</tr>
<tr>
<td>Cationic</td>
<td>PAM</td>
<td>1, 10</td>
<td>Chlorine 20 DD water 3, 6, 9 0-30 min</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1, 10</td>
<td>Chlorine 20 DD water 3, 7, 9 &gt;3 days</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>Chlorine 20 DD water 3, 6, 10 NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1, 10, 100</td>
<td>Ozone 3 DD water 3, 6, 9 0-60 min</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>Ozone NA DD water 6 NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1, 10</td>
<td>Chlorine 20 NA 3, 6, 9 0-30 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>NA</td>
<td>Chlorine NA NA 3, 6, 9 0-34 days</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1, 10</td>
<td>Chlorine 20 NA 3, 7, 9 0-20 days</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1, 10, 100</td>
<td>Ozone 0.1 NA 3, 6, 9 0-60 min</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NA</td>
<td>Ozone NA NA 30 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>Ozone 0.1 NA NA 0-10 min</td>
<td></td>
</tr>
<tr>
<td>Anionic</td>
<td>PAM</td>
<td>5</td>
<td>Chlorine 0-10 NA NA 24 h</td>
<td></td>
</tr>
<tr>
<td>Nonionic</td>
<td>PAM</td>
<td>5</td>
<td>Chlorine 0-10 NA NA 24 h</td>
<td></td>
</tr>
</tbody>
</table>

DD water: Double-distilled water; M.W.: Molecular weight; TOC: Total organic carbon; TN: Total nitrogen; ACM: Acrylamide.

(1984), who studied the ozonation of acrylamide alone and acrylamide in an anionic PAM. The removal of acrylamide monomers was rapid, with the first-order reaction rate coefficient at -0.14/min.

Formation of chloroform was detected during chlorination and the concentration increased with increasing polyelectrolyte concentrations and incubation times (Gehr and Soponkanaporn, 1990). Another study on formation of chloroform from a cationic PAM indicated that the rate and extent of polymer reaction increased with increasing pH and temperature (Gehr and Soponkanaporn, 1989).

N-nitrosodimethylylamine (NDMA) is a known animal carcinogen with oral LD$_{50}$ at 58 mg/kg for rats (NDMA Material Safety Data Sheet, 2004). It was reported that the aging of an Epi-DMA (epichlorohydrin-dimethylamine) stock solution resulted in increased NDMA production over a 5-hour period (Kohut and Andrews, 2003).

2.2 Photodegradation of Polyacrylamides

Photodegradation of polyacrylamides is believed to be a free radical process which may lead to cleavage of the polymer backbone (chain scission), cross-linking, introduction of new functional groups, and formation of lower molecular weight products (Reddy, et al., 1994; Caulfield et al., 2002). Caulfield et al. (2003) studied the stability of linear polyacrylamides under thermal and irradiation conditions. It was found that PAMs are stable under fluorescent lights and did not release detectable
levels of acrylamide at 95 °C, although hydrolysis of side-chain amide groups to acid groups was observed during the thermal aqueous degradation. Under UV irradiation at 254 nm, small levels of released acrylamide (generally below 50 parts per million repeat monomer units in the polymer) and a drop in viscosity were observed. It was concluded that the acrylamide released was due to chain scission, not unzipping of the polymer chain.

Smith et al. (1996 and 1997) investigated the degradation of a polyacrylamide thickening agent (PATA), formulated without and with a glyphosate-surfactant herbicide (GH), in distilled-deionized water, surface water and ground water samples. In laboratory controlled temperature (4, 25, and 37 °C) and light conditions (wavelength ranging 300 to 700 nm) and in outdoor environment, it was found that presence of GH either protected acrylamide and/or polyacrylamide from degradation or promoted degradation of polyacrylamide to acrylamide. They suggested that GH might act as a chromophore, absorbing photo radiation and transferring the energy to polyacrylamide, thereby breaking C-C bonds within the polymer.

However, their results have been challenged by other researchers. Vers (1999) conducted experiments under similar degradation conditions but found different results from Smith. Vers concluded that polyacrylamide can not degrade to acrylamide monomers in the presence of either sunlight or herbicide glyphosate or any combination of them. He pointed out some
deficiencies of the methods used by Smith et al. for analyzing acrylamide, such as the poor resolution between acrylamide and acrylic acid monomer, and those deficiencies might have contributed to their misleading results.

Kay-Shoemaker et al. (1998) also questioned the reliability of previous conclusions on the degradability of polyacrylamide to its monomer by Smith et al (1996 and 1997). Their study showed that UV irradiation of a high molecular weight anionic polyacrylamide resulted in reduction of the molecular weight of the polymer. However, there was no evidence for the existence of acrylamide because UV-treated PAM was not able to support bacterial growth (acrylamide monomer can serve as a sole carbon source for bacterial growth). Their results suggest that acrylamide was not formed during the degradation of polyacrylamide under UV irradiation.

The results of Smith et al (1996 and 1997) were also challenged by other researchers: Bologna et al. (1999) suggested that if depolymerization occurred, the acrylamide concentration observed would be significantly higher than that was claimed by Smith et al (1996 and 1997). It was also suggested that the regeneration of double-bond in acrylamide from PAMs is not thermodynamically feasible.

In summary, it has been generally accepted that UV irradiation can lead to molecular weight reduction of polyacrylamides, however, there is still disagreement on the degradation possibility of polyacrylamides to acrylamide monomer, which should be clarified further.
3. Flocculation Performance

The performance of a flocculant can be assessed in terms of settling rate, clarity, sediment volume, or flocculant consumption, which is influenced by the complex interplay among a number of factors that are summarized in Table 2.3.

**Table 2.3 Factors influencing polymer flocculation performance (adapted from Owen et al., 2002; Farrow and Swift, 1996)**

<table>
<thead>
<tr>
<th>Slurry Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic strength</td>
</tr>
<tr>
<td>Particle size</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Solid concentration and intensity,</td>
</tr>
<tr>
<td>Solution composition</td>
</tr>
<tr>
<td>Surface area</td>
</tr>
<tr>
<td>Surface charge</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flocculant Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge density</td>
</tr>
<tr>
<td>Functionality</td>
</tr>
<tr>
<td>Molecular weight</td>
</tr>
<tr>
<td>Polymer conformation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dynamic Aspect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agitation strength and duration</td>
</tr>
</tbody>
</table>

A number of authors have investigated the relationship between flocculation performance and the physical properties of polyelectrolytes, particularly molecular weight and charge density. For cationic PAM, charge neutralization has been suggested as the predominant flocculation mechanism, implying that increasing the charge density of a cationic polymer results in better flocculation performance (Tiravanti et al., 1985; Mabire et al., 1983). However, their conclusion has been challenged by other researchers: Smith-Palmer et al. (1994) studied the flocculation performance of a series of cationic PAMs using kaolin settling rates. It was
found that settling rates were inversely related to charge density, suggesting that bridging can play an important role in flocculation mechanism. This result was supported by Gill and Herrington (1986), who concluded that charge density was not a determining factor, but bridging was the predominant mechanism, and the differences in settling rate must be due to small differences in molecular weight.

Another factor that has been debated is the aging of PAM stock solutions (generally over periods of weeks or months). Shyluk and Stow (1969) observed that the decrease of viscosity of polyacrylamide solution over time could be described as a two stage process, with an initial rapid decrease (about 15 days) followed by a slow and steady decrease. They also reported that aging reduced the ability of the polymer to flocculate a kaolin suspension. The explanations for the mechanism of aging process have been attributed to polymer disentanglement (Gardner et al., 1978), conformation changes (Klein and Westerkamp, 1981; Kulicke and Kniewske, 1981), presence of microorganisms, or free radicals (Haas and MacDonald, 1972).

Limited data are available on the influence of oxidants on PAM flocculation performance. Gehr and Soponkanaporn (1990) reported that chlorine decreased the flocculation efficiency of a cationic PAM slightly in a 10 minute exposure, and that ozone decreased the effective polymer concentrations substantially during the first few minutes and then, the concentration remained constant.
Levine et al. (2004) studied the influence of chlorine, permanganate, UV and their combinations on the flocculation efficiency of a nonionic PAM based on finished water turbidity and time-to-filter test. It was reported that UV irradiation did not result in a significant turbidity change, but chlorine, permanganate and chlorine combined with UV exposure all resulted in decreased performance as measured by residual turbidity. However, the time-to-filter test found that exposure to UV and/or chlorine or permanganate resulted in an improvement in the “filterability” of the suspension, suggesting that larger particles might have formed from polymer flocculation providing less clogging and resistance to flow through the filter pores.

4. Chemical Analysis

It is important to determine the ultimate fate of polymers used in water treatment. A number of approaches have been studied for tracing polymer residuals in water. One approach is to employ a colloidal titration against an electrolyte of opposite charge, using dyes (Wang and Shuster, 1975; Parazak et al., 1987) or with fluorescent compounds (Tanaka and Sakamoto, 1993) as indicators. However, this method is not especially sensitive, with the lower detection limits ranging from 0.5 to 1 mg/L. A variation on this theme for cationic flocculants is to measure the light absorbance at 680 nm following progressive additions of a standard solution of an o,o′-dihydroxyazo compound, which forms an association with the polymer
Masadome (2003) also reported a similar method employing crystal violet (CV) as indicator and measuring the change of absorbance at 590 nm by a common spectrophotometer. Another similar method is to monitor turbidity by adding tannic acid to precipitate the polymer (Attia and Rubio, 1975).

Other methods have also been developed for characterizing synthetic polyelectrolytes. Goppers and Straub (1976) used thin layer chromatography to detect residual polymer and monomer associated with a cationic polyacrylamide. Size exclusion chromatography (SEC) has been used to determine the molecular weight and molecular weight distribution of polymers. It has been used to determine trace amounts of anionic partially hydrolysed polyacrylamide (Belzley, 1985), residual non-ionic polyacrylamide in an alum sludge (Keenan et al., 1998), and high molecular weight cationic polyacrylamides (Soponkanaporn and Gehr, 1987). Gel electrophoresis has also been used as a tool for determining the molecular weight distribution of long-chain synthetic polyelectrolyte (Smisek and Hoagland, 1990). It was claimed that gel electrophoresis has the advantage of higher resolution and a much broader molecular weight range than can be achieved with aqueous SEC, with an upper chain-size limit that is well above the molecular weight of any synthetic polymer of commercial significance. The disadvantage of this method is that it can only be applied for charged polymers, while SEC can also be applied to nonionic polymers.
Pyrolysis gas chromatography (Py-GC) or pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) has been an important technique in characterization of synthetic polymers, both qualitatively and quantitatively, for more than 30 years. In addition to composition identification, pyrolysis was also used to explore the structure of copolymers and study the stereoregularity of homopolymers (Wang, 1999). Black et al. (1966) employed Py-GC-MS after separation by SEC to analyze a high molecular weight, low charge density (CD) copolymer of acrylamide and sodium acrylate.

Analysis of polymer impurities is also very important, such as acrylamide residuals. The current methods used for analyzing acrylamide residual include high-performance liquid chromatography with UV detector (Vers, 1999), gas chromatography followed by an electron capture detector (ECD) (Bologna et al., 1999) or mass spectrometer (MS) (Oho et al., 2003).

5. Regulations Related to the Use of Polyacrylamides

Currently, a wide range of polyelectrolytes are available and the presence of unreacted monomer has caused concern, especially acrylamide and epichlorohydrin monomers which are toxic to human and animals. Because of these concerns, Switzerland and Japan do not permit the use of polyelectrolytes, including polyacrylamide, in drinking water treatment (Letterman and Pero, 1990). Other countries, such as the United States and the United Kingdom, set limits on contaminant levels and application doses.
In the United States, when PAM products are used in drinking water treatment, the combination of monomer and dose should not exceed 0.05% (by weight of active polymer) of acrylamide monomer dosed at 1 ppm (40 CFR 141.111), which corresponds to a maximum theoretical concentration of 0.5 µg/L monomer in water. Compared to the U.S., United Kingdom has much stricter guideline values: no single can contain more than 0.02% of free acrylamide monomer based on the active ingredient content, and the dose must average no more than 0.25 ppm and never exceed 0.50 ppm of the active ingredient (BS EN 1407:1998 and BS EN 1410:1998).

However, these regulations are focused only on the quality of the products themselves rather than the quality of the finished water. After entering a drinking water system, the PAMs and monomers can undergo a variety of reactions (as described in previous sections), which might result in increases or decreases in acrylamide residuals. None of those regulations consider the potential changes of ACM residuals in water treatment and distribution systems. Furthermore, there are no scientific guidelines for selection of polymer products in water treatment. Polyelectrolyte products are often selected empirically based on bench-scale performance and cost, and the possible degradation of polymers during treatment and distribution are typically not considered. Thus, it is essential to evaluate the degradation of polymers in water treatment system which will assist in the selection and usage of polymer products in potable water treatment.
METHODS AND MATERIALS

This chapter describes the experimental methods applied for this research. There are three major sections in this chapter: chemical degradation of PAM, UV degradation of PAM, and flocculation performance tests. The combined effect of UV and chemical oxidants on acrylamide residuals and oxidant residuals was also evaluated, which was incorporated into the first two sections. A diagram of the entire experimental design is shown in Figure 3.1.

![Diagram of experimental design](image)

**Figure 3.1 Diagram of the experimental design**

1. Polyacrylamides

   In this study, three polyacrylamide products from Polydyne Inc. were selected for investigation. Some characteristics of the polymers, such as polymer trade name, form, molecular weight, charge type, charge density,
and main components, were provided by the manufacturer, and are listed in Table 3.1. All three polymers selected were in powder form because of the high content of active polymer compared to emulsion or solution forms. Other properties of the three polymers differ from each other. For example, the anionic A-3333 P has the highest molecular weight (M.W.) of 12-16 million Daltons, whereas the cationic C-3280 has the lowest M.W. of 4-6 million Daltons. All three polymers selected represent three types of PAMs in terms of charge and component.

Before conducting tests, 0.1% polymer stock solutions (based on total solids) were made. For this study, the water matrix used was nanopure water produced by a Millipore laboratory water purification system. Before making stock solutions, the total solids of the three polymers were tested by drying a specified amount of polymer (e.g. 0.5 g) in an oven at 105 °C to 110 °C for 3 hours and measuring the weight difference before and after drying (Appendix A). Then polymers were dissolved in warm water (25 °C to 35 °C) with stirring to form 0.1 % aqueous solutions based on total solids (for example, for a 90% total solids, 1.11 gram polymer is dissolved into 1 liter water). 10 mg/L polymer work solutions were made from 0.1% stock solutions for further tests. Although lower levels of PAMs (usually less than 1 mg/L) are typically used in water treatment plants, in this study, 10 mg/L concentration was adopted for most of the experiment because of the low sensitivity of analytical methods.
Table 3.1 Polymer characteristics (Polydyne Inc., 2004)

<table>
<thead>
<tr>
<th>Polymer Trade Name</th>
<th>Polymer Form</th>
<th>Molecular Weight, Daltons</th>
<th>Type of Charge</th>
<th>Charge Density, Mole %</th>
<th>Main Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifloc N-3300 P</td>
<td>White powder</td>
<td>8~10 million</td>
<td>Neutral</td>
<td>0</td>
<td>Acrylamide homopolymer</td>
</tr>
<tr>
<td>Clarifloc A-3333 P</td>
<td>White powder</td>
<td>12~16 million</td>
<td>Anionic</td>
<td>30%</td>
<td>acrylamide &amp; sodium acrylate copolymer</td>
</tr>
<tr>
<td>Clarifloc C-3280</td>
<td>White powder</td>
<td>4~6 million</td>
<td>Cationic</td>
<td>55%</td>
<td>acrylamide &amp; Adam MeCl copolymer*</td>
</tr>
</tbody>
</table>

* Adam MeCl: Ethanaminium N,N,N-trimethyl-2-(1-oxo-2-propenyl)oxy, chloride.

2. Chemical Oxidation of Polyacrylamides

Two kinds of chemical oxidants were used in this study—free chlorine and potassium permanganate. The degradation of PAM products was evaluated through several tests, including assessment of oxidant residuals, UV spectra/absorbance, total organic carbon (TOC), acrylamide residuals, and inorganic nitrogen residuals. Changes of oxidant residuals were used as an indirect indicator for the presence and degree of reactions occurred between oxidants and polymers, since direct detection of polymer structure changes requires much more advanced techniques (e.g. Py-GC-MS). TOC and UV spectra/absorbance tests were used to evaluate the changes of total polymer contents, for example, decrease of TOC level means some of organic carbon is converted to inorganic form. Changing of acrylamide residual in the polymer solution is a big concern because of its toxicity. While
inorganic nitrogen, such as ammonia-N, was used as an indicator for polymer hydrolysis. Samples were analyzed in triplicates.

2.1 Test of Oxidant Residual—Free Chlorine

Approximately 1000 mg/L of chlorine stock solution was made from 6% commercial bleach, and the concentration was standardized against 0.025 N sodium thiosulfate standard solution (Hach) based on Standard Methods 4500-Cl G (Standard Methods for Examination of Water and Wastewater, 1998). In this experiment, the chlorine dosages adopted were 5, 10, and 15 mg/L as Cl₂ to achieve chlorine to polymer mass ratios of 0.5, 1.0, and 1.5. The detailed experimental conditions are given in Table 3.2.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Dose, mg/L</th>
<th>Cl₂, mg/L</th>
<th>KMnO₄, mg/L</th>
<th>Exposure Time, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-3300 P</td>
<td>10</td>
<td>5, 10, 15</td>
<td>2, 4, 6</td>
<td>5</td>
</tr>
<tr>
<td>A-3333 P</td>
<td>10</td>
<td>5, 10, 15</td>
<td>2, 4, 6</td>
<td>5</td>
</tr>
<tr>
<td>C-3280</td>
<td>10</td>
<td>5, 10, 15</td>
<td>2, 4, 6</td>
<td>5</td>
</tr>
</tbody>
</table>

A 200 mL aliquot of each 10 mg/L polymer solution was placed into a 250-mL glass stoppered flask, and the specified amount of chlorine stock solution was added to the flask. The glassware used in the study was acid washed. A 20 mL aliquot was removed immediately after mixing to evaluate the initial chlorine residual using the iodine titration method (Appendix B). This method uses a standard solution of sodium thiosulfate with starch as
indicator to titrate the free iodine liberated from excess potassium iodine by chlorine (Standard Methods for Examination of Water and Wastewater, 1998). Then the flask was capped with a glass stopper and sealed with aluminum foil to exclude the possible influence of UV light. The flask was placed on a mechanical shaker and shaken for 5 hours at 200 rpm. At specific time intervals, 10 mL samples were withdrawn to test chlorine residual. After a 5-hour reaction time, the reaction was stopped by adding 2-3 drops of 0.1 M sodium thiosulfate solution. The 5-hour contact time was used to allow the reactions to reach equilibrium, if possible.

2.2 Test of Oxidant Residual—Potassium Permanganate

1000 mg/L of KMnO$_4$ stock solution was made by weighing 0.1 mg of KMnO$_4$ powder (Fisher) and dissolving into 100 mL of nanopure water. The dosages of permanganate applied for oxidation of 10 mg/L polymer solution were 2, 4, or 6 mg/L as KMnO$_4$ (Table 3.2). The method described in the previous section (chlorine oxidation) was followed and the change of permanganate residual was evaluated with time. Potassium permanganate concentration was directly determined by measuring its absorbance at 525 nm using a spectrophotometer (HACH DR 4000U), because its concentration is directly proportional to the absorbance as measured at 525 nm. The detailed method is described in Appendix C.
2.3 Total Organic Carbon and UV spectra/Absorbance

The total organic carbon (TOC) of the PAM solutions (10 mg/L) was tested using a Sievers Total Organic Carbon Analyzer. The measurement of TOC is based on evaluation of the mass of carbon dioxide produced from oxidation of organic matter by the coupling of UV irradiation and ammonium persulfate oxidation under acidic conditions (Levine et al., 2004). For each measurement, about 30 mL of sample was placed into a pre-cleaned 29 x 81 mm 40 mL screw-capped vial with Teflon lined septa and then placed into the autosampler. The testing parameters were programmed using a computer system. To evaluate the impact of oxidation on organic carbon content of polyacrylamides, the TOC contents of three PAMs (10 mg/L solutions) were tested before and after oxidizing with chlorine at 5, 10, 15 mg/L and potassium permanganate at 2, 4, 6 mg/L for 5 hours.

Another method for measuring polymer residual is UV spectra/absorbance. Polymer samples before and after oxidation with chlorine/permanganate were scanned using a UV/Vis spectrophotometer (Hach DR 4000U) from 190 to 300 nm. Since previous lab studies found that polyacrylamides achieve their maximum absorbance in the range of 190 nm to 205 nm. Therefore, the absorbance of PAM solutions at 195 nm was set as a standard to compare the absorbance changes before and after oxidation reactions. The reaction durations were up to 1 hour, which is close to the residence time of some water treatment facilities.
2.4 Changing of Acrylamide Residuals

The acrylamide residual content of PAM solutions was tested using gas chromatography (GC) and electron capture detector (ECD). The acrylamide in aqueous samples was brominated by saturated bromine water (Fisher) to form 2,3-dibromopropionamide, and then extracted with ethyl acetate (Fisher) and converted to the more stable 2-propenamide. The 2-propenamide was separated in a polar DBwax (polyethylene glycol) capillary column (30 m x 0.25-mm i.d., 0.25 \( \mu \)m film thickness) (J&W Scientific) and then detected by an ECD detector. The detailed method is described in Appendix D.

Since previous studies found that cationic PAM was more susceptible to oxidation, only the acrylamide residual change of the cationic PAM solution (10 mg/L) was evaluated in this study. The solution was exposed to 15 mg/L of chlorine or 6 mg/L of KMnO\(_4\) for 30 minutes, then ACM residuals were measured. The combined effects of UV irradiation were also investigated, which will be described in section 3.

2.5 Inorganic Nitrogen Residuals

The concentration levels of ammonia-N, nitrite-N, and nitrate-N in 10 mg/L polymer solutions were detected using a spectrophotometer (Hach DR 4000U). For each measurement, the analysis procedures provided by the instrument vendor (Hach) were followed. 100 mL of 10 mg/L polymer solutions were oxidized with chlorine at 10, 15 mg/L or permanganate at 4,
6 mg/L for 1 hour, then NH$_3$-N, NO$_2^-$-N, and NO$_3^-$-N were tested and compared with the results from the control group (no oxidant added in polymer solutions).

The methods for inorganic nitrogen tests are summarized in Table 3.3. Other analytical methods used in the research are provided in appendices, which have been modified from Standard Methods or other references.

Table 3.3 Methods for inorganic nitrogen tests (Hach DR4000 Spectrophotometer Handbook, 2001)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Instrument</th>
<th>Detection Limit</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total NH$_3$-N</td>
<td>8155-2455</td>
<td>DR4000U HACH Spectrophotometer</td>
<td>0.09 ppm</td>
<td>Cu, Fe, Mg, NO$_3^-$, NO$_2^-$, PO$_4^{3-}$, SO$_4^{2-}$</td>
</tr>
<tr>
<td>NO$_2^-$-N</td>
<td>8507-2610</td>
<td>DR4000U HACH Spectrophotometer</td>
<td>0.0008 ppm</td>
<td>Pb$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, NO$_3^-$, strong oxidizing and reducing agents</td>
</tr>
<tr>
<td>NO$_3^-$-N</td>
<td>8192-2515</td>
<td>DR4000U HACH Spectrophotometer</td>
<td>0.01 ppm</td>
<td>Ca, Cl$^-$, Fe$^{2+}$, Fe$^{3+}$, NO$_2^-$, pH, strong oxidizing and reducing agents</td>
</tr>
</tbody>
</table>

3. Photodegradation of Polyacrylamides

A sunlight lamp with UV spectrum was used to study the photo-induced degradation of polyacrylamides. Polymer samples were exposed to the UV light and degradation of PAMs was evaluated based on the tests described in the following sections. The UV intensity applied for this experiment was about 7 $\mu$w/cm$^2$, because it was close to the UV intensity in real sunlight at noon during the period in which the experiment was conducted (May 2004). A 30-minute exposure time was applied because longer exposure time
might result in overheating of the polymer solutions and faster evaporation rates. To measure the volume lost caused by evaporation, 50 mL of polymer work solution was exposed to the same light for 30 minutes and the volume was measured using a graduated cylinder. The results for following studies were corrected by the percentage of evaporation lost.

3.1 UV Induced Polymer Changes

The impact of UV irradiation on PAMs’ TOC content and UV spectra was evaluated. The methods are similar to those described in section two.

3.2 Acrylamide Residual Changes by UV and Combination with Oxidants

10 mg/L Cationic PAM (C-3280) solution was exposed to UV irradiation alone and/or combined with oxidants (chlorine and/or permanganate) for 30 minutes and then tested for acrylamide residuals using GC-ECD. The experimental conditions are summarized in Table 3.4.

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Polymer Dose</th>
<th>UV</th>
<th>Chlorine</th>
<th>Potassium Permanganate</th>
<th>Exposure Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-3280</td>
<td>10 mg/L</td>
<td></td>
<td></td>
<td></td>
<td>30 min</td>
</tr>
<tr>
<td>C-3280</td>
<td>10 mg/L</td>
<td>X</td>
<td></td>
<td></td>
<td>30 min</td>
</tr>
<tr>
<td>C-3280</td>
<td>10 mg/L</td>
<td>X</td>
<td>15 mg/L</td>
<td></td>
<td>30 min</td>
</tr>
<tr>
<td>C-3280</td>
<td>10 mg/L</td>
<td>X</td>
<td></td>
<td>6 mg/L</td>
<td>30 min</td>
</tr>
<tr>
<td>C-3280</td>
<td>10 mg/L</td>
<td>X</td>
<td>15 mg/L</td>
<td>6 mg/L</td>
<td>30 min</td>
</tr>
</tbody>
</table>

3.3 Oxidant Residuals—Combination of UV with Chlorine/Permanganate

This experiment investigated the impact of UV irradiation on chlorine/permanganate oxidation of PAM solutions. 10 mg/L of PAM
solutions were exposed to UV irradiation, and a specified amount of chlorine (or permanganate) stock solution was added to achieve an initial residual of 5, 10, or 15 mg/L as Cl$_2$ (or 2, 4, 6 mg/L as KMnO$_4$ for permanganate oxidation). 10 mL samples were removed every ten minutes and the chlorine residuals (or permanganate residuals) were tested until reaction completion. The reduction of oxidant residuals in 30 minutes was compared to their reduction in 30 minutes without UV intervention.

4. Flocculation Performance

In this experiment, the flocculation performance of selected PAMs, before and after oxidation, was evaluated and compared based on the settling rate of 1.5 % kaolin slurry. The settling rate test method was modified through the study of Smith-Palmer et al. (1994). For each set of flocculation tests, 15 g of kaolin (Fisher) was stirred with 890 mL of nanopure water and 10 mL of salt solution for at least one hour. The salt solution contains $3.3 \times 10^{-1} M$ sodium chloride (Fisher), $1.5 \times 10^{-2} M$ calcium chloride (Fisher), and $5.0 \times 10^{-3} M$ magnesium chloride (Fisher). Kaolin slurry was then dispensed in 30-mL aliquots three times (totally 90 mL) into a 100-mL graduated cylinder. Thereafter, a specific amount of polymer solution was added into the cylinder, and the volume was made up to 100 mL. The cylinder was inverted for 5-minute mixing, then the settling distance (cm) in 3 minutes was measured and averaged settling rate (cm/min) was calculated. Before testing the flocculation performance of the polymers, the
settling rate of 1.5 % kaolin slurry was measured with this method as a control for further comparison.

4.1 Polymer Flocculation with No Oxidant Presented

In drinking water treatment, the dosages of PAMs usually do not exceed 1.0 mg/L, therefore, in this experiment, 0.5 and 1.0 mg/L of PAMs were applied for testing the flocculation rates of three polyacrylamide products. To reach the specified polymer concentration, 5 mL or 10 mL of 10 mg/L polymer solutions was added into the graduated cylinder containing 90 mL of kaolin slurry. For the solution containing 5 mL of 10 mg/L polymer solution, 5 mL of nanopure water was added to bring the total volume up to 100 mL. Then the cylinder was inverted for 5-minute mixing before measuring the settling rate.

4.2 Polymer Flocculation with Oxidant Presented

In this part, free chlorine and permanganate were used for oxidation of the three polymers. The oxidant dosage applied was 10 mg/L of Cl₂ or 4 mg/L of KMnO₄. The polymer dosages were 0.5 mg/L and 1.0 mg/L.

4.2.1 Polymer Flocculation with Chlorine Oxidation

Two types of oxidation methods involving chlorine were employed in this section. In the first method, a specified amount of chlorine stock solution was added into 90 mL of kaolin slurry in 100-mL graduate cylinder. After 10 minutes of contact time, the specified amount of polymer solution was added. The volume of the mixture was diluted to 100 mL with nanopure
water (if the total volume was less than 100 mL), then the graduated
cylinder was inverted for 5 minutes and the settling rate was tested. In this
method, the oxidation duration of polymer can be considered as about 5
minutes (the mixing time).

In the second method, 10 mg/L of polymer solution reacted with 10
mg/L of chlorine for 1 hour, then the specified amount of reaction product
was added into the graduated cylinder containing 90 mL kaolin slurry,
thereafter, more chlorine stock solution was added to maintain the same
initial concentration of 10 mg/L and follow the same steps as previous
sections to test the settling rate. In this method, the oxidation duration was
considered as approximately 1 hour.

4.2.2 Polymer Flocculation with Permanganate Oxidation

The methods for testing of polymer flocculation with permanganate
oxidation were similar to those described in the previous sections, except
that the permanganate dosage was different (4 mg/L of KMnO₄).
RESULTS AND DISCUSSION

In this chapter, the results are presented and discussed in four sections: chemical degradation of polyacrylamides, photodegradation of polyacrylamides and coupling effects with chemical oxidation, results of polymer flocculation performance testing, and policy significance of the study.

1. Chemical Degradation of Polyacrylamides

The degradation of polyacrylamides was investigated by exposure to chlorine or permanganate solutions with different oxidant doses and contact time. The degradation extent was evaluated by oxidant residuals, TOC and UV spectra, acrylamide residuals, and inorganic nitrogen residuals.

1.1 Oxidant Residuals

Three PAM products were oxidized with either free chlorine or potassium permanganate at different dosages for 5 hours. The concentration of oxidant residual was used as an indirect indicator for the redox reactions between oxidants and polymers. The oxidant residual was measured after initial mixing with polymers and then tested at specific intervals over a 5-hour period. The averaged amount of oxidant consumed during a 5-hour reaction time is summarized in Table 4.1 for each test.
Table 4.1 Compare the decreasing of chlorine/permanganate residuals after reacting with three PAM samples (N-3300 P, A-3333 P, and C-3280) for 5 hours.

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Initial Oxidant Residual, mg/L*</th>
<th>Final Oxidant Residual, mg/L*</th>
<th>Elapsed Time, h</th>
<th>Oxidant Degradation, mg/L*</th>
<th>Oxidant Degradation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-3300 P</td>
<td>KMnO₄ 6.029</td>
<td>KMnO₄ 6.003</td>
<td>5</td>
<td>0.026</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>KMnO₄ 3.995</td>
<td>KMnO₄ 3.969</td>
<td>5</td>
<td>0.026</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>KMnO₄ 1.974</td>
<td>KMnO₄ 1.948</td>
<td>5</td>
<td>0.026</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 15.055</td>
<td>Free Chlorine 8.508</td>
<td>5</td>
<td>6.547</td>
<td>43.49</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 9.926</td>
<td>Free Chlorine 5.459</td>
<td>5</td>
<td>4.467</td>
<td>45.00</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 5.140</td>
<td>Free Chlorine 3.368</td>
<td>5</td>
<td>1.772</td>
<td>34.47</td>
</tr>
<tr>
<td>A-3333 P</td>
<td>KMnO₄ 6.042</td>
<td>KMnO₄ 5.990</td>
<td>5</td>
<td>0.052</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>KMnO₄ 3.969</td>
<td>KMnO₄ 3.930</td>
<td>5</td>
<td>0.039</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>KMnO₄ 1.961</td>
<td>KMnO₄ 1.922</td>
<td>5</td>
<td>0.039</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 15.421</td>
<td>Free Chlorine 14.715</td>
<td>5</td>
<td>0.706</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 9.749</td>
<td>Free Chlorine 9.217</td>
<td>5</td>
<td>0.532</td>
<td>5.46</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 5.018</td>
<td>Free Chlorine 4.431</td>
<td>5</td>
<td>0.587</td>
<td>11.70</td>
</tr>
<tr>
<td>C-3280</td>
<td>KMnO₄ 6.042</td>
<td>KMnO₄ 5.468</td>
<td>5</td>
<td>0.574</td>
<td>9.50</td>
</tr>
<tr>
<td></td>
<td>KMnO₄ 3.956</td>
<td>KMnO₄ 3.630</td>
<td>5</td>
<td>0.326</td>
<td>8.24</td>
</tr>
<tr>
<td></td>
<td>KMnO₄ 1.896</td>
<td>KMnO₄ 1.674</td>
<td>5</td>
<td>0.222</td>
<td>11.71</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 15.314</td>
<td>Free Chlorine 10.458</td>
<td>5</td>
<td>4.856</td>
<td>31.71</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 9.572</td>
<td>Free Chlorine 4.963</td>
<td>5</td>
<td>4.609</td>
<td>48.15</td>
</tr>
<tr>
<td></td>
<td>Free Chlorine 4.786</td>
<td>Free Chlorine 1.383</td>
<td>5</td>
<td>3.403</td>
<td>71.10</td>
</tr>
</tbody>
</table>
Figure 4.1 Decrease in permanganate residual after oxidation of 10 mg/L Clarifloc C-3280 (KMnO₄ dose at 6 mg/L)

Figure 4.2 Decline of chlorine residual after oxidation of 10 mg/L Clarifloc N 3300 P, A-3333 P and C-3280 (chlorine dose at 15 mg/L)
As shown in Table 4.1, there was only a minimal decrease for permanganate residual when mixed with nonionic N-3300 P and anionic A-3333 P. However, an obvious decline of permanganate residual was observed when different doses of KMnO$_4$ reacted with cationic PAM C-3280, ranging from 8 % to 12 %. For free chlorine oxidation, approximately 30 to 70% of free chlorine was consumed after reacting with N-3300 P and C-3280 for 5 hours, whereas reaction with A-3333 P resulted in relatively small decrease in chlorine residuals (about 4 to 12%).

Example results of the decline of oxidant residual with time are shown in Figures 4.1 and 4.2, and other results are shown in Appendix F. The decrease of KMnO$_4$ residual with time when oxidizing cationic C-3280 is...
shown in Figure 4.1, which is close to a straight line, with a slope of 0.0019 mg/L-min and R^2 value at 0.9848 when the KMnO_4 dose was about 6 mg/L. This reaction can be considered as a zero order reaction with reaction rate at about 0.002 mgL^{-1}min^{-1}.

As shown in Figure 4.2, oxidation of anionic A-3333 didn’t result in obvious decline of chlorine residual. When mixed with nonionic N-3300 P, relatively little decrease of chlorine residual was observed in the first hour, however, the rate of reaction increased in the following 1~2 hours and decreased thereafter. One possible explanation is that certain reaction products worked as catalysts or initiators for the subsequent reactions. Cationic C-3280 was much more susceptible to oxidation reactions in the first one hour than other polymers. Thereafter, chlorine residual became relatively steady. A similar trend was observed for other chlorine doses. The decline of chlorine residuals in the first 40 minutes was plotted for N-3300 P and C-3280 (Figure 4.3). In this period, the reactions between the two polymers and chlorine are regarded as zero-order reactions with rates at about 0.007 and 0.086 mg/L-min for N-3300 P and C-3280, respectively.

1.2 UV Spectra/Absorbance

The three PAM products (10 mg/L) were placed in 5-cm cells and scanned using a UV/VIS spectrophotometer from 190 nm to 300 nm, and the spectra are shown in Figures 4.4 to 4.6. As shown, the UV spectra of
nonionic PAM and anionic PAM had a similar pattern with the maximum absorbance associated with wavelength in the range of 190 to 195 nm. Whereas the UV spectra of the cationic PAM had a relatively broad adsorption wavelength band and the maximum absorbance was found between 200 and 205 nm. To quantitatively evaluate the potential changes of UV absorbance before and after oxidation of the PAM samples, the absorbance at 195 nm was selected as a guideline for comparing those changes. The polymer samples were oxidized with KMnO₄ at 2 mg/L or free chlorine at 5 mg/L for 1 hour, and the changes of absorbance versus time are shown in Figures 4.7 and 4.8, respectively.

Figure 4.4 The UV spectra of Clarifloc N-3300 P (10 mg/L)
Figure 4.5 The UV spectra of Clarifloc A-3333 P (10 mg/L)

Figure 4.6 The UV spectra of Clarifloc C-3280 (10 mg/L)
Figure 4.7 UV absorbance changes at 195 nm (measured in 5 cm cell) for the PAM samples (10 mg/L) when exposing to 2 mg/L of KMnO₄.

Figure 4.8 UV absorbance changes at 195 nm (measured in 5 cm cell) for the PAM samples (10 mg/L) when exposing to 5 mg/L of free chlorine.
In Figure 4.7, KMnO₄ solution (2 mg/L) without addition of polymers was used as a control, with the absorbance of 0.852 at 195 nm. As shown, permanganate oxidation didn’t result in obvious changes in UV absorbance at 195 nm for any of the three PAMs during oxidation process by permanganate, which suggests that the PAMs were not mineralized to inorganic forms. However, the absorbance difference between the mixture and the control was less than the absorbance of polymer itself (although dilution ratio of 1:500 was considered), in another word, \( \text{ABS}_{\text{mixture}} < \text{ABS}_{\text{polymer}} + \text{ABS}_{\text{KMnO}_4} \), which indicates certain reactions between permanganate and PAMs must have happened.

When oxidized by free chlorine, no apparent change on UV absorbance was observed for N-3300 P and A-3333 P. The only exception was C-3280. The UV absorbance at 195 nm decreased about 20 % when chlorine was added into the 10 mg/L polymer solution for 1 minute. Then, the UV absorbance at 195 nm increased approximately 40 % in 30 minutes, and reached a relatively stable plateau. The changes of UV spectra for C-3280 are shown in Figures 4.9 and 4.10. When compared to the UV spectra of C-3280 control (Figure 4.6), a new peak formed immediately after addition of chlorine (chlorine peak), which gradually disappeared during the reaction process, which indicates that chlorine was consumed in reactions (confirmed by the oxidant residual tests). It is postulated that new products were
formed during oxidation of C-3280 by chlorine. Although the UV spectra could not determine the reaction products, it is very easy to test and the spectrophotometers are available to most of the labs in water treatment plants. In addition, the main purpose for such analysis is to avoid reactions between oxidants and polymers during polymer selection process.

Figure 4.9 The UV spectra of Clarifloc C-3280 (10 mg/L) after addition of 5 mg/L of chlorine for 1 minute

Figure 4.10 The UV spectra of Clarifloc C-3280 (10 mg/L) after addition of 5 mg/L of chlorine for 30 minute
1.3 Total Organic Carbon

A Sievers Total Organic Carbon Analyzer was used to test the impacts of chlorine and permanganate on the organic carbon content of PAM samples. The PAM samples were oxidized by different doses of chlorine or permanganate for 5 hours and total organic carbon was tested and compared with the control group (Figures 4.11 and 4.12). The results show that chlorine or permanganate did not result in an apparent loss of the total organic carbon of the PAM samples, which suggests that partial oxidation was the leading reaction. This was confirmed by Gehr and Soponkanaporn (1990) and Levine et al. (2004) who studied oxidation of polyacrylamides by chlorine. However, for permanganate oxidation, there are no comparable data. Triplicate tests show that the standard deviation of the TOC tests ranged from 0.15 to 0.25 mg/L, which is small for the analysis.
Figure 4.11 Impact of chlorine dose on the oxidizable carbon content of three PAMs (N-3300 P, A-3333 P and C-3280) after 5 hours oxidation

Figure 4.12 Impact of KMnO₄ dose on the oxidizable carbon content of three PAMs (N-3300 P, A-3333 P and C-3280) after 5 hours oxidation
1.4 Acrylamide Residuals

Because cationic PAM was more reactive with chlorine/permanganate, acrylamide residuals formed from 10 mg/L C-3280 before and after oxidation with chlorine (15 mg/L) or permanganate (6 mg/L) were evaluated. All samples were spiked with 10 µg/L acrylamide standard in case the level of acrylamide residuals was too low to be detected. The detection limit of the method was considered to be around 1 µg/L. As shown in Figure 4.13, about 36 µg/L acrylamide residual was detected in 10 mg/L C-3280 containing 10 µg/L ACM standard. The acrylamide residuals after exposure to chlorine or permanganate were shown in Figures 4.14 and 4.15. When the

![Figure 4.13 Acrylamide residual in 10 mg/L C-3280 (spiked with 10 µg/L acrylamide standard)](image)

Retention Time: 10.400 min  
Peak Area: 285645  
Concentration: 36.1 µg/L (contain 10 µg/L ACM standard)  
Analyzed by GC-ECD
Retention Time: 10.408 min
Peak Area: 267610
Concentration: 33.8 µg/L (contain 10 µg/L ACM standard)
Analyzed by GC-ECD

Figure 4.14 Acrylamide residual in 10 mg/L C-3280 (spiked with 10 µg/L acrylamide standard) after exposure to 15 mg/L chlorine for 30 minutes

Retention Time: 10.408 min
Peak Area: 74746
Concentration: 9.3 µg/L (spiked with 10 µg/L ACM standard)
Analyzed by GC-ECD

Figure 4.15 Acrylamide residual in 10 mg/L C-3280 (spiked with 10 µg/L acrylamide standard) after exposure to 6 mg/L KMnO₄ for 30 minutes
10 ppb acrylamide standard spiked in each sample was not considered, exposure to 15 mg/L chlorine or 6 mg/L permanganate resulted in reduction of ACM residuals about 9% or 100%, respectively. The degradation of acrylamide by chlorine or permanganate is compared with UV induced degradation in section 2.

1.5 Inorganic Nitrogen Residuals

As known, ammonia nitrogen is released as the result of hydrolysis of polyacrylamides under acidic or basic conditions. Therefore, the concentration of ammonia nitrogen can be used as an indicator for the extent of PAM hydrolysis in aqueous solution.

In this experiment, the concentrations of inorganic nitrogen (NH$_3$-N, NO$_2^-$-N and NO$_3^-$-N) were measured before and after oxidation by chlorine and permanganate using colorimetric method, and the detection limits for NH$_3$-N, NO$_2^-$-N and NO$_3^-$-N are 0.09, 0.0008, and 0.01 ppm, respectively (Hach DR4000 Spectrophotometer Handbook, 2001). The inorganic nitrogen residuals in fresh aqueous solutions (within 48 hours) of three types of PAM are given in Table 4.2. In each PAM solution, there were negligible amounts of inorganic nitrogen residual (<0.1 ppm). After addition of chlorine or permanganate, minor changes were observed for inorganic-N group, which suggests that addition of chlorine/permanganate had minor effects on hydrolysis of PAMs in aqueous solutions. However, it seems that
ageing of PAM solution dramatically increased the degree of PAM hydrolysis.

For example, about 0.40 mg/L of NH$_3$-N was measured in an aged PAM solution (more than 1 month), compared to 0.01 to 0.04 mg/L of NH$_3$-N in fresh solution.

Table 4.2 Inorganic nitrogen contents in three Clarifloc PAMs (N-3300 P, A-3333 P, and C-3280) before and after KMnO$_4$ (4 mg/L and 6 mg/L) and chlorine (10 mg/L and 15 mg/L) oxidation for 1 hour

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Oxidant</th>
<th>Oxidant Dose, mg/L</th>
<th>NH$_3$-N, mg/L</th>
<th>NO$_2^-$-N, mg/L</th>
<th>NO$_3^-$-N, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-3300 P</td>
<td>None</td>
<td>0</td>
<td>0.01</td>
<td>0.0032</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>KMnO$_4$</td>
<td>4</td>
<td>0</td>
<td>0.003</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>0</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Cl$_2$</td>
<td>10</td>
<td>0.05</td>
<td>0.0029</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>0.04</td>
<td>0.0035</td>
<td>0.01</td>
</tr>
<tr>
<td>A-3333 P</td>
<td>None</td>
<td>0</td>
<td>0.04</td>
<td>0.0033</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>KMnO$_4$</td>
<td>4</td>
<td>0.03</td>
<td>0.0039</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>0.02</td>
<td>0.0039</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Cl$_2$</td>
<td>10</td>
<td>0.02</td>
<td>0.0035</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>0.02</td>
<td>0.0039</td>
<td>0.01</td>
</tr>
<tr>
<td>C-3280</td>
<td>None</td>
<td>0</td>
<td>0.01</td>
<td>0.0206</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>KMnO$_4$</td>
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<td>0</td>
<td>0.0209</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>0.01</td>
<td>0.0202</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Cl$_2$</td>
<td>10</td>
<td>0.06</td>
<td>0.0166</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>0.07</td>
<td>0.0147</td>
<td>0.01</td>
</tr>
</tbody>
</table>

In summary, among three PAMs investigated, the cationic PAM was more susceptible to chemical degradation caused by chlorine and permanganate, however, for any polymer sample, only partial degradation was observed and there was no apparent loss of total polyacrylamide.
content. The oxidation of cationic PAM by chlorine (15 mg/L) and permanganate (6 mg/L) resulted in loss of acrylamide residuals by 9% and 100%, respectively.

2. Photolytic Degradation of Polyacrylamides

A sunlight lamp with UV spectrum was used to study photo-induced PAM degradation. The strength was controlled at a level close to the natural sunlight in summer (the season when UV irradiation is strongest and has the most impact). Changes in TOC, UV spectra and acrylamide residuals for three polymer samples were monitored when exposed to UV irradiation. In addition, the impact of UV irradiation on chemical oxidation of PAMs and acrylamide residuals by chlorine or permanganate was investigated. Since exposure to UV irradiation can increase solution temperature and accelerate evaporation, temperature and volume changes of a 50-mL PAM solution by exposure to UV irradiation for 30 minutes were measured. About 15 to 20 °C temperature increase and less than 1% evaporation loss were observed. All samples were tested in triplicates.
The study indicates that both total organic carbon (Figure 4.17) and UV absorbance at 195 nm (Figure 4.16) (as well as UV spectra) of the polymer samples were not apparently affected by exposure to UV irradiation. It
suggests that total polyacrylamide content was not reduced by UV irradiation.

The results of acrylamide residual tests for C-3280 by exposure to UV irradiation, chlorine, permanganate, and their combinations for 30 minutes are compared in Figure 4.18. The 10 µg/L ACM standard spiked in each sample has been subtracted from the results. The study on acrylamide residuals showed that UV irradiation had minimal effects on the level of ACM residuals. Although a slight increase was observed, it is uncertain that this increase was because of UV irradiation or random error. A slight reduction of acrylamide residuals (less than 10%) in the polymer solution was observed by exposure to 15 mg/L chlorine. However, the coupling effects of chlorine with UV irradiation dramatically reduced ACM residuals by about 90%. Exposure to 6 mg/L potassium permanganate for 30 minutes totally removed acrylamide residuals in the polymer solution, and similar results were obtained for combination of permanganate with UV and/or chlorine.
The impact of UV irradiation on chlorine/permanganate oxidation of PAMs was tested based on oxidant residuals. Three different oxidant doses were applied: 5, 10, 15 mg/L of Cl₂ or 2, 4, 6 mg/L of KMnO₄. Examples of the results are shown in Figures 4.19 and 4.20. As shown, UV irradiation dramatically increased the amount of oxidant consumption in a fixed exposure time when compared to the oxidant consumption with no UV exposure. In another sense, UV irradiation increased the reaction rates dramatically. The results from other oxidant doses showed a similar pattern. Although the exact mechanism is unknown, one possible reason is that the heat absorbed by PAM solutions increased the temperature of the solutions.
by about 15 to 20 °C, thus accelerating the chemical reactions. Another possible reason is that the energy from UV irradiation destroyed chemical bonds in PAM (i.e. C-C, C-O, or C-H) and generated polymer radicals which participated in free radical reactions with oxidants.

![Figure 4.19 Comparison of the amount of chlorine consumed during oxidation of three PAMs (10 mg/L) with free chlorine (15 mg/L) only and its combination with UV irradiation for 30 minutes](image)

**Figure 4.19** Comparison of the amount of chlorine consumed during oxidation of three PAMs (10 mg/L) with free chlorine (15 mg/L) only and its combination with UV irradiation for 30 minutes.
Figure 4.20 Comparison of the amount of permanganate consumed during oxidation of three PAMs (10 mg/L) with KMnO₄ (4 mg/L) only and its combination with UV irradiation for 30 minutes

In summary, UV irradiation didn’t result in loss of either total PAM content or acrylamide residuals. However, it accelerated the degradation reactions caused by chlorine or permanganate.

3. Polymer Flocculation Performance

The flocculation performance of the PAMs was tested based on the settling rate of kaolin slurry. This method is easy to handle and control, however, it is quite different from typical conditions and can only be used as an indicator for the true flocculation performance. In addition, the sensitivity and reproducibility of method are not very high, thus the tests were conducted in triplicate or until stable results were obtained. Example data are given in Table 4.3.
Table 4.3 Comparison of the flocculation performance of the PAMs before and after oxidation with free chlorine (10 mg/L) or potassium permanganate (4 mg/L)

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>N-3300</th>
<th>A-3333</th>
<th>C-3280</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Dose, mg/L</td>
<td>0.5</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.5% Kaolin Slurry Settling Rate, cm/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank (no polymer)</td>
<td>0.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer Only</td>
<td>4.33</td>
<td>4.73</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>5.20</td>
<td>2.67</td>
<td>3.47</td>
</tr>
<tr>
<td>Polymer &amp; Cl2 (5 min reaction)</td>
<td>4.33</td>
<td>4.67</td>
<td>3.47</td>
</tr>
<tr>
<td></td>
<td>5.36</td>
<td>2.00</td>
<td>2.60</td>
</tr>
<tr>
<td>Polymer &amp; Cl2 (~1hr reaction)</td>
<td>3.47</td>
<td>4.53</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>3.33</td>
<td>2.00</td>
<td>2.60</td>
</tr>
<tr>
<td>Polymer &amp; KMnO4 (5 min reaction)</td>
<td>5.60</td>
<td>7.00</td>
<td>4.47</td>
</tr>
<tr>
<td></td>
<td>7.50</td>
<td>4.00</td>
<td>3.47</td>
</tr>
<tr>
<td>Polymer &amp; KMnO4 (~1hr reaction)</td>
<td>3.47</td>
<td>4.53</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>3.33</td>
<td>2.00</td>
<td>2.60</td>
</tr>
</tbody>
</table>

(note: settling rate was averaged through the settling distance of slurry water interface in the first three minutes)

The flocculation performance of the polymers depended on the dosages applied and type of charge. For example, when 0.5 mg/L polymers were used, the nonionic PAM gave the highest performance, whereas when 1.0 mg/L polymers were applied, the anionic PAM showed the best performance.

Exposure to chlorine or permanganate for one hour resulted in about 20-30 % loss in flocculation performance for any polymer studied, based on settling rates of kaolin slurry. However, exposure in short time (i.e. 5 minutes) didn’t result in significant loss of flocculation performance for the nonionic and anionic PAMs, which even increased in certain situation. For cationic PAM, even short time exposure to chlorine led to loss of flocculation performance.
performance about 25-35 %, which indicated that cationic PAM was more susceptible to oxidation.

4. Policy Significance

The results from chemical degradation of PAMs indicated that when exposed to chlorine or potassium permanganate, especially in the first one or two hours, the cationic PAM was much more reactive than the anionic and nonionic PAMs. Since the reactions between the oxidants and polymers will increase the demand for both chemicals in water treatment, so this type of reactions should be avoided as best as possible during polymer selection. Some simple tests can be run to determine the reactivity of the polymers, for example, oxidant residual test and UV spectra.

The results from photodegradation of PAMs indicated that although total PAM contents were not reduced by exposure to UV, however, the UV did accelerate the chemical reaction rates between oxidants and polymers. Therefore, if possible, direct exposure to sunlight should be avoided, and some types of cover can be built, which also have other benefits such as preventing rains and other types of pollution.

The United States guideline value for application of polyacrylamide products in drinking water treatment is equivalent to 0.5 µg/L acrylamide monomer in water when dosed at 1 mg/L. In this study, the ACM residuals in 10 mg/L PAM solutions were evaluated, thus, the resulted residual should be
divided by 10 to be comparable to the guideline. 26.2 µg/L ACM residual was
found in 10 mg/L C-3280 solution, which is equivalent to 2.6 µg/L ACM
residual when the polymer is dosed at 1 mg/L. This value is well above the
U.S. guideline of 0.5 µg/L acrylamide in water, as well as the U.K. guideline
of 0.1 µg/L acrylamide monomer in drinking water. Although addition of
oxidants reduced the ACM level in water, chlorine has limited effects on
reducing ACM level without combination of UV irradiation. In addition,
chlorine removes bacteria in water which otherwise might degrade ACM
monomer to acrylic acid and ammonia (ICON, 2001). Since chlorine has
been the most widely used disinfectant in drinking water treatment in the
U.S., water treatment industry should be cautious in application of PAMs,
especially for those cationic PAMs which have higher levels ACM residual,
and for those treatment processes which only use chlorine or UV for
pre-oxidation and/or disinfection. Since the most water treatment facilities
don’t have advance analytic instruments (e.g. GC-ECD or HPLC) for testing
acrylamide monomer when selecting PAM products, certification should be
obtained from the manufactures and/or certified labs that the acrylamide
residual in 1ppm PAM aqueous solution does not exceed 0.5 ppb.

The flocculation performance tests indicated that even short time
exposure to chlorine could result in loss of performance for cationic PAM.
When selecting polymer products, the simple polymer performance test
used in this study can be done to evaluate the possible performance change for each polymer caused by oxidants used in the treatment process, and the performance change should be considered with other issues (e.g. costs).
CONCLUSIONS

This study was conducted to evaluate the degradation potential of polyacrylamides (PAMs) when exposed to oxidants and/or UV irradiation in water treatment. The major conclusions are:

(1) The cationic PAM was more susceptible to chemical degradation by exposure to chlorine or permanganate, compared to the nonionic and anionic PAMs studied. However, for any polymer sample, only partial degradation was observed and there was no apparent loss of total polyacrylamide content. The acrylamide monomer in the cationic PAM was higher than the U.S. federal regulation level, however, it can be reduced by exposure to chlorine (less than 10% removal) or permanganate (total removal).

(2) UV irradiation didn’t result in loss of either total PAM content or acrylamide residuals. However, it accelerated the degradation reactions caused by chlorine or permanganate.

(3) The flocculation performance of the polymers depended on the doses applied. Exposure to chlorine or permanganate for one hour resulted flocculation performance loss about 20 to 35% for any polymer studied. However, short time exposure didn’t result in significant loss of flocculation performance for the nonionic and anionic PAMs, which even increased in
certain situation. For cationic PAM, even short time exposure led to loss of flocculation performance about 25-35%.

(4) During selection of polymers for potable water treatment, some simple tests (e.g. oxidant residual test, polymer performance test) used in this study can be done for evaluating the potential degradation of polymers, and highly reactive polymers should be avoided in treatment processes.
RECOMMENDATIONS FOR FUTURE RESEARCH

Because of limited time and funding, this study only evaluated degradation of three PAM samples from one manufacture in simple systems. It is uncertain that whether or not the polymer from other manufactures will exert different properties. Furthermore, the water treatment systems are much more complicated than the studied conditions. Such parameters as temperature, pH, and alkalinity all can affect the chemical reactions. The water matrix is also different, for example, finished drinking water is usually used as water matrix to make polymer solutions in treatment processes. Therefore, here are several suggestions for future studies:

1. Since this study and most other studies used pure water matrix, in the future, tap water and some natural water sources can be used as water matrix, such as surface water, groundwater and sea water;

2. The impact of pH, alkalinity, and some other parameters need to be studied on polymer degradation; and

3. More polymer samples with a variety of molecular weights, charge densities, components, and purities from different polymer manufactures should be studied to compare the degradability of different types of polymers.
REFERENCES


Appendix A: Test of Total Solids

This procedure is to determine the total solids content of solution-, emulsion-, and powder-form PAM products. The procedure is not corrected for inert ingredients. Therefore, it may not give the active polymer content of the sample. The total solids test is based on an oven drying of a sample that leaves a residue of 0.45 ± 0.05 g.

1. Apparatus
   1.1 Analytical balance.
   1.2 Aluminum weighing dishes.
   1.3 Dropper pipettes or syringes, glass or plastic, 1 mL to 10 mL.
   1.4 Lab spoon, aluminum.
   1.5 Forced draft oven, capable of maintaining temperature at ±2°C of set point.
   1.6 Desiccator and desiccant.

2. Procedure
   2.1 Heat aluminum dish in oven at 105°C for a minimum of 1 hr, remove and cool in a desiccator.
   2.2 Record tare weight of dried aluminum weighing dish to nearest 0.0001 g.
   2.3 Add about 0.5 g powder-form PAM products into the aluminum weighing dish and record the total weight of the sample plus the weighing dish to the nearest 0.0001 g. For emulsion-form PAM products, add approximately 2 g using dropper pipettes or syringe. For solution-form PAM products, add approximately 10 g. Spread the sample over the surface of the aluminum weighing dish to avoid formation of a crust during drying. It may be necessary to add 3 mL to 5 mL of deionized water to assist spreading.
   2.4 Place the aluminum weighing dish containing the weighted sample in a 105°C -110°C forced draft oven for 3 hr. for emulsion- or solution-form PAM products, drying overnight (24 hr).
   2.5 Remove aluminum dish from the oven and cool in a desiccator. Weigh the cooled dish to the nearest 0.0001 g.

3. Calculation
   \[
   \text{\% total solids} = \left( \frac{\text{weight of dish + dried sample}}{\text{weight of dish + initial sample}} - \frac{\text{weight of empty dish}}{} \right) \times 100\%
   \]
**Note**
1. Samples should be run in duplicate.
2. Difference between duplicate samples should be less than $\pm 0.5$ percent.
   If greater than $\pm 0.5$ percent, the test should be rerun.

**Reference**
AWWA Standard for Polyacrylamide, 2001
Appendix B: Test of Chlorine

This method uses iodine titration to test chlorine residuals in water. Chlorine will liberate free iodine from potassium iodine (KI) solutions at pH 8 or less. The liberated iodine is titrated with a standard solution of sodium thiosulfate (Na$_2$S$_2$O$_3$) with starch as the indicator. Titrate at pH 3 to 4 because the reaction is not stoichiometric at neutral pH due to partial oxidation of thiosulfate to sulfate. The interferences of this method include other oxidizing and reducing agents, sulfuric acid, hydrochloric acid, etc. The concentrations of chlorine below 1 mg/L cannot be measured accurately by this method.

1. Reagents
   1.1 Acetic acid, conc. (Fisher)
   1.2 Potassium iodine, KI, crystals (Fisher)
   1.3 Standard sodium thiosulfate, 0.025 N (HACH)
   1.4 Standard sodium thiosulfate, 0.001 N: diluted from 0.025 N standard solution
   1.5 Starch indicator (HACH)
   1.6 Iodine solution, 0.0282 N

2. Procedure
   2.1 Preparation for titration: Place 1 mL acetic acid or enough to reduce the pH to between 3.0 and 4.0. Add about 0.1 g KI and about 20 mL nanopure water. Then put in 10 mL sample into the beaker.
   2.2 Titration: Add 0.001 N standard Na$_2$S$_2$O$_3$ solution from a buret until the yellow color of the liberated iodine almost is discharged. Add several drops of starch indicator and titrate until blue color is discharged. Record the volume of Na$_2$S$_2$O$_3$ used (A).
   2.3 Blank titration: Substitute 10 mL sample with 10 mL nanopure water. If blue color developed, follow the same titration method as sample test, and record the volume of Na$_2$S$_2$O$_3$ used (-B). If no blue color developed, titrate with 0.0282 N iodine solution until a blue color appears, then back titrate with 0.025 N Na$_2$S$_2$O$_3$ solution and record the difference (+B).

3. Calculation

   \[ \text{mg Cl as Cl}_2/L = (A \pm B) \times N \times 35450/\text{mL sample} \]

Reference
Appendix C: Test of Permanganate

This method is a direct determination of aqueous potassium permanganate solutions. The concentration is directly proportional to the absorbance as measured at 525 nm using a spectrophotometer. The interferences include turbidity and manganese dioxide.

1. Apparatus
   1.1 Spectrophotometer with 5-mm sample cell (HACH)
   1.2 Filters, 0.22 μm
   1.3 Filtration apparatus

2. Reagents
   2.1 Sulfuric acid, H₂SO₄, 20%: Add 20 g H₂SO₄ slowly, with stirring, to 80 mL nanopure water. After cooling, adjust volume to 100 mL.
   2.2 Calcium chloride solution, CaCl₂, 1 M:
   2.3 Sodium oxalate, Na₂C₂O₄ (Fisher)
   2.4 Sodium thiosulfate solution, Na₂S₂O₃, 0.025 N (HACH)
   2.5 Potassium permanganate standard, KMnO₄, 0.006 M: Dissolve 1.000 g KMnO₄ in nanopure water and dilute to 1000 mL. Standardize as follow: Accurately weigh about 0.1 g sodium oxalate and dissolve it in 150 mL nanopure water in a 250-mL Erlenmeyer flask. Add 20 mL 20% H₂SO₄ and heat to 70 to 80 °C. Titrate the warm oxalate solution with potassium permanganate standard until a pink coloration persists (60 s). Calculate the potassium permanganate concentration:

   \[
   \text{mg KMnO}_4/L = \left(\frac{W \times 1000}{2.1197 \times V}\right)
   \]

   where: \( W \) = weight of sodium oxalate, mg, and \( V \) = mL KMnO₄ titrant.

3. Procedure
   3.1 Calibration of equipment: Prepare calibration curve by diluting standardized potassium permanganate solution. Make dilutions at 0, 2.5, 5, 7.5, 10 mg/L KMnO₄ and measure the absorbance at 525 nm. Plot absorbance (y axis) versus KMnO₄ concentration and calculate a best-fit line through the points.
   3.2 Potassium permanganate analysis: Check zero on spectrophotometer at 525 nm with nanopure water. If the water is soft, add 1 mL CaCl₂ solution/L sample to aid in removal of any colloidal manganese dioxide and suspended solids. Pass 20 mL sample through a 0.22 μm filter. Rinse spectrophotometer cell twice with portions of filtrate. Fill cell and check that no air
bubbles are present in the solution or on the sides of the cell. Measure absorbance at 525 nm and record the result (A). To 100 mL sample, add 0.1 mL CaCl$_2$ solution. Add 0.1 mL sodium thiosulfate solution per 1 mg/L KMnO$_4$. Pass through a 0.22 µm filter and measure absorbance (B).

4. Calculation

Corrected absorbance = A – B

Where: A = absorbance of sample, and
      B = absorbance of blank.

Reference
Appendix D: Test of Acrylamide by GC-ECD

1. Introduction
This method is used to determine trace amounts of acrylamide monomer in aqueous matrices. The procedure is based on bromination of the acrylamide double bond. The reaction product (2,3-dibromopropionamide) is extracted from the reaction mixture with ethyl acetate, after salting out sodium sulfate. The extract reacts with triethylamine to form more stable 2-bromo-propenamide, which can be analyzed by gas chromatography with electron capture detection (GC/ECD) using a capillary column. Figure A-1 illustrates the reaction sequence.

\[
\begin{align*}
 &\text{I: } \text{H}_2\text{C} = \text{C} - \text{NH}_2 \\
 &\text{II: } \text{H}_2\text{C} = \text{C} - \text{NH}_2 \\
 &\text{III: } \text{H}_2\text{C} = \text{C} - \text{NH}_2
\end{align*}
\]

Figure A-1 Reaction sequence showing conversion of acrylamide (adapted from Raymer, et al., 1993)

2. Apparatus and Materials
2.1 Gas chromatography system
2.1.1 Gas chromatography (Hewlett-Packard 5890 Series II)
2.1.2 GC column: DB-WAXter capillary column (30 m, 0.25 µm I.D., df = 0.25 µm) (J & W Scientific).
2.1.3 Detector: electron capture detector.
2.2 Separatory funnel, 250-mL.
2.3 Flasks with glass stoppers, 100-mL.
2.4 Amber glass vial, 40-mL.
2.5 Glass vial, 20-mL.
2.6 Microsyringes: 5-µL.
2.7 Pipets.

3. Reagents
3.1 Deionized water.
3.2 Solvent.
3.2.1 Ethyl acetate, HPLC grade (Fisher).
3.2.2 Methanol, HPLC grade (Fisher).
3.3 Saturated bromine water (Fisher)
3.4 Sodium sulfate (anhydrous): Preheat at 400°C for 4 hours in a shallow tray.
Appendix D (Continued)

3.5 Sodium thiosulfate, 1 M aqueous solution, prepared from powder form.
3.6 Potassium bromide (Fisher).
3.7 Hydrobromic acid, 20% (Fisher).
3.8 Acrylamide, > 99% purity (Sigma-Aldrich).
3.9 Stock standard solution, 1000 mg/L
   Dissolve (100 mg)/(% purity) of acrylamide monomer in deionized water in a 100-mL volumetric flask, and dilute to the mark with DI water. Reverse to mix.
3.10 Calibration standards
   Dilute the acrylamide stock solution with DI water to produce standard solutions containing 0, 5.0, 10.0, 50.0, 100 \( \mu \text{g/L} \) of acrylamide.
3.11 Triethylamine, HPLC grade (Fisher)

4. Procedure
4.1 Bromination
   4.1.1 Pipet 50 mL of sample into a 100-mL glass-stoppered flask. Dissolve 7.5 g of potassium bromide into the sample, with stirring.
   4.1.2 Adjust the pH of the solution with hydrobromic acid until the pH is between 1 and 3.
   4.1.3 Wrap the flask with aluminum foil in order to exclude light. Add 2.5 mL saturated bromine water, with stirring. Store the flask and contents in the dark, at 0\(^{\circ}\)C, for at least 1 hour.
   4.1.4 After reaction, decompose the excess of bromine by adding 1 M sodium thiosulfate solution, drop by drop, until the solution becomes colorless.
   4.1.5 Add 15 g sodium sulfate and stirring vigorously using a magnetic stirrer.
4.2 Extraction
   4.2.1 Transfer the solution into a 250-mL separatory funnel. Rinse the reaction flask with 2-mL DI water. Transfer the rinses into the separatory funnel.
   4.2.2 Extract the aqueous solution with 10 mL ethyl acetate. Shake vigorously for 2 minutes. Drain the bottom layer (water layer) into original sample flask, and remove the ethyl acetate layer to a 40-mL glass vial. Extract the aqueous phase again with 10-mL ethyl acetate. Combine the organic extracts and dry with 1 g anhydrous sodium sulfate.
   4.2.3 Transfer 5 mL dried organic phase to a 20-mL glass vial and add 100 \( \mu \text{L} \) triethylamine.
Appendix D (Continued)

4.3 Gas chromatography conditions
  Carrier gas: He, 12 psi
  Makeup gas for ECD: N₂
  Column temperature: 100 °C (0 min) – 12 °C/min – 240 °C, initial hold 0.1 min
  Detector: ECD
  Injector temperature: 250°C
  Detector temperature: 300°C
  Injection volume: 1µL

4.4 Calibration
  4.5.1 Inject 1 µL of a method blank (deionized water carried through bromination and extraction procedures) into the GC.
  4.5.2 Brominate and extract each standard acrylamide solution and injection 1 µL of each into the GC, record the instrument response.
  4.5.3 Plot the response as a function of concentration in aqueous sample. Obtain calibration equations from the calibration curve.

4.5 Sample analysis
  Inject 1 µL of each sample extract into the gas chromatography, and record the response. Calculate the concentration using the equation obtained from calibration curve.

Reference
Appendix E: Material Safety Data Sheet

MATERIAL SAFETY DATA SHEET

1. IDENTIFICATION OF THE PRODUCT AND THE COMPANY

CLARIFLOC® N-3300P POLYMER

Supplier: POLYDYNE INC.
PO Box 279
Ricoboro, GA 31323
Tel: 800-848-7659  Fax: 912-884-8770

2. COMPOSITION/INFORMATION ON INGREDIENTS


The product is not considered hazardous in accordance with OSHA Federal Regulation 29 CFR 1910.1200.

3. HAZARDS IDENTIFICATION

Aqueous solutions or powders that become wet render surfaces extremely slippery.

4. FIRST AID MEASURES

Inhalation: Move to fresh air.
Skin contact: Wash with water and soap as a precaution. In case of persistent skin irritation, consult a physician.
Eye contact: Rinse thoroughly with plenty of water, also under the eyelids. In case of persistent eye irritation, consult a physician.
Ingestion: The product is not considered toxic based on studies on laboratory animals.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media: Water, water spray, foam, carbon dioxide (CO2), dry powder
Special fire-fighting precautions: Aqueous solutions or powders that become wet render surfaces extremely slippery.
Protective equipment for firefighters: No special protective equipment required.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions: No special precautions required.
Appendix E (Continued)

CLARIFLOC® N-3300P POLYMER

Environmental precautions
Do not contaminate water.

Methods for cleaning up
Do not flush with water. Clean up promptly by sweeping or vacuum. Keep in suitable and closed containers for disposal. After cleaning, flush away traces with water.

7. HANDLING AND STORAGE

Handling
Avoid contact with skin and eyes. Avoid dust formation. Do not breathe dust. Wash hands before break and at the end of workday.

Storage
Keep in a dry, cool place (0-30°C).

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering controls
Use local exhaust if dusting occurs. Natural ventilation is adequate in absence of dusts.

Personal protection equipment

- Respiratory protection
  Dust safety masks are recommended where concentration of total dust is more than 10 mg/m³.

- Hand protection
  Rubber gloves.

- Eye protection
  Safety glasses with side-shields. Do not wear contact lenses.

- Skin protection
  Chemical resistant apron or protective suit if splashing or repeated contact with solution is likely.

Hygiene measures
Wash hands before breaks and at the end of workday. Handle in accordance with good industrial hygiene and safety practice.

9. PHYSICAL AND CHEMICAL PROPERTIES

Form
Granular solid

Color
White

Odor
None

pH:
4 - 6 @ 5 g/l polymer. See Technical Bulletin for specific value.

Melting point (°C)
Not applicable.

Flash point (°C)
Not applicable.

Autoignition temperature (°C)
Not applicable.

Vapour pressure (mm Hg)
Not applicable.
Appendix E (Continued)

CLARIFLOC® N-3300P POLYMER

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**10. STABILITY AND REACTIVITY**

**Stability:**
Product is stable. No hazardous polymerization will occur.

Oxidizing agents may cause exothermic reactions.

**Hazardous decomposition products**
Thermal decomposition may produce: nitrogen oxides (NOx), carbon oxides.

**11. TOXICOLOGICAL INFORMATION**

**Acute toxicity**
- **Oral:** LD50/dermal/rat > 5000 mg/kg

- **Dermal:** The results of testing on rabbits showed this material to be non-toxic even at high dose levels.

- **Inhalation:** The product is not expected to be toxic by inhalation.

**Irritation**
- **Skin:** The results of testing on rabbits showed this material to be non-irritating to the skin.

- **Eyes:** Testing conducted according to the Draize technique showed the material produces no corneal or iridal effects and only slight transient conjunctival effects similar to those which all granular materials have on conjunctivae.

**Sensitization:** The results of testing on guinea pigs showed this material to be non-sensitizing.

**Chronic toxicity:** A two-year feeding study on rats did not reveal adverse health effects. A one-year feeding study on dogs did not reveal adverse health effects.

**12. ECOLOGICAL INFORMATION**

- **Fish:** LC50/Danio rerio/96hr > 100 mg/L (OECD 203)

- **Algae:** EC50/Chlorella vulgaris/72hr > 100 mg/L (OECD 201)

- **Daphnia:** EC50/Daphnia magna/48hr > 100 mg/L (OECD 202)
Appendix E (Continued)

CLARIFLOC® N-3300P POLYMER

Environmental fate:
LogP ow: 0
Bioaccumulation: Does not bioaccumulate.
Persistence / degradability: Not readily biodegradable

13. DISPOSAL CONSIDERATIONS

Waste from residues / unused products: In accordance with federal, state and local regulations.

Contaminated packaging:
Rinse empty containers with water and use the rinse water to prepare the working solution. Can be landfilled or incinerated, when in compliance with local regulations.

14. TRANSPORT INFORMATION

Not regulated by DOT.

5. REGULATORY INFORMATION

All components of this product are on the TSCA and DSL inventories.

RCRA status: Not a hazardous waste.
Hazardous waste number: Not applicable
Reportable quantity (40 CFR 352): Not applicable
Threshold planning quantity (40 CFR 353): Not applicable

California Proposition 65 information:
The following statement is made in order to comply with the California Safe Drinking Water and Toxic Enforcement Act of 1986: This product contains a chemical(s) known to the State of California to cause cancer: residual acrylamide.

EMIS & NIEA Ratings

- Health: 1.1.1
- Flammability: 1
- Reactivity: 0

NEPA

1

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### 1. IDENTIFICATION OF THE PRODUCT AND THE COMPANY

**CLARIFLOC® A-3333P POLYMER**

**Supplier:**
POLYDYNE INC.
PO Box 279
Riceboro, GA 31323
Tel: 800-848-7659  Fax: 912-884-8770

### 2. COMPOSITION/INFORMATION ON INGREDIENTS

Identification of the preparation: Anionic water-soluble polymer

### 3. HAZARDS IDENTIFICATION

Aqueous solutions or powders that become wet render surfaces extremely slippery

### 4. FIRST AID MEASURES

<table>
<thead>
<tr>
<th>Condition</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inhalation</td>
<td>Move to fresh air.</td>
</tr>
<tr>
<td>Skin contact</td>
<td>Wash with water and soap as a precaution. In case of persistent eye irritation, consult a physician.</td>
</tr>
<tr>
<td>Eye contact</td>
<td>Rinse thoroughly with plenty of water, also under the eyelids. In case of persistent eye irritation, consult a physician.</td>
</tr>
<tr>
<td>Ingestion</td>
<td>The product is not considered toxic based on studies on laboratory animals.</td>
</tr>
</tbody>
</table>

### 5. FIRE-FIGHTING MEASURES

<table>
<thead>
<tr>
<th>Condition</th>
<th>Action</th>
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</thead>
<tbody>
<tr>
<td>Suitable extinguishing media</td>
<td>Water, water spray, foam, carbon dioxide (CO2), dry powder</td>
</tr>
<tr>
<td>Special fire-fighting precautions</td>
<td>Aqueous solutions or powders that become wet render surfaces extremely slippery</td>
</tr>
<tr>
<td>Protective equipment for firefighters</td>
<td>No special protective equipment required</td>
</tr>
</tbody>
</table>

### 6. ACCIDENTAL RELEASE MEASURES

<table>
<thead>
<tr>
<th>Condition</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Personal precautions</td>
<td>No special precautions required.</td>
</tr>
<tr>
<td>Environmental precautions</td>
<td>Do not contaminate water.</td>
</tr>
<tr>
<td>Methods for cleanup</td>
<td>Do not flush with water. Clean up promptly by sweeping or vacuum. Keep in suitable and closed containers for disposal. After cleaning, flush away traces with water.</td>
</tr>
</tbody>
</table>
Appendix E (Continued)

7. HANDLING AND STORAGE

Handling  Avoid contact with skin and eyes. Avoid dust formation. Do not breathe dust. Wash hands before breaks and at the end of workday.

Storage  Keep in a dry, cool place (0-35°C).

18. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering controls  Use local exhaust if dusting occurs. Natural ventilation is adequate in absence of dusts.

Personal protective equipment

- Respiratory protection  Dust safety masks are recommended where concentration of total dust is more than 10 mg/m³.
- Hand protection  Rubber gloves.
- Eye protection  Safety glasses with side-shields. Do not wear contact lenses.
- Skin protection  Chemical resistant apron or protective suit if splashing or contact with solution is likely.

Hygiene measures  Wash hands before breaks and at the end of workday. Handle in accordance with good industrial hygiene and safety practice.

9. PHYSICAL AND CHEMICAL PROPERTIES

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Form</td>
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<tr>
<td>pH:</td>
<td>4-9 @ 5 g/l</td>
</tr>
<tr>
<td>Melting point (°C)</td>
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<tr>
<td>Flash point (°C)</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Autoignition temperature (°C)</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Vapour pressure (mm Hg)</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Bulk density</td>
<td>See Technical Bulletin</td>
</tr>
<tr>
<td>Water solubility</td>
<td>See Technical Bulletin</td>
</tr>
<tr>
<td>Viscosity (mPa s)</td>
<td>See Technical Bulletin</td>
</tr>
</tbody>
</table>
10. STABILITY AND REACTIVITY

**Stability:** Product is stable. No hazardous polymerization will occur.

**Conditions to avoid:** Oxidizing agents may cause exothermic reactions

**Hazardous decomposition products:** Thermal decomposition may produce: nitrogens oxides (NOx), carbon oxides

11. TOXICOLOGICAL INFORMATION

**Acute toxicity:**
- Oral: LD50/oral/rat > 5000 mg/kg
- Dermal: The results of testing on rabbits showed this material to be non-toxic even at high dose levels.
- Inhalation: The product is not expected to be toxic by inhalation.

**Irritation:**
- Skin: The results of testing on rabbits showed this material to be non-irritating to the skin.
- Eyes: Testing conducted according to the Draize technique showed the material produces no corneal or iridal effects and only slight transient conjunctival effects similar to those which all granular materials cause on contact.

**Sensitization:** The results of testing on guinea pigs showed this material to be non-sensitising.

**Chronic toxicity:** A two-year feeding study on rats did not reveal adverse health effects. A two-year feeding study on dogs did not reveal adverse health effects.

12. ECOLOGICAL INFORMATION

- **Fish:** LC50/Danio rerio/96 hr > 100 mg/L (OECD 203) (Based on results obtained from tests of analogous products.)
- **Algae:** EC50/Scenedesmus subspicatus/72hr > 100 mg/L (OECD 201) (Based on results obtained from tests of analogous products.)
- **Daphnia:** EC50/Daphnia magna/48 hr > 100 mg/L (OECD 202) (Based on results obtained from tests of analogous products.)

**Bioaccumulation:** Does not bioaccumulate.

**Persistence / degradability:** Not readily biodegradable.

13. DISPOSAL CONSIDERATIONS
Appendix E (Continued)

CLARIFLOC® A-3333P POLYMER

Waste from residues / unused products
In accordance with federal, state and local regulations.

Contaminated packaging
Rinse empty containers with water and use the rinse water to prepare the working solution. Can be landfilled or incinerated, when in compliance with local regulations.

14. TRANSPORT INFORMATION

Not regulated by DOT.

15. REGULATORY INFORMATION

All components of this product are on the TSCA and DSL inventories.

RCRA status
Not a hazardous waste.

Hazardous waste number
Not applicable

Reportable quantity (40 CFR 302)
Not applicable

Threshold planning quantity (40 CFR 355)
Not applicable

California Proposition 65 Information
The following statement is made in order to comply with the CA Safe Drinking Water and Toxic Enforcement Act of 1986. This product contains a chemical known to the State of California to cause cancer: residual acrylamide.

<table>
<thead>
<tr>
<th>HMR &amp; NFPA Ratings</th>
<th>NFPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Health</td>
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<tr>
<td>Flammability</td>
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</tr>
<tr>
<td>Reactivity</td>
<td>0</td>
</tr>
</tbody>
</table>

16. OTHER INFORMATION

Person to contact
Regulatory Affairs Manager
Appendix E (Continued)

MATERIAL SAFETY DATA SHEET

1. IDENTIFICATION OF THE PRODUCT AND THE COMPANY

CLARIFLOC® C-3280 POLYMER

POLYDYNE INC.
PO Box 279
Riceboro, GA 31323
Tel: 900-940-7656 Fax: 912-984-8770

2. COMPOSITION/INFORMATION ON INGREDIENTS

Identification of the preparation: Cationic water-soluble polymer.

The product is not considered hazardous in accordance with OSHA Federal Regulations 29 CFR 1910.1200.

3. HAZARDS IDENTIFICATION

Aqueous solutions or powders that become wet render surfaces extremely slippery.

4. FIRST AID MEASURES

Inhalation: Move to fresh air.

Skin contact: Wash with water and soap as a precaution. In case of persistent skin irritation, consult a physician.

Eye contact: Rinse thoroughly with plenty of water, also under the eyelids. In case of persistent eye irritation, consult a physician.

Ingestion: The product is not considered toxic based on studies on laboratory animals.

5. FIRE-FIGHTING MEASURES

Suitable extinguishing media: Water, water spray, foam, carbon dioxide (CO2), dry powder

Special fire-fighting precautions: Aqueous solutions or powders that become wet render surfaces extremely slippery.

Protective equipment for firefighters: No special protective equipment required.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions: No special precautions required.

Environmental precautions: Do not contaminate water.
Appendix E (Continued)

Methods for cleaning up

Do not flush with water. Clean up promptly by scoop or vacuum. Keep in suitable and closed containers for disposal. After cleaning, flush away traces with water.

7. HANDLING AND STORAGE

Handling
Avoid contact with skin and eyes. Avoid dust formation. Do not breathe dust. Wash hands before breaks and at the end of workday.

Storage:
Keep in a dry, cool place (0 - 35°C).

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering controls
Use local exhaust if dusting occurs. Natural ventilation is adequate in absence of dusts.

Personal protective equipment

- Respiratory protection
  Dust safety masks are recommended where concentration of total dust is more than 10 mg/m³.

- Hand protection:
  Rubber gloves.

- Eye protection:
  Safety glasses with side-shields. Do not wear contact lenses.

- Skin protection
  Chemical resistant apron or protective suit if splashing or contact with solution is likely.

Hygiene measures
Wash hands before breaks and at the end of workday. Handle in accordance with good industrial hygiene and safety practice.

9. PHYSICAL AND CHEMICAL PROPERTIES

Form: granular solid

Color: white

Odor: none

pH: 2.5 - 4.3 @ 5g/l for product series. See Technical Bulletin for specific value.

Melting point (°C): Not applicable.

Flash point (°C): Not applicable.

Autoignition temperature (°C): Not applicable.

Vapour pressure (mm Hg): Not applicable.

Bulk density: See Technical Bulletin

Water solubility: See Technical Bulletin
## Appendix E (Continued)

**CLARIFLOC® C-3280 POLYMER**

<table>
<thead>
<tr>
<th>Viscosity (mPa.s)</th>
<th>See Technical Bulletin</th>
</tr>
</thead>
</table>

### 10. STABILITY AND REACTIVITY

**Stability:**  
Product is stable, no hazardous polymerization will occur.  
Oxidizing agents may cause exothermic reactions.

**Hazardous decomposition products:**  
Thermal decomposition may produce hydrogen chloride gas, nitrogen oxides (NOx), carbon oxide.

### 11. TOXICOLOGICAL INFORMATION

#### Acute toxicity

- **Oral:**  
  L50 oral/rat > 5000 mg/kg

- **Dermal:**  
The results of testing on rabbits showed this material to be non-toxic even at high dose levels.

- **Inhalation:**  
The product is not expected to be toxic by inhalation.

#### Irritation

- **Skin:**  
The results of testing on rabbits showed this material to be non-irritating to the skin.

- **Eyes:**  
  Testing conducted according to the Draize technique showed the material produces no corneal or iridal effects and only slight transitory conjunctival effects similar to those which all granular materials have on conjunctiva.

#### Sensitization

- **Sensitization:**  
The results of testing on guinea pigs showed this material to be non-sensitizing.

#### Chronic toxicity

- **A two-year feeding study on rats did not reveal adverse health effects. A one-year feeding study on dogs did not reveal adverse health effects.**

### 12. ECOLOGICAL INFORMATION

**Ecotoxicity:**

The effects of this product on aquatic organisms are rapidly mitigated through hydrolysis and by the presence of dissolved organic carbon in the aquatic environment.

- **Fish:**  
  LC50/Danio rerio/96 hr = 5-10 mg/L (OECD 203)

- **Algae:**  
  Algal inhibition tests are not appropriate. The flocculating characteristics of the product interfere directly in the test medium preventing homogeneous distribution which invalidates the test.
Appendix E (Continued)

CLARIFLOC® C-3280 POLYMER

- Daphnia : EC50/Daphnia magna 48 hr = 20-50 mg/L (OECD 202)

Environmental fate:

Log Pow = 0

Bioaccumulation : Do not bioaccumulate.

13. DISPOSAL CONSIDERATIONS

| Waste from residues | In accordance with federal, state and local regulations. |
| unused products     |                                                                 |

Contaminated packaging: Rinse empty containers with water and use the rinse water to prepare the working solution. Can be landfilled or incinerated, when in compliance with local regulations.

14. TRANSPORT INFORMATION

Not regulated by DOT.

15. REGULATORY INFORMATION

All components of this product are on the TSCA and DSL inventories.

RCRA status: Not a hazardous waste.

Hazardous waste number: Not applicable

Reportable quantity (40 CFR 392): Not applicable

Threshold planning quantity (40 CFR 355): Not applicable

California Proposition 65 Information: The following statement is made in order to comply with the California Safe Drinking Water and Toxic Enforcement Act of 1986: This product contains a chemical(s) known to the State of California to cause cancer: residual Acrylamide
Appendix E (Continued)

CLARIFLOC® C-3280 POLYMER

<table>
<thead>
<tr>
<th>HMIS &amp; NFPA Ratings</th>
<th>NFPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Health</td>
<td>1</td>
</tr>
<tr>
<td>Flammability</td>
<td>1</td>
</tr>
<tr>
<td>Reactivity</td>
<td>0</td>
</tr>
</tbody>
</table>

16. OTHER INFORMATION

Person to contact: Regulatory Affairs Manager

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guide for safe handling, use, processing, storage, transportation, disposal and release, and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process unless specified in the text.
Appendix F Data and Graphs

Figure F-1 Decline of permanganate residuals when reacting with 10 ppm PAM solutions (KMnO₄ dosed at 6 ppm)

Figure F-2 Decline of permanganate residuals when reacting with 10 ppm PAM solutions (KMnO₄ dosed at 4 ppm)
Figure F-3 Decline of permanganate residuals when reacting with 10 ppm PAM solutions (KMnO₄ dosed at 2 ppm)

Figure F-4 Decline of chlorine residuals when reacting with 10 ppm PAM solutions (Cl₂ dosed at 10 ppm)
Appendix F (Continued)

Figure F-5 Decline of chlorine residuals when reacting with 10 ppm PAM solutions (Cl₂ dosed at 5 ppm)

Figure F-6 Comparison of chlorine consumed in 30 minutes for three PAMs with and without the effects of UV (Cl₂ dosed at 5 ppm)
Figure F-7 Comparison of chlorine consumed in 30 minutes for three PAMs with and without the effects of UV (Cl₂ dosed at 10 ppm)

Figure F-8 Comparison of KMnO₄ consumed in 30 minutes for three PAMs with and without the effects of UV (KMnO₄ dosed at 2 ppm)
Appendix F (Continued)

Figure F-9 Comparison of KMnO₄ consumed in 30 minutes for three PAMs with and without the effects of UV (KMnO₄ dosed at 6 ppm)

Figure F-10 Chromatogram of acrylamide residual in 10 ppm C-3280 (spiked with 10 ppb ACM standard) after exposure to UV for 30 min

Migration Time: 10.400 min
Peak Area: 295396
Conc.: 37.3 ppb (contain 10 ppb ACM standard)
Analyzed by GC-ECD
Figure F-11 Chromatogram of acrylamide residual in 10 ppm C-3280 (spiked with 10 ppb ACM standard) after exposure to UV and 6 ppm KMnO$_4$ for 30 min

Migration Time: 10.400 min
Peak Area: 74796
Conc.: 9.3 ppb (spiked with 10 ppb ACM standard)
Analyzed by GC-ECD

Figure F-12 Chromatogram of acrylamide residual in 10 ppm C-3280 (spiked with 10 ppb ACM standard) after exposure to UV and 15 ppm chlorine for 30 min

Migration Time: 10.400 min
Peak Area: 96388
Conc.: 12.0 ppb (spiked with 10 ppb ACM standard)
Analyzed by GC-ECD