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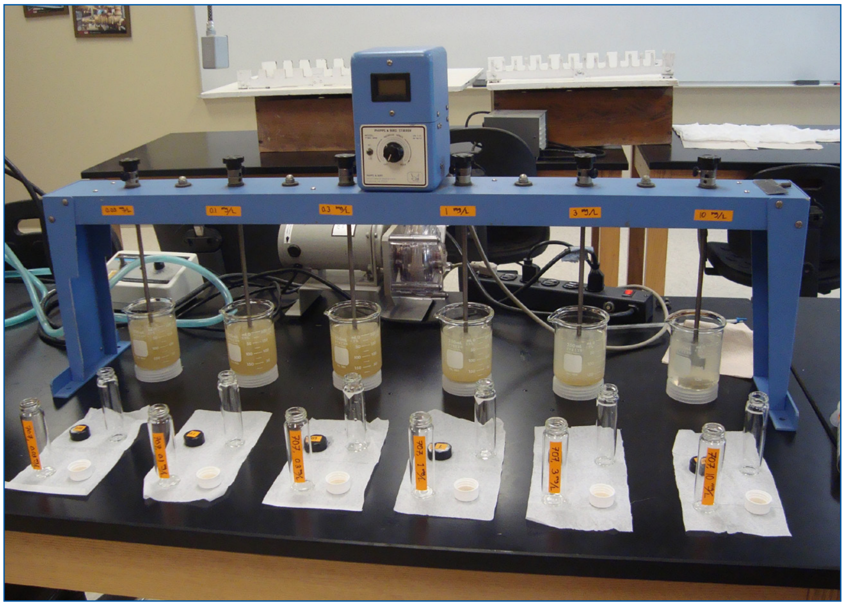
Using Flocculation to Reduce Turbidity of Construction Site Runoff



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Using Flocculation to Reduce Turbidity of Construction Site Runoff

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Disclaimer

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ABSTRACT

Construction of highways usually requires large areas of land disturbance, which may result in accelerated soil erosion. The stormwater runoff from highway construction sites typically contains a large amount of fine particles that are difficult to remove using conventional best management practices. Stormwater with high turbidity levels can negatively affect the water quality of receiving waters and natural habitats of rivers, lakes, and streams. Flocculation with polyacrylamide (PAM) is a promising technology that can be used to reduce the turbidity levels in construction site runoff. The objectives of this study were to determine the effectiveness of different PAMs in reducing turbidity of construction site runoff in South Dakota, and to provide recommendations on PAM applications for stormwater runoff treatment. Four different soils were collected from active construction sites in South Dakota and synthetic runoff was created for each soil. Laboratory flocculation experiments were conducted to evaluate various factors that can affect turbidity reduction from synthetic runoff. The results showed that PAM flocculation effectively reduced turbidity from synthetic runoff. PAMs with higher charge densities and molecular weight generally performed better than PAMs with lower charge densities and molecular weight. The optimum polymer dose was approximately 1 mg/L for anionic PAMs. Cold temperatures negatively affected the PAM flocculation of soil solutions, especially at low dosages. PAM flocculation efficiency increased with increasing mixing intensity, mixing time, and settling time. High calcium and low pH conditions improved PAM flocculation. It is recommended that lab testing of specific soil samples should be performed to determine the optimum PAM type and dosage for construction site runoff treatment. For stormwater runoff treatment under cold temperatures, the PAM dose can be increased to compensate for the loss of flocculation efficiency. Adequate mixing and settling conditions should be provided when using PAM for construction site runoff treatment.

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1. EXECUTIVE SUMMARY

1.1 Introduction

Construction of highways usually requires large areas of land disturbance, which may result in accelerated soil erosion. The stormwater runoff from highway construction sites typically contains a large amount of fine silt and clay particles that are difficult to remove using conventional best management practices (BMPs), such as silt fences, mulching, and sedimentation basins. Stormwater with high turbidity levels can negatively affect the water quality of receiving waters and natural habitats of rivers, lakes, and streams. The turbidity of stormwater runoff from highway construction sites can be affected by many factors, including soil type, site slope, precipitation patterns, and the implemented BMPs. The runoff from construction sites can have turbidity up to several thousand nephelometric turbidity units (NTU), even with the use of conventional BMPs. It is important to develop technologies that can effectively reduce the turbidity of runoff from highway construction sites in order to meet regulatory requirements and protect natural water resources.

Polyacrylamide (PAM) flocculation has been demonstrated to be a cost-effective and practical BMP for erosion and sediment control. PAM is a class of long-chain polymers that vary in net charge, molecular weight, and charge density. PAM can react with fine particles to form larger particles, thereby improving particle removal through sedimentation or filtration. The results of laboratory experiments and field trials suggest that PAM flocculation is effective in reducing turbidity levels of construction runoff. The effectiveness of PAM is affected by many parameters, including soil type, pH, temperature, organic matter, and the type and dose of PAM. The optimum PAM flocculation conditions are site-specific. Therefore, it is critical to investigate the flocculation effectiveness for specific soil types and environmental conditions in order to determine the optimum PAM treatment conditions to achieve low effluent turbidity.

1.2 Research Objectives

The objectives of this study were to determine the effectiveness of different PAMs in reducing turbidity of construction site runoff in South Dakota, and provide recommendations on PAM applications for construction site runoff treatment. In this study, four different soils were collected from active construction sites in South Dakota. Synthetic runoff was created for each soil and laboratory flocculation experiments were conducted to develop an understanding of the PAM's ability to promote flocculation of South Dakota soils. Different PAMs and various PAM doses were evaluated for each runoff sample. In addition, mixing intensity, mixing time, and settling time were also varied during the experiments to determine the required operating conditions for successful PAM flocculation systems. Many of the previous PAM studies focused on relatively warm environments. The impact of low temperatures on PAM effectiveness has not been carefully investigated. A set of flocculation experiments were performed under low temperatures for each runoff sample. Therefore, this research provides an understanding of the low temperature impact on PAM flocculation of the stormwater runoff from highway construction sites. This will have significant implications for the application of PAM in cold regions.

1.3 Research Work

A total of nine anionic and non-ionic PAMs with varying molecular weight and charge density were obtained for this study. Four soil samples were collected from active construction sites in the cities of Aberdeen, Brookings, Rapid City, and Sioux Falls, SD. A synthetic runoff solution designed to mimic actual field conditions was created by mixing each soil sample with distilled water in a column reactor. The runoff solutions were collected after large particles had settled. The initial turbidity of the synthetic runoff was maintained at approximately 1,500 NTU. A standard jar test unit was then used to flocculate the soil solutions with different PAMs under controlled conditions to evaluate turbidity reduction. The flocculation experiments were divided into two phases. In the Phase 1 study, the PAM doses, temperatures, and mixing times were varied to determine their impacts on PAM flocculation. All of the nine PAMs and four soil samples were tested during Phase 1 experiments.

The goal of Phase 2 study was to determine the impact of important water quality parameters and flocculation conditions on PAM flocculation. These factors included the solution pH value, calcium and dissolved organic matter concentrations, and flocculation mixing and settling conditions. One of the PAMs with medium molecular weight and charge density, and Brookings soil sample were selected for the Phase 2 flocculation experiments. The water quality parameters and mixing and settling conditions were varied to simulate a wide range of field PAM flocculation conditions during Phase 2 experiments.

1.4 Research Findings

The flocculation experiment results showed that PAM flocculation is an effective technology to reduce turbidity from simulated construction site runoff. In general, PAMs with higher charge densities and molecular weight performed better than PAMs with lower charge densities and molecular weight. The long-chain polymers in high molecular weight PAMs may have contributed to the effective attachment between soil particles and PAM, which led to higher flocculation efficiency. The optimal polymer dose was approximately 1 mg/L for anionic PAMs. Flocculation with the anionic PAMs at a dose of 1 mg/L was able to reduce the runoff solution turbidity from an initial value of 1,500 NTU to less than 200 NTU after the treatment. Further increasing PAM doses beyond the optimal dose deteriorated the PAM flocculation performance. Nonionic and APS polymers were less effective compared with anionic PAMs at low doses. Cold temperatures negatively affected the PAM flocculation of soil solutions, especially at low doses. However, different PAMs generally achieved similar levels of turbidity reduction at different temperatures when an optimal dose of 1 mg/L was used.

Brookings soil sample and Superfloc A-130 were used to determine the impact of important water quality parameters and flocculation conditions on PAM and soil flocculation. The results showed that the PAM flocculation efficiency increased when increasing the mixing intensity from 50 to 150 rpm. The effects of mixing intensity on turbidity and total suspended solids (TSS) reduction was more pronounced at a PAM dose of 0.1 mg/L than a dose of 1 mg/L. PAM doses lower than the optimal dose require higher mixing intensity to achieve better turbidity and TSS reduction. The turbidity and TSS removal during PAM flocculation was also improved with increasing mixing time. The PAM flocculation efficiency at a dose of 0.1 mg/L showed continuous improvement when increasing mixing time up to 10 minutes. When a PAM dose of 1 mg/L was used, the PAM flocculation process completed within two minutes. Further increasing mixing time at this dose had little impact on turbidity and TSS reduction. The sedimentation process after PAM flocculation generally completed within two minutes for various PAM doses and mixing conditions. After that, further increasing the settling time showed no additional gains in turbidity and TSS reduction.

Adding calcium ions to the solution enhanced PAM flocculation. This trend was most obvious when the runoff was underdosed (< 1 mg/L) or overdosed (>1 mg/L) with polymer. Calcium concentrations has limited impact on PAM flocculation when an optimal dose of 1 mg/L was applied. Within the pH range (5-9) tested, the lower the pH of the runoff solution, the more efficient the flocculation process was. Similar to the calcium addition test, the pH effects on PAM flocculation were more obvious at very low or high PAM doses. Dissolved organic matter in the soil solution had little effect on PAM flocculation.

1.5 Recommendations

The results of this study suggest that PAM flocculation is an effective technology to remove fine particles and reduce turbidity of construction site stormwater runoff. Different PAM behaved differently when treating soil samples collected from four construction sites in South Dakota. Therefore, it is recommended to perform lab testing of specific soil samples to determine the optimum PAM type and dosage for construction site runoff treatment. Although there is an optimal polymer dose to achieve the minimum turbidity of the treated water, this study shows that only a fraction of this dose may be needed to lower the turbidity to the target value. When cold temperatures are present on a construction site, the PAM dose may need to be increased to compensate for the loss of flocculation efficiency. The results of the calcium addition tests indicate that bridging by divalent cations is an important mechanism of soil flocculation using anionic polyacrylamide. When natural divalent cations in the soil are scarce, calcium additions could be used to enhance flocculation or decrease the amount of PAM needed for turbidity reduction. The flocculation experiments of this study also suggest that mixing intensity, mixing time, and settling time are critical factors that can affect final turbidity levels. Increasing mixing intensity, mixing time, and settling time could help achieve better final runoff turbidity, especially when relatively low PAM doses are applied. Therefore, adequate mixing and settling conditions should be provided when using PAM for construction site runoff treatment.

2. INTRODUCTION

2.1 Background

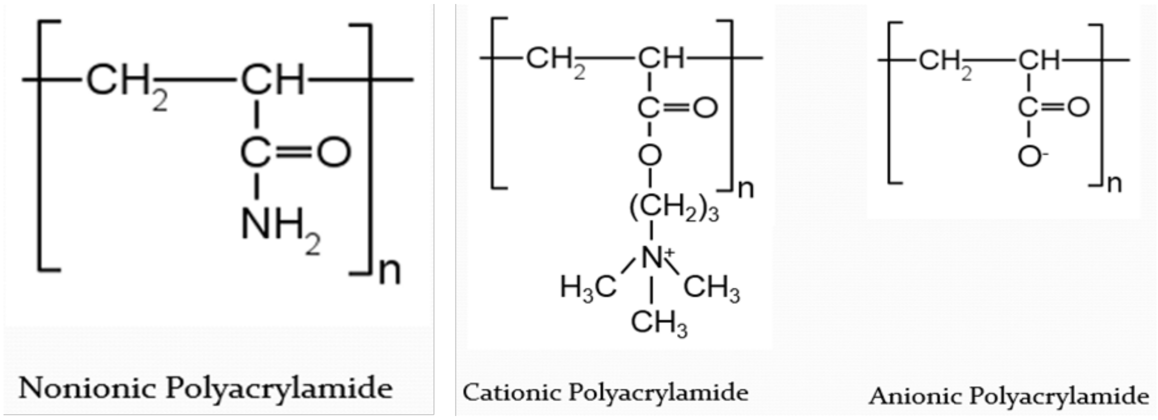
The disturbance of earth and the subsequent increase in migration of soil material in stormwater runoff have caused concerns about the impact of construction activity on water quality. The fine clays and silts carried in runoff leaving a construction site can lead to substantial increases in the turbidity of the receiving water. Turbidity is a measure of the loss of transparency of water due to the suspended solids that it contains, and is measured in nephelometric turbidity units (NTU). In 2009, the Environmental Protection Agency (EPA), as part of updating its National Pollutant Discharge Elimination System (NPDES) permit, proposed a numerical turbidity limit of 280 NTU for stormwater runoff from construction sites. This proposal was eventually withdrawn by the EPA as a result of challenges by stakeholders. However, federal and state agencies have been evaluating the current practices of construction activities regarding runoff water quality. New regulations on turbidity can be potentially proposed in the future.

Current best management practices (BMPs), such as mulching, erosion control blankets, silt fences, rock or fiber check dams, or sedimentation ponds, are generally not effective in controlling turbidity in runoff. McCaleb and McLaughlin (2008) tested a number of different sediment trapping devices on a North Carolina construction site and found that while those devices were effective in reducing the total sediment load in the water leaving the site, even the best discharges had turbidities over 1,000 NTU. Clearly, alternative or supplemental processes need to be implemented in order to lower the turbidity of construction site runoff. One of the most promising technologies is the use of polyacrylamide (PAM), as flocculants to adhere fine soil particles together and quickly settle them out.

2.2 Polyacrylamide

Polyacrylamide comprises very long polymer chains made up of many identical acrylamide monomer units. The length of the molecules gives PAM one of its primary advantages: the ability to attach to multiple particles at once during floc formation. There are three main characteristics that diversify PAM: charge type, charge density (CD), and molecular weight (MW).

Charge type indicates the overall net charge of the polymer chain. PAMs can be cationic (positively charged), nonionic (no net charge), or anionic (negatively charged). The charge of a PAM is determined by the substitution of the amine (NH_2) group on the monomer unit with a cationic or anionic comonomer (Mortimer, 1991) or by using a post-polymerization reaction process. Figure 2.1 shows a single unit in a nonionic, a cationic, and an anionic PAM. For a cationic polymer, the amine group has been substituted with a positively charged comonomer, while for the anionic one, it has been substituted with oxygen, making the overall charge of that monomer unit negative. The second major characteristic of a PAM is its charge density, which is defined as the percent of the monomer units in the polymer chain that have a positive (for cationic) or negative (for anionic) net charge. A PAM that has a CD less than 10% is considered to be low charged, 10% – 30% is moderately charged, and greater than 30% CD is high charged (Barvenik, 1994). A polymer that is nonionic usually has a very low anionic CD (1% – 2%) due to the manufacturing process (Halverson and Panzer, 1980).



Nonionic Polyacrylamide

Cationic Polyacrylamide

Anionic Polyacrylamide

Figure 2.1 Polyacrylamide Monomer Units with Various Charges

Cationic PAMs are typically used in processes such as the flocculation of sewage and industrial wastes, and are used heavily in the paper pulp industry (Barvenik, 1994). They work by attaching directly to negatively charged sites on a particle in suspension and either bridging between multiple particles or reducing the surface charge of the particles to the point where they no longer repel each other (Theng, 1982). However, cationic PAM is also toxic to aquatic life, and specifically to fish. Fish gill damage caused by cationic PAM has been reported in the literature (Biesinger and Stokes, 1986). Therefore, although it is suitable for industrial applications, it cannot be implemented in places open to the environment, including construction sites.

Anionic PAM, on the other hand, has been shown to have very little or no toxicity toward aquatic life, making it much more suitable for widespread environmental applications (Biesinger and Stokes, 1986), including soil conservation in agriculture and construction activities. Most particles suspended in natural water are negatively charged, as is anionic PAM, but there are a few mechanisms by which it can flocculate the particles. The first is the compression of the diffuse double layer of ions that surrounds suspended particles, neutralizing their charge and allowing the PAM to adsorb onto them. For this method to work, usually an additive, such as gypsum, is needed to initiate the compression (Letey, 1994; Shainberg and Levy, 1994). Another possible flocculation mechanism is interparticle bridging. In this case, polyvalent cations, the most common being calcium (Ca^{2+}) and magnesium (Mg^{2+}), form a bridge by neutralizing one negative charge on the particle and one on the PAM molecule (Theng, 1982; Peng and Di, 1994; McLaughlin and Bartholomew, 2007). A third method may involve the reduction of the solution's zeta potential. This reduction would occur when polymer binds to the particle surface, displacing the shear plane around the particle, and causing an apparent change to its surface charge (Mpofu et al., 2003). There is still debate over which of these mechanisms is the primary one, although it is likely that most of the time all three are in effect to some degree.

The final defining property of a PAM is its MW. Because polyacrylamide is a long repeating chain of single monomer units, the MW of a PAM simply indicates the length of this polymer chain. Like with CD, PAMs can be classified based on their molecular weight. Table 2.1 displays the categories based upon MW. Higher MW PAMs are generally used in environmental purposes, but the higher the MW of a PAM, the more viscous the solution will be, so there are limits to what can be practically used (Barvenik, 1994). A number of studies have tested PAMs with varying MWs (Shainberg and Levy, 1994; Green et al., 2000; Mamedov et al., 2007; Yang et al., 2011; Rounce et al., 2012). The results show that the impact of MW on PAM performance is site-specific.

Table 2.1 Polymer Classification by Molecular Weight (from Barvenik, 1994)

Classification	Molecular Weight (g mole^{-1})
Low MW	$< 10^5$
Medium MW	10^5-10^6
High MW	1-5×10^6
Very High MW	$> 5 \times 10^6$

Three main forms of PAM have been used for construction sites: dry granules, liquid, and an inverse emulsion. Granular PAM is typically applied directly to the soil using a spreader (Sojka et al., 2007). Its advantages include a longer product life in addition to being easier and cheaper to transport (Barvenik, 1994). Liquid PAM is simply granular PAM that has already been dissolved in water, and is commonly applied by spraying from trucks or an existing irrigation system. Liquid PAM is generally effective at rapid flocculation. The third common PAM form is an inverse emulsion, where the PAM is trapped in droplets in oil, and is only released when mixed with water again. Its advantage over liquid PAM is its lower viscosity and higher polymer concentration, making it easier to transport (Barvenik, 1994). In addition to these main forms of PAM, a proprietary product, FlocLog, has been developed by Applied Polymer Systems for environmental applications. FlocLog is essentially a brick of different types of polymer and other additives, and is placed in a stormwater channel. FlocLog is usually held there with a string, and dissolved as water flows over it, releasing the polymer into the runoff.

When used on a construction site, polymer can be applied using a number of different strategies, including active and passive dosing systems. Active systems use pumps to mix the PAM with a certain amount of runoff, which is then discharged to a settling basin or a filter before being released to the environment. Passive systems use PAM that is either in granular form or in solution and applied to the land regularly between storm events. Another type of passive system is the use of FlocLogs as described previously. Passive treatments in particular can be utilized in conjunction with other best management practices, including mulch, check dams, rock dams, and excelsior wattles (McLaughlin et al., 2009; McLaughlin and McCaleb, 2010).

2.3 Factors Affecting Polyacrylamide Use

There are many factors that affect the use of polyacrylamide in flocculating soils. In the past few decades, many studies have been conducted to evaluate factors affecting PAM's efficiency. These factors include soil classification (texture) and clay mineralogy, temperature, the presence of cations, organic matter, pH, and PAM dose.

Soil particle sizes have a significant effect on PAM treatment performance. Soil particles can be classified as clay (< 2 µm in diameter), silt (2 – 62.5 µm), and sand (62.5 µm up to 2 mm). With regard to flocculation, McLaughlin and Bartholomew (2007) tested a number of soils with different textures using various PAMs. They found that of the subsoils tested, the ones that responded best to flocculation with PAM were those in which kaolinite mineralogy was dominant, specifically those that were >14% clay and 22% silt. In contrast, those that had higher percentages of silt and sand showed poor flocculation efficiencies. However, Bhardwaj and McLaughlin (2008) found that, in some cases, having coarser soil particles in suspension is beneficial to PAM flocculation.

Temperature is known to affect coagulation and flocculation with alum. Low temperatures cause smaller, less-dense, and more fragile flocs (Hanson and Cleasby, 1990; Morris and Knocke, 1984; Exall and Vanloon, 2000). However, little has been done to test polyacrylamide in a cold environment. This may be in part because it is currently used more frequently in the southern United States, where extreme cold temperatures are rarer. Mpofu et al. (2004) conducted flocculation testing with PAM and polyethylene oxide (PEO) and found that the negative zeta potential magnitude increased with increasing temperature (20°C – 60°C), indicating the thickness of the adsorbed layer of ions around the soil particles decreased. PAM and PEO adsorption also increased with temperature. They proposed that with increasing temperature, PAM chains collapsed upon the surface due to the changes in the surface's conditions, forming less effective flocs. However, this study only covered a range of temperatures higher than room temperature and did not deal with the colder ones that could be observed on a northern U.S. construction site.

The presence of divalent cations, such as calcium and magnesium, in runoff can also affect PAM flocculation. It is known that these cations can form a bridge between negatively charged soil particles and the negative groups of anionic polymer (Theng, 1982). However, studies have reported different results on the impact of divalent cations on the effectiveness of soil flocculation using polyacrylamide. Laird (1997), Entry et al. (2003), McLaughlin and Bartholomew (2007), Lu et al. (2002), and Shrestha et al. (2006) found that the presence of calcium ions in runoff solution enhances flocculation via the theoretical bridging model, while others (Peng and Di, 1994; Lee et al., 2012) determined that divalent cations had a detrimental effect on flocculation. Lee et al. (2012) proposed two different mechanisms by which anionic PAM could interact with calcium ions: particle-binding and polymer-binding. In the particle-binding model, calcium bridging allows PAM molecules to attach to soil particles while extending into the surrounding solution, allowing them to attach to other sites on different particles. Polymer-binding is when the PAM molecule attaches at many sites on the particle's surface and calcium ions that attach to its surface will attract more PAM molecules.

Natural organic matter (NOM) in soils can be formed by decay of plant and animal matter. A number of studies have found that the presence of NOM has an adverse effect on flocculation with anionic PAM (Nadler and Letey, 1989; Lu et al., 2002). Lu et al. (2002) found that reducing the NOM in fine soils, such as Linne clay loam and Imperial silty clay, had a much more marked effect on PAM sorption than in coarse soils, such as Palouse silt loam and Arlington loamy sand. They attributed this to the fact that particulate organic matter more easily cements clay particles together, covering up adsorption sites that could otherwise be used by PAM.

The change in pH of a solution also has an effect on flocculation with PAM. Peng and Di (1994) found that in very low pH (<5) PAM molecules tend to lose their anionic and extendibility characteristics due to multivalent metallic cations adsorbed onto the hydrocarbon chain, which leads to low kaolin flocculation efficiency. At high pH values (>9), adsorption of calcium and calcium hydroxide on anionic PAM surface and precipitation onto kaolin surface covers active functional groups, which inhibits hydrogen bonding. Between 5 and 9, the pH was inversely proportional to the flocculation efficiency. Taylor et al. (2002) stated that pH was shown to vary the adsorption capacity by influencing the extent of electrostatic repulsion between the PAM and kaolinite components. Their study confirmed the results of Peng and Di (1994) in that the adsorption capacity of the solution decreases as pH value increased from 4.5 to 8.5.

Finally, PAM dose is one of the most important factors that affect PAM flocculation effectiveness. Multiple studies have found that there is an optimal dose of anionic PAM for a soil solution at which it reduces turbidity most effectively, and beyond which turbidity values begin to increase again (Shrestha et al., 2006; McLaughlin and Bartholomew, 2007; Rounce et al., 2012). For many of these, the optimal dose (concentration) was around 1 mg/L. Nasser and James (2006) suggested that this relatively low optimal dose was due to the anionic nature of the polymer chain, which tends to stretch out, repelling itself and other PAM molecules. This facilitates the formation of large, open-structure flocs. It is thought that after this optimal dose, when available attachment sites on soil particles are taken, additional PAM will only cause the PAM molecules to repel the soil particles and each other, stabilizing the solution (Shrestha et al., 2006).

3. EFFECT OF POLYMER TYPE AND CONCENTRATION ON CONSTRUCTION SITE SOIL FLOCCULATION

3.1 Research Objectives

The objective of the first phase of this research was to determine the impact of different types of PAMs and their doses on the efficiency of flocculation of construction site soils. We collected soil samples from various South Dakota construction sites. Simulated construction site stormwater runoff solutions were created using soil samples in the laboratory. A jar test unit was then used to flocculate the soil solutions with different PAMs under controlled conditions to evaluate turbidity reduction.

The goal of these flocculation experiments was to determine which polymers and concentrations (doses) were most effective at turbidity reduction. PAM characteristics that were investigated included charge, charge density, and molecular weight. In addition, these experiments were performed under different temperatures, ranging from 5 to 30 degrees Celsius, in order to determine the temperature effects on the PAM flocculation process. Finally, a number of flocculation experiments were also conducted with varying mixing times of the PAM with the soil solution to determine the mixing conditions required for sufficient flocculation. The overall purpose of these tests was to analyze effects of temperature and polymer dose and properties on PAM flocculation and provide recommendations about implementation of this technology in controlling construction site turbidity.

3.2 Experimental Materials and Methods

3.2.1 Soil Sample Collection

Three soil samples were collected from highway and development construction sites in Aberdeen, Brookings, and Sioux Falls, all in the eastern side of South Dakota. Figures 3.1 and 3.2 show the construction sites in Aberdeen and Sioux Falls, respectively, where soil samples were taken. The Brookings soil sample was collected at a construction site located in South Dakota State University. The samples were taken so as to represent native clays, which are found deeper than the organic topsoils.

Figure 3.1 Aberdeen construction site

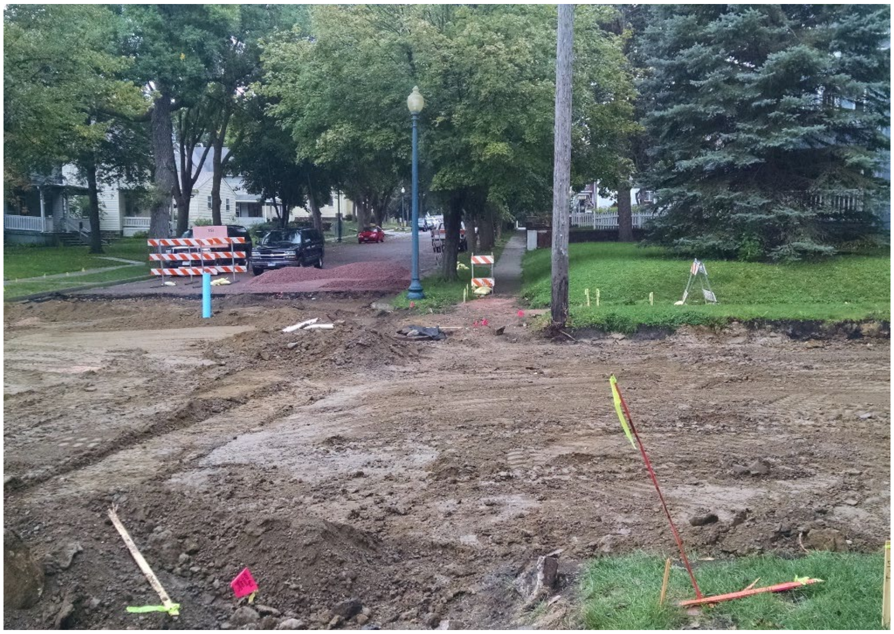


Figure 3.2 Sioux Falls construction site

Subsamples of the collected soils were sent to Midwest Laboratories, Inc., in Omaha, Nebraska, for analyzing several chemical properties. Table 3.1 presents the soil analytical results. The three soils have low organic matter content (0.4% – 0.5%) and the pH values of all three soils are basic (8.0 – 8.2). The calcium contents of the three soils were one order of magnitude higher than potassium and magnesium contents. The calcium and magnesium (both divalent cations) contents, as well as the cation exchange capacity (CEC), may give a good indication of the ability of PAM to flocculate the soil particles (Theng, 1982; Laird, 1997).

Table 3.1 Properties of soils collected in field

Sample	Organic Matter (%)	K (mg/kg)	Mg (mg/kg)	Ca (mg/kg)	pH	CEC (meq/100g)
Aberdeen	0.4	137	241	2680	8.0	15.8
Brookings	0.4	92	443	3052	8.1	19.2
Sioux Falls	0.5	114	419	3209	8.2	20.4

3.2.2 Simulated Stormwater Runoff Creation

An artificial runoff solution designed to mimic actual field conditions was created for each soil sample. First, the soil samples were processed to remove large aggregates, such as rocks and pebbles. This was done by crushing soil clods using a heavy-duty mortar and pestle and passing all soil content through a set of sieves with a #10 sieve (2-mm opening size). Soil particles with sizes less than 2mm were collected to prepare simulated stormwater runoff. Figure 3.3 shows a processed soil sample.

Figure 3.3 A processed soil sample for simulated stormwater runoff creation

Once soil was pre-processed, it was used to create an artificial runoff solution with a turbidity of ~1500 nephelometric turbidity units (NTU). This relatively high turbidity was used to model a realistic high-turbidity runoff from a construction site (Line et al., 2011; Rounce, 2012). Because all soil solutions had this common starting point, differences in final turbidity values after flocculation could be attributed to soil properties and flocculation conditions rather than varying initial turbidities.

The solutions were prepared in a column reactor (Figure 3.4), which was filled to a depth of 23 inches with distilled water. A specific mass of soil was added to the top of the reactor (e.g., 300 grams) and the stirrer in the reactor was turned on high speed for 5 minutes. The reactor was then turned off and, after an initial one-minute period to dissipate turbulence, the solution was allowed to settle for 20 minutes. According to Stoke's Law, these experimental conditions allowed for particles roughly larger than 20 μm to settle to the bottom. It was desirable to maintain only smaller particles, as these are the primary cause of turbidity during stormwater events, as well as the fact that the smallest clay particles prove the most difficult to settle out of actual construction site runoff.

Figure 3.4 The column reactor and holding tank for simulated stormwater runoff

Once larger particles had been settled out, the runoff was removed from the reactor via a port near the bottom and transferred to a large holding tank where it was continuously stirred. By measuring the turbidity of the solution coming out of the first reactor and the slurry in the holding tank, the initial soil amount put into the column reactor for each batch was varied, and a final turbidity of ~1500 NTU was achieved once all necessary solution for testing had been created.

3.2.3 Polyacrylamides

The flocculants used in this study were all polyacrylamides of the anionic or nonionic varieties. Because cationic polyacrylamides have been shown to be harmful to the aquatic environment, they were excluded in this study (Biesinger and Stokes, 1986; Green and Stott, 2001). Table 3.2 presents a list of the PAMs used. It includes seven anionic PAMs, as well as one nonionic, all from the Superfloc® series (SF) manufactured by Kemira, a chemical company headquartered in Finland. The polymers were chosen to obtain a range of different molecular weights and charge densities, the two main PAM properties. The nonionic PAM was used as a comparison to the anionic ones. One more PAM was also included, APS 706b, a proprietary product from Applied Polymer Systems (Atlanta, GA). Although the properties of APS 706b were not disclosed, it was included because it is currently being sold and used for turbidity reduction in stormwater. APS 706b PAM is a mixture of anionic PAM and other constituents. All polyacrylamides used in this study were obtained in granular form from their manufacturers. Laboratory PAM stock solutions at concentrations of 100 mg/L and 1000 mg/L, respectively, were prepared by adding each PAM product to nanopure water and stirring with a magnetic stirrer for at least 24 hours.

Table 3.2 Polyacrylamide properties

PAM Name	Charge Type	Molecular Weight (Mg/mol)	% Charge Density
SF N-300	Nonionic	15	0
SF A-110	Anionic	10-12	16-18
SF A-110 HMW	Anionic	10-14	16-18
SF A-130 LMW	Anionic	3-4	35
SF A-130	Anionic	10-12	35
SF A-130 HMW	Anionic	N/A	35
SF A-150	Anionic	10-12	50
SF A-150 HMW	Anionic	17	50
APS 706b	Anionic (mixed)	N/A	N/A

3.2.4 Temperature Variation Flocculation Tests

The created runoff solutions and the selected polymers were used, along with a modified jar test setup, to test the effectiveness of the polymers on flocculation of the suspended soil particles with the goal of reducing final supernatant turbidity. Soil solutions were dosed with six different doses of each polymer, including 0.03, 0.1, 0.3, 1, 3, and 10 mg/L. The selected PAM doses encompass the effective ranges of most anionic polymers (McLaughlin and Bartholomew, 2007; Rounce, 2012). A six-position jar tester (Phipps & Bird, Richmond, VA) was used for the flocculation experiments. In place of the 2-L plastic jars normally used, 200-mL glass beakers were used in order to reduce the amount of synthetic runoff and PAM stock needed. Accordingly, a set of scaled-down paddle blades was used for stirring during the tests. Standard blades measure 1-inch by 3-inch, while the modified ones were cut down to 4-cm by 1.33-cm. This scaling down was proportionally equivalent to the scaling down of the original jars to the 200-mL beakers. Figure 3.5 shows the modified jar tester setup for the flocculation experiments.

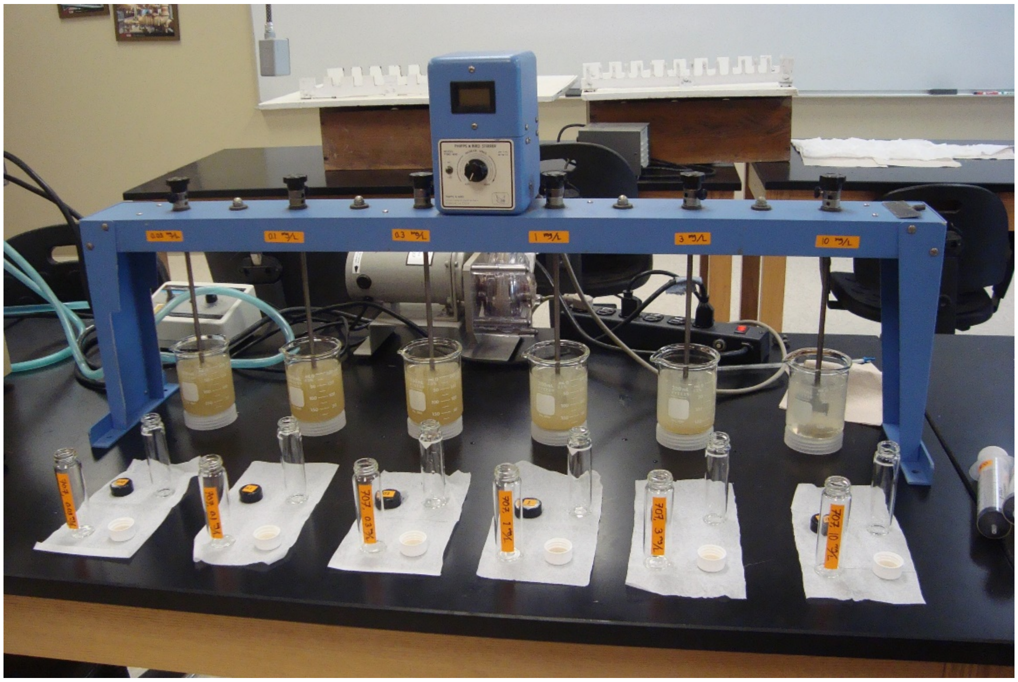


Figure 3.5 Jar tester used for flocculation experiments

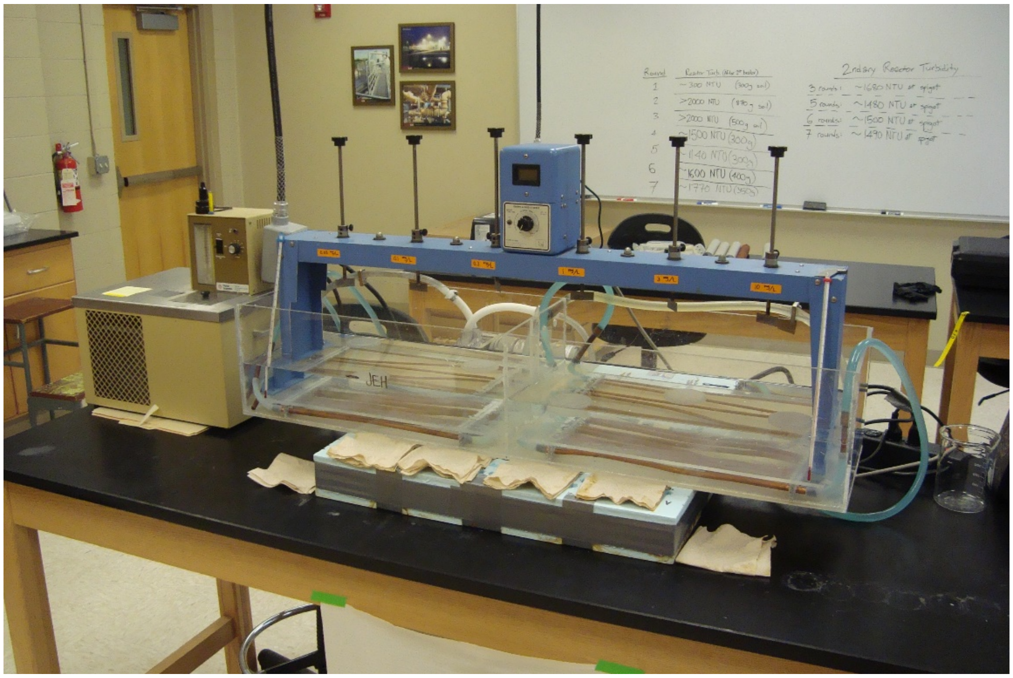


Figure 3.6 Temperature control unit for the jar tester

The other major variable evaluated during the first stage of the research was temperature. Little research has been done dealing with the effects of extreme natural temperatures on soil flocculation with anionic polyacrylamide. In order to determine the effects of varying the temperature, the desired temperature of the synthetic runoff had to be maintained throughout the flocculation process. This was done by placing the entire jar test unit into a specially built water bath attached to a temperature-control unit (Fisher Scientific, Waltham, MA), which allowed the temperature of the solution in the beakers to be maintained by the water in the bath. Figure 3.6 presents the temperature control unit for the jar tester. Four different temperatures were tested, which included 30, 20, 10, and 5 degrees Celsius. These temperatures were chosen to roughly cover the range of ground-level temperatures during which the runoff and flocculation process might take place on a construction site. The temperature-control unit was able to maintain the bath at all of the temperatures except 5°C, when ice needed to be added to the bath in order to keep the temperature low enough. The temperature of the synthetic runoff solutions was kept the respective experimental temperature before each flocculation experiments. The solution was put into the 2-L jar containers and temperature was moderated overnight. For 30°C, the containers were placed into a warm water bath (Blue M Electric Co., Blue Island, IL.); for 20°C, they were put into an incubator (Thermo Fisher Scientific, Waltham, MA); for 10°C, they were put into a cooler incubator/refrigerator (Hotpoint, Woodston, Peterborough, UK); and for 5°C, they were put into a cold walk-in refrigerator (Sherer, Auckland, NZ).

During a flocculation test, each solution was first mixed at ~250 revolutions per minute (rpm) for at least two minutes, in order to re-suspend all soil that had settled to the bottom overnight. The solution was then transferred to each of the six glass beakers, which were filled to the 200-mL line and placed into the temperature bath. At the same time, a small sample was also taken from the plastic jar to test the initial turbidity and make sure it was approximately 1500 NTU. Once the beakers were under the modified jar test unit, the unit was turned on and allowed to stir at 150 rpm for at least two minutes in order to make sure that the temperature had stabilized and all soil in solution was fully suspended. Then different doses of PAMs were added to the solutions. The stirrer was immediately turned up to 300 rpm and the solution was rapid-mixed for 30 seconds. Next, the stirrer was turned down to 100 rpm for five minutes of slow mixing, after which it was turned completely off. The samples were allowed to settle for five minutes. Plastic syringes were used to transfer supernatant solution from the beakers into turbidity vials. The vials were shaken up and placed into the turbidimeter and a hand timer was started. Turbidity was measured at 15 seconds, 20 seconds, and 25 seconds, and the values were averaged to achieve a final value for that beaker.

3.2.5 Temperature Variation with Mixing Variation

A final set of flocculation tests was conducted to investigate the effect of slow-mix time on the flocculation effectiveness. The Brookings soil sample and SF A-130 PAM were used for this set of tests. The A-130 PAM was chosen because it represents an average-molecular-weight and average-charge-density anionic polymer. After dosing with A-130 PAM at 0.1 and 1 mg/L, the solutions were rapid-mixed at 300 rpm for 30 seconds. After that, the paddle blades were pulled out of the beakers after 0, 0.5, 1, 2, 5, and 10 minutes of slow mixing at 100 rpm. All other experimental parameters, including the temperatures, and the settling time of five minutes remained the same as the initial temperature tests. The purpose of these tests was to determine the effect of temperature variation on the flocculation kinetics of the synthetic runoff dosed with PAM. In other words, would a higher/lower temperature reduce the amount of mixing time needed to flocculate and settle most of the turbidity? Also, did a longer mixing time necessarily help reduce turbidity?

3.3 Results and Discussion

3.3.1 Effects of Polymer Type and Dose on Flocculation

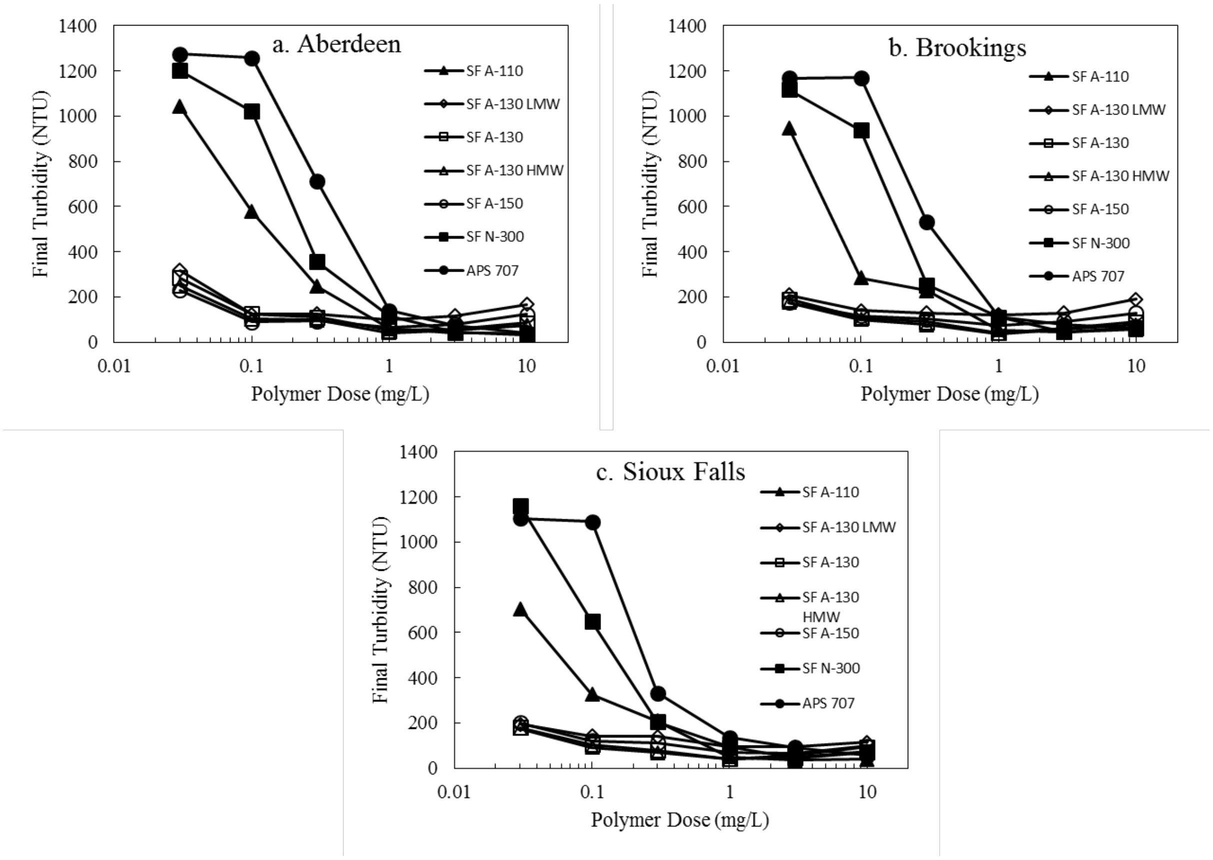


Figure 3.7 Final turbidities of synthetic runoff solutions after flocculation at 20°C

Figure 3.7 presents the final turbidities of synthetic runoff solutions after flocculation with different PAMs at a temperature of 20ºC. The final turbidity levels generally reduced with increasing PAM dose from 0.03 mg/L to 1 mg/L. The final turbidities did not vary substantially when further increasing the dose to 10 mg/L. It seems that there was an optimal polymer concentration at which the final solution turbidity reaches a low point, beyond which turbidity begins to increase again. During the flocculation experiments, it was visually observed that as the polymer dose approached the optimal dose, floc size increased until, at the optimal dose, there was essentially just a single "megafloc" (see Figure 3.8). After this dose was surpassed, floc size again diminished. Nasser and James (2007) explained that while cationic PAMs rely on charge neutralization to cause soil particles to attach together, anionic PAM primarily uses a bridging mechanism. If cationic PAM is overdosed, it can cause surface saturation of the particles and they will again begin to repel each other. Anionic PAM, on the other hand, attaches to soil particles only at a few specific sites. Because both the polymer and the particles are negatively charged, the long anionic PAM molecule extends out into the solution, producing loops and tails, and is able to attach at a few points to many other soil particles. This is what could form the large, open-structure floc that was observed, especially closer to the optimal dose of polymer. Turbidity increased again after this optimal dose, probably because the majority of available bridging sites on the clay particles had been used up by PAM molecules, and additional PAM molecules in the solution only served to repel each other and the soil particles (Shrestha et al., 2006).

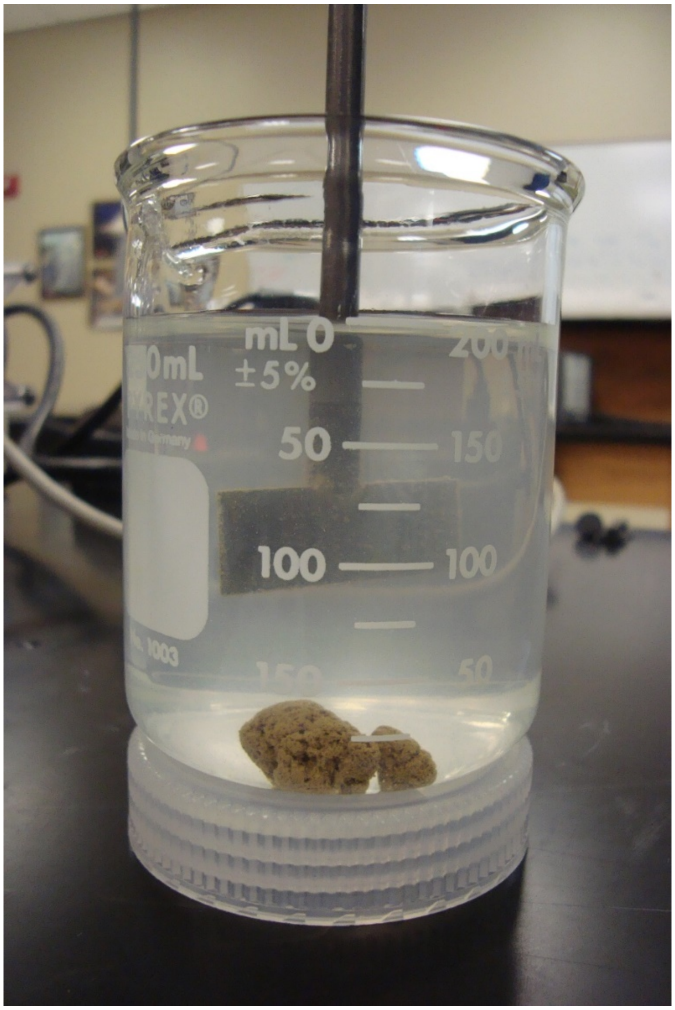


Figure 3.8 Single large floc created by the optimal dose of an anionic polymer (1 mg/L)

The optimal PAM dose was observed for the anionic Kemira polymers tested, although not for the Applied Polymer Systems or nonionic ones. It is possible that the APS polymer, being a mixed proprietary product, has a much lower charge density than the other anionic PAMs. SF N-300 is a nonionic polymer, and so theoretically has no surface charge. Nasser and James (2006) dosed a soil solution with a much higher-concentration range of PAMs of all charge types and densities, and found that the higher the charge density of an anionic PAM, the poorer it performed. They suggested that because both the clay particles in suspension and the anionic PAM are negatively charged, the optimal flocculation point was when the interparticle bridging mechanism, which involves the divalent cations such as calcium and magnesium, was working optimally. The optimal PAM dose observed during flocculation experiments was normally 1 mg/L for anionic polymers. Beyond that point, dosing with more anionic PAM introduces more negative charge into the environment, causing the soil particles to tend to repel one another (Lentz et al., 1996; McLaughlin and Bartholomew, 2007). The SF N-300 and APS 707 polymers did not show the tendency to re-suspend the soil particles as the dose increased to 10 mg/L. It is possible that the optimal point has not been greatly surpassed under the conditions of this study. Rounce (2012) dosed a runoff solution with up to 100 mg/L of similar polymers (SF N-300 and APS 705) and found that after about 10 mg/L, final turbidity did begin to increase slightly again.

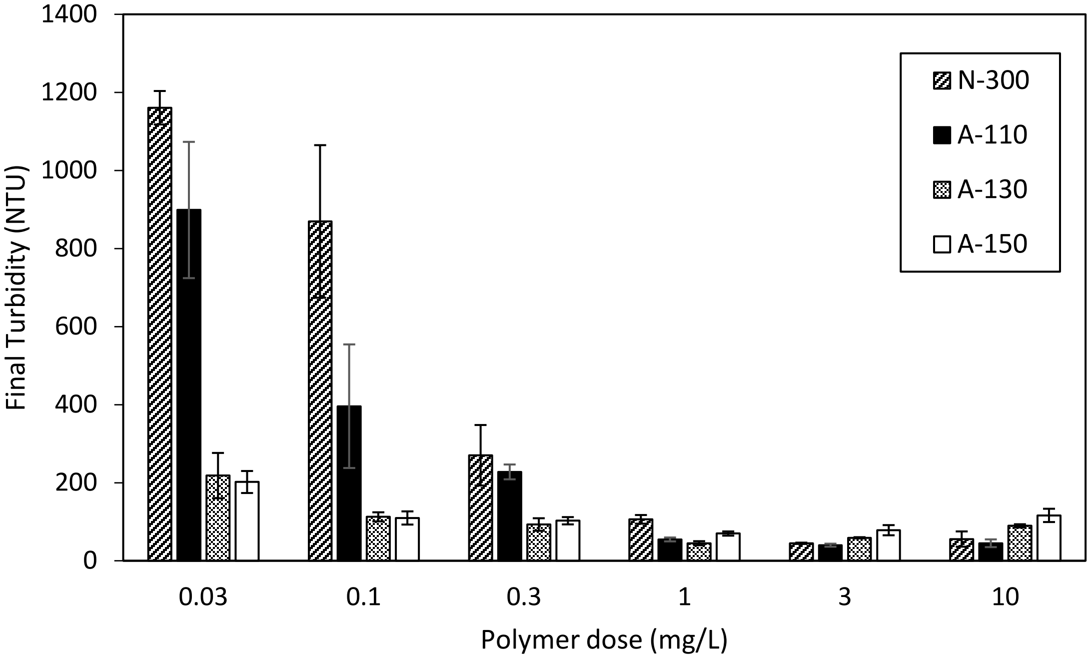


Figure 3.9 Averaged final turbidity values of Aberdeen, Brookings, and Sioux Falls soil solutions dosed with PAMs of varying charge densities

Figure 3.9 shows the average final turbidities of the three synthetic runoff solutions (Aberdeen, Brookings, and Sioux Falls) after flocculation with polymers of different charge densities. The polymers with higher charge densities, A-130 and A-150, perform better than polymers with lower charge densities, N-300 and A-100, when low dose range of 0.03 to 0.3 mg/L was used. All four polymers showed effective turbidity removal at a dose of 1 mg/L. After that, the polymers with the lower charge densities, N-300 and A-110, yielded lower turbidities, though only by a small margin. They also yielded lower ultimate turbidities than the higher charge density PAMs for the selected doses. Standard two-tailed t-tests were used to compare average final turbidities of the three soil samples when dosed with either A-110 or A-150 PAM. At a 95% confidence level ($P < 0.05$), the final values for A-110 were significantly higher for 0.03, 0.1, and 0.3 mg/L doses, while those for A-

150 were higher at 1, 3, and 10 mg/L doses. It should be noted though, that if the EPA limit were to be set at ~280 NTU and the main goal of an operation were simply to reduce the turbidity below this value in a cost-effective manner, dosing with a lower amount of a higher charge density polymer would probably make the most sense. At the lowest dose, 0.03 mg/L, A-130 and A-150 had already met the limit, while N-300 and A-110 did not reduce the turbidity below the limit until 0.3 mg/L, using 10 times as much polymer.

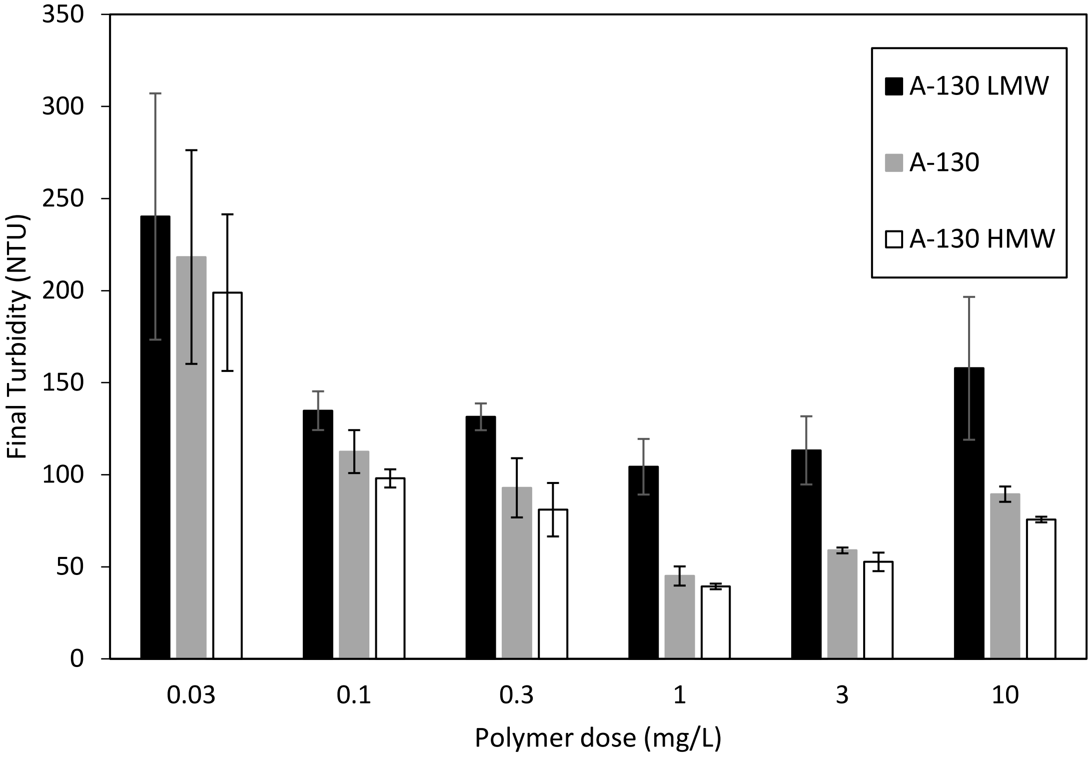


Figure 3.10 Averaged final turbidity values of Aberdeen, Brookings, and Sioux Falls soil solutions dosed with anionic PAMs of varying molecular weights

Figure 3.10 shows the average final turbidities of the three synthetic runoff solutions tested with three polymers of identical charge density, but differing molecular weight. The molecular weight showed a consistent trend during the flocculation tests. In general, anionic PAMs with higher molecular weight performed better than their lower-MW counterparts. However, the molecular weight does not have a noteworthy effect on the final turbidity at the lowest dosage of 0.03 mg/L. It is only at a dose of 0.1 mg/L and higher that its effect can be clearly seen. For the most part, Superfloc A-130 HMW (high molecular weight) performed better than SF A-130, which performed better than SF A-130 LMW (low molecular weight). A standard two-tailed t-test was used to compare the final turbidities of the soil samples (averaged) dosed with A-130 LMW PAM to the final turbidities of those dosed with A-130 HMW PAM. As expected, at all doses except 0.03 mg/L, the PAM with the higher molecular weight yielded significantly (95% confidence level) lower turbidities. It is thought that the longer polymer molecule in HMW PAM is able to attach to more clay particles and sites on particles, and therefore it is more effective at forming flocs (Moss and Dymond, 1978; Theng, 1982).

Yang et al. (2011) and Mamedov et al. (2007) performed erosion potential analyses on a soil surface dosed with anionic PAMs of differing charge densities and molecular weights. They concluded that the optimal charge density and molecular weight of a PAM depends greatly on the properties of the soil being treated. Yang et al. (2011) found that high-molecular weight and charge density PAMs were more effective in treating coarse loamy sand, medium-molecular weight and charge density PAMs were most effective for silty loam, and low-molecular weight and high-charge density PAMs were best for silty clay. McLaughlin and Bartholomew (2007) tested different polymers with synthetic runoff solutions with the goal of turbidity reduction. They found that no polymer of a specific molecular weight or charge density really had a distinct advantage over others, and this was probably due to the variety of soil samples that the PAMs were tested on. It is likely that the soils tested during the experiments were fairly similar in texture. But during commercial use, it would be prudent to do trial tests to determine the most efficient polymers to use on a specific site.

3.3.2 Effects of Temperature Variation on Flocculation

The influence of temperature on the PAM flocculation process was one of the most important variables tested during this research, in part because only limited information is available in the literature, but also because temperature can vary greatly on an outdoor construction site. Figure 3.11 displays the final turbidities of the three soil samples dosed with A-130 LMW polymer under all four temperatures tested. In general, colder temperatures yielded worse flocculent performance (i.e., higher final turbidities). It is clear that the influence of cold temperature is much greater at low polymer doses than at high ones. For example, for the Aberdeen soil, at a 0.03 mg/L PAM dose, the final turbidity levels were 216 and 642 NTU, respectively, for 30°C and 5°C. At the optimal dose, 1 mg/L, the final turbidities are very similar, indicating that at the optimal polymer dose, varying the temperature does not have a marked effect on the flocculation efficiency.

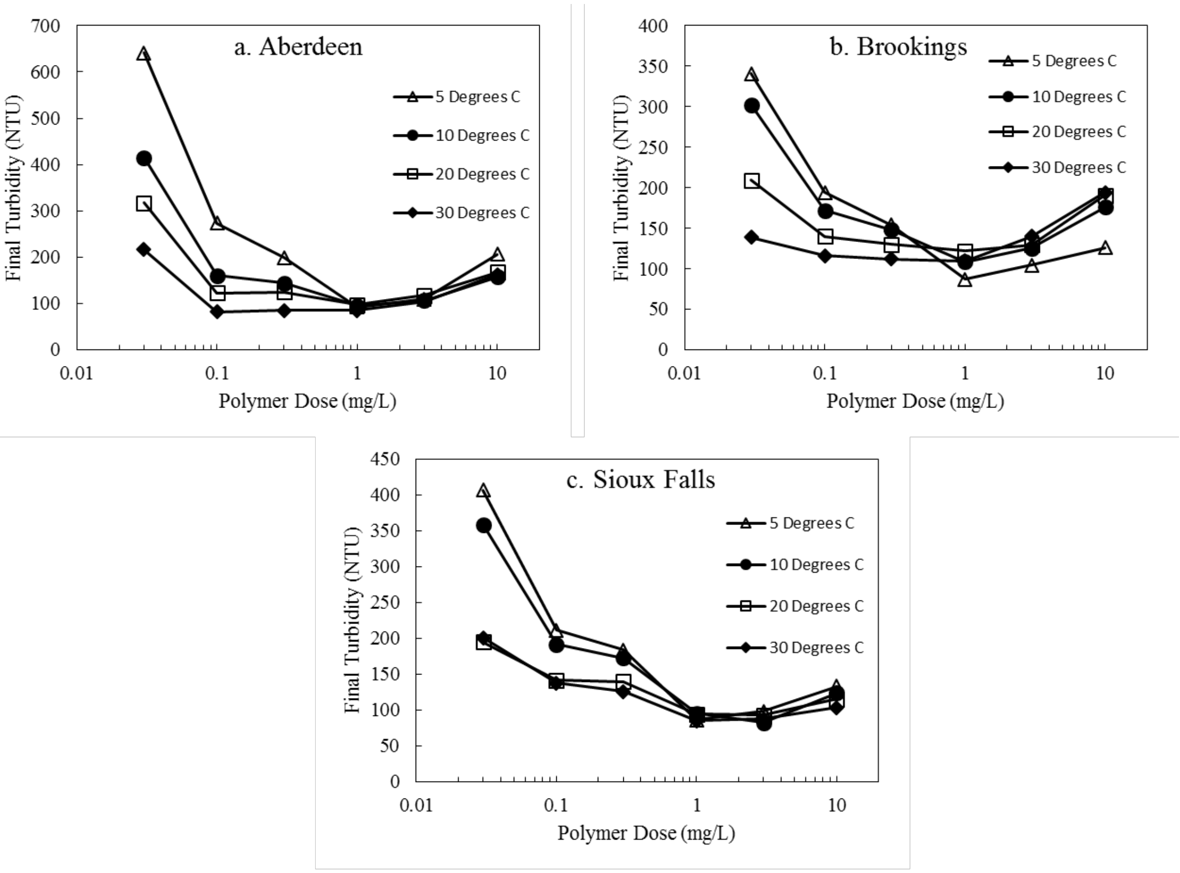


Figure 3.11 Final turbidities of synthetic runoff solutions dosed with A-130 LMW polyacrylamide under varying temperatures

A number of two-tailed standard t-tests were run to compare the final turbidities from the three soil samples at 30°C with those flocculated at 5°C. This was done for all polymers used at both the lowest dose, 0.03 mg/L, and the observed optimal dose, 1 mg/L. The tests revealed that for all but one anionic polymer (SF A-110), at a 0.03 mg/L dose, there was a statistically significant difference in mean final turbidity between 30°C and 5°C at a 90% confidence level ($P < 0.1$). As was expected, at the optimal dose of 1 mg/L, no significant difference was found between final turbidities with varied temperature. For the two polymers that were not strictly anionic, N-300 and APS 707, the only statistically significant differences observed between extreme temperatures were for 0.1 mg/L, and at a 90% confidence level. This was because at a very low dose, the polymer had little effect on final turbidity, while at 1 mg/L, the PAMs were converging on their optimal dose (see Figure 3.12).

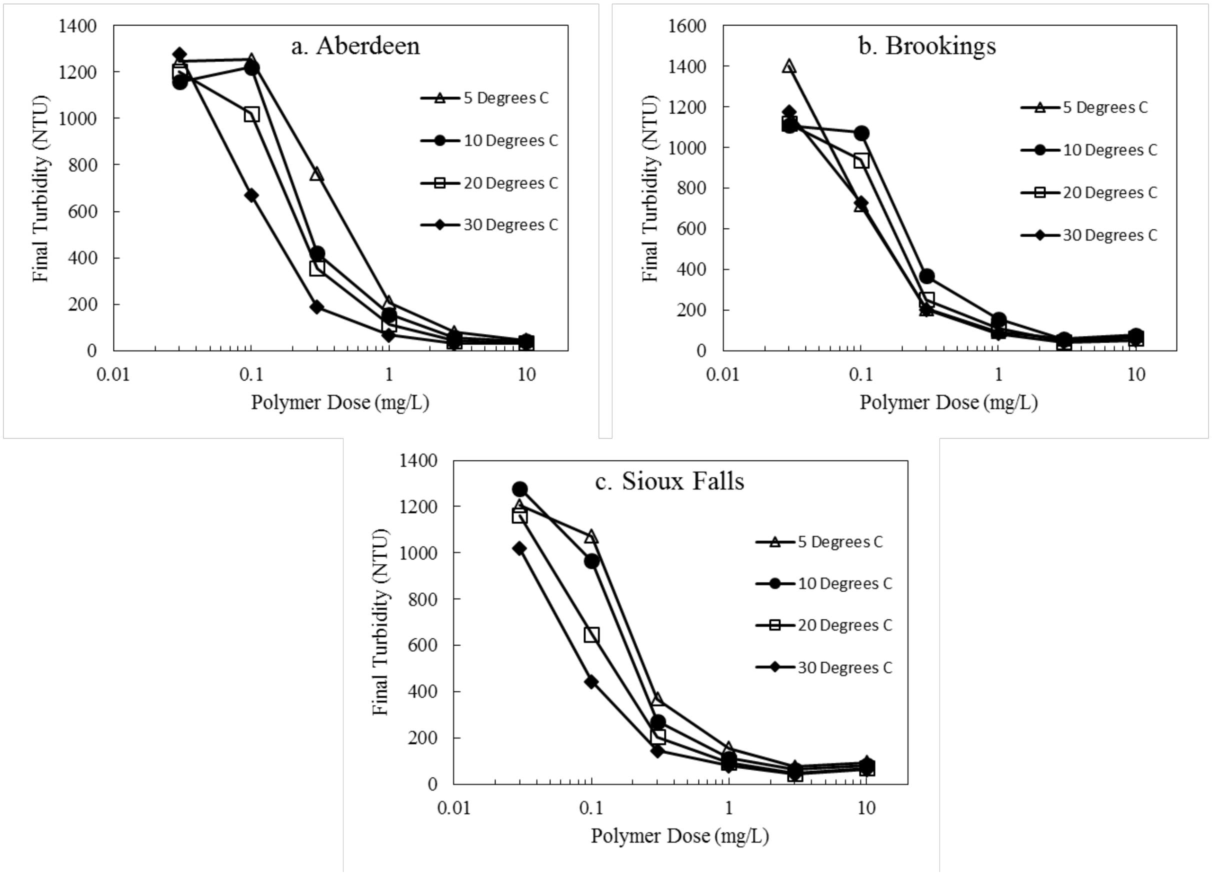


Figure 3.12 Final turbidities of synthetic runoff solutions dosed with N-300 polyacrylamide under varying temperatures

It is not known exactly why very low temperatures have a negative impact on flocculation with PAM. Based on the research done by Mpofu et al. (2004), it is possible that increasing solution temperature compresses the layer of ions around soil particles, allowing more PAM to be adsorbed. During the flocculation experiments of this study, it is likely that the PAM-particle adsorption process improved as temperature increased from 5°C to 30°C, which promoted flocculation efficiency during this study. When cold temperatures were used, the PAM chain did not unfold as completely, making them less available to form open structure flocs. In addition, higher viscosity at low temperatures could impede the mixing and settling mechanics.

3.3.3 Effects of Mixing Variation at Different Temperatures on Flocculation

Figure 3.13 shows the effects of mixing time on the final turbidities. In this test, a low A-130 PAM dose, 0.1 mg/L, and the optimal dose, 1 mg/L, were used to flocculate particles from the Brookings soil sample under different mixing times and temperatures. It is apparent for both polymer doses that a longer slow mix time reduced turbidity more effectively compared with a short one. This indicates that a longer slow mix time would promote floc growth and lead to lower final turbidity levels. Similar to previous experiments, the turbidity was once again more easily reduced under warm temperatures (20°C and 30°C) than cold ones (5°C and 10°C). The results in Figure 3.13 also suggests that mixing time played a more important role in flocculation for 0.1 mg/l dose than for 1 mg/L. At a relatively low dose of 0.1 mg/L, high turbidity levels (500 – 800 NTU) were observed after rapid mixing but before any slow mixing. The final turbidity levels declined rapidly with increasing slow mixing time from 0 to 5 minutes and only moderate decreases in turbidity were observed when further increasing the mixing time to 10 minutes. It would take approximately five minutes to reduce the turbidity below the proposed limit of 280 NTU when the flocculation temperatures were 5°C and 10°C. The PAM flocculation exhibited high efficiencies when an optimal dose of 1 mg/L was used. The final turbidity decreased to below 100 NTU after rapid mixing alone for all temperatures. Additional slow mixing time further decreased the final turbidity levels, and the flocculation process appeared to be completed after two to five minutes of slow mixing. After that, no further reduction in turbidity was observed. These results suggest that a longer mixing time would be needed to effectively reduce turbidity levels when low doses of PAMs are used for construction site runoff treatment.

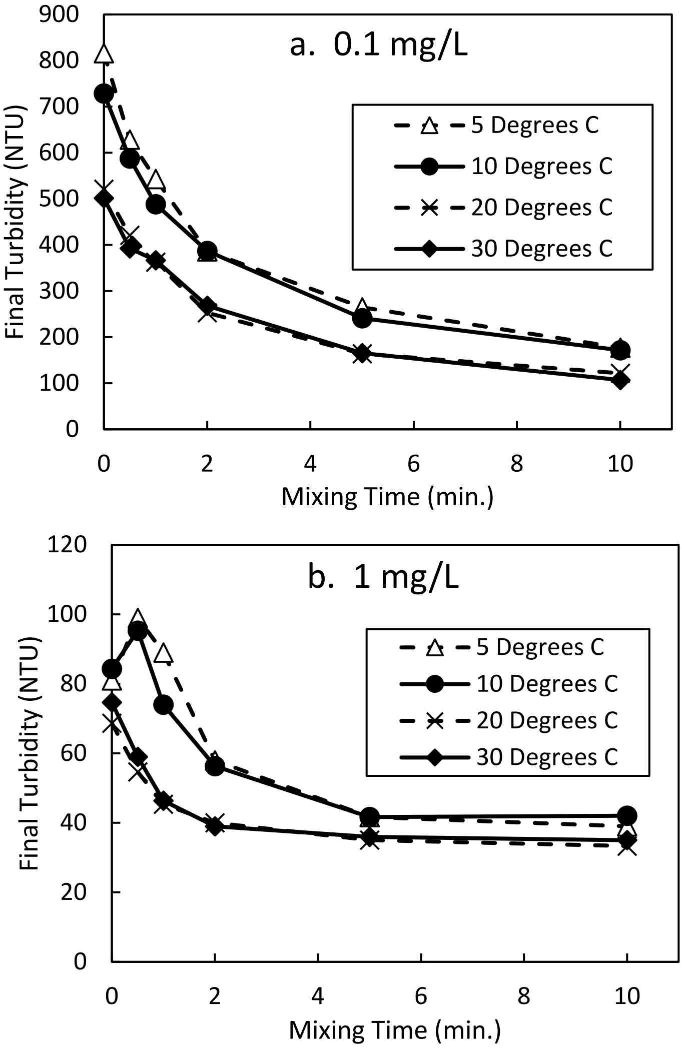


Figure 3.13 Final turbidities of Brookings soil solution dosed with A-130 PAM under different mix times

3.3.4 Rapid City Soil Sample

One more soil sample was collected from a construction site in Rapid City, SD, on the western side of the state. Figure 3.14 shows the construction site at Rapid City where the soil sample was taken. The soil data are presented in Table 3.3. This soil has a characteristic red color and a high organic content. The Rapid City soil behaved differently from the other three samples, therefore the results for this soil sample are discussed separately.

Figure 3.14 Rapid City construction site

Table 3.3 Properties of Rapid City soil sample

Sample	Organic Matter (%)	K (mg/kg)	Mg (mg/kg)	Ca (mg/kg)	pH	CEC (meq/100g)
Rapid City	1.7	95	184	3249	8.0	18

Figure 3.15 presents the PAM flocculation results at 20ºC for the Rapid City soil. The optimal dose of anionic polymers for this soil sample was about 1 mg/L, which is similar to other soils. However, most of the PAMs were much less effective at flocculating soil particles, and the final turbidities were generally much higher at all doses. A-130 and A130 HMW are the two PAMs that showed relatively high flocculation efficiencies at a dose range of 0.03 to 1 mg/L. This indicates that it is important to perform flocculation experiments to select optimum PAMs for a specific soil type. Figure 3.16 shows the effect of temperatures on flocculation with A-130 and A-130 HMW PAMs. The final turbidity levels generally decreased with increasing temperatures for a PAM dose range of 0.03 to 1 mg/L. However, the magnitude of temperature impact was much less compared with other soils. The specific soil type and texture may have caused the unique PAM flocculation performance. The Rapid City sample had a significantly higher organic matter content than the other three soil samples, which could have a detrimental effect on flocculation with PAM (Lu et al., 2002). The magnesium content was also markedly lower, which may affect interparticle bridging during flocculation. McLaughlin and Bartholomew (2007) and Bhardwaj and McLaughlin (2008) also found that the differing percentages of sand, silt, and clay, all smaller particle sizes, can determine the effectiveness of PAM flocculation. It is highly possible that the Rapid City soil sample had a unique gradation when compared with the other three soils, which made it less responsive to flocculation with PAM.

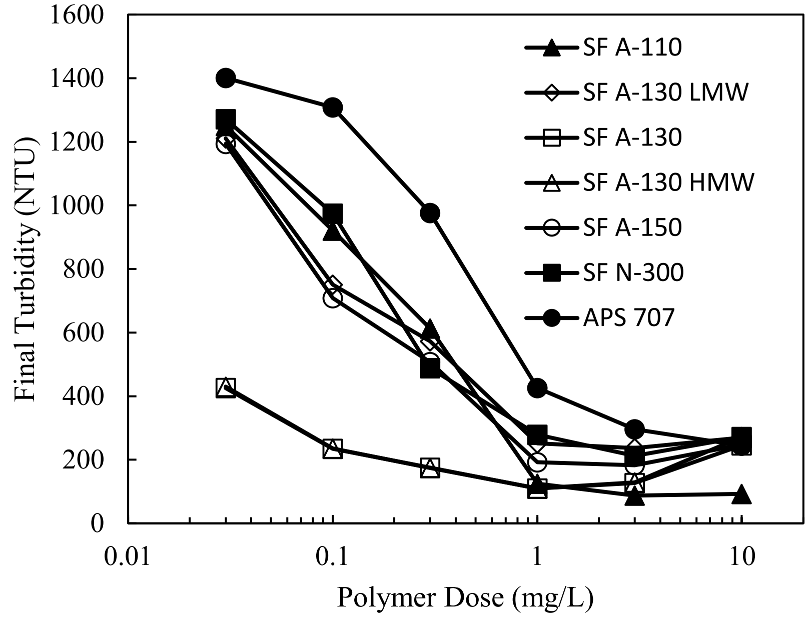


Figure 3.15 Final turbidities of Rapid City soil sample solution dosed with different polymers

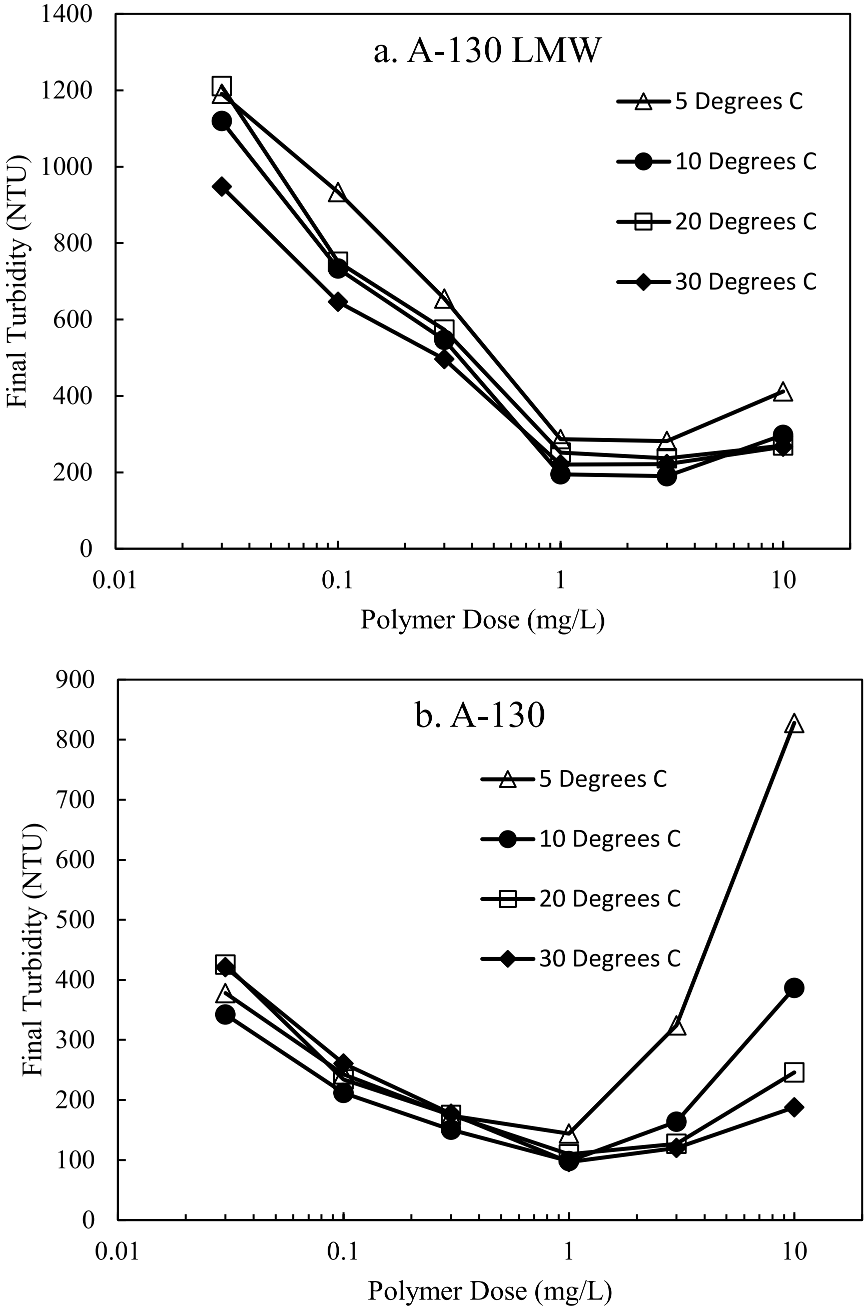


Figure 3.16 Effect of temperatures on PAM flocculation of Rapid City soil sample

3.3.5 Summary of PAM Type and Concentration Effects on Flocculation

During the first part of this research, four simulated construction site runoff solutions were created using soil samples from construction sites at Aberdeen, Brookings, Rapid City and Sioux Falls, SD. These solutions were flocculated with seven different PAMs under a temperature range of 5°C to 30°C. The flocculation experiment results showed that PAM flocculation is an effective technology to reduce turbidity from simulated construction site runoff. The optimal polymer dose was approximately 1 mg/L for anionic PAMs, and after that the final turbidity increased again. Nonionic and APS polymers were less effective compared with anionic PAMs at low doses. The anionic PAMs formed large and dense flocs at the optimal dosage.

In general, PAMs with higher charge densities and molecular weight performed better than PAMs with lower charge densities and molecular weight. However, those with a lower charge density reached a lower final turbidity with higher dosage, probably because of their reduced tendency to cause particles to repel each other when the polymer is overdosed. The long-chain polymers in high molecular weight PAMs may have contributed to the effective attachment between soil particles and PAM, which led to higher flocculation efficiency.

Cold temperatures negatively affected the PAM flocculation of soil solutions, especially at low dosages. It is possible the reduced flocculation kinetics and PAM activity that led to less flocculation efficiencies at low temperatures. However, different PAMs generally achieved similar levels of turbidity reduction at different temperatures when an optimal dose of 1 mg/L was used. Mixing time had a marked impact on PAM flocculation, especially at low dosages. Flocculation with PAMs was generally a fast process. Mixing times between two and five minutes were typically required to achieve highest turbidity reduction.

4. EFFECT OF WATER QUALITY AND FLOCCULATION CONDITIONS ON CONSTRUCTION SITE SOIL FLOCCULATION

4.1 Research Objectives

The goal of the second part of this research was to investigate the impact of important water quality parameters and flocculation conditions on PAM and soil flocculation. These factors included the solution pH value, calcium and dissolved organic matter concentrations, and flocculation mixing and settling conditions. During PAM flocculation of construction site runoff, the mixing intensity, mixing time, and settling time can vary substantially based on specific site conditions. These flocculation conditions will affect the final turbidity levels after PAM treatment. Therefore, it is necessary to evaluate these conditions on PAM performance to optimize the field application conditions to reduce runoff turbidity.

The presence of divalent cations such as calcium is generally thought to aid flocculation using anionic PAM. Calcium and magnesium are ubiquitous in almost all soils, but the concentration can vary. In this study, different quantities of calcium were added to the simulated construction site runoff to determine the impact of calcium concentrations on PAM flocculation. The pH of construction site runoff is an important water quality parameter that can affect PAM flocculation. Sulfuric acid or sodium hydroxide were added to the runoff solution prior to the flocculation in order to observe how the pH variation influences the process. Finally, organic matter present in the runoff may affect PAM performance. Dissolved organic carbon (DOC) was added to runoff solution in the form of fulvic acid before flocculation, and final turbidity and total suspended solid (TSS) were measured.

Some of the variables tested during this second part of the research are characteristics of a construction site that probably couldn’t feasibly be altered, such as pH and organic matter. However, it may be important to know the conditions of the site before the application of PAM flocculation. Other factors, such as the mixing conditions and cation concentration, can potentially be altered to make conditions more favorable for the successful use of PAM.

4.2 Experimental Materials and Methods

4.2.1 Soil Sample Collection and Runoff Creation

Simulated construction site runoff solutions were created using soil samples collected from a construction site at Brookings, SD. The soil sample was mixed with water, and larger soil particles were allowed to settle in the primary reactor. The solution was then transferred to a secondary reactor and mixed continuously prior to use. The initial turbidity levels of the solutions were maintained at about 1500 NTU before PAM flocculation experiments. An anionic PAM, Superfloc A-130, was chosen for the second part of this research. A-130 PAM has a medium charge density and molecular weight. The experimental temperature was controlled at 20°C.

4.2.2 Mixing and Settling Variation

The factors that vary the most during soil flocculation using PAM on a construction site are the mixing and settling conditions. These conditions include the natural energy that is imparted to the water as well as any mechanical mixing devices that might be used to help promote the flocculation. A number of tests were performed in order to determine how much of an effect the mixing and settling factors have on reducing the runoff turbidity. Three different variables were tested during the flocculation experiments: the mixing time, the mixing intensity, and the settling time.

A six-position jar tester (Phipps & Bird, Richmond, VA) was used for the flocculation experiments. The sample volume for each flocculation experiment was 200 mL. At the beginning of the experiment, the soil solution was dosed with 0.1 or 1 mg/L of A-130 PAM. After that, the solution was immediately stirred for 10 seconds at 250 rpm to mix the polymer. The PAM and soil solution was then mixed at 50, 100, and 150 rpm for 0, 1, 2, 5, and 10 minutes. After each designated mixing time, the solution was allowed to settle for five minutes before taking samples for turbidity and TSS analyses. TSS was tested in order to compare it to final turbidity.

The effects of settling time were tested separately from the mixing time and intensity. The soil solutions were also dosed with 0.1 or 1 mg/L with A-130 PAM. After that, the samples were rapidly mixed for 10 seconds, and the slowly mixed at 100 rpm for 1 or 5 minutes. After the slow mixing was complete, the solutions were left to settle for 0, 1, 2, 5, and 10 minutes. Final turbidity and TSS were measured for each sample.

4.2.3 Calcium Addition

It has been reported that the presence of divalent cations, such as calcium and magnesium, promotes the flocculation of negatively charged clays using anionic polyacrylamide (Theng, 1982; Laird, 1997). However, little is known of the effects of varying calcium concentrations on construction site runoff PAM flocculation. A calcium chloride stock solution (44.4 g/L) was prepared to dose the synthetic runoff with varying calcium contents. Six 200-mL beakers were filled with runoff solution and placed under the jar tester. Calcium chloride stock solution was added to each beaker to achieve a range of calcium added concentrations of 0, 10, 20, 40, 80, and 160 mg/L. The beakers were then dosed with 0.03, 0.1, 0.3, 1, 3, or 10 mg/L of A-130 polymer. Each sample was stirred at 250 rpm for 10 seconds and then allowed to slow mix at 100 rpm for five minutes, after which the sample was allowed to settle for five minutes. Final samples were taken for determining turbidity, TSS, and calcium. Calcium concentration was measured by a standard hardness titration method after the sample being filtered through a 0.45-µm membrane filter. The quantity of the calcium adsorbed onto the soil particles can be determined by comparing the initial and final calcium concentrations in the sample.

4.2.4 Variation of pH

During the pH variation experiment, five beakers of synthetic runoff solution were dosed with varying amounts of either sulfuric acid stock solution or sodium hydroxide stock solution to adjust the pH of the runoff. The selected final pH values were 5, 6, 7, 8, and 9 to cover a wide range of pH conditions in construction site runoff. The five beakers were dosed with A-130 polymer at concentrations of 0.03, 0.1, 0.3, 1, 3, or 10 mg/L. Each sample was stirred at 250 rpm for 10 seconds and then allowed to slow mix at 100 rpm for five minutes, after which the runoff was allowed to settle for another five minutes. Turbidity and TSS were measured for each sample.

4.2.5 DOC Addition

It has been suggested that natural organic matter has a detrimental effect on fine soil flocculation using PAM. Some of the organic compounds can be adsorbed onto the clay particles, leading to less available surface area for the adsorption of polymer. This results in less PAM being adsorbed and consequently less effective flocculation (Lu et al., 2002). Stormwater runoff typically contains certain amounts of dissolved organic carbon. However, the impact organic matter has on PAM flocculation is largely unknown (Eganhouse and Kaplan, 1981). Suwannee River Fulvic Acid, obtained from the International Humic Substances Society, was used as a model organic matter to achieve different levels of DOC in the simulated runoff solutions. The fulvic acid was added to the samples at levels of 0, 1, 3, 5, 10, and 20 mg/L DOC. After that, the samples were dosed with 0.1, 1, or 3 mg/L of A-130

PAM. Each sample was stirred at 250 rpm for 10 seconds and then allowed to slow mix at 100 rpm for five minutes. Turbidity and TSS samples were taken after five minutes of settling.

4.2.6 Zeta Potential

Zeta potential is a measure of net electrokinetic potential in a particle dispersion. It indicates the extent that particles in the solution will repel each other. Zeta potential was measured for the simulated runoff while adjusting three parameters: PAM dosage, calcium, and pH. During the PAM tests, polymer was added to the synthetic runoff in a 42-mL vial in order to achieve a concentration range of 0.5, 1, 1.5, 2, 3, and 10 mg/L. The vial was then hand-shaken by inversion for one minute, after which solution was withdrawn using a syringe. Zeta potential was measured using a Lazer Zee Meter Model 501 (PenKem Inc., Bedford Hills, NY). An identical process was used for both calcium and pH variation. For calcium, the vials were dosed with varying amounts of calcium chloride stock, with resulting concentrations in the vial being 0, 10, 20, 40, 80, and 160 mg/L. Sodium hydroxide or sulfuric acid stock solutions were used to adjust the pH of the solution to the target pH values of 5, 6, 7, 8, and 9. The purpose of these tests was to determine the impact of these variables on the zeta potentials and their relationship with PAM flocculation performance.

4.3 Results and Discussion

4.3.1 Mixing and Settling Variation

Although anionic PAM has been tested for turbidity reduction from construction site stormwater runoff, the effect of field mixing and settling conditions on PAM performance has not been carefully evaluated. The PAM dosing and treatment system will require proper mixing and settling conditions before the runoff is allowed to enter the environment. It is important to design the mixing and settling zones to maximize the effectiveness of the PAM in reducing turbidity in the runoff water.

Figure 4.1 shows the final turbidity and total suspended solids after PAM flocculation of Brookings soil samples at different mixing intensity and duration. Throughout the test, increasing the mixing intensity from 50 to 150 rpm improved the removal of turbidity and TSS. The mixing intensity had a larger impact on turbidity removal for the 0.1 mg/L PAM dose than for the 1 mg/L PAM dose. For example, the final turbidity levels after treatment with 0.1 mg/L PAM were 183, 112, and 61 NTU, respectively, for mixing at 50, 100, and 150 rpm after 10 minutes. The corresponding turbidity levels were 66, 49, and 35 NTU when a PAM dose of 1 mg/L was used. This indicates that PAM doses lower than the optimal dose require higher mixing intensity to achieve better turbidity reduction.

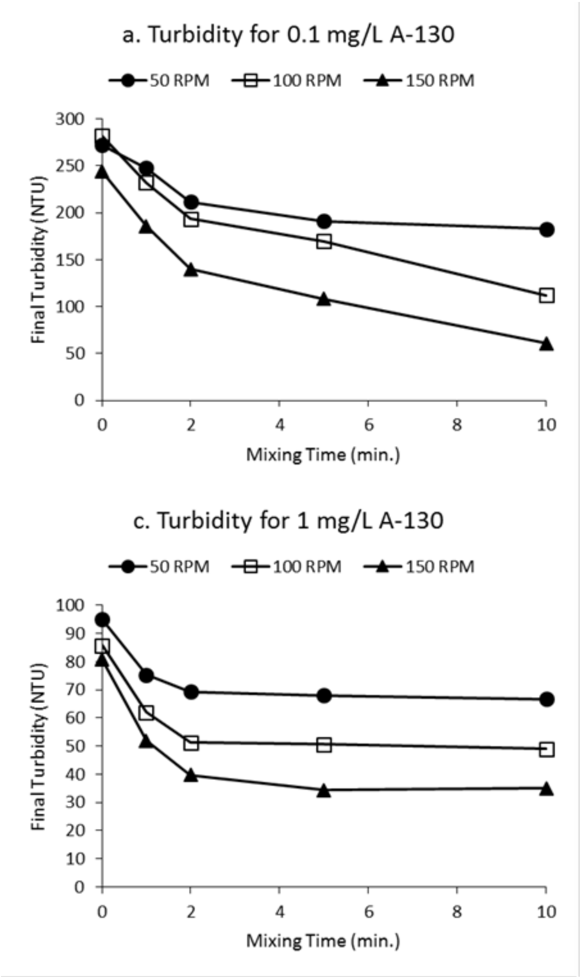


Figure 4.1 Final turbidity and total suspended solids after flocculation with A-130 PAM at different mixing speeds and time periods

The mixing time also had a marked effect on final turbidity and TSS. For the solutions dosed with 0.1 mg/L of PAM, the turbidity and TSS levels decreased quickly when increasing mixing time up to two minutes. After that, the turbidity and TSS continued to decrease at a slower rate until a mixing time of 10 minutes was reached. For solutions dosed with 1 mg/L of A-130, the turbidity and TSS levels also showed sharp decreases between 0 and 2 minutes. However, turbidity and TSS levelled off after two minutes. Additional mixing did not lead to improvement in either parameter. PAM and soil particles flocculation exhibited faster reaction kinetics at an optimal dose of 1.0 mg/L than at a lower dose of 0.1 mg/L, and the flocculation process was completed within two minutes due to higher efficiency. It should be noted that 0.1 mg/L A-130, one-tenth of the optimal dose, also showed good soil flocculation performance. It is recommended that adequate mixing conditions should be provided when low PAM doses are used for construction site runoff turbidity removal.

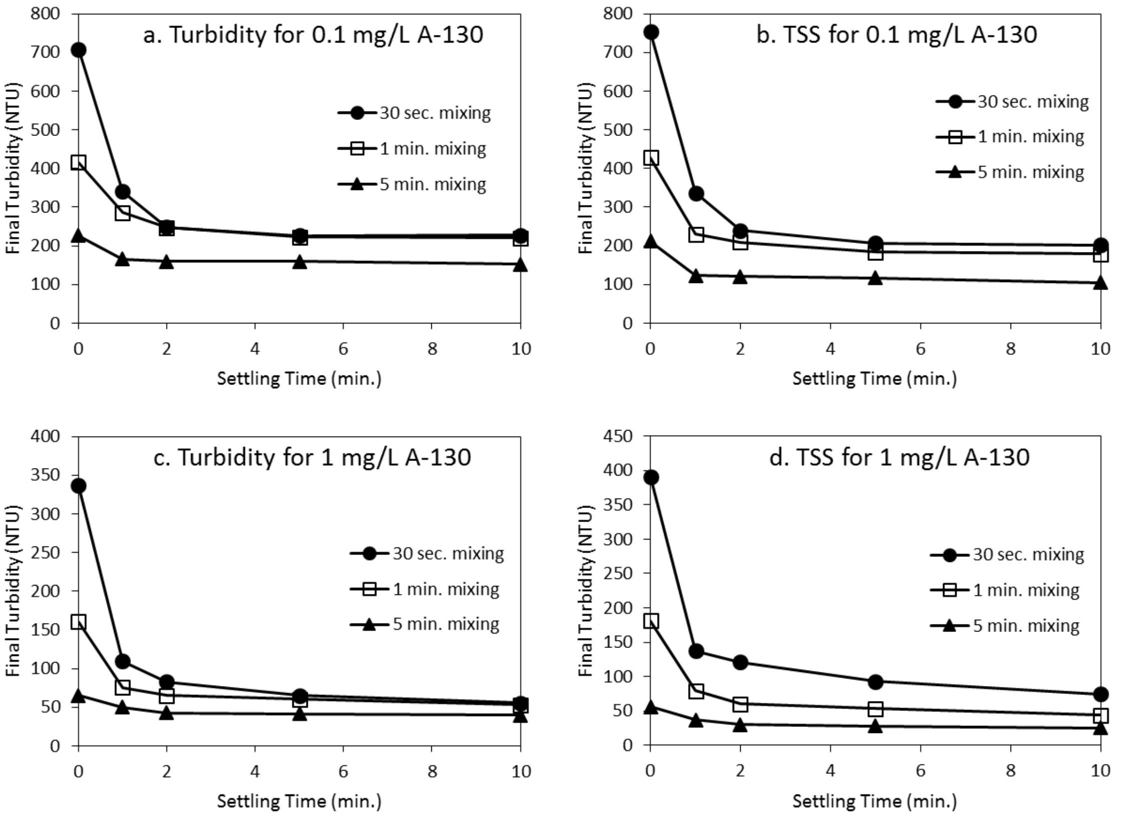


Figure 4.2 Final turbidity and total suspended solids after flocculation with A-130 PAM at different settling time periods

Figure 4.2 presents the final turbidity and total suspended solids after PAM flocculation of Brookings soil samples at different settling times. In general, increasing the settling time decreased final turbidity and TSS. However, the effect was much more pronounced in samples with shorter mixing times. For example, for PAM flocculation at a dose of 0.1 mg/L and a mixing time of 30 seconds, the turbidity decreased from 700 to 250 NTU when increasing settling time from 0 to 2 minutes. The turbidity only decreased from 230 to 160 NTU at the same settling time when the solution was mixed for five minutes. Similar results were also observed for 1 mg/L dose of PAM. The turbidity and TSS settling processes nearly completed within two minutes since these parameters did not vary much between 2- and 10-minute settling periods.

It is interesting to note that mixing intensity, mixing time, and settling time all affect PAM flocculation of the synthetic runoff solution. These three parameters should be considered simultaneously when designing and operating PAM treatment systems for construction site runoff. Increasing any of the variables will improve flocculation efficiency. On a construction site, if it is prohibitive to add a mechanical mixing system, allowing runoff to be retained for even a short settling period could greatly improve turbidity. In the same way, even if there were no room to allow for any settling structure, adding certain mechanical or static mixing elements after the PAM dosing point could be critical to meet effluent turbidity goals.

4.3.2 Calcium Addition

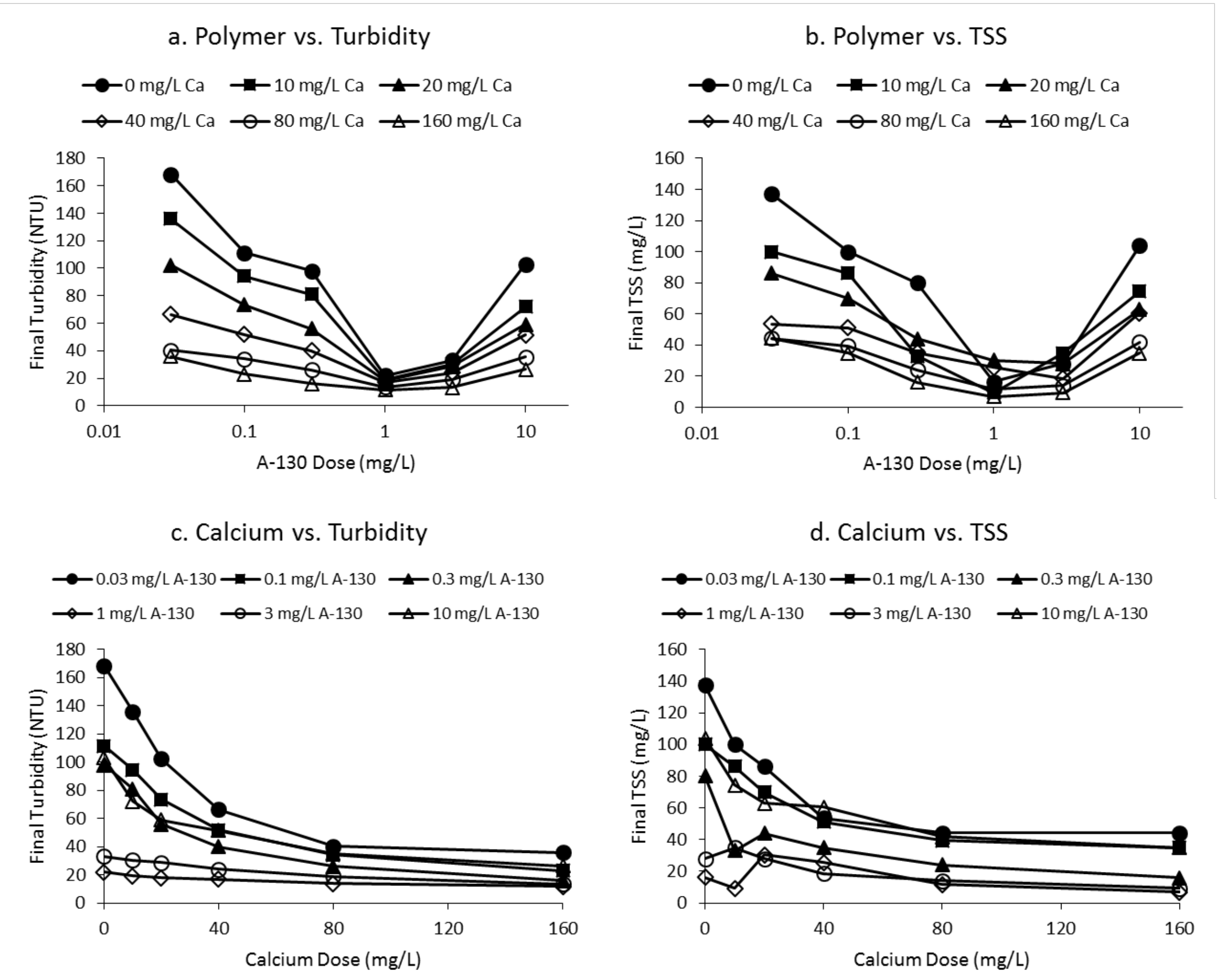


Figure 4.3 Effect of calcium addition on PAM flocculation

Figure 4.3 presents the effect of varying calcium concentrations on turbidity and TSS removal during PAM flocculation of Brookings soil runoff samples. Parts a and b in this figure show that turbidity and TSS removal improved with increasing calcium concentrations. The calcium effect on PAM flocculation was much more substantial at very low (0.03 mg/L) or very high (10 mg/L) PAM doses compared with the optimal dose (1 mg/L). Calcium had limited impact on final turbidity and TSS at the optimal PAM dose, perhaps because of the high flocculation efficiency at this dose. Parts c and d in Figure 4.3 reveal that calcium had a diminishing return effect when the added concentration exceeded 80 mg/L. Further increasing calcium beyond this point did not increase flocculation effectiveness.

Calcium concentrations in each sample before and after the flocculation experiment were determined using the titration method. Table 4.1 shows the adsorbed calcium concentrations during the PAM flocculation experiments. The adsorbed amounts of calcium increased with increasing polymer doses and initial calcium concentrations. However, the impact of increasing calcium concentrations was much more pronounced than increasing PAM doses. As indicated by Figure 4.3, a calcium dose of 80 mg/L led to the optimum condition for improving turbidity and TSS removal. There was a continual increase in calcium adsorption when further increasing the dose to 160 mg/L. However, the adsorbed calcium at this dose had limited impact on turbidity and TSS removal compared with the dose of 80 mg/L. It is possible that most of the available attachment sites on the soil particles were exhausted at the calcium dose of 80 mg/L, and further increasing calcium doses caused more calcium adsorption onto polymer chains, but did not aid in flocculation.

Table 4.1 Adsorbed calcium concentrations during flocculating with A-130 PAM

A-130 Dose (mg/L)	**$CaCl_2$ Dose (mg/L)**					
	0	**10**	**20**	**40**	**80**	**160**
0.03	0.0	1.6	3.1	11.0	24.2	47.4
0.1	0.0	2.5	3.2	11.1	23.2	49.3
0.3	0.0	2.5	5.1	12.1	25.1	49.4
1	0.9	4.4	6.0	13.0	25.1	50.2
3	1.8	5.3	7.9	13.9	27.0	51.1
10	1.8	5.4	7.9	13.9	27.0	52.1

4.3.3 Variation of pH

Varying the pH of the synthetic runoff solution also had an important effect on turbidity and TSS reduction. Figure 4.4 shows the turbidity and TSS reduction at different solution pH values and different doses of A-130 PAM. In general, within the pH range of 5 – 9, the lower the pH, the more effective the flocculation was. As seen with the calcium addition test, the pH effect was more evident at very low (underdosed) and high (overdosed) polymer concentrations. It seems that when the optimal dose of A-130 PAM (1 mg/L) is applied, variation of other factors has little effect. Peng and Di (1994) found that when the pH value gradually lowered from 9 to 5, flocculation efficiency increased, but when pH was below 5, efficiency dropped sharply. The pH levels can affect adsorption between PAM and soil particles by changing the electrostatic potential in the solution and the adsorption of dissolved ions onto both the clay particle and the PAM molecule (Peng and Di, 1994; Taylor et al., 2002). This in turn affects the attachment between PAM and clay particles and the effectiveness of PAM flocculation. The results of the pH test indicate that low pH conditions favor the PAM flocculation of simulated construction runoff. Varying the pH of construction site runoff may not be a viable option during runoff treatment. However, every construction site is different, and the pH of the runoff leaving the site is an important parameter that should be taken into account when designing a flocculation system since it has a considerable impact on the process.

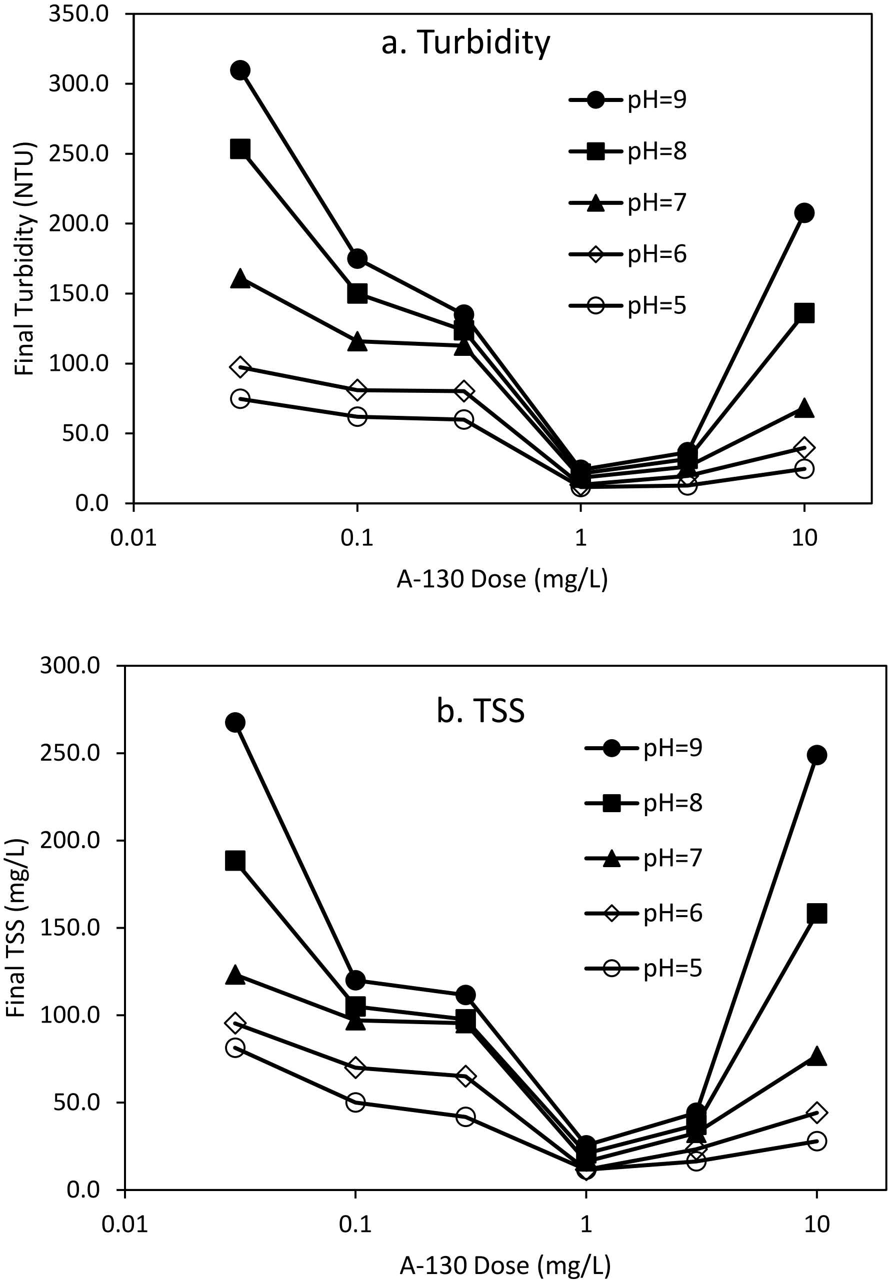


Figure 4.4 Effect of pH on turbidity and total suspended solids remvoal during PAM flocculation

4.3.4 DOC Addition

Tables 4.2 and 4.3 show the effects of DOC concentrations on the turbidity and TSS removal during flocculation using A-130 PAM. Fulvic acid was used as a source of DOC for this set of experiments. It has been determined that the presence of organic matter is detrimental to flocculation because the organic matter cements clay particles together in such a way that effective attachment sites are covered up (Lu et al., 2002). However, increasing DOC concentrations did not have a major effect on PAM flocculation during this study. The final turbidity increased by 37 NTU when increasing DOC levels from 0 to 20 mg/L for a PAM dose of 0.1 mg/L. The DOC concentrations had little impact on final turbidity for PAM doses of 1 and 3 mg/L. Similar results were also observed for TSS reduction. It is possible that the organic matter effect on PAM flocculation is site specific. Different soil organic matter and PAM flocculation conditions may have different impact on PAM effectiveness.

Table 4.2 Effect of DOC concentrations on turbidity levels during PAM flocculation

A-130 Dose (mg/L)	**Fulvic Acid Dose (mg C/L)**					
	0	**1**	**3**	**5**	**10**	**20**
0.1	192	194	190	176	216	229
1	62	62	58	63	66	63
3	56	57	55	57	62	53

Table 4.3 Effect of DOC concentrations on TSS levels during PAM flocculation

A-130 Dose (mg/L)	**Fulvic Acid Dose (mg C/L)**					
	0	**1**	**3**	**5**	**10**	**20**
0.1	149	151	160	144	181	191
1	53	51	51	51	58	56
3	51	51	49	49	56	47

4.3.5 Zeta Potential

The results of the zeta potential experiments are shown in Figure 4.5. When A-130 PAM was added to raw runoff solution, the resulting particle zeta potential decreased with increasing PAM doses. This is the opposite of some other studies that showed kaolinite particle zeta potential increased slightly in the presence of anionic PAM (Nasser and James, 2006; Mpofu et al., 2003). It was proposed that this effect was caused by a shift in the position of the plane of shear due to the negative polymer chains. However, Rounce (2012) found that all anionic PAMs decreased the zeta potential of soil particles collected from construction sites. The difference between these studies may have been caused by different particles used in the experiments. In the previous experiments, the addition of calcium chloride to the runoff solution improved flocculation effectiveness, especially with low doses of PAM. The analysis of zeta potential at different calcium concentrations showed that zeta potential increased from -25.7 mV to -22.5 mV when increasing calcium from 0 to 160 mg/L. The added calcium ions reduced the magnitude of the negative charge of particles likely because of the adsorption onto the particles, which contributed to the improved PAM flocculation effectiveness. Varying solution pH also had a noticeable effect on the zeta potential of the runoff solution. As the pH increased from 5 to 9, the zeta potential decreased from -19 mV to -27 mV. Peng and Di (1994) also found that increasing the pH of a kaolin slurry from 2 to 10 caused a decrease in zeta potential from 0 to -40 mV. They stated that the drop in zeta potential could be attributed to the change in oxygenic surfaces of the kaolin caused by the pH change. The reduced negative charge of particles at low pH conditions could explain at least in part the improved PAM flocculation performance.

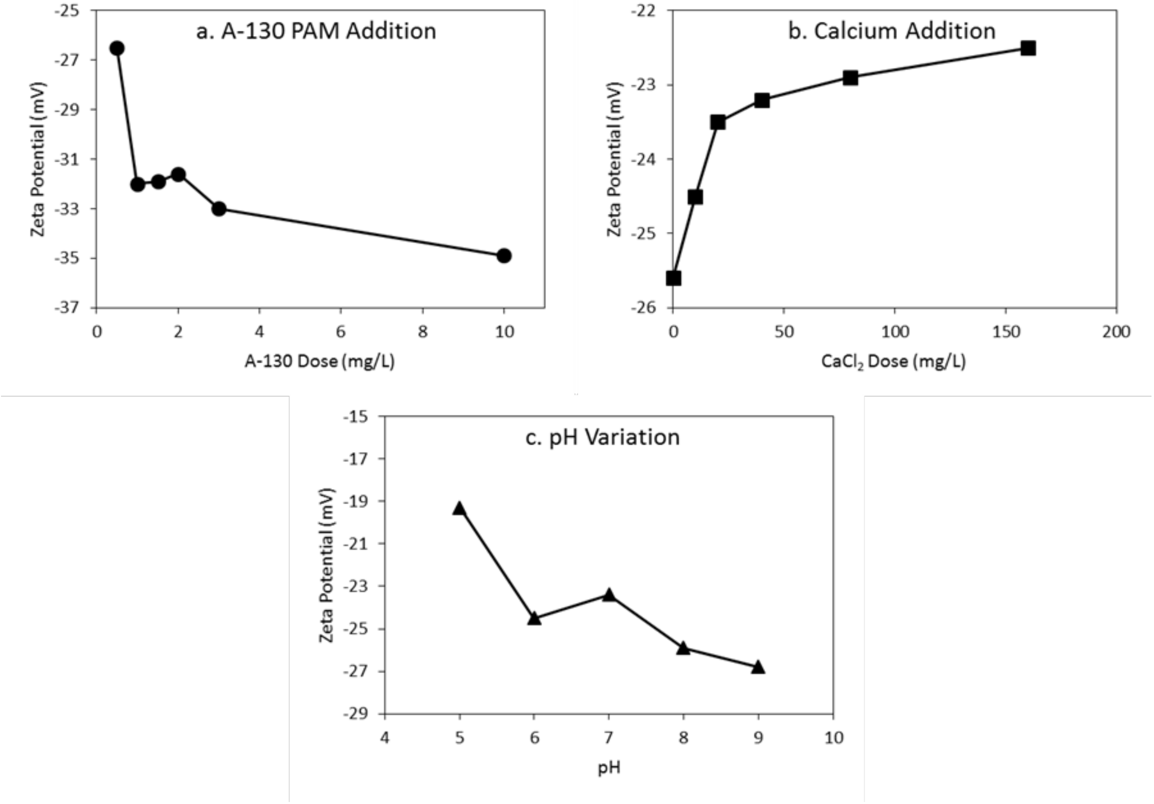


Figure 4.5 Effect of PAM, calcium, and pH variation on zeta potential of Brookings synthetic runoff

4.4 Summary of Effects of Water Quality and Mixing Regime on PAM Flocculation

During the second part of this research, one soil sample, from a construction site in Brookings, South Dakota, and one anionic polymer, Superfloc A-130, were used to determine the impact of important water quality parameters and flocculation conditions on PAM and soil flocculation. The flocculation mixing intensity, mixing time, and settling time were varied during the PAM flocculation experiments to evaluate their effects on final turbidity and TSS. The calcium concentration, the synthetic runoff pH, and the dissolved organic matter content were also varied to understand their roles in PAM flocculation. Finally, solution zeta potential was measured as a function of polymer dose, calcium concentration, and pH level.

The PAM flocculation efficiency increased when increasing the mixing intensity from 50 to 150 rpm. The effects of mixing intensity on turbidity and TSS reduction was more pronounced at a PAM dose of 0.1 mg/L than a dose of 1 mg/L. PAM doses lower than the optimal dose require higher mixing intensity to achieve better turbidity and TSS reduction. The turbidity and TSS removal during PAM flocculation was also improved with increasing mixing time. The PAM flocculation efficiency at a dose of 0.1 mg/L showed continuous improvement when increasing mixing time up to 10 minutes. When a PAM dose of 1 mg/L was used, the PAM flocculation process completed within two minutes. Further increasing mixing time at this dose had little impact on turbidity and TSS reduction. Therefore, the PAM flocculation kinetics was much higher at a dose of 1 mg/L than at a dose of 0.1 mg/L. Allowing the solution more time to settle after mixing improved the removal of turbidity and TSS. The sedimentation process after PAM flocculation generally completed within two minutes for various PAM dose and mixing conditions. After that, further increasing the settling time showed no additional gains in turbidity and TSS reduction.

In all tests performed, adding calcium ions to the solution enhanced PAM flocculation. This trend was most obvious when the runoff was underdosed (< 1 mg/L) or overdosed (>1 mg/L) with polymer. Calcium concentrations has limited impact on PAM flocculation when an optimal dose of 1 mg/L was applied. The results of these tests point to divalent cation bridging as a major mechanism of PAM flocculation. Within the pH range (5 – 9) tested, the lower the pH of the runoff solution, the more efficient the flocculation process was. Similar to the calcium addition test, the pH effects on PAM flocculation were more obvious at very low or high PAM doses. Addition of dissolved organic matter had little effect on the flocculation of fine soils with PAM.

Initial zeta potential of the soil solution was negative. The addition of anionic A-130 PAM slightly decreased this value. The zeta potential of the soil solution increased with increasing calcium concentrations but decreasing pH values. The reduced negative charge of particles at high calcium and low pH conditions could explain at least in part the improved PAM flocculation performance.

5. CONCLUSIONS AND RECOMMENDATIONS

Construction of highways usually requires large areas of land disturbance, which may result in accelerated soil erosion. The stormwater runoff from highway construction sites typically contains a large amount of fine particles that can negatively affect the water quality of the receiving water. PAM flocculation has been demonstrated to be a cost-effective and practical BMP for erosion and sediment control. The application of PAM in construction sites requires an evaluation of specific soil types and climate conditions. The objective of this research is to evaluate various factors that can affect PAM flocculation performance and provide recommendations on construction site runoff treatment using PAM.

During the first phase of this study, four simulated construction site runoff solutions were created using soil samples from construction sites at Aberdeen, Brookings, Rapid City, and Sioux Falls, SD. These solutions were flocculated with seven different PAMs under controlled lab conditions. The flocculation experiment results showed that PAM flocculation is an effective technology to reduce turbidity from simulated construction site runoff. In general, PAMs with higher charge densities and molecular weight performed better than PAMs with lower charge densities and molecular weight. The long-chain polymers in high molecular weight PAMs may have contributed to the effective attachment between soil particles and PAM, which led to higher flocculation efficiency. The optimal polymer dose was approximately 1 mg/L for anionic PAMs. Flocculation with the anionic PAMs at a dose of 1 mg/L was able to reduce the runoff solution turbidity from an initial value of about 1,500 NTU to less than 200 NTU after the treatment. Further increasing PAM doses beyond the optimal dose deteriorated the PAM flocculation performance. Nonionic and APS polymers were less effective compared with anionic PAMs at low doses. Cold temperatures negatively affected the PAM flocculation of soil solutions, especially at low dosages. However, different PAMs generally achieved similar levels of turbidity reduction at different temperatures when an optimal dose of 1 mg/L was used.

During the second phase of this research, Brookings soil samples and Superfloc A-130 were used to determine the impact of important water quality parameters and flocculation conditions on PAM and soil flocculation. The results showed that the PAM flocculation efficiency increased when increasing the mixing intensity from 50 to 150 rpm. The effects of mixing intensity on turbidity and TSS reduction was more pronounced at a PAM dose of 0.1 mg/L than a dose of 1 mg/L. PAM doses lower than the optimal dose require higher mixing intensity to achieve better turbidity and TSS reduction. The turbidity and TSS removal during PAM flocculation was also improved with increasing mixing time. The PAM flocculation efficiency at a dose of 0.1 mg/L showed continuous improvement when increasing mixing time up to 10 minutes. When a PAM dose of 1 mg/L was used, the PAM flocculation process completed within two minutes. Further increasing mixing time at this dose had little impact on turbidity and TSS reduction. The sedimentation process after PAM flocculation generally completed within two minutes for various PAM dose and mixing conditions. After that, further increasing the settling time showed no additional gains in turbidity and TSS reduction.

In all tests performed, adding calcium ions to the solution enhanced PAM flocculation. This trend was most obvious when the runoff was underdosed (< 1 mg/L) or overdosed (>1 mg/L) with polymer. Calcium concentrations have limited impact on PAM flocculation when an optimal dose of 1 mg/L was applied. Within the pH range (5 – 9) tested, the lower the pH of the runoff solution, the more efficient the flocculation process was. Similar to the calcium addition test, the pH effects on PAM flocculation were more obvious at very low or high PAM doses. Addition of dissolved organic matter had little effect on the flocculation of fine soils with PAM. The zeta potential of the soil solution increased with increasing calcium concentrations but decreasing pH values. The reduced negative charge of particles at high calcium and low pH conditions could explain at least in part the improved PAM flocculation performance.

The results of this study suggest that PAM flocculation effectively removed fine particles and reduced turbidity of construction site runoff. Different PAMs behaved differently when treating soil samples collected from four construction sites in South Dakota. Therefore, it is recommended to perform lab testing of specific soil samples to determine the optimum PAM type and dosage for construction site runoff treatment. Although there is an optimal polymer dose to achieve the minimum turbidity of the treated water, this study shows that only a fraction of this dose may be needed to lower the turbidity to the target value. When exceptionally cold temperatures are present on a construction site, the PAM dose may need to be increased to compensate for the loss of flocculation efficiency. The results of the calcium addition tests indicate that bridging by divalent cations is an important mechanism of soil flocculation using anionic polyacrylamide. When natural divalent cations in the soil are scarce, calcium addition could be used to enhance flocculation or decrease the amount of PAM needed for turbidity reduction. The flocculation experiments of this study also suggest that mixing intensity, mixing time, and settling time are critical factors that can affect final turbidity levels. Increasing mixing intensity, mixing time and settling time could help achieve better final runoff turbidity, especially when relatively low PAM doses are applied. Therefore, an adequate mixing and settling condition should be provided when using PAM for construction site runoff treatment.

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