A Technology for Enhanced Control of Erosion, Sediment and Metal Leaching at Disturbed Land Using Polyacrylamide and Magnetite Nanoparticles

by

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Abstract

Urbanization and human disturbance of land often result in serious soil erosion and releases of fine sediments and soil-bound toxic metals, which can lead to contamination of downstream water bodies and cause water treatment plant failure. Yet, effective technologies for rapid soil stabilization at disturbed sites have been lacking. The study tested the effectiveness of a commercial soil conditioner, known as polyacrylamide (PAM), in combination with a class of polymer-bridged magnetite nanoparticles for simultaneous control of soil erosion and metal leaching from disturbed sites. A small-scale box-test setup was constructed to test the releases of sediments and soluble metals from two disturbed surface under simulated rainfall conditions. Sandy loam soil from a local quarry mining site and Smith Farm loam soil were used as the model soils. Polymer-bridged magnetite nanoparticles were prepared using PAM or a water soluble starch as bridging agents. Arsenic (V) was used as a model soluble toxic metal. PAM stabilized magnetite nanopartilces (Total Fe=0.1g/L) had significant effects on runoff concentration control (90.8% reductions for Vulcan Site soil, 89.1% reduction for Smith Farm soil) and significant amount of turbidity removal (83.0% reductions for Vulcan Site soil, 90.5% reduction for Smith Farm soil), with 30% reduction of viscosity compared to PAM only. Starch partially stabilized magnetite nanoparticles associated with PAM application successfully immobilized the arsenate in soils (below 8% arsenate is leachable). Vulcan site soil is more vulnerable to runoff but easier to be stabilized by nanoparticles when contaminated than SmithFarm soil. Low pH value (pH: 5.46) and high dosage of Fe nanoparticles (total Fe = 1g) as well as the soil texture presents better removal efficiency for arsenate immobilization. Batch adsorption test and immobilization kinetics test reinforced the above findings.

Key words: Arsenate immobilization; Magnetite nanoparticles; Polyacrylamide (PAM); Runoff; Sediment; Soil erosion; Water pollution control.

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Chapter 1 Introduction

1.1 Overview

Various human activities, such as construction and mining, can result in serious soil disturbance, leading to soil erosion and releases of large quantities of fine sediments and even toxic metals into aquatic systems. For example, soil erosion and runoff during and after mining operations and other mining activities often generate large amounts of silts and sediments that can pose environmental problems including changes in the water quality in nearby bodies of water, changes in the stream morphology, alterations of hydrologic and hydraulic characteristics, impacts on aquatic habitat, and increased flooding (Codner, 2001; Sansalone and Buchberger, 1997). Polluted storm water runoff often ends up in local rivers or streams (MPCA, 2001). The recovery time from sediment is measured in years. Furthermore, waters draining active and, in particular, abandoned mines and mine wastes in a quarry are often acidic (sometimes extremely acidic). Such waters typically pose an additional risk to the environment by the fact that they often contain elevated concentrations of metals (iron, aluminum and manganese, and possibly other heavy metals) and metalloids of which arsenic is generally of greatest concern, which are otherwise stable in the environment, can then be dissolved and mobilized.

To mitigate soil erosion and the associated water pollution problems, various rules and regulations have been enacted. Since mining activities involve major changes to the landscape with associated erosion, sediment releases, and dust propagation, mining sites are subjected to numerous federal environmental laws such as the Clean Water Act (CWA) and Clean Air Act (CAA) (Kogel et al., 2006). The CWA was amended in 1987 to empower the United States Environmental Protection Agency (EPA) to establish a phased National Pollutant Discharge Elimination System (NPDES) permit program. Phase I NPDES required any construction activity with a start date in 1990 or later and that would impact greater than five acres to comply with the permit requirements and to comply with certain land management requirements during and after the operations. In 2003, Phase I NPDES requirements were tightened to become Phase II NPDES. Under Phase II NPDES, construction activities (pollutants include sediments and erosion from these sites) that disturb greater than one acre of land are subject to the NPDES permit requirements. To control erosion and sediment release, operators of regulated sites are required to develop and implement storm water pollution prevention plans and to obtain the required permits from an authorized state agency or from the US EPA. There are other federal environmental laws that could impact quarrying operations, such as the Fish and Wildlife Resource Management Act, the Fish and Wildlife Coordination Act, and the Endangered Species Act (Kogel et al., 2006). Federal occupational health and safety laws apply to all sectors of the mining industry. In addition to these federal laws, there are local and state laws that regulate the operation of these sites. For example, in Maine, mining is governed by the general land-use regulations as well as several other specific environmental statutes and rules to protect wetlands, beaches, dunes, water bodies, wildlife habitat, and other environmentally sensitive areas (MDEP 2008). Another example would be North Carolina’s Mining Act of 1971 (as amended through 2000), which required any aggregate mining operation of one acre or more to apply for a North Carolina mining permit and post a reclamation bond. In 2008, the US EPA proposed effluent limitation guidelines, mandating construction sites to reduce initial turbidity level to 13 NTU

(US EPA, 2008). At the conclusion of the mining operation, the sites must be reclaimed before the reclamation bond is released. As a result of these various laws, Erosion and Sediment Control Plan is often required to control anticipated erosion and to prevent sediment from leaving the site.

Water soluble anionic polyacrylamide (PAM) has been considered as an economical, safe, and environmental friendly soil conditioner that appears to have a variety of beneficial soil amendment properties such as reducing storm water runoff, controlling soil erosion, and stabilizing soil structure (Flanagan et al., 2002a, b; Sojka, 2008). In addition, PAM has been shown to have the potential for reducing the associated contamination. Unfortunately, PAM has some key limitations when used at mining sites. The main limitation is that negatively charged anionic PAMs are ineffective for binding with soil particles and colloids that carry the same surface charge. Since the soils from most mining sites are negatively charged (i.e. the point of zero charge (PZC) is negative), PAMs would need to be modified. Another limitation is that PAMs are less effective in soils with a low metal presence or with clay or silt content ("sandy soils"). Still another limitation is that PAMs have a higher molecular weight with the result that PAM poorly penetrates into aggregates to an ineffective depth (Mamedov et al., 2007). In addition, the large PAM molecules have greater viscosity when in a solution or in an emulsion with the result that soil hydraulic conductivity is reduced and surface re-vegetation is prevented (Malik and Letey, 1992). Any approach or strategy for modifying PAM products would need to extended molecular size/structure without increasing the viscosity and the soil pore blockage behaviors.

PAM has been widely studied for controlling erosion and sediment in furrow irrigation, but very little research has been done on the use of PAM on very steep slopes (4:1 to 2:1) that are typical of a mining site (Flanagan et al., 2002; McLaughlin and Brown, 2006).

Water soluble PAM has amide and carboxylic functional groups. These groups can interact with metal. There is no known research on how this behavior can help with the retainment of metals in runoff. Gonzalez et al (2006) analyzed the movement of solids and heavy metals in runoff waters and they noted that it would be desirable to control both erosion and metal dispersal. Thus, there is a need to study PAM effectiveness for metal immobilization as well as for soil stabilization.

Of all the metals and metalloids, arsenic (chemical symbol: As) is the greatest concern, because it is present in many areas in the US (Cebrian et al., 1983; Chowdhury et al., 1999; Dhar et al., 1997; Karim, 2000; Mondal et al., 2006). The soil functions as an important sink for arsenic compounds, because the accumulation is greater than the uptake by plants or by leaching or by erosion (Smith et al., 1998). Soil sorbed arsenic is sensitive to mobilization due to weathering actions, soil erosion, and human actions (Mohan and Pittman, 2007). Mackenzie et al. (1979) estimated that soil erosion contributed 612 x 10^5 kg per year and that leaching contributed 2,380 x 10^5 kg per year of dissolved and suspended arsenic to the oceans.

Most environmental arsenic problems have come from mobilization. Arsenic and other toxic metals such as chromium, cadmium, and mercury, have been reported in various mining sites in the drainage and tailings (Smith et al., 1998). The most common form of arsenic in the soil is the arsenate compound (Bowell, 1994; Garcia-Manyes et al., 2002). Under the authority of the Safe Drinking Water Act, the EPA required public water systems to meet by January 23, 2006 the arsenic standard of 10 parts per billion or less (An et al., 2005). The previous standard was 50 parts per billion or less; the tighter standard was a great challenge to many water utilities, because the presence of arsenic in all sources had to be addressed (An et al., 2011). There remains an urgent need for developing innovative technologies to control soil erosion and the associated mobilization of toxic metals such as arsenic at various disturbed sites.

Iron oxides have been widely studied for the removal of arsenic from contaminated soil and groundwater (Guo and Chen, 2005; Manning et al., 2003; Pierce and Moore, 1982; Raven et al. 1998). Iron oxides applied to garden soils have shown decreases as much as 50% in water extractable arsenic concentration, together with lower accumulation levels in plant tissues (Mench et al., 1998). The surfaces of iron oxides are known to be involved in arsenic adsorption from soils (Jacob et al., 1970; Lumsdon et al., 1984; Waychunas et al., 1993).

Commonly used iron oxides include bulk crystalline Fe(III) oxide such as goethite and hematite (Coker et al., 2006; Giménez et al., 2007; Pierce and Moore, 1982; Raven et al., 1998) can cause less removal of arsenic in the presence of other iron oxides and tend to bind to filters (Shipley et al., 2010). Synthetic nanoparticles have an advantage over bulk crystalline iron oxides due to the increased surface area, which would allow for more sorption action of arsenic (Banfield and Navrotsky, 2003; Rusanov, 2005). Amorphous iron oxides have equal to or greater specific surface area than bulk crystalline iron, but amorphous iron oxides are often difficult to separate and can leave iron residuals in the water after treatment (Hering et al., 1997).

Recently, magnetite nanoparticles have gained increasing interest due to the potential application of adsorbing contaminants from aqueous effluents with increased adsorption capacity (Bowell, 1994; Giménez et al., 2007; Moeser et al., 2002; Shipley et al., 2009 and 2010; Yavuz et al., 2006; Yean et al., 2005) and also they can be easily separated from solution with low field magnets or filters (Moeser et al., 2002). Herein, magnetite nanoparticles were used in this research.

1.2 Goals and objectives

The overall research goal was to test a modified technology that would combines PAM and bridged magnetite nanoparticles for controlling soil erosion and releases of sediments and arsenic compounds. The aim would be to modify the molecular configuration of PAM by taking advantage of the strong interactions (complexation) between PAM and the nanoparticles. The specific objectives are:

1. Prepare a new class of nanoparticle-modified PAM (Nano-PAM) emulsion by in situ synthesizing magnetite nanoparticles in the presence of commercially available PAM products.
2. Test the effectiveness of the new materials for controlling erosion, sediment, and runoff of two model soils under various environmental conditions.
3. Test the effectiveness of the Nano-PAMs or bridged magnetite nanoparticles for immobilization of arsenic in disturbed surface soils.

Chapter 2 Soil Erosion Tests with Simulated Rainfall

2.1 Introduction

2.1.1 Soil erosion

Soil erosion is exposed soil caused by the loss of vegetation by water, wind, and ice with the result of reduced soil-water capacity and with the reduced soil productivity due to the losses of sediments, nutrients, etc., by runoff (Bertol et al., 2007). It can lead to pollution and eutrophication in water bodies where the eroded materials are deposited (Pote et al., 1996). Soil erosion has been considered a major form of soil degradation that is a naturally occurring process and that can be accelerated by human activities (Sepaskhah and Mahadi-Hosseinabadi, 2008) and it is one of the most serious eco-environmental problems in the world (Srivastava et al., 2010).

Construction sites and other locations with disturbed soil are very susceptible to soil erosion, especially during the critical period before vegetation has become well established. Lack of vegetal cover coupled with high slope gradients and lengths combine to leave these sites extremely vulnerable to soil loss (Flanagan et al., 2002b). In coal mining areas, soil erosion has resulted in more than just the transformation of fertile and cultivated land into wasteland, the greater problem is siltation (the pollution of water by fine particles such as heavy metals) into nearby water bodies with the great loss of aquatic biodiversity and economic wealth. This is worst of geo-environmental disasters (Wong et al., 2003).

There is a marked relationship between rainfall and erosion, where heavy rainfall accelerates soil degradation (Marques et al., 2007). Soil is vulnerable on steep slopes and erosion can cause nutrient loss from the ecosystem (Fu and Chen, 2000). Soil erosion on steep slopes can lead to time-consuming and costly repairs.

Construction activity erosion control best management practices (BMPs) are typically designed to prevent soil erosion and to reduce sediment transport. BMPs that reduce runoff volume are typically able to reduce soil erosion and sediment transport (Beighley et al., 2010). One BMP is to use anionic polyacrylamide (PAM) for reducing soil erosion along with other practices for dealing with rain fed areas (Murphy et al., 2010).

2.1.2 Polyacrylamides (PAMs)

PAMs are a class of polymeric compounds synthesized by the polymerization of acylamide monomers. PAMs that are used for erosion control, tend to be copolymerized macromolecules with a fraction (20-70%) of amide groups substituted by carboxylic groups as shown in Figure 2.1.

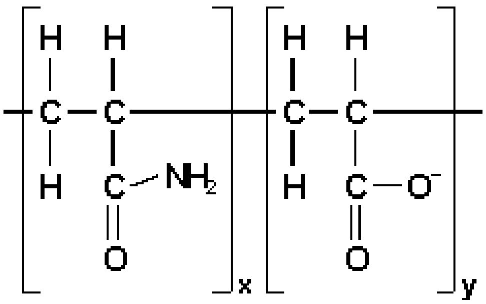

Figure 2.1. The Repeating Functional Units of an Anionic PAM.

Note: The amine (NH2) and carboxylic groups (COO-) can interact strongly with soil minerals and metals.

Soil stabilizing polymers were used during World War II to aid in road and runway construction (Wilson and Crisp, 1975). The concept was adapted for agricultural uses in the early 1950s (Weeks and Colter, 1952). Typically, the polymers are one in five chain segments that provide a charged site for bonding. The erosion control PAMs are large (12-15 megagrams per mole), water soluble (non-cross-linked) anionic molecules, and containing less than 0.05% acrylamide monomers. These PAM products are also effective flocculants for accelerating the separation of solids from aqueous suspensions (Sojka, 2008).

PAM molecules can aggregate fine soil particles (mainly with the clay/silt fractions) through Coulombic and Van der Waals forces (Orts et al., 1999, 2000). This PAM molecule behavior enhances particle cohesion forces and increases resistance to shear-induced detachment, thereby consolidating the soil structure and preventing sediment transport in runoff. Any escaped particles are quickly flocculated by the PAM molecules and the particles settle out of the transport stream.

PAMs have been sold in the US since 1995 for reducing irrigation-induced erosion and for enhancing infiltration. The soil stabilizing and flocculating properties can greatly improve runoff water quality by reducing the presence of sediments, N, P, COD (chemical oxygen demand), pesticides, weed seeds, and microorganisms (Agassi et al., 1995; Jiang et al., 2010; Lentz et al., 1998). The first series of field tests for using anionic PAM for irrigation erosion control on medium to fine textured soils were conducted in the U.S. in 1991 with the result that an average reduction of 94% (80-99% range) of sediment loss and an increase of 15-50% relative infiltration when compared to untreated controls fields were achieved (Sojka, 2008).

PAMs can be used either as soil binders to stabilize top soil or as flocculants to aggregate suspended solids (SS) in wastewater, the soil binding usage is much more economical (Gannon, 1999). For soil stabilization, PAM is mixed at a ratio of approximately 1 lb. per 1,000 gallon of water and sprayed over the disturbed surface. (Each 1,000 gallon solution covers approximately 1 acre.) Flanagan et al. (2002) reported on a study conducted at a Vulcan Materials Company aggregate pit in West Lafayette, Indiana under simulated rainfall conditions. The results indicated that the use of a PAM product (applied at 80 kg ha^{-1}) reduced the total runoff by 40% to 52%, and sediment loss by 83% to 91% for the test plots.

The optimum application rate of PAM is influenced by the soil slope (Sepaskhah and Bazrafshan-Jahromi, 2006). Only a few number of studies has focused on PAM effectiveness on steep slopes (from 1% to 25% incline) (Cochrane et al., 2005; Flanagan and Canady, 2006 a&b; Lee et al., 2010; Martinez-Rodriguez et al., 2007; McLaughlin and Brown, 2006). Even less is known about its effectiveness on much steeper slopes (4:1 to 2:1) that is typical of quarrying sites. Wallace et al. (1986) conducted laboratory studies on small plots at 58% slopes, with PAM applied at rates ranging from 16 to 161 kg[ha.sup.$^{-1}$] (14 to 144 lb[sac.sup^{-1}]), and they found that soil loss rates decrease with increasing rates of PAM application. Flanagan et al. (2002a) used simulated rainfall to test PAM sprayed on a 32% constructed slope of bare clay loam subsoil. Then they modified the experiment to test PAM alone (80kgha^{-1}) and PAM plus 5Mgha^{-1} gypsum with test parameters of under natural rainfall, on a silt loam soil, and at 45% slope (Flanagan et al., 2002b). The results showed that PAM alone and PAM plus gypsum significantly reduced the average sediment loss from 40% to 54% as compared to an untreated control plot. Hayes et al. (2005) tested three North Carolina Department of Transportation construction sites (located outside of the Appalachian Mountains and foothills areas of the state) by using 10.5kgha^{-1} PAM or less on 20% and 50% of fill slopes, but in contrast to the results of Flanagan et al. (2002b), they did not notice any significant benefits with the PAM products applied to moderate to steep slopes. Shoemaker (2009) evaluated anion PAM with different application rates and application methods on slopes that mimic conditions similar to highway embankment with 3:1 incline. His results showed that dry PAM with an application rate of 35 lbs per acre performed the best by significantly reducing initial turbidity level by 97% and eroded soil by 50% when compared to a bare soil control plot. Liquid PAM without any time to dry before the execution of the rain simulation performed the worst. As indicated by these different findings, more research on steeper slopes is needed.

Research has shown that water soluble anionic PAMs that contain less than 0.05% acrylamide monomer are safe and are environmentally friendly soil conditioners (Sojka, 2008). Environmental and safety considerations of anionic PAMs have been thoroughly reviewed (Barvenik, 1994; Bologna et al., 1999; Seybold, 1994). The most significant environmental effects of any PAM use is its soil erosion reduction, its protection of surface waters from sediment, and its protection of surface waters from other contaminants flowing from eroding fields. In any soil, PAMs degrade at a rate of about 10% per year as a result of physical, chemical, biological and photochemical processes and reactions (Azzam et al., 1983; Tolstikh, et al., 1992; Wallace et al., 1986)). Unlike anionic PAMs, cationic and neutral PAMs have toxicities warranting caution or preclusion from sensitive environmental uses. In 2000, National Resources Conservation Service specified soil treated with anionic PAM as a BMP for controlling soil erosion. The US EPA and the US Food and Drug Administration have also approved anionic PAM products for use in food processing, in water treatment and in many other sensitive applications (Sojka and Lentz, 1997). PAMs are economical costing between $4.50 to $12 per kilogram of active ingredient, are able to be effective at low rates (1 to 5 kg per hectare per season), and are relatively easy to use (Sojka, 2008).

Although PAMs have shown great promise for rapid control of soil erosion and sediment at agricultural settings, this technology has some key technical limitations that call for further improvement of this approach, especially when this technology is applied at quarrying sites. These are:

First, because anionic PAMs are negatively charged, the effectiveness is greatly reduced for binding with soil particles or colloids that carry similar negative surface charges. PAMs are also less effective for soils of low metal or clay/silt content (e.g. sandy soils), and it often fails to bind with soils of high organic matter (OM) (Lu et al., 2002). Soils from most quarrying sites are negatively charged (i.e. the PZC is below the surrounding water or soil pH). Fine sandy particles and sandy soils have been fairly common at aggregates production facilities and have been accumulating for years. Therefore, modifications of PAMs would be needed in order to enhance the effectiveness at quarrying sites.

Second, it is generally believed that since PAMs have a higher molecular weight (MW) and have longer molecules, the result would be more efficient binding of fine soil particles (the larger "grappling distance" behavior) (Theng, 1982). However, a PAM of a high MW would penetrate poorly into aggregates with the result of in a less effective depth (Mamedov et al., 2007). Furthermore, the large PAM molecules have the behavior of greater viscosity in a solution or emulsion with the result that soil hydraulic conductivity is reduced (Malik and Letey, 1992), which is harmful to the subsequent surface re-vegetation. Therefore, a highly desired strategy is one that would result in extended molecular size and structure without increasing the viscosity and soil pore blockage.

Third, PAM has been widely studied for controlling soil erosion and for controlling sediment accumulation in furrow irrigation, but much less is known about its effectiveness on very steep slopes (4:1 to 2:1) typical of quarrying sites (Flanagan et al., 2002; McLaughlin and Brown, 2006). Therefore, research is needed to facilitate applications of the PAM-based technology at quarrying sites.

Lastly, water soluble PAMs carry amide and carboxylic functional groups, both of these can interact with metal cations such as Pb^{2+} and Cd^{2+}. However, there has been no documented research on its effectiveness for retaining anion metals such as arsenic in runoff. Gonzalez et al. (2006) analyzed mobilization of solids and metals in quarries runoff waters and they noted that it would be desirable to control both erosion and moving metals. Therefore, there is a need to study the effectiveness of PAMs for metal immobilization as well as the effect of metal ions on the performance of PAMs for soil stabilization.

2.1.3 PAM and nanoparticles

Nanotechnology is the manipulation of matter for use in a particular application through certain chemical or physical processes or both to create materials with specific properties. There are two commonly used methods. One method is the top down nanotechnology that can be achieved by scaling down lithographic techniques, miniaturizing patterns, and creating nanostructure; the other method is the bottom-up nanotechnology in which small molecules or particles are assembled into large 2D to 3D structures (Sijbesma and Meijer, 2008).

Polymers are perfectly fitted to bridge the gap between the top down and bottom up nanotechnologies since the polymer's size is between the atomic and macroscopic scale. It was hypothesized that combining the commercial PAM with magnetite nanoparticles will achieve some synergistic effects that are beneficial for soil erosion control and in situ immobilization of leachable metals. First, given the anionic functional groups of PAM, strong interactions between PAM and the magnetite particles are expected. As a result, the nanoparticles may serve as "joints" or "bridges" between multiple PAM molecules, forming a polymeric network that is supposedly more effective for binding fine soil particles, and thus, soil erosion control; and second, the PAM molecules serve as a bridging agent that prevent the nanoparticles from agglomeration, and thus, maintaining high specific surface area and sorption capacity for binding leachable toxic metals such as arsenic.

Herein, PAM was introduced to magnetite nanoparticles synthesis, where we plan to take advantage of the size scale of the polymers. In addition, nanoparticles can enhance the particle-aggregating ability of PAM molecules as illustrated in Figure 2.2. Since PAM is integrated into nanoparticles, its viscocity will surely be reduced as the molecule size goes down. Again, our goal is to obtain larger Nano-PAM complexes that can capture more fine particles without increasing the viscosity of the emulsions.

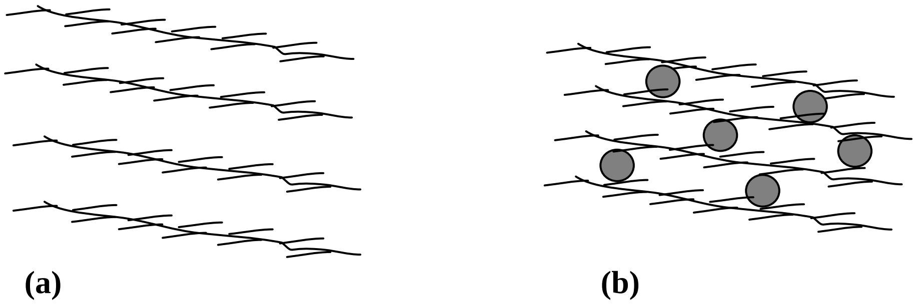

Figure 2.2 (a) PAM molecules are loose and discrete without the nanoparticles. (b) PAM molecules are bridged together with nanoparticles.

Note: Nano-PAM offers much stronger power for trapping fine soil/sediment particles and for sorption of heavy metals without increasing viscosity.

2.2 Materials and methods

2.2.1 Soils

Two sample field soils were used in this study, one sample from the Vulcan Materials Company’s Notasulga Facility (8938 Alabama Highway 14, Loachapoka AL 36865) (Figure 2.3(a), (b), and (c)) and the other sample from the Auburn University E.V. Smith Research Farm (about half way between Auburn and Montgomery near Interstate 85) (Figure 2.3(d), (e), and (f)). Both soils were sampled from the top 0-0.3m layer. Raw soils were used for small scale box soil erosion test aiming to simulate the natural soil erosion process under rainfall.

Figure 2.3 (a) Vulcan Material Company Notasulga Quarry; (b) Vulcan Construction Site Runoff View; (c) Vulcan Soil Sample Collecting Site; (d) E.V. Smith Research Center; (e) Smith Farm Soil Collecting Site; (f) Close View of Smith Farm Surface Soil.

The potentiometric titration method was used to determine the soil point of zero charge (PZC) (Vanraij and Peech, 1972). The other soil selected soil properties in Table 2.1 were analyzed by Auburn University Soil Testing Lab. Elements were determined simultaneously by

Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry using a Varian Vista-MPX Spectrometer. Soil texture analysis was conducted by Bouyoucos Hydrometer Method.

Table 2.1 Selected Physical and Chemical Properties of the Studied Soils

	Vulcan Site Soil	**Smith Farm Soil**
pH	5.67	4.76
Organic Matter (%)	0.5	1.3
CEC[a] (meq/100g)	0.31	0.29
Fe (mg/L)	39	104
Al (mg/L)	84	132
Ca (mg/L)	294	52
Mg (mg/L)	306	80
P (mg/L)	9	3
Mn (mg/L)	39	35
Sand (%)	80.0	36.3
Silt (%)	2.5	45.6
Clay (%)	17.5	18.1
Texture Class	Sandy Loam	Loam

Note: CEC[a] = cation exchange capacity.

2.2.2 Box test setup

2.2.2.1 Small scale box test facility

The Auburn University Harbert Engineering Center Loading Area was used for this researcher's small scale box test. The wood frames for supporting the rain simulation system were custom built by mounting on the handrails in north side of the loading area and contained features specifically tailored for this research (Figure 2.4). Electricity from nearby electrical outlets was used to power the instruments.

Figure 2.4 Small-Scale Test Facility

Figure 2.5 Rainfall Simulator

2.2.2.2 Rainfall simulator

The construction of the rainfall simulator (Figure 2.5) consisted of a half-inch (1.27 cm) diameter PVC pipe, support wood, a garden hose, and electrical wiring for the solenoid valve.

A sprinkler system for simulating natural rainfall was constructed by mounting a specialty nozzle (FullJetTM ½HH – 30WSQ, Spraying System Co., Carol Stream, Illinois, USA) to a wood frame 10 ft above the concrete floor. The overall rainfall simulator extended 7.5 ft (2.25m) horizontally by supporting wood from the building concrete column. The nozzle was connected with a solenoid valve (ASCOTM 2-way 8210 series, ASCO Valve, Inc., Florham Park, NJ, USA) and a pressure regulator (NorgrenTM R43-406-NNLA, Norgren, Littleton, CO, USA) that could create medium to large droplets with a wide angle uniform sprayer that could produce a distribution pattern similar to natural rainfall. A pressure gauge was attached to the pressure regulator for monitoring the operating water pressure and thus allow for any necessary adjustments to be made during the operation in order to ensure a constant flow. Local tap water, which originated from Lake Ogletree, Auburn, AL, was used as the rain water.

2.2.2.3 Rain uniformity

To determine and analyze rainfall uniformity, an 8 ft x 8 ft (2.4 m x 2.4 m) grid was placed beneath the simulator. The dimensions of the gird covered approximately the total spray area of the rainfall simulator. At 1 ft (0.3 m) intervals, using intersecting gridlines, marks were placed on the floor (the concrete floor slab) and 2.5-quart (2,365 ml) containers were placed at these locations to collect the "rainfall" (Figure 2.6). To ensure uniformity of the water sprayer, three trial runs at three different operating pressures of 5, 10, and 20 psi for a total duration of 10 minutes were used.

Figure 2.6 Rain Uniformity Test Setup

The Christian Uniformity Coefficient in equation (1) was used to quantify rainfall distribution as a uniformity percentage (ASAE Standards, 2000). Generally, the uniformity coefficient ranged from 80% to 100%, which is acceptable. A test area was determined to be a 4×4 ft^2 area right underneath the sprayer nozzle; yellow water-proof tape was used to mark the boundary of this area. The calculations for different variables are shown in Table 2.2. (Notice that “Test Plot Area” is the 16 ft^2 area located directly under rainfall simulator nozzle). Referring to Shoemaker (2009), 10 psi is used in this research.

$$\mathrm{CUc} = 100 \times \left[1 - \frac{\sum_{i=1}^{n} vi - \bar{v}}{\sum_{i=1}^{n} vi}\right] \qquad (1)$$

Where,

CUc = Christian Uniformity Coefficient,

n = number of collectors,

vi = volume of water in the ith collector, and

$\bar{v}$ = mean volume of water in all collectors.

Table 2.2 Christian Uniformity Coefficients for Rainfall Simulator

Trial	**Entire 8´×8´ spray area**	**Test Plot Area**
5 psi		
1	78.9%	87.4%
2	79.1%	88.7%
3	79.3%	88.6%
Average	**79.1%**	**88.2%**
10 psi		
1	77.8%	85.5%
2	79.9%	87.6%
3	78.9%	87.3%
Average	**78.9%**	**86.8%**
20 psi		
1	75.6%	87.0%
2	74.2%	86.3%
3	74.4%	87.5%
Average	**74.7%**	**86.9%**

2.1.2.4. Test plots construction and setup

Two parallel boxes (Figure 2.7(a) and (b)) were built for holding the soil samples. Each box would simulate a plot of 12 inches in width 36 inches in length, and 3 inches in depth. The design and construction of the boxes were similar to the test plots recommended by McLaughlin and Brown (2006) and Shoemaker (2009) with the only difference is that the widths of the boxes were a half scale less than Shoemaker's boxes.

The boxes were constructed from pressurized timber, consisting of a half-inch (1.27 cm) plywood base and one-by-threes to form the perimeter. At the down-slope end, a metal strip with 3/8-inch holes was drilled to prevent water ponding, as recommended by McLaughlin and Brown (2006). A PVC pipe was cut in half and installed below the metal strip to catch potentially soil infiltration.

In addition to the metal strip and the PVC pipe, plastic gutters were fabricated and installed at the down-slope end to function as a runoff collection device. Figure 2.7(c) show how the gutters were attached to one of the test boxes.

Reduction in weight and ease of setup offers greater amount of flexibility for this small scale box test. Two commercial grade sawhorses were purchased to support the test boxes and to allow a sleep slope for testing. Cinderblocks were used to support the down-slope end and raise the elevation of test boxes to allow for collection buckets to be placed under the gutter discharge point. This testing setup allowed for a test slope of 3:1 to be established. See Figure 2.7 (d) for photos of the completed test plot boxes.

To reach the desired level of compaction, the test soil must be near the recommended moisture content of 15% as determined twenty-four hours before the experiment (Shoemaker, 2009). Soil and water were thoroughly mixed in a basin. Part of the mixture was placed into a test box and then hand-tamped for 90 drops (Shoemaker, 2009) or until the layer is one inch deep. More mixture is added and the hand-tamping is repeated. When the layer is two inches thick (Figure 2.8), then the test plots are treated with the selected applications as required for the experimentation.

For each experiment run, a test plot was prepared in accordance with the following five steps:

1. Determine the existing water content of the soil samples.
2. Compact the soil samples.
3. Apply the treatment agents.
4. Position the boxes at the desired slope.
5. Run the simulated rain test.

Figure 2.7 (a) Front View of Test Plots; (b) Side View of Test Plots; (c) Runoff Collection Device; (d) The Testing Setup of Slope of 3:1.

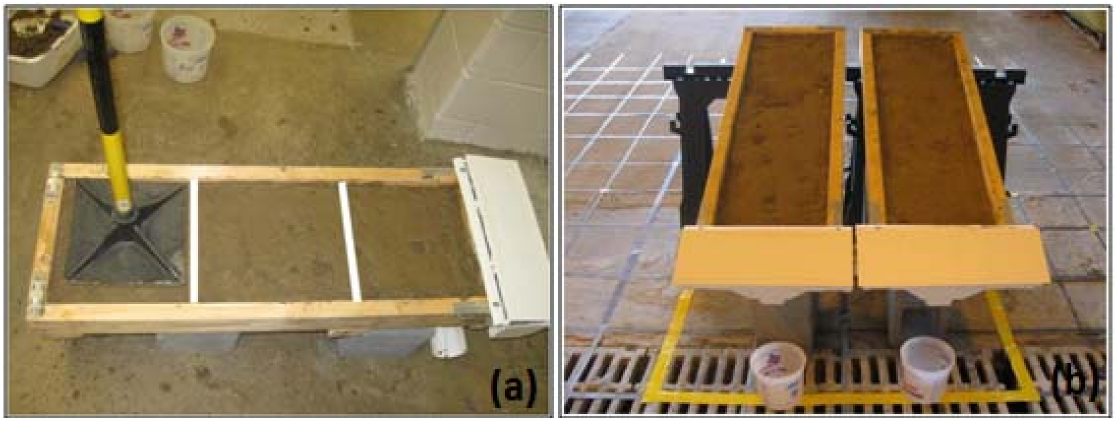

Figure 2.8 (a) 3 Sections to Compact the Soils; (b) Compacted Soil (i.e. Smith Farm Soil)

2.2.3 Soil treatment

A commercially available soil conditioner known as APS#705 or PAM 705 was used to treat the soil samples (see Table 2.3 for information on the soil conditioner properties). The polymers in a granular form came from Applied Polymer System, Inc. (Woodstock, GA, USA) (Figure 2.9).

Applied Polymer System, Inc. provided information on the recommended amount of water needed for mixing with the PAM products in order to achieve the proper water to PAM ratio (3,000 gallons per acre). Applied Polymer System, Inc. adjusts the ratio for clay soil (10 lbs of PAM product and 1,000 gallon water) and for sandy soil (50 lbs of PAM product and 1,000 gallon). The necessary amount of PAM solution required for all experiments was based on 3,000 gallons per acre, which when converted to experimental scale worked out to be 0.261L/ ft^2. For this scale, only 782ml of PAM 705 solution is needed for one 3 ft^2 plot.

Table 2.3 APS 700 Series PAM Properties (Given by APS Manufacture)

Properties	
Appearance	white, granular
Bulk Density	40-50 lbs/cubic foot
Percent Moisture	15% maximum
pH 0.5% solution	6~8
Shelf Life	up to 5 years

At least four hours prior to the experiment, the liquid form of PAM 705 was prepared by mixing granular PAM 705 (Figure 2.9) with tap water at a polymer-to-water ratio between 0.25:100 and 0.3:100. The dissolved PAM was used within one hour and it was applied with a garden sprayer onto a targeted soil plot. Our results indicated that the soil binding effectiveness decreased when the dissolved PAM was used two days later. This agreed with Gregory (1988), who pointed out that a particle-to-particle encounter will result in bridge formation only when the particles carry an active polymer. i.e., freshly absorbed polymer with long loops. Since the active state of a polymer is in a transient, nonequilibrium state, the result is a limited lifetime. With each PAM application, the test plots were allowed to completely dry and to stabilize for three days before being subjected to a simulated rainfall event. PAM 705 application performance is evaluated in duplicate. To compare the effect of the soil stabilizers, control tests were run in parallel with the same compacted soil plot, but without application of the soil stabilizers.

Figure 2.9 Granular PAM705

2.2.4 Preparation of PAM-bridged magnetite nanoparticles

The following chemicals (ACS grade or higher) were purchased:

1. From Fisher Scientific (Pittsburgh, PA, USA):
    a. $FeCl_3$
    b. NaOH
    c. HCl
2. From Acros organics (Morris Plains, NJ, USA).
    a. $FeSO_4 \cdot 7H_2O$

All solutions were prepared with ultrapure deionized (DI) (18.2 MΩcm^{-1}) water.

To achieve simultaneous control of soil erosion and leaching of toxic metals (e.g. arsenic), a new class of PAM-bridged magnetite nanoparticels were prepared for this work.

PAM-bridged magnetite nanoparticles were prepared at room temperature (21^{o}C) as follows:

1. The liquid form of 1% PAM 705 stock solution was prepared by mixing granular PAM 705 with deionized (DI) water at 1:100 polymer-to-water ratio for at least 4 hours ahead to allow complete dissolution.

2. A ferrous-ferric stock solution was prepared at an Fe^{2+}/Fe^{3+} molar ratio of 1:2 by dissolving respective iron salts ($FeSO_4 \cdot 7H_2O$ and $FeCl_3$) in deoxygenated deionized water.
3. Under nitrogen-purging, 1,380 ml of ferrous-ferric stock solution was mixed with 600 ml of 1 wt. % of the PAM 705 solution to give 0.1g/L as total iron and 0.3% of PAM 705.
4. About 20 ml of a 2M NaOH solution was injected into the Fe-PAM mixture, which resulted in a final pH of ~11.
5. The resultant magnetite nanoparticles suspension was sealed and placed in the dark to allow nanoparticles to grow mature for at least 12 hrs.
6. The mixture pH was brought down to ~7.0 by adding ~2ml of a 2M HCl stock solution under nitrogen purging and the mixture was allowed to stay still for one hour when a steady pH was reached.

Then, 782 ml of PAM 705 stabilized nanoparticles (see Figure 2.10) were rapidly poured out from the 2,000 ml nanoparticle stock solution to the garden sprayer reservoir and this was carefully sprayed evenly on each test plot. The test plots were allowed to dry for three days.

Figure 2.10 0.3% PAM705 Stabilized Magnetite with 0.1g/L Total Fe

2.2.5 Viscosity of PAM and nano-PAM emulsions

In addition to collecting soil erosion and runoff data, the viscosity of the PAM and of the Nano-PAM emulsions would be measured with a Gilmont falling ball viscometer (Gilmont Instruments, Barnant Company, Barrington, IL, USA).

2.2.6 Simulated rainfall tests

A rainfall event was designed based on Shoemaker (2009) guidance. These would consist of four 15 minute events at 10 psi that generates a rain intensity of 4.39 in/hr. These four events would be used to simulate the desired 2-year, 24-hour storm event and thus would allow a researcher to examine the long term effectiveness of PAM treatments (Shoemaker, 2009). A period of no rainfall would be observed to allow researchers time to collect data in between the events.

Effluent runoff samples were collected at the one-minute point, at the 5 minute point, and every five minutes thereafter until the 60 minute point is reached. The weight and volume of the samples were measured. The initial turbidity and turbidity changes over time were measured using a HACH 2100N Laboratory Turibidimeter (Hach Co., Loveland, Colorado, USA) for all the samples. Sediment samples would be collected by transferring the runoff samples into labeled beakers and dried in a conventional oven overnight at 105 ^oC and weighed afterwards.

2.2.7 Statistical analysis

Statistical analysis on the experimental data was carried out by using Statistical Analysis System (SAS) and Microsoft Excel. All the results were expressed as means ± S.D. (standard deviation) of replicates when possible. Experimental results under various conditions were analyzed by one-way analyses of variance (ANOVA) or by a t-test to compare the differences. Differences were considered significant at $p < 0.05$.

2.2.8 Chemical analysis

Solution or suspension pH was measured using an Oakton pH meter (pH 510 Benchtop Meter, Oakton Instruments, Vernon Hills, IL, USA).

2.3 Results and discussion

2.3.1 Physical and chemical characteristics of two soils

The surface property of a soil sample depended upon the activities of the potential determining ions ($H^+$and OH^-) and electrolyte concentrations (ionic strength, I) (Van Olphen, 1963). The pH value where the net total particle charge is zero is called the PZC, which is one of the most important parameters used to describe variable charge surfaces (Morais et al., 1976; Park and de Bruyn, 1962). Generally, soil PZC was determined by potentiometric titration method (Vanraij and Peech, 1971). The PZCs of Vulcan site soil and Smith Farm soil are 5.03 and 4.86, respectively as shown in Figure 2.11 and Figure 2.12. Compared to soil pH value (pH=5.67), the Vulcan site soil has a net negative charge and predominately exhibited an ability to exchange cations, while the Smith Farm soil tended to retain anions (electrostatically) because its pH value (pH= 4.76) is slightly below its PZC.

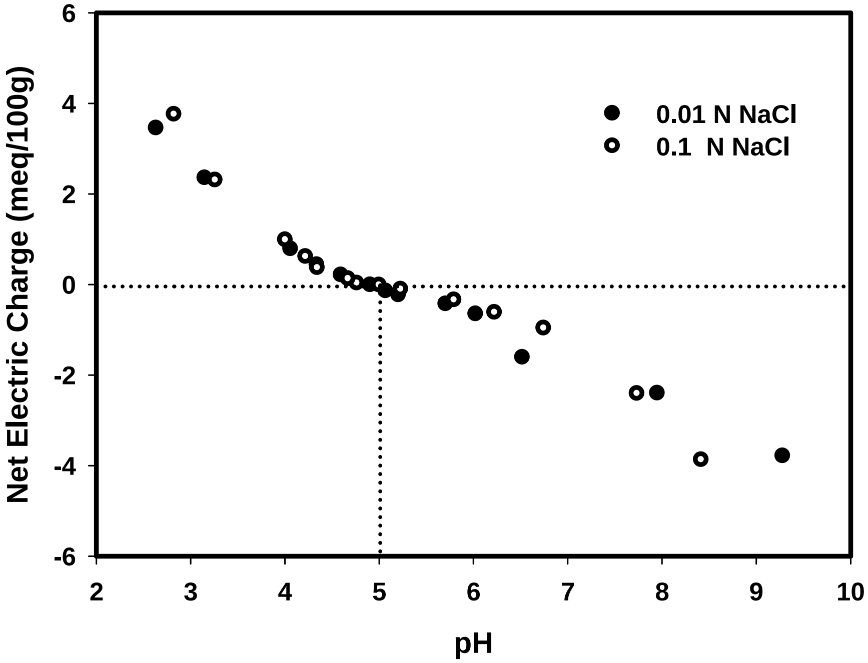

Figure 2.11 The Surface Charge of Vulcan Site Soil as Determined by Potentiometric Titration.

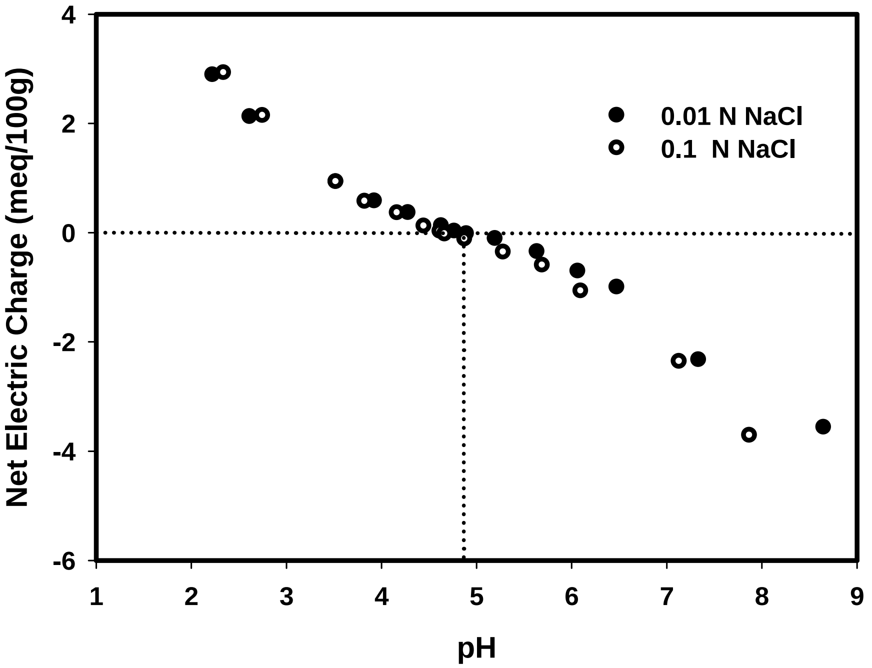

Figure 2.12 The Surface Charge of Smith Farm Soil as Determined by Potentiometric Titration.

2.3.2 Soil erosion tests under simulated rainfall

Rapid soil erosion may be attributed to combination of bare, loose soil conditions resulting from various disturbances such as tillage, logging, mining, or construction activities. The steep slope (greater than 25%) is typical of agricultural production in many regions of the world as well as many forested regions and construction sites within the US, can experience extreme soil loss. Santos et al. (2003) claimed that a 5% slope was responsible for a 52% increase in sediment loss for ten representative soils at a southern Portugal site. Many engineered activities, such as construction of highways, landfills, and aboveground reservoirs, often result in embankments of steep slopes (3:1 to 2:1). In this study, a representative steep slope of 3:1 was selected in all of the soil erosion tests.

2.3.2.1 Vulcan site soil erosion test

0.3% PAM 705 and 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe=0.1g/L) treatments are illustrated in Figure 2.13, Figure 2.14, and Figure 2.15, respectively. The following sub paragraphs will discuss the figures in more details.

2.3.2.1.1 Runoff flowrate

Figure 2.13 showed that under the same rain fall intensity, the differences in runoff flow profiles were statistically insignificant ($p < 0.05$) for untreated soils and for soils treated with PAM or the suspension of PAM-magnetite mixture.

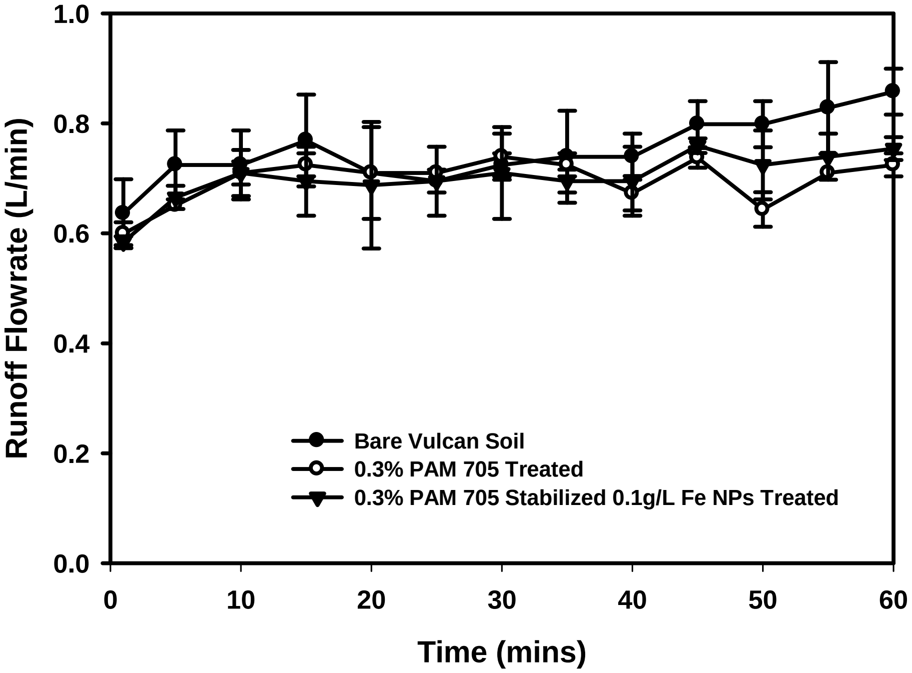

Figure 2.13 Comparison of Bare and Treated Vulcan Site Soils Runoff Flow Rate Variation with Time

2.3.2.1.2 Average runoff concentration of sediments

Figure 2.14 showed that the average runoff concentration of sediments on the control plots increased rapidly to 32.6 g/L and then slowly decreased to about 19.4 g/L at the end of the simulation run. Larger error bars exist due to sandy loam texture of the Vulcan site soil. The average sediment yields for the control and the PAM only treated group kept constant at 19.58±3.42g and 0.49±0.15g respectively, while it kept increasing for the PAM nanoparticles treated group. However, both PAM treatments resulted in significant reductions in the sediment yield compared to the control plots ($p < 0.05$). The sediment yield for the PAM only treated group was almost negligible for the entire run. Sediment yields for PAM treatments were statistically significantly different ($p < 0.05$) from one another. The cumulative sediment yield for the study period indicated that a significant reduction of 97.5% and 90.8%, respectively, for PAM only and PAM nanoparticles treatments as compared to the control plots. This finding is supported by Flanagan et al. (1997), who found that sediment runoff was reduced in PAM-amended silt loam soil plots compared to the control plots under the same runoff conditions. Also, agreement was reached with Zhang and Miller (1996) who found that an application of 15 or 30 kg/ha of PAM sprayed on the soil surface and allowed to dry greatly reduced soil loss in a rainfall simulation study on a Cecil sandy loam soil.

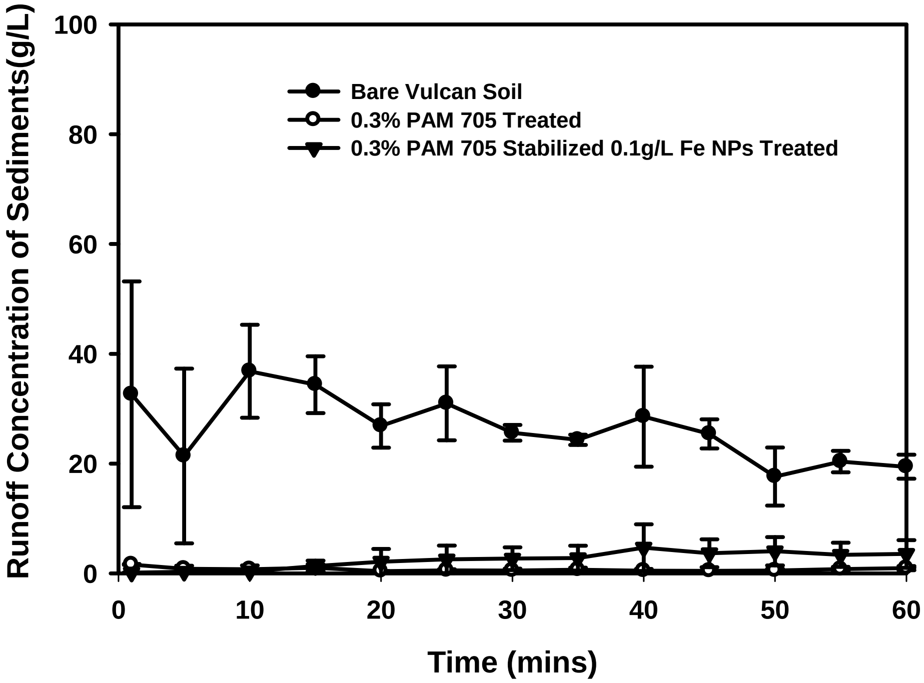

Figure 2.14 Comparison of Bare and Treated Vulcan Site Soils Runoff Concentration of Sediment Variation with Time

2.3.2.1.3 Initial runoff turbidity

The proposed EPA effluent limitations guideline would mandate that construction sites would need to reduce the initial turbidity to 13 NTU (US EPA, 2008). However, up to date, while this thesis is written, EPA (US EPA, 2010) proposed a revised limit for Construction and Development Effluent Limitation Guideline. The regulation is effective on February 1, 2010. After this date, all permits issued by EPA or states must incorporate the final rule requirements. All construction sites required to obtain permit coverage must implement a range of erosion and sediment controls and pollution prevention measures. Beginning on August 1, 2011 all sites that disturb 20 or more acres of land at one time are required to comply with the turbidity limitation. On February 2, 2014 the limitation applies to all construction sites disturbing 10 or more acres of land at one time. These sites must sample stormwater discharges and comply with a numeric limitation for turbidity. The limitation is 280 NTU (nephelometric turbidity units).

For this work, 13 NTU was set as the ultimate goal for turbidity reduction. Figure 2.15 compared the initial turbidity histories of the control test plots and PAM or PAM-magnetite treated plots for the Vulcan site soil during the one hour rain event. For the control plots, the runoff initial turbidity level remained high with an average turbidity of 244.5±27.5 NTU throughout the test period. When treated with either 0.3% PAM 705 or 0.3% PAM 705 stabilized magnetite nanoparticles (0.1 g/L as Fe), the turbidity was consistently suppressed during the test period, with an average turbidity reduction of 89% and 83%, respectively. Apparently, the addition of the nanoparticles slightly decreased effectiveness of the PAM product for controlling soil erosion. This could be attributed to the fact that preemptive binding of PAM with the nanoparticles reduced the sites available for binding with soil particles; thus this would lessen the PAM product's capacity for erosion control. It was expected that by combining PAM and magnetite nanoparticles, the result would be to offer the advantage of controlling both soil erosion and leachable arsenic. Another apparent advantage with the mixed PAM-magnetite suspension is the reduction in viscosity. In actual practice, the PAM concentration had been limited by its viscosity. High viscosity prevented the polymeric molecules from penetrating into the soil with the result of limited treatment depth. With the addition of the magnetite nanoparticles (0.1 g/L as Fe), the viscosity for 0.3% PAM was reduced from 13.04 centipoises to 9.09 centipoises, which is a 30% reduction. The runoff sample turbidity from the PAM and PAM nanoparticles treatment plots increased during the rain event may have been caused by rainfall shear force, that is, some of the PAM was flushed away. Another possibility is that since any PAM treatment weakens over time, the PAM treatment was becoming ineffective due to age.

Statistical analysis via t-tests indicated that the runoff NTU levels were significantly different ($p < 0.05$) for each of the treatments.

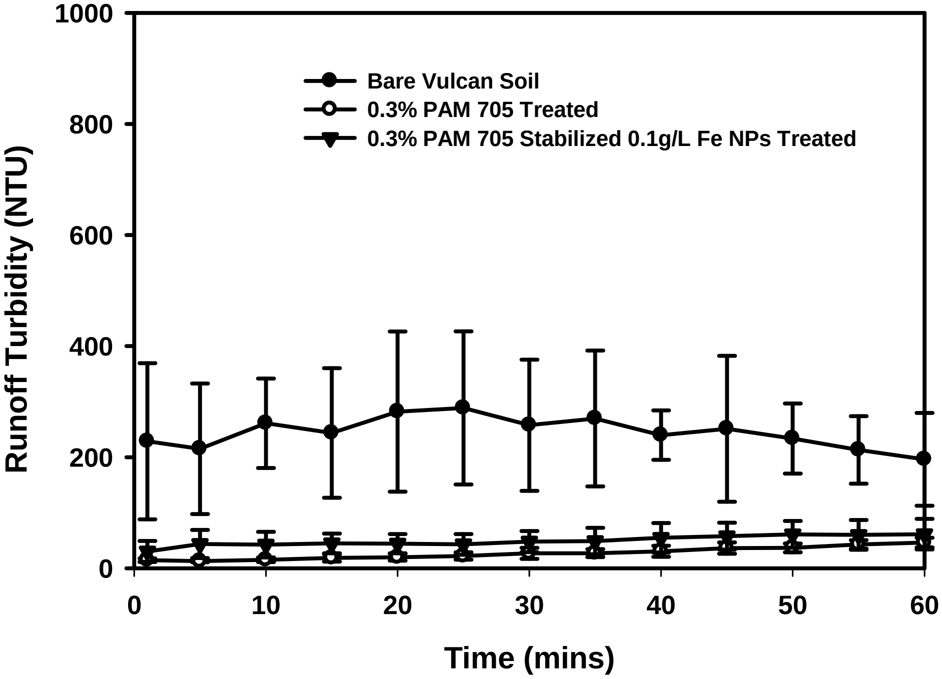

Figure 2.15 Comparison of Bare and Treated Vulcan Site Soils Runoff Turbidity Variation with Time

2.3.2.1.4 Turbidity kinetics

Further investigations were conducted on turbidity kinetics measurements to determine relative performance between treatments and control. Overall runoff samples average turbidity variation over time for control, 0.3% PAM 705 and 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe=0.1g/L) treatments are illustrated in Figure 2.16, Figure 2.17, and Figure 2.18, respectively.

The collected data were representative of the time required for suspended soil particles in the runoff to settle out. The turbidity of runoff samples decreased for all cases. The turbidity slowly decreasing over time for the control plots with the 96 hour point being the time for all runoff samples to clear up the initial turbidity of 244.5±27.5 NTU down to 13NTU. Treated plots cleared up faster; 8 hours for the PAM only treated plots and 48 hours for the PAM nanoparticles treated plots for turbidity to drop down to 13 NTU. Turbidity is generally the result of clay-size sediment in suspension. PAM is particularly effective at stabilizing soil against detachment and transport of fines as well as flocculating and removing fines from runoff. Small soil aggregates were visually observed for PAM treatment groups due to the fact that as rainfall and surface runoff activated the PAM molecular, these were introduced into the storm water and bonded with suspended soil particles, promoting flocculation and settling. Liquid PAM that was allowed to dry thoroughly on the soil surface provides a thin layer of protection against soil erosion. This layer effectively prevented the soil particles from being detached and becoming transported in the storm water.

However, no aggregates were observed for the control group, the sediment detached from the test plot were the surface soil. Fewer aggregates were found in PAM nanoparticles treated group since the PAM was used as a stabilizer for nanoparticles, but no brownish color was observed in the runoff. This means Fe nanoparticles stayed in the soil matrix potentially serving as contaminant absorbent.

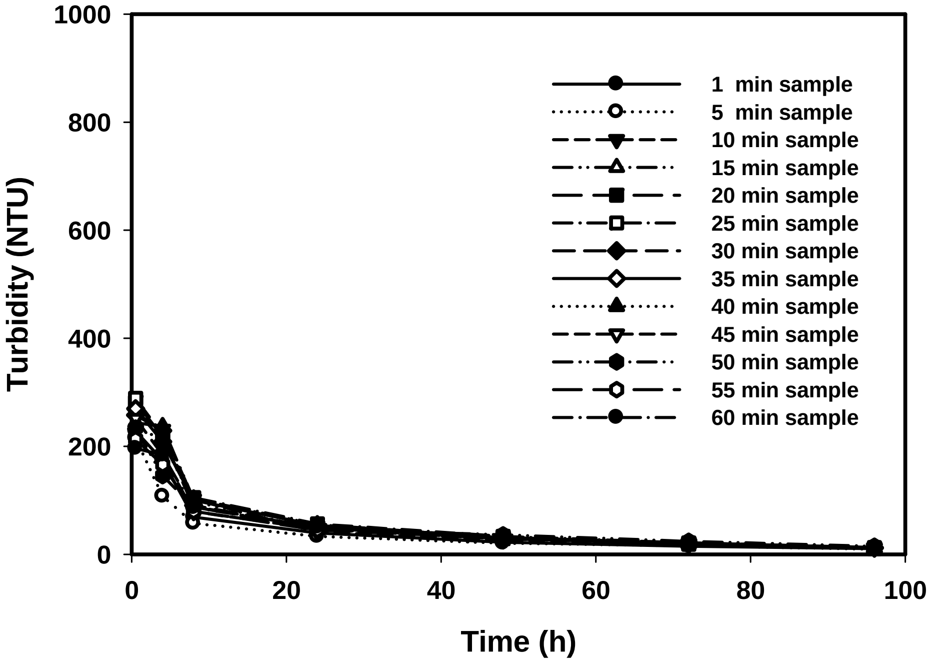

Figure 2.16 Bare Vulcan Site Soil Runoff Samples Turbidity Variation with Time

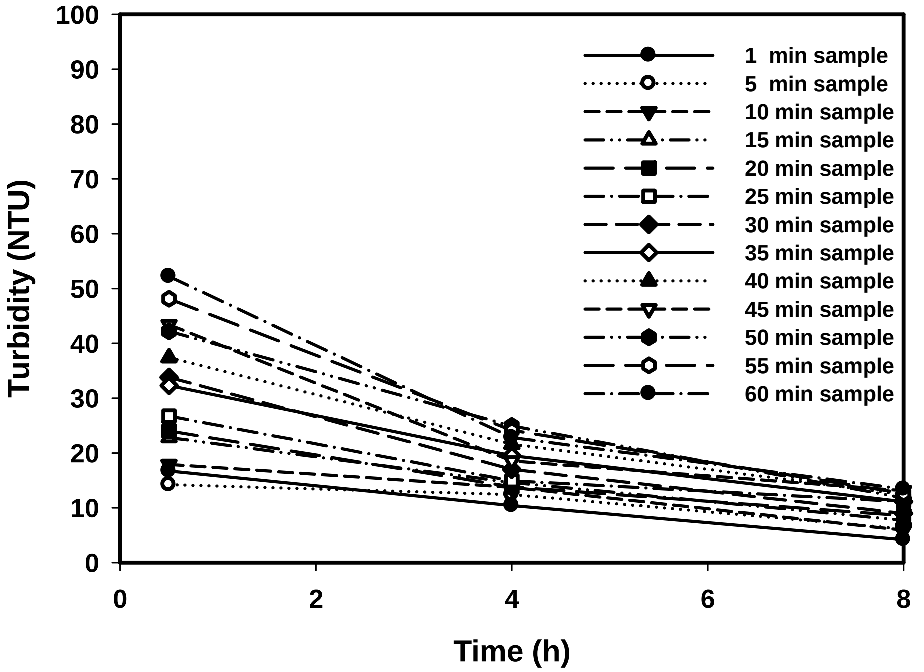

Figure 2.17 0.3% PAM705 Treated Vulcan Site Soil Runoff Samples Turbidity Variation with Time

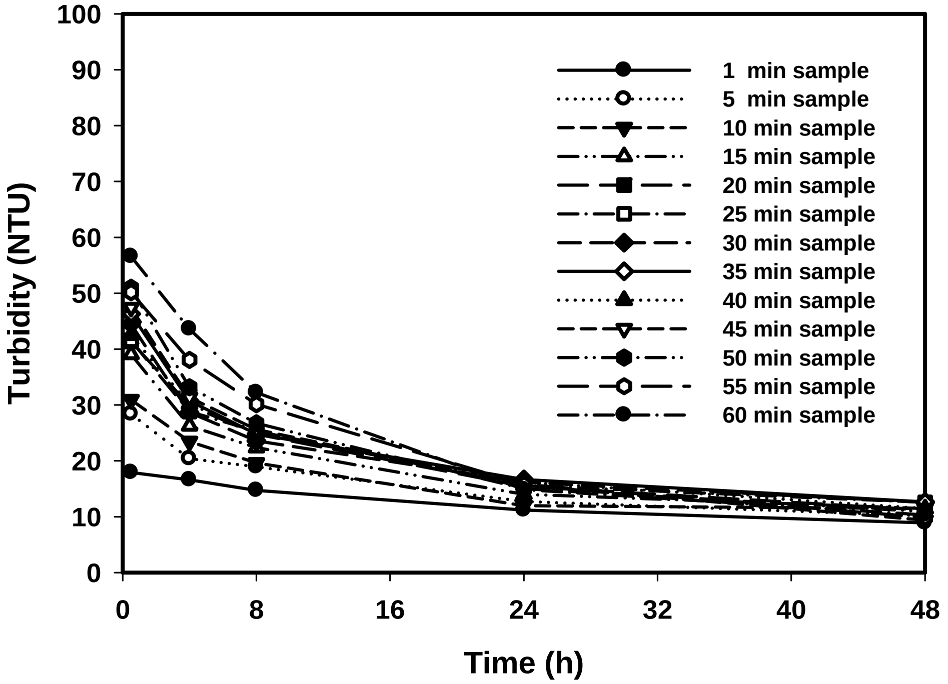

Figure 2.18 0.3% PAM705 Stabilized Magnetite Nanopartilces(total Fe= 0.1g/L) Treated Vulcan Site Soil Runoff Samples Turbidity Variation with Time

2.3.2.1.5 Summary

Relatively high proportions of silt and sand in the upper top soil may cause infiltration and runoff problems, leading to sediment loss and erosion (Santos et al., 2003; Shainberg et al., 1991). The Vulcan site soil had 80% of sand and this would definitely cause severe runoff problems. Treating sandy soils with PAM, PAM would act as a binding agent and settling agent. Such treated sandy soils would have aggregate stability, would have increased infiltration, and would have reduced runoff and reduced sediment loss. The PAM applications on steep slopes have improved parameters and are statistically significant difference when compared to a control plot; this indicates that PAM treatments have significant effect on the surface runoff. The research findings are similar to Roa et al. (1998) where they claimed that in their three years of studies on construction sites, PAM provided 60 to 70% reduction in runoff sediment and to

Flanagan et al. (2002a, b) where they reported good successes when they applied PAM for erosion control on steep slopes.

2.3.2.2 Smith Farm soil erosion test

2.3.2.2.1 Runoff flowrate

The same soil erosion tests were performed on Smith Farm soil samples in order to compare the PAM effectiveness on this different type of soil. The overall average runoff flow rate, the concentration, and the initial turbidity for the control, 0.25% PAM 705, 0.3% PAM 705, and 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe=0.1g/L) treatments are illustrated in Figure 2.19, Figure 2.20, and Figure 2.21, respectively.

No statistically significant differences ($p < 0.05$) were found for the runoff flow rates (Figure 2.19).

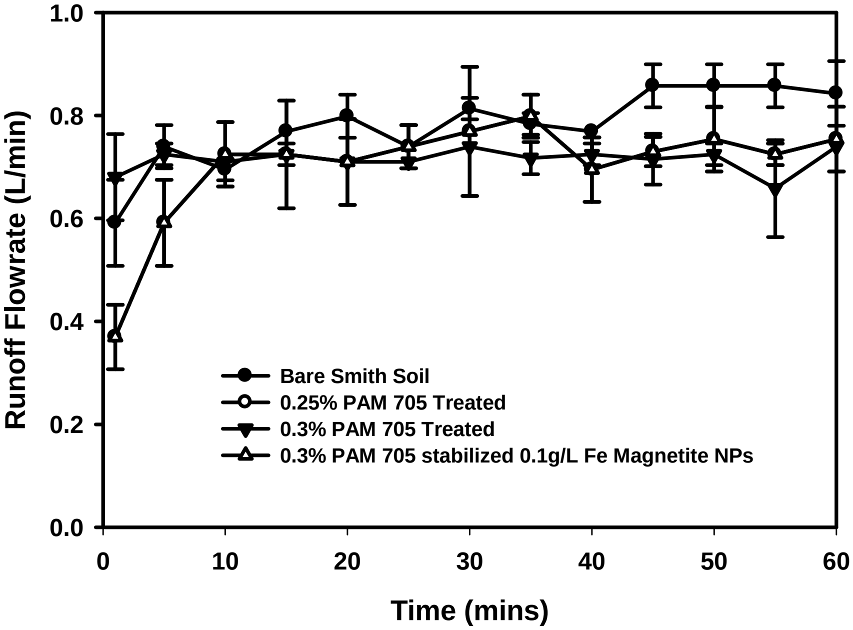

Figure 2.19 Comparison of Bare and Treated Smith Farm Soils Runoff Flow Rate Variation with Time

2.3.2.2.2 Average runoff concentration of sediments

Figure 2.20 showed the average runoff concentration of sediments for the control plots is 50.49±8.43 g/L. Average runoff concentration of sediments for the treated plots are 2.79±1.72 g/L, 0.02±0.01 g/L and 5.49±1.91 g/L. Compared to the control plot, the average runoff concentration of sediments were reduced by 95% and 100% for the plots treated with 0.25% and 0.3% PAM respectively. The results also indicated that when the PAM dosage is increased, SS concentration in the runoff is decreased. When PAM magnetite nanoparticles (0.3% PAM+0.1 g/L Fe) were applied, the runoff SS concentration was reduced by 89.1%.

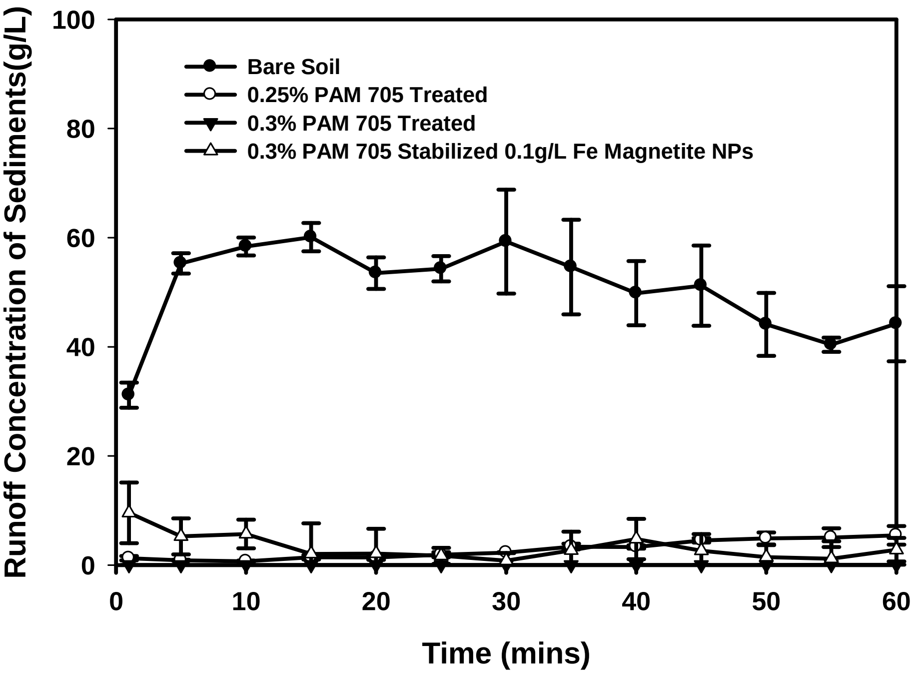

Figure 2.20 Comparison of Bare and Treated Smith Farm Soil Runoff Concentration Variation with Time

2.3.2.2.3 Runoff initial turbidity

Figure 2.21 compared the runoff turbidity levels for the untreated and the treated Smith Farm soils. The initial turbidity of the control plots increased rapidly to 627±25.5 NTU following the inception of the rainfall and gradually decreased to ~243.5±54.5 NTU at the end of the run.

In all cases, the effective reduction of the sediment loss was evident. The average turbidity was reduced to 21.9±5.2 NTU, 95.6% reduction and 7.2±1.4 NTU, 98.6% reduction when the soil was treated with 0.25% and 0.3% PAM, respectively. For 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe=0.1 g/L) treatment, the turbidity increased gradually from 25.8±3.0 NTU to 79.4±2.2 NTU, a 90.5% average turbidity reduction was achieved for this case. Again, PAM efficiency is lessened as the rainfall continued.

Individual treatments were evaluated by t-test, statistical significant differences ($p < 0.05$) were found among each group. This means that the Smith Farm soil is sensitive to different PAM application methods.

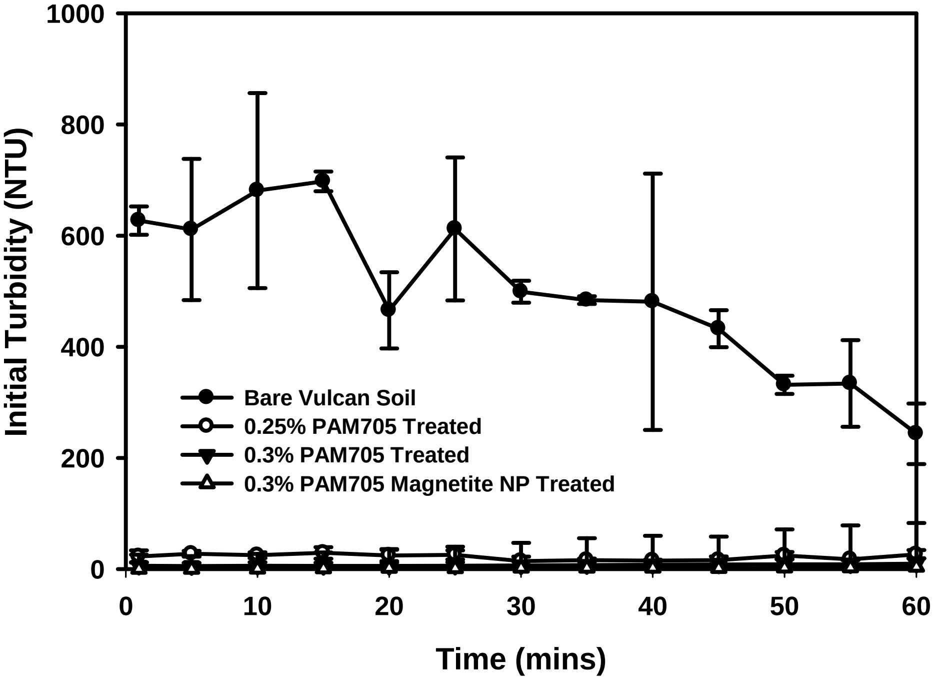

Figure 2.21 Comparison of Bare and Treated Smith Farm Soils Runoff Turbidity Variation with Time

2.3.2.2.4 Turbidity kinetics

Turbidity kinetics in selected effluent samples was followed under stagnant condition to evaluate the effect of PAM addition on the settleability of SS in the runoff. The initial turbidity for 0.3% PAM 705 treated group was below 13NTU. Figure 2.22, Figure 2.23, Figure2.24 showed that the average turbidity changed over time in the collected runoff water from all of the plots. The turbidity of the runoff samples went down for all cases as the SS in the runoff precipitated over time. The turbidity slowly decreased for the control plots; it took 17 days for the turbidity to drop below 13 NTU. When a plot was treated with 0.25% PAM 705 or 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe=0.1g/L), it took only 4 hours for the turbidity to drop down to 13 NTU.

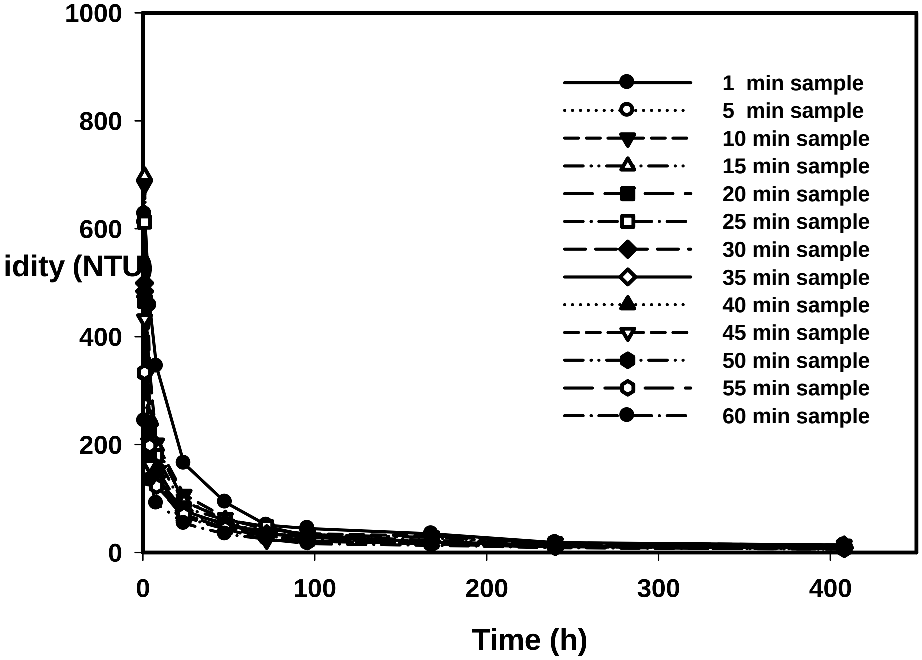

Figure 2.22 Bare Smith Farm Soil Runoff Samples Turbidity Variation with Time

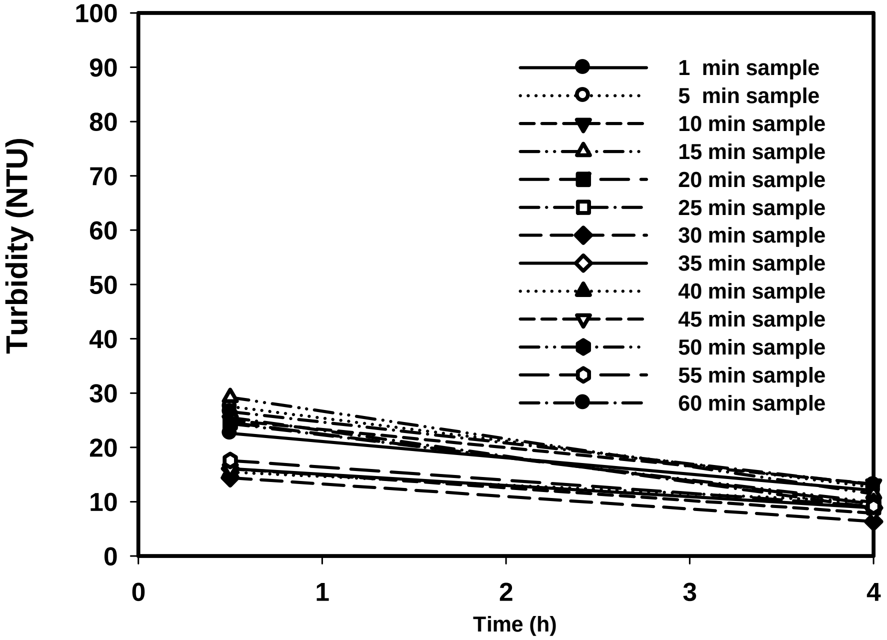

Figure 2.23 0.25% PAM705 Treated Smith Farm Soil Runoff Samples Turbidity Variation with Time

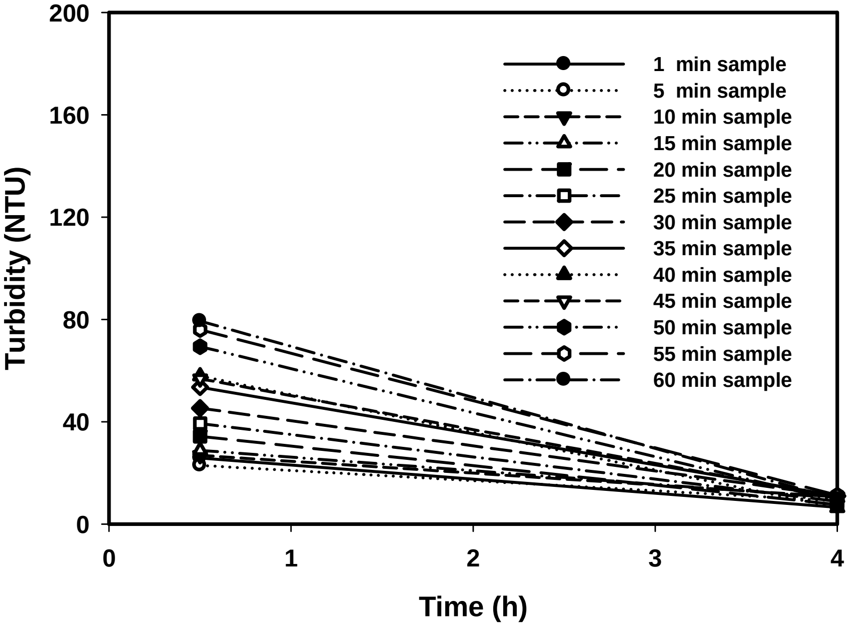

Figure 2.24 0.3% PAM705 Stabilized Magnetite Nanopartilces(Total Fe= 0.1g/L) Treated Smith Farm Soil Runoff Samples Turbidity Variation with Time

2.3.2.2.5 Summary

PAM molecules can aggregate fine soil particles (mainly with the clay/silt fractions) through Coulombic and Van der Waals forces (Orts et al., 1999, 2000). As a result of these two forces, the Smith Farm soil (45.6% silt and 18.1% clay) could combine more with the PAM. This enhanced particle cohesion force and the increased resistance to shear-induced detachment resulted consolidating the soil structure and preventing sediment transport in runoff. Any escaped particles are quickly flocculated by the PAM molecules and the particles are settled out of the transport stream.

2.3.3 Effectiveness of PAM treatment for two soils

During the simulated rainfall events, the sediment loss and turbidity profiles differed markedly for the two sample soils. Very significant soil erosion was observed for the loam soil (Smith Farm soil) than for the sandy loam (Vulcan site soil). Smith Farm loam soil has more silt and slightly higher clay content than the Vulcan site sandy loam soil. Therefore, the elevated erosion of the loam soil could be attributed to the higher silt content. The findings of Sepaskhah and Shahabizad (2010) also indicated that soils with higher clay or silt contents are more susceptible to erosion. Also, longer time was needed for the Smith Farm soil runoff samples to settle down compared to the Vulcan site soil. This is due to soil particle size distribution and the Smith Farm soil contained more fine particles. With the treatment of 0.3% application of PAM 705 and PAM 705 nanoparticles, the reduction in sediment loss was better for the Smith Farm soil and the turbidity in the runoff water decreased more rapidly for the Smith Farm soil than for the Vulcan site soil.

In addition to the Smith Farm soil containing more fine particles, another possible reason might be that the PZC value is 4.86 and the pH value is 4.76. The Vulcan site soil had a PZC value of 5.03 and a pH value of 5.67. These elevated values reflect a net negative charge that would tend to repel anionic PAM whereas the Smith Farm soil would tend to retain anions.

2.4 Conclusions

A new class of nano-PAM emulsion was synthesized. The new PAM product was evaluated for erosion control and compared with other PAM treatments on two different types of soils. Various soil runoff parameters (runoff flow rate, runoff concentration, initial turbidity, and sample turbidity kinetics) were investigated. The major findings for this chapter are as follows:

1. For Vulcan site soil, under identical runoff flow rate:
    a. The cumulatived sediment yield for the study period indicated that there were significant reduction of 97.5% and 90.8% respectively, for PAM only and PAM nanoparticles treatments, compared to control. Sediment yields for PAM treatments were statistically significant different ($p < 0.05$) based on t-tests.
    b. When treated with either 0.3% PAM 705 or 0.3% PAM 705 stabilized magnetite nanoparticles (0.1 g/L as Fe), the turbidity was consistently suppressed during the test period, with an average turbidity reduction of 89% and 83%, respectively. Statistical analysis via t-tests indicated that the runoff NTU levels were significantly different ($p < 0.05$) for each of the treatments.
    c. With addition of the magnetite nanoparticles (0.1 g/L as Fe), the viscosity for 0.3% PAM was reduced from 13.04 centipoises to 9.09 centipoises, which is a 30% reduction.
    d. The turbidity slowly decreasing over time for the Vulcan site soil control plots. It was the 96 hour point when the last runoff samples achieved a value of 13 NTU from an initial turbidity value of 244.5±27.5 NTU. The PAM only

achieved the 13 NTU value in 8 hours and the PAM with nanoparticles achieved the same 13 NTU in 48 hours. Sediments in any PAM treatment were capable of settling out much quickly than the control.

2. For Smith Farm soil, under identical runoff flow rate:
    a. Compared to the control plot, the average runoff concentration was reduced by 95% and 100% for the plots treated with 0.25% and 0.3% PAM respectively. The results also indicated that when the PAM dosage increased, the SS concentration in the runoff decreased. When PAM-magnetite (0.3% PAM+0.1 g/L Fe) was applied, the runoff SS concentration was reduced by 89.1%.
    b. The average turbidity had a 95.6% reduction and a 98.6% reduction when the soil was treated with 0.25% and 0.3% PAM, respectively. For 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe=0.1 g/L) treatment, the turbidity was reduced by 90.5%. PAM efficiency did lessen as the rainfall continued.
    c. Initial turbidity for the 0.3% PAM 705 treated group was well below 13 NTU. The turbidity slowly decreased over time for the control plots, where the turbidity went down to below 13 NTU after 17 days. When a soil plot was treated with 0.25% PAM 705 or 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe=0.1 g/L), it took only 4 hours for the turbidity to drop down to 13 NTU.
    d. Smith Farm soil is more sensitive and more responsive to different PAM application methods.

Overall, soil properties play a big role on PAM treatment performance.

Chapter 3 Arsenate Adsorption and Immobilization Batch Tests

3.1 Introduction

Arsenic was first documented by Albertus Magnus in 1250 (Emsley, 2001). This chemical element's atomic number is 33. It is a silver-gray brittle crystalline solid with an atomic weight of 74.9, a specific gravity of 5.73, a melting point of 817 °C (at 28 atm), a boiling point of 613 °C and a vapor pressure of 1mm Hg at 372 °C. It is ubiquitous and it ranks 20th as a natural occurring metalloid or in combination and it comprise about 0.00005% of the earth's crust; in seawater it ranks 14th and in the human body it ranks 12th (Mandal and Suzuki, 2002). Its concentration in most rocks ranges from 0.5 to 2.5 mg/kg, although higher concentrations are found in finer grained argillaceous sediments and phosphorites (Kabata-Pendias and Pendias, 2000; Mandal and Suzuki, 2002). This element has been a continuous center of controversy for environmental and for health reasons.

In this chapter, various polymer bridged magnetite nanoparticles were studied to determine their arsenic removal efficiency in batch tests. Starch bridged magnetite nanoparticles showed superior advantage over the other nanoparticles in arsenic immobilization in aqueous phase. Then, they were further investigated in batch tests in order to evaluate arsenic adsorption capacity in two soils, and arsenic immobilization on two contaminated soils. It is shown that Smith Farm soil have more affinity to arsenic thus nanoparticles are less accessible to arsenic which is associated with soil particles.

3.1.1 Arsenic contamination

Increasing amounts of arsenic are being introduced into the soil and the water environments from natural processes and from human activities (Smith et al., 1998). Arsenic is ranked the second most common inorganic pollutant in the various US superfund sites (Davis et al., 2001). Arsenic contamination of ground and surface water pose significant threats to human health (WHO, 2001).

Arsenic contamination of drinking water sources has been reported in Banglades (Chowdhury et al., 2000), in India (Chakraborti et al., 2003), in China (Zhang, 2003), in Taiwan (Guo, 2003), in Thailand (Choprapawon and Rodcline, 1997), in the United States of America (Kim et al., 2002) and in Canada (Wang and Mulligan, 2006). Hungary, Germany, Greece, Finland, Romania, and Spain also face arsenic problems in their drinking water utilities (Katsoylannis and Zouboulis, 2006). Arsenic has been associated with various carcinogenic and other health issues. Triggered by numerous risk concerns, the US EPA announced in October 2001 a new ruling to lower the Maximum Contaminate Level (MCL) of arsenic from the then current 50 µg/L (established in 1942) to 10µg/L with a compliance date of January 22, 2006.

However, high arsenic concentrations ranging from 10 to greater than 1,000 mg/kg have been observed worldwide and are typically caused by human activities (Smith et al., 1998). Seventy percent of the world's arsenic production (WHO, 2001) and 90% of the US arsenic production is intended for the wood preservation industry; in this industry, arsenic is used as a compound (chromated copper arsenate or CCA) (National Toxicology Program, 2005).

Mining activities, fossil fuels combustion, use of arsenic in pesticides, herbicides, and crop desiccants, and use of arsenic additives in livestock feed create additional environmental impacts (Mohan and Pittman , 2007).

Natural soil concentration of arsenic typically ranges from 0.1 to 40 mg/kg with an average of 5 to 6 mg/kg (WHO, 2001; National Toxicology Program, 2005) and rarely exceeds 15 mg/kg in North America (Smith et al., 1998). Arsenic in the soil is a possible threat to humans (Khan et al., 2004). A growing concern has been expressed over the potential impact of soil containing arsenic on human health, particularly children who are most likely to come in contact with soil (Dagan et al., 2006).

3.1.2 Arsenic chemistry

The chemical behavior and hence speciation of arsenic determines its uptake by plants and soil biota (Otte et al., 1991). An improved understanding of arsenic chemistry within a soil system should lead to improved management of arsenic contaminated soils (Hartley et al., 2004).

Arsenic exists in the −3, 0, +3 and +5 oxidation states (Smedley, 2002). Environmental forms include arsenious acids (H_3AsO_3, H_3AsO_3, $H_3AsO_3^{2-}$), arsenic acids (H_3AsO_4, H_3AsO^{4-}, $H_3AsO_4^{2-}$), arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, arsine, etc. Arsenic(III) is a hard acid and preferentially complexes with oxides and nitrogen. Conversely, arsenic(V) behaves like a soft acid, forming complexes with sulfides (Bodek et al., 1998). Inorganic forms of arsenic most often exist in water supplies (Bodek et al., 1998). Under oxidizing conditions such as those prevailing in surface waters, the predominant species is pentavalent arsenic, which is mainly present with the oxyanionic forms ($H_2AsO_4^-$, $HAsO_4^{2-}$) with pKa = 2.19; pKb = 6.94; respectively. In mildly reducing conditions such as found in ground waters, the normal pH values would induce As(III) (the thermodynamically stable form or arsenic) to form the non-ionic form of arsenious acid (H_3AsO_3, pKa = 9.22) (Cullen and Reimer, 1989). As(III) may react to a smaller extent with most solid surfaces and as a result it is more difficult to extract it by conventional methods (Clifford and Lin, 1991). As a result, a preoxidation step is usually required to transform the trivalent form to pentavalent. Arsenic is uniquely sensitive to mobilization (pH 6.5–8.5) and under both oxidizing and reducing conditions among heavy metalloids (Smedley and Kinniburgh, 2005). Trivalent arsenites predominate in moderately reducing anaerobic environments such as groundwater; Pentavalent species predominate and are stable in oxygen rich aerobic environments. (Greenwood, 1984). Redox potential (Eh) and pH control arsenic speciation (Tallman and Shaikh, 1980).

3.1.3 Arsenic and magnetite nanoparticles

Arsenic may be removed through chemical methods such as coagulation and filtration, ion exchange, membrane, and adsorption technologies (Mohan and Pittman, 2007).

Numerous research papers have demonstrated that iron oxides have a high affinity for the adsorption of arsenite and arsenate (Pierce and Moore, 1982; Raven et al., 1998). Iron-based arsenic removal technologies make use of this strong (geo) chemical association of arsenic with iron by removing arsenic through the direct adsorption processes (Mohan and Pittman, 2007; Sylvester et al., 2007; Yuan et al., 2002). Commonly used iron oxides include bulk crystalline Fe(III) such as goethite and hematite, (Coker et al., 2006;; Giménez et al., 2007; Pierce and Moore, 1982; Raven et al., 1998; Waychunas et al., 1993) and to a lesser effect the mixed iron [Fe(II)/(III)] oxide, magnetite (Dixit and Hering, 2003; Ohe et al., 2010). Their work showed that iron oxides can adsorb arsenic, especially arsenate, from a solution.

The surface properties of iron oxides are key factors in adsorption. A limitation to larger particulate sorbents is the surface area, which can cause less removal in the presence of other species, and in some cases, large quantities (greater than 1 g/L) of the solid is needed to remove arsenic to levels below MCL, while amorphous colloids produced by adding iron(III) salts are difficult to remove and tend to bind to filters (Shipley et al., 2010). Using synthetic nanoparticles can be advantageous over using bulk crystalline iron oxides due to the increased surface area, which would provide more sorption sites for arsenic removal (Banfield and Navrotsky, 2003; Rusanov, 2005). Likewise amorphous iron oxides have high specific surface areas equal to or greater than most iron oxide nanoparticles, but these are often difficult to separate and can leave iron residuals in the water after treatment (Hering et al., 1997).

In natural occurring sediments, both crystalline and amorphous iron oxide minerals can coexist; recent studies have also shown that amorphous iron oxides are transformed to magnetite during reductive dissolution (Benner et al., 2002; Fredrickson et al., 1998). Mayo et al. (2007) claimed that nanocrystalline magnetite is not only more efficient in the removal of arsenic, but also more easily recovered.

In this research effort, magnetite nanoparticles were used since this magnetite compound has an affinity for arsenate and can be easily separated from a solution with low field magnets or filters (Moeser et al., 2002). Another reason for using this magnetite compound is that it has a greater adsorption capacity when compared with bulk magnetite particles (Yavuz et al., 2006; Yean et al., 2005).

3.1.4 Parameters influence Arsenic adsorption by magnetite and magnetite nanoparticles

Potential environmental parameters that influence arsenic adsorption by magnetite and magnetite nanoparticles are very critical when design a treatment method. A short review is as follows to show the relationship between the treatment efficiency with those parameters.

3.1.4.1 Sorption kinetics and isotherm

A first order (Shipley et al., 2010) and pseudo-second order rate equations (Giménez et al., 2007) were used to describe the arsenic sorption kinetics for magnetite nanoparticles and magnetite. Giménez et al. (2007) studied the arsenic sorption kinetics on magnetite and they claimed that the rate constant for arsenite is always higher than arsenate. This claim seems to be consistent with Bowell's (1994) work.

Langmuir adsorption isotherm has been found to fit the arsenic adsorption to magnetite nanoparticles very nicely (Yavuz et al., 2006; Yean et al., 2005). Giménez et al. (2007) agreed that arsenic sorption to magnetite can be fitted to the Langmuir isotherm and this indicates a monolayer coverage on the iron mineral surface.

3.1.4.2 Particle size

Ohe et al. (2010) compared the high surface area magnetite (up to 245 m^2/g) with natural magnetite (0.89 m^2/g) and they noted that the adsorption capacity of arsenite and arsenate was 348 and 164 times greater than that of natural magnetite. Mayo et al. (2007) indicated that the removal efficiency depended greatly on the size of the Fe_3O_4 sorbents. The adsorption capacity of As(V) on 12 nm magnetite was nearly 200 times greater than those of As(V) on some 20 and 300 nm commercially available magnetites. The adsorption capacities of As(V) were higher than those of As(III). Yean et al. (2005) claimed that increased adsorption maximum capacities were observed while decreasing the magnetite size. Yean et al. (2005) found 20 and 300nm magnetite showed significant size dispersion and irregular shapes with the same PZC value of pH 6.8. However, there were no appreciable differences in the surface acid-base properties. Arsenite adsorption to 300nm magnetite particles is 1/18 less than those of 20nm. In the desorption test, Yean et al. (2005) indicated that desorption of both arsenite and arsenate from 300nm magnetite nanoparticles appeared to be irreversible, the complete desorption hysteresis was observed for arsenite and arsenate from 20nm particles. With three steps of desorption only 20-25% and 1% of arsenite and arsenate were desorbed from 300 and 20nm particles.

3.1.4.3 pH values

The sorption behavior of arsenic is strongly influenced by a solution's pH value and by the oxidation state of arsenic.

Wakui et al. (2005) noted that arsenic(V) was quantitatively adsorbed over the pH range of values. The distribution coefficient K_d was almost constant at a pH value between 3 and 7. The anionic arsenate was the predominant species adsorbed to magnetite. The K_d value decreased along with an increase of the pH values above 7. Jönsson et al. (2008) found that As(V) and As(III) sorbs to magnetite by forming inner-sphere surface bidentate corner sharing complex. No evidence of redox transformation for As(V) at a pH value of 10.6 or for As(III) at a pH value of 7 was found. Dissimilatory reduction of iron oxides, followed by precipitation of magnetite would release the dissolved As(V) when the pH value is greater than 8, however, As(III) sorption was enhanced with ever increasing pH values. Dixit and Hering (2003) investigated the sorption edges of arsenic on iron oxide and they found that the sorption of arsenite on magnetite increased gradually over most of the pH range (pH values from 4 to 10). Yean et al. (2005) found that for pH values of 4.8, 6.1, and 8.0, the adsorption of arsenite for two different types of nanopartilces was not sensitive to these pH values. However, when Yean et al. (2005) increased the pH values above 8, the maximum adsorption capacity of arsenate for both particles decreased with each increasing pH value. Shipley et al. (2009) noted similar observations for pH values of 7.7, 8.0, and 8.3).

3.1.4.5 Effect of common aqueous species in environment

The effect of competing species in solution was studied. Previous work by Shipley et al. (2009) showed that potassium had a negligible effect on arsenic adsorption to magnetite nanoparticles. Furthermore, Shipley et al. (2010) revealed that the difference in the adsorbed arsenate and arsenite concentrations is due to the presence of calcium, magnesium, or sulfate in concentrations commonly encountered in potable waters, which is about 10% or less. The addition of fulvic acid decreased the arsenite removal more than the arsenate removal. Phosphate, bicarbonate, and silica at high concentrations had the most significant effect on arsenic adsorption. The amount of removed arsenic decreased as the bicarbonate and silica concentrations increased. Wakui et al. (2005) found that the sulfate did not interfere with the adsorption of arsenate when the amount is less than 0.2 M. On the contrary, a marked decrease of K_d was observed when the phosphate concentration is increased. Wakui et al. (2005) suggested that the reaction of arsenic took place on the surface of the magnetite crystals. Su and Puls (2008) found that minute amounts of manganese impurities in the magnetite samples may have been responsible for arsenite oxidation and the structural Fe(III) in magnetite and hydroxyl radicals in a solution; thus the manganese could serve as an oxidant for arsenite as well.

To summarize, the magnetite and magnetite nanoparticles are a suitable sorbent media to removal arsenic, on removal efficiencies as related to surface area and particle size, on the range of initial concentrations, and on the presence of other elements, variations of pH values, variations in ionic strength, and variations in the temperature for impacting the sorbent behaviors. A basic understanding of both the target contaminant and the sorbent behavior is useful for determining the feasibility of a particular treatment application.

3.2 Materials and methods

3.2.1 Soils and soil spiking

The raw soils were washed with tap water several times to remove all soluble components such as dissolved organic matter and other soluble impurities until the supernatant was clear.

The resulting soil was air dried at room temperature for several days, then sieved through a 2-mm standard screen (#10). The background arsenic concentrations were determined by using the EPA method 3050B in triplicate.

To achieve an arsenic level of 270.3 mg/kg in the Vulcan site soil and 359.1mg/kg in the Smith Farm soil, the spiking method was used to add arsenate to the soil samples. Specifically, As(V) was added to the soils using a sodium arsenate ($AsHNa_2O4{\cdot}7H_2O$, Sigma-Aldrich, St. Louis, MO, USA) stock solution that contained a 1:10 g/ml suspension in 10^{-3} M $CaCl_2$ (Fisher Scientific, Pittsburgh, PA, USA) solution; this follows what was described by Yang et al. (2003). The pH value of the slurry was adjusted by adding dilute NaOH. After 12 days, the soil suspension was centrifuged and the supernatant was decanted. This was wash soil twice to remove any traces of the original soluble arsenate. The decanted supernatant and the rinse water were filtered through a 0.22µm membrane of mixed cellulose esters (Millipore Corp., Billerica, MA, USA). The filtrate was then acidified with 5% nitric acid (Mallinckrodt Chemicals, Phillipsburg, NJ, USA). The soil residues were digested using EPA 3050B in order to verify the mass balance. Two batches of each soil were spiked with different arsenate concentration for batch test and immobilization in small scale box test.

3.2.2 Preparation of polymer-bridged magnetite nanoparticles

Typically the erosion of disturbed soil is couple with leaching of various toxic chemicals. Thus it is necessary to control both soil erosion and metal leaching. To reduce arsenic leaching, a class of starch-bridged magnetite nanoparticles was prepared based on the protocol used by An et al. (2011).

The desired magnetite nanoparticles were prepared by modifying the co-precipitation approach in the presence of a suitable concentration of a water soluble starch. First, a solution of Fe^{3+} and Fe^{2+} (from $FeCl_3{\bullet}6H_2O$ and $FeSO_4{\bullet}7H_2O$, respectively) was prepared at a ferric-to-ferrous molar ratio of 2:1 at room temperature (21 °C). To avoid oxidation during the preparation process, deionized (DI) water was first deoxygenated by nitrogen purging.

2% (w/w) of a starch stock solution was made by mixing 20 g of starch in 980 ml DI water and heated to the boiling point under magnetic stirring and kept boiling for 15 minutes, followed by cooling down to room temperature before use.

The cooled starch stock solution was mixed with the Fe^{3+}/Fe^{2+} solution under N_2 purging at a starch concentration ranging from 0.04 to 0.1 wt.%. Next, a 2 M NaOH solution was added drop wise into the solution under vigorous stirring until a pH value of about 11 was obtained. When the color changed from brown to black, this indicated the formation of the nanoparticles (Schwertmann and Cornell, 2000). Then the starch bridged magnetite solution was nitrogen-purged for 20 minutes. Finally, the suspension was sealed and placed in a dark place for 12 hours in order to allow the magnetite nanoparticles to grow. The pH value was lowered back to about 7.0 with trace amounts of 2 M HCl and the suspension was used within one hour.

For comparison, a starch-bridged magnetite particles solution was prepared with 0.3% PAM 705 and the same steps were followed. A small volume of 0.3% PAM 705 stabilized magnetite nanoparticles solution was prepared based on the steps described in section 2.2.4.

3.2.3 Arsenic immobilization isotherm test in aqueous phase

A simple batch test was performed to study the effectiveness of various polymer-bridged magnetite nanoparticles in terms of arsenate removal from aqueous phase only. A series of batch equilibrium sorption tests were performed with the polymer-bridged magnetite nanoparticles in duplicate. First, the particles were prepared at 0.1 g/L as total Fe with 0.3% PAM only, or 0.1 g/L Fe with 0.04, 0.1 wt.% of starch in absence or presence of 0.3% PAM in 30 ml plastic vials. The concentrated particles were then mixed with 1 ml arsenate stock solution, which yielded the following initial arsenic concentration of 3.711 mg/L. The systems were equilibrated on a slowly rotating rack (Glas-Col, Terre Haute, IN, USA) that provided gentle end-over-end tumbling (40 rpm) for 12 days. At the end of this period of time, the solution was filtrate with a 0.025µm membrane filter mixed cellulose esters hydrophilic membrane (Millipore Corp., Billerica, MA, USA). Acidify was used for analyzing the arsenate. The following mass balance equation (2) was employed to determine the arsenate uptake:

$$q_e = \frac{V(C_0 - C_e)}{M} \qquad (2)$$

Where, q_e (mg/g) is the equilibrium mass uptake of arsenic,

V (L) is the solution volume,

C_0 and C_e (mg/L) are the initial and final concentration of arsenic, respectively,

M (g) is the mass of sorbent added calculated as Fe.

3.2.4 Arsenic adsorption isotherm test in two soils

Arsenate sorption isotherms were constructed for the two soils through batch equilibrium experiments to probe the absorbability of arsenic on two soils. The initial arsenic concentration ranged from 0.8mg/L to 200mg/L in a simulated solution containing 0.01 M of $NaNO_3$. The adsorption tests were initiated by mixing 3g each of an air-dried clean soil sample with 30ml of the arsenate solutions 30 ml plastic vials. The solution pH was maintained at 6.5 through intermittent adjustment with dilute HNO_3 or NaOH solutions. The mixtures were equilibrated on the rotator operated at 40 rpm for 12 days at room temperature (~21 ^{o}C), which was found sufficient to reach equilibrium through separate kinetic tests. The mixtures were then centrifuged at 5000 rpm for 10 min, the supernatants were filtered through 0.22μm Millipore Membrane Filters, and the filtrate were then acidified with 5% nitric acid, and then analyzed for total As and Fe. All experiments were performed in triplicate.

3.2.5 Arsenic immobilization kinetics test in contaminated soils

The effectiveness of starch-bridged magnetite nanoparticels for immobilization of arsenate preloaded in the two soils was probed through batch kinetic tests. The experiment was carried out at an initial pH value of 6.5. The experiment consisted of using 15ml tubes where each tube received 1.5 g of an arsenate loaded soil sample and 15ml of the nanoparticle suspension (Fe = 0.25 g/L, starch 0.1%). Control tests were carried out under otherwise identical conditions, but with the absence of nanoparticles. The pH value of each solution was measured immediately after each sampling. Then the samples were filtered through a 0.025μm membrane of mixed cellulose esters to remove the nanoparticles and soil. The resulting filtrate was acidified with 5% nitric acid, and analyzed for As and Fe. All experiments were performed in triplicate.

3.2.6 Chemical analysis

The solution or suspension pH values were measured using an Oakton pH meter (pH 510 Benchtop Meter, Oakton Instruments, Vernon Hills, IL, USA). All arsenate concentrations were analyzed using the PERKIN ELMER Graphite Atomic Absorption Spectrometer 3110 (connected with HGA 600 and EDL system 2). The detection limit for arsenic was 3 ppb as As. Dissolved iron was measured using a Flame Atomic Absorption Spectrometer (Varian Spectra 220 FS) (detection limit = 0.05 mg/L).

3.3 Results and discussion

3.3.1 Soil arsenic concentration

The background arsenic concentration in both soils was determined to be zero per EPA method 3050B in triplicate. The results showed that both soils have no arsenic contamination initially. These clean washed and sieved soils were used for adsorption experiments.

Arsenic contaminated Vulcan Site soil and Smith Farm soil with 270.3mg/kg and 359.1mg/kg concentration of arsenic were used for desorption kinetics experiment and they were contaminated in the laboratory.

3.3.2 Arsenate immobilization kinetics batch test

An et al. (2011) found that the starch-bridged magnetite nanoparticles removed 5 times more arsenic than bare magnetite particles under otherwise identical conditions, and the bridged nanoparticles can be easily separated from water by gravity. Inspired by his findings, in order to compare the effectiveness of various polymer-bridged magnetite nanoparticles in terms of arsenate removal from aqueous phase only, a simply batch test was performed for this purpose. The effect of 0.3% PAM 705 stabilized magnetite nanoparticles on arsenate immobilization was compared with four other types of magnetite nanoparticles. The As(V) removal percentage for each nanoparticles type is shown in Figure 3.1.

With the same amount of iron (0.1g/L), 0.04% and 0.1% starch-bridged magnetite nanoparticles removed 94.5% and 98.0% of arsenate respectfully. The addition of 0.3% PAM 705, resulted in the 0.04% and the 0.1% starch-bridged magnetite nanoparticles removing less arsentate (72.3% and 75.9%). However, 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe = 0.1g/L) did not show any advantages for removing arsenate (the removal efficiency was 58.6%). This may be due to the fact that the large polymer molecules do not work as efficiently as the starch does for being a nanoparticles stabilizer—this behavior is necessary in order to enhance the nanoparticles dispersion during synthesis. The Fe nanoparticles may partially bind to the PAM instead of the starch when both are uses as nanoparticle stabilizer, thus, the particle size is not smaller enough to offer more surface area to adsorb arsenate. Whereas, starch-bridged magnetite nanoparitlces showed significant advantage on arsenate removal.

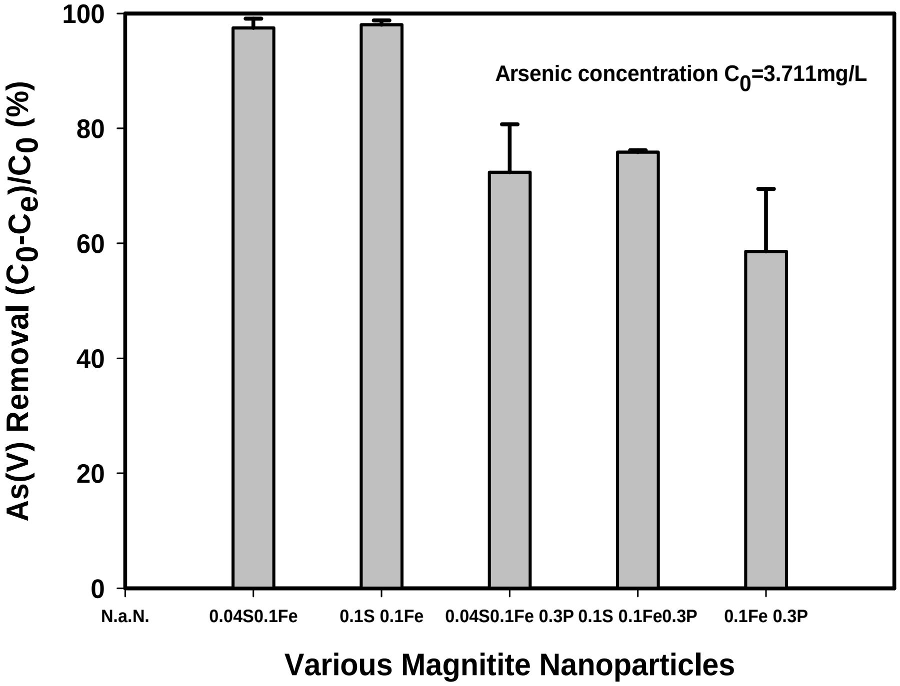

Figure 3.1 Arsenic Removal Efficiency Comparison of Various Magnetite Nanoparticles with Total Fe of 0.1g/L

Despite lower efficiency, the PAM stabilized magnetite nanoparticles are still capable of removing arsenate. When it is applied to the surface soil, it works on non specific point contaminant removal in the surface runoff by immobilizing trace heavy metals as well as controlling soil erosion. As indicated by Kumpiene et al. (2006), stabilization of trace elements can be achieved by adding soil amendments that can absorb, can bind, or can coprecipitate the contaminating elements, of course, PAM stabilized magnetite nanoparticles can be used for this purpose.

In this research, in order to simulate the point contamination with high concentration of contaminants under surface soil runoff threat, starch-bridged magnetite nanoparticles were used to immobilize contaminants with the aim to obtain the best removal efficiency. Therefore, magnetite nanoparticles with a starch stabilizer were further utilized for arsenate removal study in the following batch tests and the small scale immobilization tests.

3.3.3 Adsorption Test

Further studies were conducted to elucidate the arsenate adsorption behavior in the soils by batch tests. As noted by Smith et al. (1998), adsorption is one of the most important arsenic retention mechanisms in any soil. The duration and behavior of arsenic in any soil is dependent upon the processes of adsorption and desorption/release (Zhang and Selim, 2005).

Our arsenic adsorption tests were conducted for two different types of soils over a 12 days period at room temperature in an environment with pH values around 6.5. Differences were noticed for aqueous and sorbed arsenate. Results of the adsorption isotherm batch experiments for the Vulcan site soil and the Smith Farm soil are presented in Figure 3.2.

The Freundlich equation is used to describe such adsorption isotherms as below,

$$\mathbf{S=K_FC^b} \tag{3}$$

Where, S represents the total amount of adsorption (mg/kg),

K_F is the distribution or partition coeffi带ent (L/kg),

b is the dimensionless reaction order commonly less than one.

The results indicated that arsenate adsorption by these two soils was highly nonlinear, the b values after 12 days retention are 0.22 and 0.21 for Smith Farm soil and Vulcan site soil. Such small Freundlich b values for arsenate adsorption have been reported by Buchter et al. (1989), Manning and Goldberg (1997), and Zhang and Selim (2005). The sorption nonlinearity also implies that arsenic mobility in a solution tends to increase as the concentration increases.

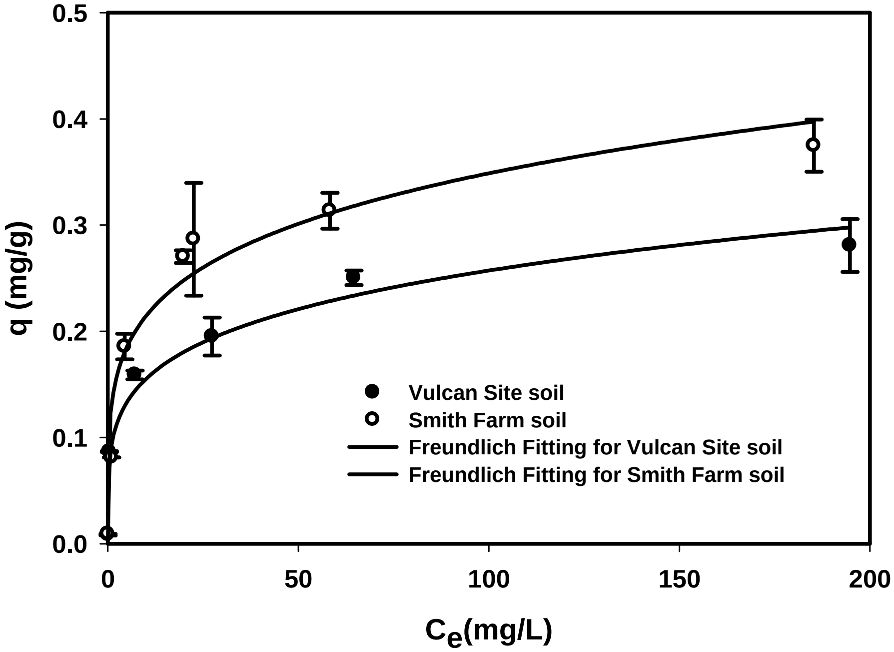

Figure 3.2 Arsenate Adsorption Isotherm for Vulcan Site Soil and Smith Farm soil with Freundlich Fitting.

The isotherms also revealed that the adsorption ability for the two soils. The Smith Farm soil showed more affinity for arsenate than the Vulcan site soil. It is well established that Fe and Al oxides and hydroxides have a high affinity for arsenic (Jacobs et al., 1970; Manning and Goldberg, 1997; Zhang and Selim, 2005). Also, the adsorption of arsenic has been shown to increase at low pH values and it declines when there is an increase in pH values (Polemio et al., 1982). As indicated in the soil properties, the Smith Farm soil had more Fe and Al and was slightly more acidic pH (pH = 4.76) than the Vulcan site soil (pH = 5.67); as a result the Smith Farm soil is more affinitive to arsenate.

The soil type and its properties had significant effect on metalloids leachate concentrations. This observation agrees with Hartley et al. (2004) work.

3.3.4 Batch experiment kinetics study of arsenate immobilization from contaminated soils

Magnetite in a nanoscale form is effective for remediating arsenic (Mohan and Pittman, 2007; Yavuz et al., 2006; Yean et al., 2005). The effectiveness of the partially stabilized magnetite nanoparticles for the removal of soil-sorbed arsenate was tested in a series of batch experiments.

Figure 3.3 and Figure 3.4 showed the transient release of arsenic when 1.5g of the arsenate spiked soil samples were mixed with 15ml of the nanoparticle suspension containing 0.1% starch-bridged 0.25g/L Fe at an initial pH value around 6.5. For comparison, arsenate desorption kinetic data in DI water at pH about 6.5 are also superimposed in these two figures.

The figures clearly showed the changes in the concentration of arsenate in the aqueous phase over time for the different soil samples. Initially, the rate of arsenate desorption was rapid and was followed by gradual or somewhat slow reactions, since sorbed arsenic is relates to the solid phase with different strengths as indicated by Zhang and Selim (2005).

The nanoparticles treated groups reached equilibrium at about the 168 hour point. The DI water based groups reached equilibrium at about the 48 hour point for the Vulcan site soil and at about the 12 hour point for the Smith Farm soil. About 60.7% of the arsenate was desorbed from the Vulcan site soil when the nanoparticles were absent. In contrast, when the 0.1% starch-bridged 0.25 g/L Fe nanoparticles were present, about 8.3% of the arsenate was released. The Smith Farm soil had opposite results. About 27% of the arsenate was desorbed from the soil when the nanoparticles were absent. In contrast, when the 0.1% starch-bridged 0.25 g/L Fe nanoparticles were present, about 10.0% of the arsenate was released.

Magnetite nanoparticles arsenate removal capacity is 0.065 mgAs/mgFe for the Vulcan site soil and 0.024 mgAs/mgFe for the Smith Farm soil. The observations indicate that a small dose of the magnetite nanoparticles was able to reduce greatly the arsenate leachability. Again, the batch arsenate immobilization tests confirmed that sandy loam has shorter arsenate residence time and this would make it easier to leach out and to adsorbe the arsenate by nanoparticles. Whereas, Smith Farm soil has more affinity to arsenate, magnetite nanoparticles are less accessibility to the arsenate which is associated with the soil particles.

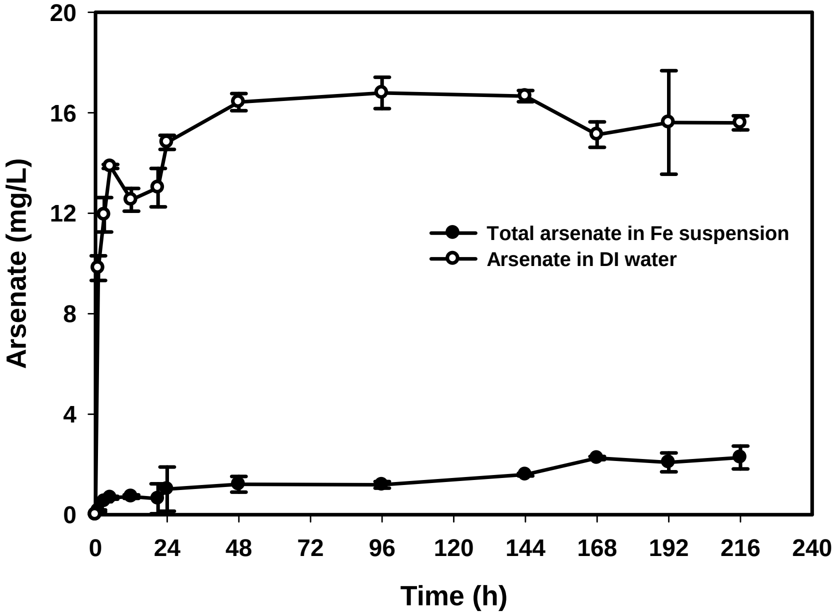

Figure 3.3 Leaching of Arsenate form A Contaminated Vulcan Soil with Nanoparticle Suspension (Total Fe= 0.25g/L, 0.1% Starch) or DI Water(Solution Volume=15ml, Soil=1.5g)

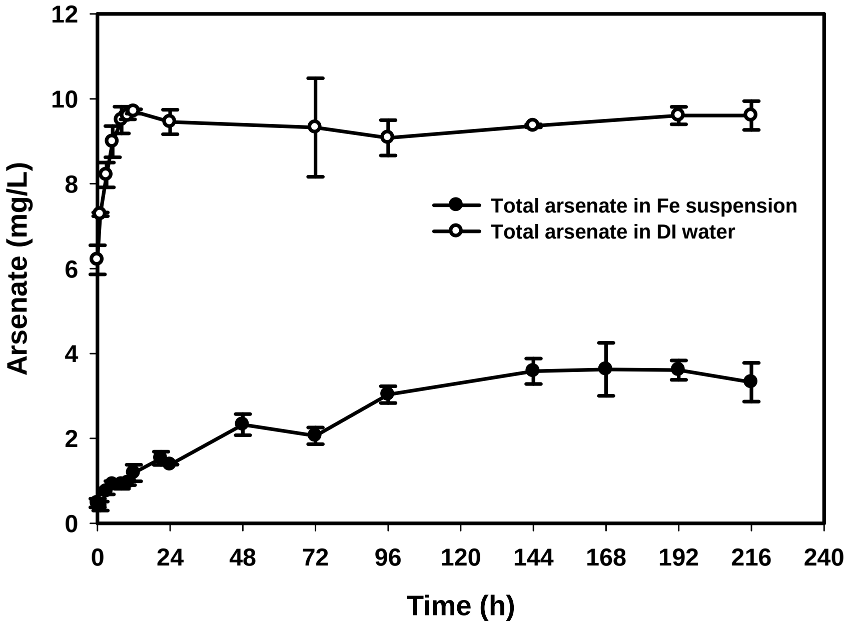

Figure 3.4 Leaching of Arsenate form A Contaminated Smith Farm Soil with Nanoparticle Suspension (Total Fe =0.25g/L, 0.1% Starch) or DI Water.(Solution Volume=15ml, Soil=1.5g)

3.4 Conclusions

Major findings from series of batch tests are as following:

1. A simply batch test was performed to study the effectiveness of various polymer-bridged magnetite nanoparticles in terms of arsenate removal from aqueous phase only. With the same amount of iron (0.1 g/L), 0.04% and 0.1% starch-bridged magnetite nanoparticles removed 94.5% and 98.0% of arsenate respectfully. By adding 0.3% PAM 705, 0.04% and 0.1% starch-bridged magnetite nanoparticles could not remove as much arsenate (72.3% and 75.9%). However, 0.3% PAM 705 stabilized magnetite nanoparticles (total Fe = 0.1 g/L) did not show any advantage in arsenate removal (removal efficiency, 58.6%) over the other nanoparticles.

2. The results indicated that arsenate adsorption by the two different soil samples was highly nonlinear, the b values after 12 days retention are 0.22 for the Smith Farm soil and 0.21 for the Vulcan site soil. Apparently, the Smith Farm soil showed more affinity to arsenate than the Vulcan site soil. Soil type and properties had significant effect on metalloids leachate concentrations.
3. Magnetite nanoparticles arsenate removal capacity is 0.065 mgAs/mgFe for the arsenic contaminated Vulcan site soil and 0.024 mgAs/mgFe for the arsenic contaminated Smith Farm soil. Again, batch arsenate immobilization tests confirmed that sandy loam soil has a shorter arsenate residence time, and this makes it easier to leach out and to adsorbe the arsenate by the nanoparticles. The Smith Farm soil showed more affinity to arsenate; the magnetite nanoparticles are less accessibility to the arsenate when associated with the soil particles.

Chapter 4 Immobilization of Arsenate at Disturbed Surface Soils in Small Scale Box Test

In this chapter, small scale box study was conducted to investigate the performance of starch bridged magnetite nanoparticles in presence of PAM in terms of arsenic immobilization in two soils under simulated rainfall. pH and dosage effect of nanoparticles was also evaluated.

4.1 Introduction

Human activities that contribute arsenic to the soil environmental originate from primary and secondary industries. As a byproduct of mining, many contaminates are generated and dumped onto the ground (Anawar et al., 2006; Casado et al., 2007) and these amounts substantially exceed any reasonable guidelines. For example, in the United Kingdom the limit is 50 mg/kg for agricultural soils (MAFF, 1993), which is exceeded by many mining operations.

Arsenic is a natural component in lead, zinc, copper, and gold ores. Consequently, contamination during mining and smelting could add arsenic to the atmosphere, to the ground, to above ground bodies of water, and to underground water sources (Smith et al., 1998).

Studies that monitor the leachate forms of heavy metal contaminated soils have found that these metals remain closely bound to soil matrix and are relocated only under extremes of physical and chemical conditions (i.e. high water fluxes and extreme E_h or pH values) or after excessive accumulations on the site (Schirado et al., 1986). Where soils are acidic or alkaline, where metal loadings are high, where the shallow soil profiles reflects a poor retentive nature, and where the area is subjected to large water fluxes, then the potential exists for heavy metal contamination of groundwater (Carey et al., 1996).

Mining operations and vegetation removal can also lead to the formation of sinkholes (Langer, 2001) and to the acceleration of soil erosion (EBP, 2008). In sub-surface quarrying, the production of Acid Mining Drainage (ARD) can be a potentially serious environmental problem. This is the case when the rocks contain elevated amounts of sulfide minerals (often pyrite) are removed from the quarrying pit. After being exposed to air and water, the metal sulfides undergo oxidation and begin to generate acid products. Equation (1) depicts the stoichiometry of this process:

$$2FeS_2(s) + 7O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4SO_4^{2-}(aq) + 4H^+(aq) \qquad (1)$$

The oxidation of the metal sulfides to a sulfate solubilizes form such as ferrous iron, which in turn is subsequently oxidized to ferric iron:

$$4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Fe^{3+}(aq) + 2H_2O(l) \qquad (2)$$

These reactions can occur spontaneously and can be catalyzed by microorganisms. The ferric irons produced can also oxidize additional pyrite:

$$FeS_2(s) + 14Fe^{3+}(aq) + 8H_2O(l) \rightarrow 15Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 16H^+(aq) \qquad (3)$$

The net effect of these reactions is to release H^+, which turns the water into an acidic solution. Under an extremely acidic condition, toxic metals such as copper, zinc, lead, arsenic, and manganese become unstable and are dissolved to become a mobilized solution. ARD contamination of surface and groundwater by toxic metals has been an extremely challenging environmental problem for decades. The sediment recovery time is measured in years. Therefore, mining operators are frequently required to have an Erosion and Sediment Control Plan with provisions for handling and for controlling any anticipated erosion and to prevent sediment from leaving the site.

The fate and the behavior of arsenic in soils depend greatly on the adsorption process and desorption/release process (Bowell, 1994; Williams et al., 2003; Zhang and Selim, 2005). Arsenic mobility and bioavailability in the soil environment and the aquatic environment are a function of pH values, the redox potential, the presence and type of adsorbing surfaces (primary iron oxyhydroxides), and the microbial population (Dowdle et al., 1996; Masscheleyn et al., 1991; McGeehan and Naylor, 1994).

In this research project, arsenic contaminated soils were subjected to intensive rainfall in small-scale box tests. The test was designed to mimic the extreme situations that exist in a mining site. In this extreme situation, we used starch-bridged magnetite nanoparticles with different pH values and different Fe dosages in order to discover the best approach for immobilizing arsenic from contaminated soils. The PAM products were used as a soil stabilizer and as a runoff reduction agent. Different combinations were applied to discover the best one for reducing runoffs.

4.2 Materials and methods

4.2.1 Soils and preloaded arsenate concentration

To facilitate the arsenic immobilization in small-scale box tests, two air-dried clean soils were spiked with As(V). The Vulcan site soil had a soil-phase concentration of 380 mg/kg and the Smith Farm soil had a soil-phase concentration of 548 mg/kg.

4.2.2 Preparation of starch-bridged magnetite nanoparticles

A solution of $Fe^{3+}$and Fe^{2+} (from $FeCl_3$•$6H_2O$ and $FeSO_4$•$7H_2O$, respectively) was prepared at a ferric-to-ferrous molar ratio of 2:1 at room temperature (21°C). Then, the 2% starch stock solution was mixed with the Fe^{3+}/Fe^{2+} solution under N_2 purging at a starch concentration of 0.1 wt.%. Then, a 2 M NaOH solution was added drop wise into the solution under vigorous stirring until a pH value of about 11 was obtained. When the color changed from brown to black, this meant that the formation of the nanoparticles had taken place (Schwertmann and Cornell, 2000). Then, the starch-magnetite solution was nitrogen-purged for 20 minutes. Finally, the suspension was sealed and placed in a dark area for 12 hours in order to allow the magnetite nanoparticles to grow. Then the pH value was lowered back to the desired pH value with 2 M HCl, the suspension was used within the hour.

4.2.3 Arsenate immobilization in small-scale box tests

Immobilization of arsenic in simulated surface soil was tested using the same box test setup. However, only one-third of a box was loaded with a soil sample. (To achieve this, the box volume was reduced through the use wooden blocks in order to form a one-foot by one-foot smaller box. The resulting boxes were filled with about two inches of the soil samples. Upon proper compacting, the one-inch soil in the center area (4.33×4.33 cm^2) was removed and replaced with the arsenate laden soil. The arsenic-loaded soil needed for each plot was 200 g of dry soil with about 30 g of water added in order to reach the 15% water content, which is a requirement for having a constant saturation ratio during the tests. The mixtures were allowed to dry for one day. After this drying period, the 0.3% PAM 705 (w/w) 260 ml was sprayed onto the test plots permitted to dry for three days. Nanoparticles in the arsenic-laden soil were aged for four days before the soil was subjected to a rainfall test. During the simulated rainfall tests, runoff samples were collected every 5 minutes for 60 minutes. The samples were then filter through 25nm membrane filter (0.025μm VSWP, Millipore, USA) and the resulting filtrates were analyzed for arsenic and iron concentrations. The steps are shown in Figure 4.1.

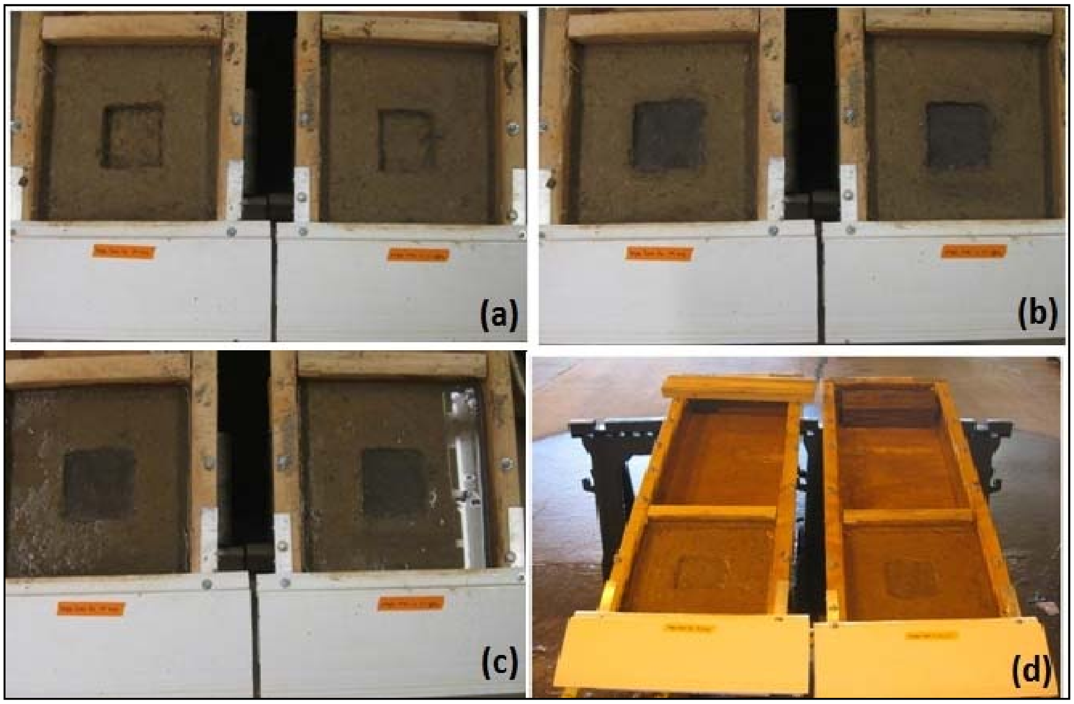

Figure 4.1 (a) Compacted Soil with One Inches Cubic Soil Taking Out; (b) Filled The Plots with Nanoparticles Amended Arsenate Contaminated Soils; (c) PAM 705 Applied; (d) Test Plots Under Rain Simulation Event.

To further study the effect of nanoparticles treatment performance, starch-bridged magnetite nanoparticles with different initial pH and dosage were used to amend the contaminated soils.

4.3 Results and discussion

In chapter three, Figure 3.1 showed that starch stabilized magnetite nanoparticles (total Fe = 0.1g/L) were able to reduce arsenate release by over 94.5% when compared to the control plots, whereas 0.3% PAM 705 stabilized magnetite nanoparticles with the same amount of stabilized magnetite nanoparticles only reduce the arsenate release by a much lower 58.6%. Therefore, magnetite nanoparticles with starch as a stabilizer were further utilized for arsenate removal studies in batch tests and in small-scale box tests.

Recalling the small-scale soil erosion test results in chapter two, the runoff concentrations were very high for the bare soil plots without the application of any PAM solutions. For these test runs, it is clear that the arsenic compounds would be washed off the contaminated soil samples or would be leached out from the contaminated soil samples. Studies on the PAM product's efficacy to promote flocculation of agricultural contaminants indicate that the PAM products are very effective as a sediment flocculant. The resulting material and water would have reduced contaminants (such as nutrients, pesticides, and biological oxygen demand (BOD) (Lentz and Smith, 2000). Lentz et al. (1998) reported that removing suspended sediment in runoff water was positively correlated with other contaminant removals. Thus, in order to avoid unnecessary contamination and to take advantage of PAM in terms of soil erosion control and in terms of arsenate leaching behavior, the 0.3% PAM 705 treatment would be used in one-third of the runoff tests.

Arsenic stabilization in soils can be achieved with the addition of iron based chemicals or other treatment solutions in order to decrease the leachability of arsenic from contaminated soils (Warren et al., 2003). Different iron dosages for starch-bridged magnetite nanoparticles with different pH values were used to immobilize the arsenate in soils ex situ. The low permeability of construction site soils is due to compaction, which apparently hinders the nanoparticles transport into the contaminated soil with the result could definitely weaken the efficiency of the nanoparticles. For this test, in order to thorough mix and promote sufficient remediation, an ex situ method was used for arsenate immobilization. PAM was applied in the same way as was done in the soil erosion tests. Surface runoffs were collected every five minutes during the simulated rainfall for a total of twelve samples. The arsenate masses in the effluents of the Vulcan site soil and of the Smith Farm soil for different starch-bridged magnetite nanoparticles treatments verse rainfall duration are showed in Figure 4.2 and Figure 4.4.

4.3.1 Arsenic immobilization in Vulcan Site soil

Figure 4.2 shows the arsenate masses for the control (no iron nanoparticles treatment) and for the 0.1% starch-bridged magnetite nanoparticles with 0.5g total Fe (pH = 6.65) , 0.5g total Fe (pH = 5.46), and 1g total Fe (pH = 6.95) for the three treated Vulcan site soil plots. As shown in Figure 4.2, the arsenate mass of the control plot had a sharp drop during the first ten minutes when the arsenate mass was extremely high. After five minutes the arsenate mass was at 3,037.73μg. After a passage of another five minutes, the arsenate mass was at 795.55μg. It took more time to gradually reduce the arsenate mass down to 82.55μg. As mentioned in the soil properties, 75.9mg of arsenate by calculation was introduced to the Vulcan site soil. With the PAM application, 7.8% arsenate mass was leached in terms of cumulative arsenate mass during the rainfall event without nanoparticles treatment. The arsenate masses for the three PAM treatments continued to decrease while the "rain" fell.

Raven et al. (1998) claimed that the sorption behavior of arsenic is strongly influenced by a solution's pH value and this is due to the fact that arsenic is more strongly retained at low pH values. Our work used magnetite nanoparticles with 0.5g total Fe (pH = 6.65), with 0.5g total Fe (pH = 5.46), and with 1g total Fe (pH = 6.95) for reducing the arsenate mass leaching. The results showed a reduced arsenate mass leaching of 1.18%, 0.54% and 0.22%, respectively.

When the magnetite nanopartilces compounds contained the same amount of iron (Fe = 0.5g), but different pH values, the results showed different efficiency for arsenate immobilization.

A lower pH value (pH = 5.46) was more efficient with 54.6% of the arsenate was immobilized. This result agrees with the Yean et al. (2005) results.

Treated plots with 1g of iron (pH = 6.95) tended to have arsenate masses in the effluent range of 8.49 to about 23.15μg in the runoff samples. This is an 81.4% arsenate mass reduction when compared to treated plots with 0.5g total iron (pH = 6.65). This shows that the aqueous arsenate concentrations do decrease when the magnetite nanoparticles concentration is increased. Shipley et al. (2009 and 2010) had the similar conclusion. The incorporation of magnetite to arsenic contaminated soils resulted in a decrease in mobile arsenic concentrations, which agrees with Hartley et al. (2004) research.

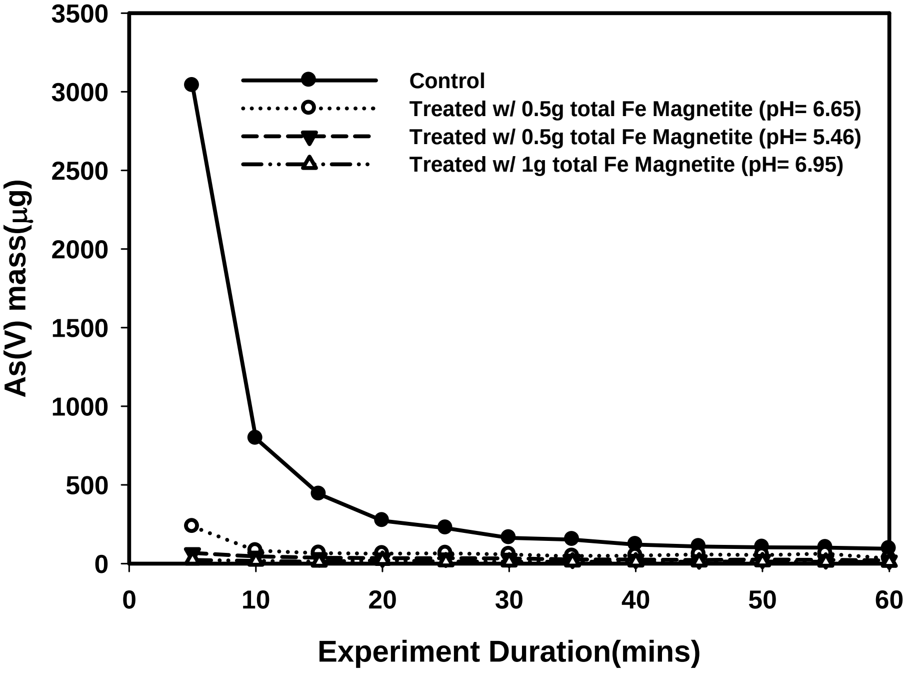

Figure 4.2 Runoff As(V) Mass in Three Magnetite Nanoparticles Treated As(V) Ladened Vulcan Site Soil

As indicated by the properties of two soils in Chapter two Table 2.1 Vulcan site soil itself contains Fe 39mg/L. In Figure 4.3, the effluent Fe mass were evaluated. Compared to control plot, 0.1%, 0.18% and almost none of total Fe were leached out from 0.5g total Fe (pH=6.65), 0.5g total Fe (pH=5.46) and 1g total Fe (pH=6.95)magnetite nanoparticles. The results showed that most of the iron nanoparticles, if not all, stayed in the soil matrix working as an arsenate absorbent.

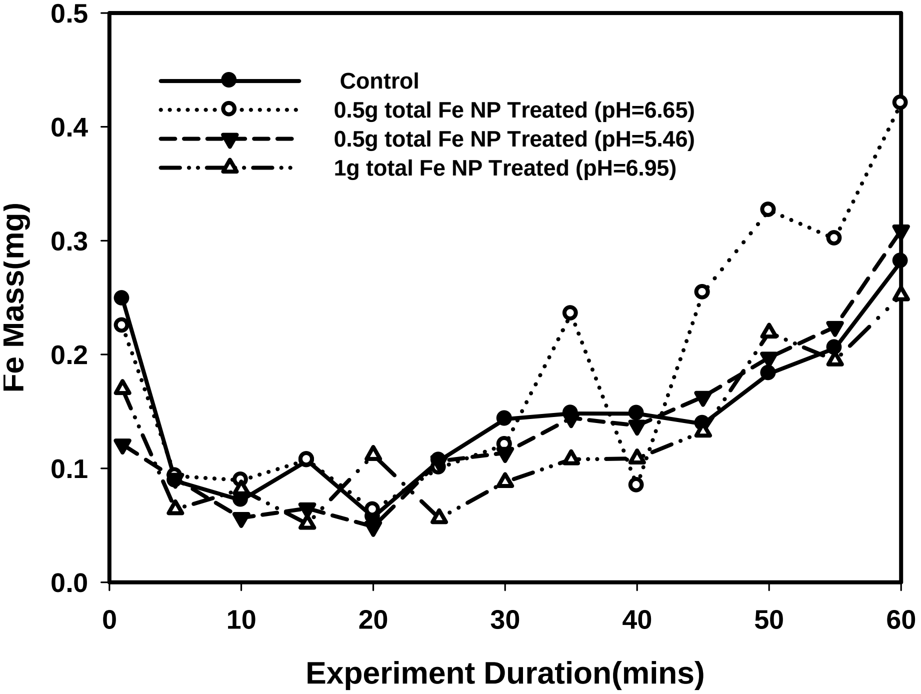

Figure 4.3 Fe Mass in Three Kinds of Magnetite NanoparticlesTreated As(V) Ladened Vulcan Site Soil Runoff Samples

4.3.2 Arsenic immobilization in Smith Farm soil

Figure 4.4 shows the arsenate masses for the control (no iron nanoparticles treatment) and for the bridged magnetite nanoparticles with 0.5g total Fe (pH = 7.04), 1g total Fe (pH = 6.65) and 1g total Fe (pH = 5.46) treated plots for Smith Farm soil, respectively. The average arsenate masses are 72.42±15.91µg, 50.68±10.06µg, 39.17±9.71µg, and 29.93±6.12µg, respectfully. The arsenate mass increased gradually for all cases when 109.5 mg arsenate was introduced to the Smith Farm soil as calculated. After the PAM applications, 0.86% arsenate was leached from the control plot, 0.61%, 0.46%, and 0.36% of arsenate masses were leached from the 0.5g total Fe (pH = 7.04), the 1g total Fe (pH = 6.65) and the 1g total Fe (pH = 5.46) treated plots. Clearly, the arsenate masses were reduced as the total iron mass in the nanoparticles increased. Lower pH values with higher amounts of total iron in the magnetite nanoparticles performed the best.

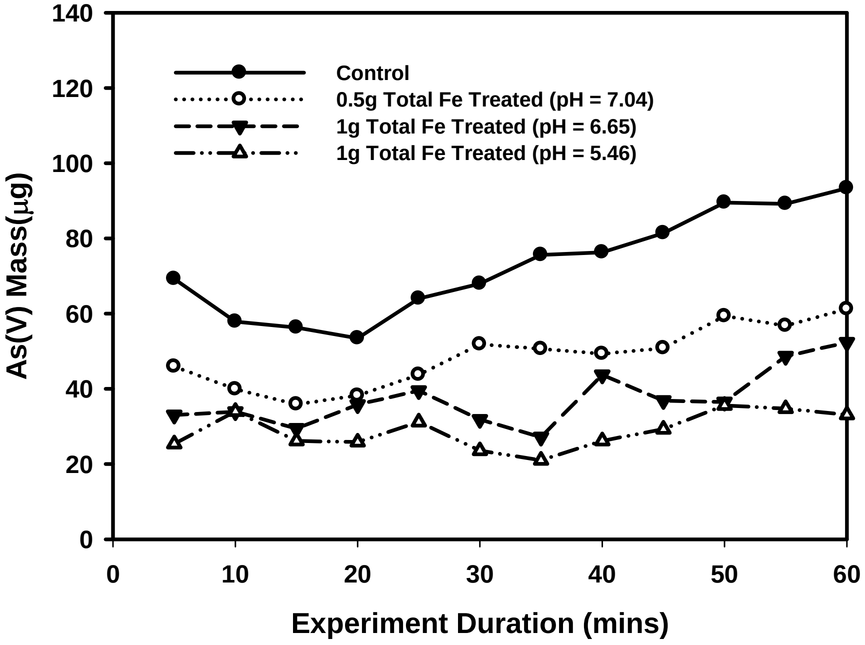

Figure 4.4 Runoff Arsenate Mass in Three Magnetite Nanoparticles Treated Arsenate Laden Smith Farm soil

Similar results were observed for Fe mass in three kind of magnetite nanoparticles treated arsenate laden Smith Farm soil runoff samples (Figure 4.5). 0.08%, almost none and 0.15% of total Fe were leached out from 0.5g total Fe (pH = 7.04), 1g total Fe (pH = 6.65) and 1g total Fe (pH = 5.46) treated plots for Smith Farm soil compared to control.

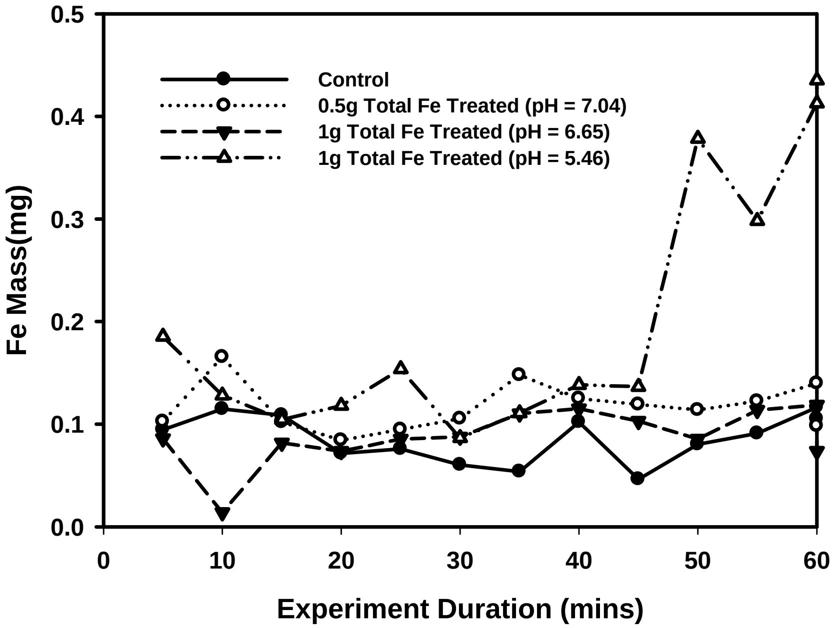

Figure 4.5 Fe Mass inThree Kinds of Magnetite NanoparticlesTreated Smith Farm Soil Runoff Samples

4.3.3 Summary

The sorptive capacity of soil is important for its role in binding arsenic (Woolson et al., 1971). The magnetite nanopartilces were more effective for absorbing the leaching arsenic in the Vulcan site soil than for the Smith Farm soil. If a soil is sandy or has a low clay content, it is less probable that arsenic can be readily bounded when compared to a soil that has high organic matter, silt, or clay content (Fraust et al., 1987a, b). It has been demonstrated that arsenic has a shorter residence time in sandy soils, especially under alkaline conditions (Gullens et al., 1979; Masscheleyn et al., 1991).

PAM 705 prevent soil erosion significantly, thus most of arsenate was stabilized in the surface soil during the simulated rain event. The contaminated Vulcan site soil was more vulnerable than the Smith Farm soil, because more arsenate leached out due to the soil texture. However, magnetite nanoparticles worked more efficient on the Vulcan site soil, because the adsorption capacity for 0.5g total Fe (pH = 6.65), 0.5g total Fe (pH = 5.46), and 1g total Fe (pH = 6.95) magnetite nanoparticles are 10.05mg As(V)/g Fe, 11.02mg As(V)/g Fe, and 5.75mg As(V)/g Fe respectfully in terms of arsenate removal for PAM treated surface soil runoff. Whereas, the adsorption capacities for starch partially stabilized magnetite nanoparticles with 0.5 g total Fe (pH = 7.04), 1g total Fe (pH = 6.65), and 1g total Fe (pH = 5.46) are 0.55mg As(V)/g Fe, 0.44mg As(V)/g Fe, and 0.55mg As(V)/g Fe respectfully as far as arsenate removal in surface soil runoff is concerned.

Arsenic is known to be less mobile in acidic soils (Madejón and Lepp, 2007). The Smith Farm soil (pH = 4.76) had a higher affinity to arsenate and thus the arsenate is more difficult to be desorbed from the soil. The extent of adsorption is also strongly influenced by the mineral PZC (Matera and Le Hecho, 2001). The Vulcan site soil contained a negative charge that would repel the arsenate anion whereas the Smith Farm soil had a greater affinity to arsenate due to its different PZC. Therefore, the physical and chemical properties of soil, such as texture and pH values, are very important when considering remediation options.

4.4 Conclusions

From the small-scale box test from this chapter, the arsenic immobilization behavior from the two soil samples is as follows:

1. For Vulcan site soil, with PAM application, 7.8% arsenate mass was leached out in terms of cumulative arsenate mass during the simulated rainfall event. Applying starch bridged magnetite nanoparticles with 0.5g total Fe (pH = 6.65), 0.5g total Fe (pH = 5.46), and 1g total Fe (pH = 6.95) in combination with PAM application, the result was

that the arsenate mass leaching dropped down to 1.18%, 0.54%, and 0.22% respectively in terms of cumulative mass during the rainfall duration.

2. The Smith Farm soil without nanoparticles treatment saw 0.86% arsenate was leached from the control plot. After PAM application and 0.5g total Fe (pH = 7.04), 1g total Fe (pH = 6.65), and 1g total Fe (pH = 5.46) starch bridged magnetite nanoparticles, the result was that the arsenate mass leaching dropped down to 0.61%, 0.46%, and 0.36% respectively in terms of cumulative mass during the rainfall duration.
3. For both soil samples, the maximum adsorption capacity of arsenate for both magnetite particles studied decreased with increasing pH, arsenate concentrations decreased with increasing magnetite nanoparticle concentration. Most of the nanoparticles stayed in the soil matrix as a soil absorbent.
4. PAM prevent soil erosion significantly, thus most of arsenate was stabilized in the surface soil during the rain event.
5. Smith Farm soil had higher affinity to arsenate thus arsenate is more difficult to be desorbed from the soil as compared to the Vulcan site soil.

Chapter 5 Summary of Conclusions

A technology for enhanced control of soil erosion, sedimentation, and metal leaching at disturbed lands using polyacrylamide and a class of polymer-bridged magnetite nanoparticles were introduced in this research. We endeavored to take advantage of the commercially available PAMs for use as a soil binder and to take advantage of magnetite nanoparticles for use as a contaminant absorbent when addressing soil erosion and the associated metal leaching problems that commonly occurred in construction and in mining sites. The research was done as a small scale box test with a steep slope (3:1) using soils from two very different locations in the state of Alabama (Vulcan site and Smith Farm) and with simulated rainfall, PAM only and PAM stabilized magnetite nanopartilces (Total Fe = 0.1 g/L) treatments were used. Data was collected on runoff flow rates, on runoff concentrations, on initial turbidity, and on sample turbidity kinetics. Analysis was performed and the results were compared with the untreated control soil plots. The results revealed that nano-PAM emulsion can significantly reduce 90.8% and 89.1% runoff concentrations and 83.0% and 90.5% turbidity for the Vulcan site soil and the Smith Farm soil, respectively. These results were achieved with only 70% viscosity in the nano-PAM solutions. Furthermore, our approach could more than satisfy the strict US EPA runoff effluent standard.

Arenic(V) was used as the targeted contaminant. A series of batch tests were conducted to study the arsenic adsorption and immobilization effectiveness with various polymer bridged magnetite nanoparticles. The intent was to discover the best the nanoparticles recipe for arsenic immobilization in small scale box test. The starch bridged magnetite nanoparticles associated with PAM application was successfully used immobilized the arsenate in soils (below1.28% arsenate is leachable) in our small scale box study. By inducing low pH values and by using a high dosage of nanoparticles, we found that more arsenic could be immobilized.

Soil properties played a big role in both the soil erosion control test and the metal leaching test. The Vulcan site soil was more sensitive to soil erosion and to metal leaching, but the nanoparticles were more able to immobilize the arsenic compound. In contrast, the Smith Farm soil had opposite behaviors.

To summarize, the PAM product applications with starch bridged magnetite nanoparticles were very effective in controlling soil erosion in arsenic disturbed soils.

References

Agassi, M., Letey, J., Farmer, W.J., Clark, P., 1995. Soil-erosion contribution to pesticide transport by furrow irrigation. Journal of Environmental Quality 24, 892-895.

American Society of Agricultural Engineers (ASAE), 2000. Testing procedure for determining uniformity of water distribution of center pivot and lateral move irrigation machines equipped with spray or sprinkler nozzles. ASCE-S436.1, 48h Ed.,St. Joseph, Mich.

An, B., Liang, Q.Q., Zhao, D.Y., 2011. Removal of arsenic(V) from spent ion exchange brine using a new class of starch-bridged magnetite nanoparticles. Water Research 45, 1961-1972.

An, B., Steinwinder, T.R., Zhao, D.Y., 2005. Selective removal of arsenate from drinking water using a polymeric ligand exchanger. Water Research 39, 4993-5004.

Anawar, H.M., Garcia-Sanchez, A., Murciego, A., Buyolo, T., 2006. Exposure and bioavailability of arsenic in contaminated soils from the La Parrilla mine, Spain. Environmental Geology 50, 170-179.

Azzam, R., El-Hady, O.A., Lofty, A.A., Hegela, M., 1983. San-RAPG combination simulating fertile clayey soils, parts I-IV. Int. Atomic Energy Agency. SM-267/15, 321-349.

Barvenik, F.W., 1994. Polyacrylamide characteristics related to soil applications. Soil Sci. 158, 235-243.

Banfield, J.F., Navrotsky, A., 2003. Nanoparticles and the environment. Reviews in mineralogy and geochemistry. Geochimica et Cosmochimica Acta, Washington DC, 67, 1753.

Beighley, R.E., Scholl, B., Faucette, L.B., Governo, J., 2010. Runoff Characteristics for Construction Site Erosion Control Practices. Journal of Irrigation and Drainage Engineering-Asce 136, 405-413.

Benner, S.G., Hansel, C.M., Wielinga, B.W., Barber, T.M., Fendorf, S. 2002. Reductive dissolution and biomineralization of iron hydroxide under dynamic flow conditions. Environ. Sci. Technol. 36, 1705-1711.

Bertol, O.J., Rizzi, N.E., Bertol, I., Roloff, G., 2007. Soil and water loss and quality of surface runoff associated with interrill erosion in no-tillage area treated with chemical and organic fertilizers. Revista Brasileira De Ciencia Do Solo 31, 781-792.

Bodek, I., Lyman, w.J., Reehl, W.F., Rosenblatt, D.H., 1998. Environmental Inorganic

Chemistry: properties, Process and Estimation Methods, Pergamon Press, USA.

Bologna, L.S., Andrawes, F.F., Barvenik, F.W., Lentz, R.D., Sojka, R.E., 1999. Analysis of residual acrylamide in field crops. Journal of Chromatographic Science 37, 240-244.

Bowell, R.J., 1994. Sorption of arsenic by iron-oxides and oxyhydroxides in soils. Applied Geochemistry 9, 279-286.

Buchter, B., Davidoff, B., Amacher, M.C., Hinz, C., Iskandar, I.K., Selim, H.M., 1989. Correlation of Freudlich k_d and n retention parameters with soils and elements. Soil Science 148, 370-379.

Carey, P.L., McLaren, R.G., Cameron, K.C., Sedcole, J.R., 1996. Leaching of copper, chromium, and arsenic through some free-draining New Zealand soils. Australian Journal of Soil Research 34, 583-597.

Casado, M., Anawar, H.M., Garcia-Sanchez, A., Santa-Regina, I., 2007. Arsenic bioavailability in polluted mining soils and uptake by tolerant plants (El cabaco mine, spain). Bulletin of Environmental Contamination and Toxicology 79, 29-35.

Cebrian, M.E., Albores, A., Aguilar, M., Blakely, E., 1983. Chronic arsenic poisoning in the north of Mexico. Human Toxicology 2, 121-133.

Chakraborti, D., Mukherjee, S.K., et al., 2003. Arsenic groundwater contamination in middle Ganga Plain, Bihar, India:a future danger? Environ. Health Persp. 111, 1194-1201.

Choprapawon, C., Rodcline, A., 1997. Chronic arsenic poisoning in Ronpibool NakhonSri Thammarat, the southern province of Thailand. In: Abernathy, C.O., Calderon, R.L., Chappell, W.R. (Eds.), Arsenic Exposure and Health Effects. Chapman and Hall, London, pp. 69-77.

Chowdhury, T.R., Basu, G.K., Mandal, B.K., Biswas, B.K., Samanta, G., Chowdhury, U.K., Chanda, C.R., Lodh, D., Lal Roy, S., Saha, K.C., Roy, S., Kabir, S., Quamruzzaman, Q., Chakraborti, D., 1999. Arsenic poisoning in the Ganges delta. Nature 401, 545-546.

Clifford, D.A., Lin, C.C., 1991. Arsenic(III) and arsenic(V) removal from drinking water in San Ysidro, New Mexico. Project summary for USEPA, EPA report EPA/600/S2-91/011, Washington, USA.

Cochrane, B.H.W., Reichert, J.M., Eltz, F.L.F., Norton, L.D., 2005. Controlling soil erosion and runoff with polyacrylamide and phosphogypsum on subtropical soil. Transactions of the Asae 48, 149-154.

Codner, S., 2001. Iowa studies ways to control highway erosion. Biocycle 42, 42-42.

Coker, V.S., Gault, A.G., Pearce, C.I., van der Laan, G., Telling, N.D., Charnock, J.M., Polya, D.A., Lloyd, J.R., 2006. XAS and XMCD evidence for species-dependent partitioning of arsenic during microbial reduction of ferrihydrite to magnetite. Environmental Science & Technology 40, 7745-7750.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem Rev. 89, 713-64.

Dagan, R., Bitton, G., Townsend, T.G., 2006. Metal transport and bioavailability in soil contaminated with CCA-treated wood leachates. Soil & Sediment Contamination 15, 61-72.

Davis, A., Sherwin, D., Ditmars, R., Hoenke, K.A., 2001. An analysis of soil arsenic records of decision. Environmental Science & Technology 35, 2401-2406.

Dhar, R.K., Biswas, B.K., Samanta, G., Mandal, B.K., Chakraborti, D., Roy, S., Jafar, A., Islam, A., Ara, G., Kabir, S., Khan, A.W., Ahmed, S.A., Hadi, S.A., 1997. Groundwater arsenic calamity in Bangladesh. Current Science 73, 48-59.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environmental Science & Technology 37, 4182-4189.

Dowdle, P.R., Laverman, A.M., Oremland, R.S., 1996. Bacterial dissimilatory reduction of arsenic(V) to arsenic(III) in anoxic sediments. Applied and Environmental Microbiology 62, 1664-1669.

EBP, 2008. Environment Bay of Plenty, Quarry Guidelines,
ttp://www.envbop.govt.nz/Land/Land-Use/Quarry-Guidelines.asp

Emsley, J., 2001. Nature's Building Blocks: An A-Z Guide to the Elements. Oxford: Oxford University Press. pp. 43,513,529. ISBN: 0-19-850341-5.

Flanagan, D.C., Canady, N.H., 2006a. Use of polyacrylamide in simulated land application of lagoon effluent: Part I. Runoff and sediment loss. Transactions of the Asabe 49, 1361-1369.

Flanagan, D.C., Canady, N.H., 2006b. Use of polyacrylamide in simulated land application of lagoon effluent: Part II. Nutrient loss. Transactions of the Asabe 49, 1371-1381.

Flanagan, D.C., Chaudhari, K., Norton, L.D., 2002a. Polyacrylamide soil amendment effects on runoff and sediment yield on steep slopes: Part I. Simulated rainfall conditions. Transactions of the Asae 45, 1327-1337.

Flanagan, D.C., Chaudhari, K., Norton, L.D., 2002b. Polyacrylamide soil amendment effects on runoff and sediment yield on steep slopes: Part II. Natural rainfall conditions. Transactions of the Asae 45, 1339-1351.

Flanagan, D.C., Norton, L.D., Shainberg, I., 1997. Effect of water chemistry and soil amendments on a silt loam soil - Part 1: Infiltration and runoff. Transactions of the Asae 40, 1549-1554.

Fraust, S.D., Winka, A.J., Belton, T., 1987a. An assessment of chemical and biological significance of arsenical compounds in the Maurice River drainage basin (N.J.). I. Distribution in water and river and lake sediments. J. Environ. Sci. Health A22, 209-237.

Fraust, S.D., Winka, A.J., Belton, T., 1987b. An assessment of chemical and biological significance of arsenical compounds in the Maurice River drainage basin (N.J.). II. Partitioning of arsenic into bottom sediments. J. Environ. Sci. Health A22, 239-262.

Fredrickson, J.K., Zachara, J.M., Kennedy, D.W., Dong, H., Onstott, T.C., Hinman, N.W., Li, S. M., 1998. Geochim. Cosmochim.Acta, 62, 3239-3257.

Fu, B.J., Chen, L.D., 2000. Agricultural landscape spatial pattern analysis in the semi-arid hill area of the Loess Plateau, China. Journal of Arid Environments 44, 291-303.

Gannon, J., 1999. A review of sediment control measures. Erosion Control.
http://www.forester.net/ec_9911_review_sediment.html

Garcia-Manyes, S., Jimenez, G., Padro, A., Rubio, R., Rauret, G., 2002. Arsenic speciation in contaminated soils. Talanta 58, 97-109.

Gimenez, J., Martinez, M., de Pablo, J., Rovira, M., Duro, L., 2007. Arsenic sorption onto natural hematite, magnetite, and goethite. Journal of Hazardous Materials 141, 575-580.

Gonzalez, E.P., Lopez, J.S., Martin, J.D., Burgos, A.J., Agudo, J.P., 2006. Analysis of the mobilization of solid loads and heavy metals in runoff waters from granite quarries. Environmental Geology 50, 823-834.

Gregory, J., 1988. Polymer adsorption and flocculation in sheared suspensions. Colloids Surf. 31, 231-253.

Gullens, J., Champ, D.R., Jackson, R.E., 1979. Influence of redox environments on the mobility of arsenic in ground water. Chemical modelling in aqueous solution. ACS Symp. Ser. 7. AmericanChemical Society, Washington, DC, 81.

Guo, H.R., 2003. Arsenic in drinking water and cancers in Taiwan. In: Murphy, T., Guo, J. (Eds.), Aquatic Arsenic Toxicity and Treatment. Backhuys Publisher, Leiden, The Netherlands, pp. 51-67.

Guo, X.J., Chen, F.H., 2005. Elimination of As(III)) from groundwater by bead cellulose adsorbent loaded with Fe(beta-FeOOH). Chemical Journal of Chinese Universities-Chinese 26, 1258-1263.

Hartley, W., Edwards, R., Lepp, N.W., 2004. Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests. Environmental Pollution 131, 495-504.

Hayes, S.A., McLaughlin, R.A., Osmond, D.L., 2005. Polyacrylamide use for erosion and turbidity control on construction sites. Journal of Soil and Water Conservation 60, 193-199.

Hering, J.G., Chen, P.Y., Wilkie, J.A., Elimelech, M., 1997. Arsenic removal from drinking water during coagulation. Journal of Environmental Engineering-Asce 123, 800-807.

Jacobs, L.W., Syere, J.K., Keeney, D.R., 1970. Arsenic sorption by soils. Soil Sci. Soc. Am. Proc. 34, 750-754.

Jiang, T., Teng, L.L., Wei, S.Q., Deng, L.L., Luo, Z.B., Chen, Y.P., Flanagan, D.C., 2010. Application of polyacrylamide to reduce phosphorus losses from a Chinese purple soil: A laboratory and field investigation. Journal of Environmental Management 91, 1437-1445.

Jonsson, J., Sherman, D.M., 2008. Sorption of As(III) and As(V) to siderite, green rust (fougerite) and magnetite: Implications for arsenic release in anoxic groundwaters. Chemical Geology 255, 173-181.

Karim, M., 2000. Arsenic in groundwater and health problems in Bangladesh. Water Research 34, 304-310.

Katsoylannis, I.A., Zouboulis, A.I., 2006. Use of iron- and manganese-oxidizing bacteria for the combined removal of iron, manganese and arsenic from contaminated groundwater. Water Quality Research Journal of Canada**,** 41, 117-129.

Khan, B.I., Solo-Gabriele, H.M., Dubey, B.K., Townsend, T.G., Cai, Y., 2004. Arsenic speciation of solvent-extracted leachate from new and weathered CCA-treated wood. Environmental Science & Technology 38, 4527-4534.

Kim, M.J., Nriagu, J., Haack, S., 2002. Arsenic species and chemistry in groundwater of southeast Michigan. Environ. Pollut. 120, 379-390.

Langer, W.H., 2001. Potential Environmental Impacts of Quarrying Stone in Karst – A Literature Review, USGS Open-File Report of-01-0484.

Lee, S.S., Gantzer, C.J., Thompson, A.L., Anderson, S.H., 2010. Polyacrylamide and gypsum amendments for erosion and runoff control on two soil series. Journal of Soil and Water Conservation 65, 233-242.

Lentz, R.D., Sojka, R.E., 2000. Applying polymers to irrigation water: Evaluating strategies for furrow erosion control. Transactions of the Asae 43, 1561-1568.

Lentz, R.D., Sojka, R.E., Robbins, C.W., 1998. Reducing phosphorus losses from surface-irrigated fields: Emerging polyacrylamide technology. Journal of Environmental Quality 27, 305-312.

Lu, J.H., Wu, L.S., Letey, J., Farmer, W.J., 2002. Anionic polyacrylamide effects on soil sorption and desorption of metolachlor, atrazine, 2,4-D, and picloram. Journal of Environmental Quality 31, 1226-1233.

Lumsdon, D.G., Fraser, A.R., Russell, J.D., Livesey, N.T., 1984. New infrared band assignments for the arsenate ion adsorbed on synthetic goethite (α-FeOOH). J. Soil Sci. 35, 381-386.

Lund, U., fobian, A., 1991. Pollution of two soils by arsenic, chromium, and copper, Denmark. Geoderma 49,83-103.

Kabata-Pendias, A., Pendias, H., 2000. Trace element in soils and plants, CRC Press, Boca Raton, FL.

Kogel, J.E., Trivedi, N.C., Barker, J.M., Krukowsk, S.T., 2006. Industrial Minerals & Rocks: Commodities, Markets, and Uses, 7th Ed., Society for Mining Metallurgy. http://books.google.com/books?id=zNicdkuulE4C&printsec=frontcover&source=gbs_summary_r&cad=0#PPA153, M1

Kumpiene, J., Ore, S., Renella, G., Mench, M., Lagerkvist, A., Maurice, C., 2006. Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. Environmental Pollution 144, 62-69.

Mackenzie, E.T., Lamtzy, R.J., Petorson, V., 1979.Global trace metals cycles and predictions, J. Int. Assoc. Math. Geol. 6, 99-142.

Malik, M., Letey, J., 1992. Pore size dependent apparent viscosity for organic solutes in saturated porous media Soil Sci. Soc. Am. J. 56, 1032-1035.

Mamedov, A.I., Beckmann, S., Huang, C., Levy, G. J., 2007. Aggregate Stability as Affected by Polyacrylamide Molecular Weight, Soil Texture, and Water Quality. SSSAJ, 71, 1909-1918.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review, Talanta. 58, 201-235.

Manning, B.A., Fendorf, S.E., Suarez, D.L., 2003. Arsenic(III) complexation and oxidation reactions on soil, in: Cai, Y., Braids, O.C. (Eds.), Biogeochemistry of Environmentally Important Trace Elements, pp. 57-69.

Manning, B.A., Goldberg, S., 1997. Arsenic(III) and arsenic(V) absorption on three California soils. Soil Science 162, 886-895.

Moeser, G.D., Roach, K.A., Green, W.H., Laibinis, P.E., Hatton, T.A., 2002. Water-based magnetic fluids as extractants for synthetic organic compounds. Industrial & Engineering Chemistry Research 41, 4739-4749.

MPCA, 2001. Stormwater phase II final rule (MS4 stormwater program overview. Water/stormwater # 1.04, January 2001. Minnesota Pollution Control Agency.

URL: http://www.pca.state.mn.us/publications/wq-sw1-04.pdf.

Marques, M.J., Bienes, R., Jimenez, L., Perez-Rodriguez, R., 2007. Effect of vegetal cover on runoff and soil erosion under light intensity events. Rainfall simulation over USLE plots. Science of the Total Environment 378, 161-165.

Martinez-Rodriguez, G.A., Vazquez, M.A., Guzman, J.L., Ramos-Santana, R., Santana, O., 2007. Use of polyacrylamide as an erosion control strategy in a highly eroded soil of Puerto Rico. Journal of Agriculture of the University of Puerto Rico 91, 87-100.

Masscheleyn, P.H., Delaune, R.D., Patrick, W.H., 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. Environmental Science & Technology 25, 1414-1419.

Matera, V., Le Hecho, I., 2001. Arsenic behavior in contaminated soils: mobility and speciation. In: Selin H.M., Sparks D.L. (Eds) Heavy Metal Release in Soils. CRC Press, Boca Raton (Chaper 10).

Mayo, J.T., Yavuz, C., Yean, S., Cong, L., Shipley, H., Yu, W., Falkner, J., Kan, A., Tomson, M., Colvin, V.L., 2007. The effect of nanocrystalline magnetite size on arsenic removal. Science and Technology of Advanced Materials 8, 71-75.

McGeehan, S.L., Naylor, D.V., 1994. Sorption and redox transformation of arsenite and arsenat in 2 flooded soils. Soil Science Society of America Journal 58, 337-342.

McLaughlin, R.A., Brown, T.T., 2006. Evaluation of erosion control products with and without added polyacrylamide. Journal of the American Water Resources Association 42, 675-684.

MDEP, 2008. Mining, Maine Department of Environmental Protection. http://www.maine.gov/dep/blwq/docstand/miningpage.htm#qrule Accessed in Mar, 2010.

Mench, M., Vangronsveld, J., Lepp, N.W., Edwards, R., 1998. Physico-chemical aspects and efficiency of trace element immobilization by soil amendments. In: Vangronsveld, J. and Cunningham, S.D., Editors, 1998. Metal-Contaminated Soils: In Situ Inactivation and Phytorestoration, Springer-Verlag, 151-182.

Moeser, G.D., Roach, K.A., Green, W.H., Laibinis, P.E., Hatton, T.A., 2002. Water-based magnetic fluids as extractants for synthetic organic compounds. Industrial & Engineering Chemistry Research 41, 4739-4749.

Mondal, P., Majumder, C.B., Mohanty, B., 2006. Laboratory based approaches for arsenic remediation from contaminated water: Recent developments. Journal of Hazardous Materials 137, 464-479.

Mohan, D., Pittman, C.U., 2007. Arsenic removal from water/wastewater using adsorbents - A critical review. Journal of Hazardous Materials 142, 1-53.

Morais, F.E., Page, A.L., Lund L.J., 1976. The effect of pH, salt concentration, and nature of electrolytes on the charge characteristics of Brazilian tropical soils. Soil Sci. Soc. Am. J., 40, 521-527.

Murphy, C.A., Thompson, A.L., Gantzer, C.J., 2010. Polyacrylamide influence on runoff and sediment detachment from a silt loam soil. Transactions of the Asabe 53, 31-38.

National Toxicology Program, 2005. 11th ROC: arsenic compounds, inorganic, 2007, Research Triangle Park, NC.

Ohe, K., Oshima, T., Baba, Y., 2010. Adsorption of arsenic using high surface area magnetites. Environmental Geochemistry and Health 32, 283-286.

Orts, W.J., Glenn, G.M., Nobes, G.A.R., 1999. Use of natural polymer flocculating agents to control agricultural soil loss. Abstracts of Papers of the American Chemical Society 217, 366-PMSE.

Orts, W.J., Sojka, R.E., Glenn, G.M., 2000. Biopolymer additives to reduce erosion-induced soil losses during irrigation. Industrial Crops and Products 11, 19-29.

Otte, M.L., Dekkers, M.J., Rozema, J., Broekman, R.A., 1991. Uptake of arsenic by aster-tripolium in relation to rhizosphere oxidation. Canadian Journal of Botany-Revue Canadienne De Botanique 69, 2670-2677.

Park, G. A., de Bruyn, P.L., 1962. The zero point charge of oxides. J. Phys. Chem. 66, 957-973.

Pierce M.L., Moore C.B., 1982. Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Res. 15, 1247.

Polemio, M., Senesi, N., Bufo, S.A., 1982. Soil contamination by metals-a survey in industrial and rural-areas of southern Italy. Science of the Total Environment 25, 71-79.

Pote, D.H., Daniel, T.C., Sharpley, A.N., Moore, P.A., Edwards, D.R., Nichols, D.J., 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. Soil Science Society of America Journal 60, 855-859.

Raven, K.P., Jain, A., Loeppert, R.H., 1998. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. Environ. Sci. Technol. 32, 344.

Roa, A., Bubenzer, G. D., Miyashita E.S., 1998. Determination of PAM use potential in erosion control. In: Proceedings of the First European Conference of Water and the Environment Innovation Issues in Irrigation and Drainage, L.S. ereria et al. (Editors). Portuguese National Committee of ICID (International Commission on Irrigation and Drainage), 49-57.

Rusanov, A.I., 2005. Surface thermodynamics revisited. Surface Science Reports 58, 111-239.

Sansalone, J.J., Buchberger, S.G., 1997. Partitioning and first flush of metals in urban roadway storm water. Journal of Environmental Engineering-Asce 123, 134-143.

Santos, F.L., Reis, J.L., Martins, O.C., Castanheira, N.L., Serralheiro, R.P., 2003. Comparative assessment of infiltration, runoff and erosion of sprinkler irrigated soils. Biosystems Engineering 86, 355-364.

Schirado, T., Vergara, I., Schalscha, E.B., Pratt, P.F., 1986. Evidenc for movement of heavy-metals in a soil irrigated with untreated waste-water. Journal of Environmental Quality 15, 9-12.

Schwertmann, U., Cornell, R.M., 2000. Iron oxide in the laboratory Wiley-vch, Weinheim, Germany.

Sepaskhah, A.R., Bazrafshan-Jahromi, A.R., 2006. Controlling runoff and erosion in sloping land with polyacrylamide under a rainfall simulator. Biosystems Engineering 93, 469-474.

Sepaskhah, A.R., Mahdi-Hosseinabadi, Z., 2008. Effect of polyacrylamide on the erodibility factor of a loam soil. Biosystems Engineering 99, 598-603.

Sepaskhah, A.R., Shahabizad, V., 2010. Effects of water quality and PAM application rate on the control of soil erosion, water infiltration and runoff for different soil textures measured in a rainfall simulator. Biosystems Engineering 106, 513-520.

Seybold, C.A., 1994. Polyacrylamide review: Soil conditioning and environmental fate Comm. Soil Sci. Plant Anal. 25, 2171-2185.

Shainberg, I., Gal, M., Ferreira A.G., Goldstein D., 1991. Effect of water quality and amendments on the hydraulic properties and erosion from several Mediterranean soils. Soil Technology, 4, 135-146.

Shipley, H.J., Yean, S., Kan, A.T., Tomson, M.B., 2009. ADSORPTION OF ARSENIC TO MAGNETITE NANOPARTICLES: EFFECT OF PARTICLE CONCENTRATION, pH, IONIC STRENGTH, AND TEMPERATURE. Environmental Toxicology and Chemistry 28, 509-515.

Shipley, H.J., Yean, S., Kan, A.T., Tomson, M.B., 2010. A sorption kinetics model for arsenic adsorption to magnetite nanoparticles. Environmental Science and Pollution Research 17, 1053-1062.

Shoemaker, A.E., 2009. Evaluation of anionic polyacrylamide as an erosion control measure using intermediate-scale experimental procedures. Auburn University Master Thesis, USA.

Sijbesma, R.P., Meijer, E.W., 2008. Polymers in Nanotechnolog: Molecular Recognition and Surface Modification. Gildeprint Drukkerijen B.V., Enschede. pp.1. ISBN: 978-90-386-1348-2

Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J., Tullio, J.O., 2002. Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina. Applied Geochemistry 17, 259-284.

Smith, E., Naidu, R., Alson, A.M., 1998. Alston A.M. Arsenic in the soil environment: A review, in Advance in Agronomy, Vol 64. Academic Press Inc: San Diego. 149-195.

Sojka, R.E., 2008. The use of PAM -- a linear polyacrylamide for use in irrigation water, USDA-Agricultural Research Service, Northwest Irrigation and Soils Research Laboratory. http://www.naicc.org/meeting/2001/UseofPAM.html

Sojka, R.E., Lentz, R.D., 1997. Reducing furrow irrigation erosion with polyacrylamide (PAM) J. Prod. Agric. 10, 1-2 and 47-52.

Srivastava, N.K., Ram, L.C., Masto, R.E., 2010. Role of selected riparian herbs in reducing soil erosion and nutrient loss under simulated rainfall. Environmental Earth Sciences 61, 405-417.

Su, C.M., Puls, R.W., 2008. Arsenate and arsenite sorption on magnetite: Relations to groundwater arsenic treatment using zerovalent iron and natural attenuation. Water Air and Soil Pollution 193, 65-78.

Sylvester, P., Westerhoff, P., Mooller, T., Badruzzaman, M., Boyd, O., 2007. A hybrid sorbent utilizing nanoparticles of hydrous iron oxide for arsenic removal from drinking water. Environmental Engineering Science 24, 104-112.

Tallman, D.E., Shaikh, A.U., 1980. Redox stability of inorganic (III) and arsenic(V) in aqueous-solution. Analytical Chemistry 52, 197-199.

Theng, B.K.G., 1982. Clay–polymer interaction: Summary and perspectives Clays Clay Miner. 30, 1-10.

Tolstikh, L.I., Akimov, N.I., Golubeva, I.A., Shvetsov, I.A., 1992. Degradation and stabilization of polyacrylamide in polymer flooding conditions Int. J. Polymeric Material. 17, 177-193.

Van olpen, H., 1963. Introduction to clay colloid chemistry. Interscience Publishers. New York.

Vanraij, B., Peech, M., 1972. Electrochemical properties of some oxisols and alfisols of tropics. Science Society of America Proceedings 36, 587-&.

United States Environmental Protection Agency (U.S. EPA), 2008. Effluent limitations Guideline and Standards for the Construction Minimum Control Measure. EPA Federal Register, 73, 72561-72614.

United States Environmental Protection Agency (U.S. EPA), 2010. http://water.epa.gov/scitech/wastetech/guide/construction/index.cfm#proposed

Wakui, Y., Persulessy, A.E., Ikeda, T., Ebina, T., Onodera, Y., Suzuki, T.M., 2005. Separation and enrichment of arsenic(V) with composite resin beads containing magnetite crystals. Analytical Sciences 21, 433-435.

Wallace, A., Wallace, G.A., Abouzamzam A.M., 1986. Effects of excess levels of a polymer as a soil conditioner on yields and mineral nutrition of plants. Soil Sci. 141, 377-379.

Wang, S., Mulligan, C.N., 2006. Occurrence of arsenic contamination in Canada: sources, behavior and distribution. Sci. Total Environ. 366, 701-721.

Warren, G.P., Alloway, B.J., Lepp, N.W., Singh, B., Bochereau, F.J.M., Penny, C., 2003. Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides. Science of the Total Environment 311, 19-33.

Waychunas, G.A., Rea, B.A., Fuller, C.C., Davis, J.A., 1993. Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. Geochim. Cosmochim. Acta 57, 2251-2269.

Weeks, L.E., Colter, W.G., 1952. Effect of synthetic soil conditioners on soil erosion control. Soil Science 73, 473-484.

WHO, 2001. Arsenic in drinking water.
Available from: http://www.who.int/mediacentre/factsheets/fs210/en.

Williams, L.E., Barnett, M.O., Kramer, T.A., Melville, J.G., 2003. Adsorption and transport of arsenic(V) in experimental subsurface systems. Journal of Environmental Quality 32, 841-850.

Wilson, A.D., Crisp, S., 1975. Rigid highly carboxylated ionic polymers. IN: Ionic Polymers. L. Holiday (ed.). Chapman and Hall, New York, 208-257.

Woolson, E.A., Axely, J.H., Kearney, P.C., 1971. The chemistry and phytotoxicity of arsenic in soils. Soil Sci.Am. Proc. 35, 938-943.

Wong, H.K., Ludmann, T., Baranov, B.V., Karp, B.Y., Konerding, P., Ion, G., 2003. Bottom current-controlled sedimentation and mass wasting in the northwestern Sea of Okhotsk. Marine Geology 201, 287-305.

Yang, J.K., Barnett, M.O., Jardine, P.M., Brooks, S.C., 2003. Factors controlling the bioaccessibility of arsenic(V) and lead(II) in soil. Soil & Sediment Contamination 12, 165-179.

Yavuz, C.T., Mayo, J.T., Yu, W.W., Falkner, J.C., Yean, S., Kan, A.T., Tomson, M.B., Colvin, V.L., 2006. Switchable magnetism for arsenic removal and biomagnetic separations. Abstracts of Papers of the American Chemical Society 231, 31-INOR.

Yean, S., Cong, L., Kan, A., Colvin, V., Tomson, M., 2005. Sorption/desorption of arsenic to magnetite nanoparticles. Abstracts of Papers of the American Chemical Society 229, 154-IEC.

Yuan, T., Hu, J.Y., Ong, S.L., Luo, Q.F., Ng, W.J., 2002. Arsenic removal from household drinking water by adsorption. Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering 37, 1721-1736.

Zhang, H., 2003. Arsenic pollution and arseniasis in Hetao area, China. In:Murphy, T., Guo, J. (Eds.), Aquatic Arsenic Toxicity and Treatment. Backhuys Publisher, Leiden, The Netherlands, pp. 19-26.

Zhang, H., Selim, H.M., 2005. Kinetics of arsenate adsorption-desorption in soils. Environmental Science & Technology 39, 6101-6108.

Zhang, X.C., Miller, W.P., 1996. Physical and chemical crusting processes affecting runoff and erosion in furrows. Soil Science Society of America Journal 60, 860-865.