Green Remediation of Acid Mine Drainage (AMD)-Impacted Soil and Water

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GREEN REMEDIATION OF ACID MINE DRAINAGE (AMD)-IMPACTED SOIL
AND WATER

A DISSERTATION

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by
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ABSTRACT
GREEN REMEDIATION OF ACID MINE DRAINAGE (AMD)-IMPACTED SOIL AND WATER
By
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Although mining industries such as coal and minerals generate revenue, they are responsible for a number of negative environmental consequences, and the production of acid mine drainage (AMD) and acid sulfate soil are the most concerning among them. Current AMD management practices are expensive, ineffective, or unsustainable. This study evaluated the potential of a cost-effective and environment-friendly “green” technology in treating AMD-impacted water and soil that utilizes the metal-binding and acid-neutralizing capacity of an industrial by-product, namely drinking-water treatment residuals (WTRs) and the extensive root system of a metal hyper-accumulating, fast-growing, non-invasive, high biomass perennial grass, vetiver (Chrysopogon zizanioides L.) to prevent soil erosion. AMD-impacted soil and water were collected from the Tab-Simco mine, an abandoned coal mine in Carbondale, IL. Two locally produced WTRs: Al-WTR and Ca-WTR were used for this study. A field-scale, gravity flow 208L WTR-filter was prepared following the laboratory batch sorption and laboratory-scale WTR-filter column experiments. A 1:6 sand-WTR ratio with a 1:1 Al-WTR and Ca-WTR was optimized for the filter media. The results showed that pH of AMD-water was increased from 2.27 to 7.8, and the concentration of Fe, Al, Zn, As, Pb, and Mn was decreased by 99% after the filtration. Different WTR application rates (2.5%, 5%, and 10% w/w) were
tested during a 60 days soil incubation study. A follow-up four-month long greenhouse column study was performed using 5% and 10% w/w WTR application rates. Vetiver grass was grown on the soil-WTR mixed media. Turbidity and Total Suspended Solids (TSS) analysis of leachates showed that soil erosion decreased in the soil-WTR-vetiver system over time. Finally, a scaled-up simulated field study was performed using a 5% WTR application rate and Vetiver for four months. Soil pH increased from 2.6 to 7.7, and soil erosion indicators such as turbidity (99%) and TSS (95%) in leachates were significantly reduced. Results from the study showed that this “green,” inexpensive, and sustainable remediation technique has the potential to effectively treat AMD–impacted water and soil.
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DEDICATION

To my Grandfather:

Late Dr. KarunaCharan RoyChowdhury

He is my true hero and the inspiration of my life. His principles have taught me that to be successful in your life you first need to be a good person. I know his blessings are always there for me.
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LIST OF ABBREVIATIONS

Acid Base Accounting (ABA)
Acid Mine Drainage (AMD)
Aluminum (Al)
Arsenic (As)
Bed Volume (BV)
Below Method Detection Limit (BDL)
Cadmium (Cd)
Calcium (Ca)
Carbon Hydrogen Nitrogen Sulfur Analyzer (CHNS)
Chromium (Cr)
Copper (Cu)
Drinking-Water Treatment Residuals (WTR)
Electrical Conductivity (EC)
Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
Ion Chromatography (IC)
Iron (Fe)
Iron hydroxide (Fe(OH)_3)
Lead (Pb)
Manganese (Mn)
Maximum Potential Acidity (MPA)
Net Neutralization Potential (NNP)
Neutralization Potential (NP)
Nickel (Ni)
Parts per billion (ppb)
Parts per million (ppm)
Pyrite (FeS_2)
Resource Conservation and Recovery Act (RCRA)
Solid Solution Ratio (SSR)
Sulfate Reducing Bioreactor (SRB)
Sulfate (SO_4^{2-})
Surface Mining Control and Reclamation Act (SMCRA)
Total Suspended Solid (TSS)
Toxicity Characteristic Leaching Potential (TCLP)
Translocation Factor (TF)
United States Environmental Protection Agency (USEPA)
Zinc (Zn)
CHAPTER 1
Cause of AMD-pollution, common AMD-Remediation techniques, and need for this study

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Abstract

The formation of Acid Mine Drainage (AMD), a highly acidic and metal-rich solution, is the biggest environmental concern associated with coal and mineral mining. Once produced, AMD can severely impact the surrounding ecosystem due to its high toxicity and various other deleterious consequences. Hence, implementations of effective post-mining management practices are necessary to control AMD pollution. Due to the existence of a number of federal and state regulations, it is necessary for private and government agencies to come up with various AMD treatments and/or control technologies. This review describes some of the widely used AMD remediation technologies in terms of their general working principles, advantages, and shortcomings. AMD treatment technologies can be divided into two major categories; namely prevention and remediation. Prevention techniques mainly focus on inhibiting AMD formation reactions by controlling the source. Remediation techniques focus on the treatment of already produced AMD before their discharge into water bodies. Remediation technologies can be further divided into two broad categories: active and passive. Due to high cost and intensive labor requirements for maintenance of active treatment technologies, passive treatments are widely used all over the world.
Besides the conventional passive treatment technologies such as constructed wetlands, anaerobic sulfate reducing bioreactors, anoxic limestone drains, open limestone channels, limestone leach beds, and slag leach beds, this paper also describes emerging passive treatment technologies such as phytoremediation. More intensive research is needed to develop an efficient and cost-effective AMD treatment technology, which can sustain persistent and long term AMD load.

**Keywords:** Acid Mine Drainage (AMD); Active AMD Treatment; Passive AMD Treatment; Phytoremediation.
1.1 Introduction

While coal and mineral mining is an important revenue generating industry, several environmental consequences are associated with it. The formation of a metal-rich acid solution known as Acid Mine Drainage (AMD) is a major environmental problem associated with mining operations. Once exposed to AMD, the quality of adjacent surface water degrades drastically and eventually becomes unsuitable for sustaining biodiversity. Additionally, soils exposed to AMD become structurally unstable and highly prone to erosion (Ferguson and Erickson, 1988; U.S. Forest Service, 1993; Lapakko, 1993; USEPA, 1994). Mostly, AMD is produced due to the oxidation of pyrite (FeS$_2$). In the presence of oxygen and water, pyrite oxidizes to form Fe$^{2+}$, SO$_4^{2-}$ and H$^+$ ions (Stumm and Morgan, 1981).

\[
\text{FeS}_2 + 3.5 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad [\text{i}]
\]

The produced Fe$^{2+}$ ion then reacts with O$_2$ to form Fe$^{3+}$. This reaction is facilitated by the sulfur oxidizing bacteria \textit{(Thiobacillus thiooxidans, Thiobacillus ferrooxidans)} as they utilize the produced energy from this reaction for their metabolism.

\[
\text{Fe}^{2+} + 0.25 \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 0.5 \text{H}_2\text{O} \quad [\text{ii}]
\]

In addition, the produced Fe$^{3+}$ further oxidizes pyrite to form Fe$^{2+}$, SO$_4^{2-}$ and H$^+$ ions.

\[
\text{FeS}_2 + 14 \text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad [\text{iii}]
\]
The abiotic rate of pyrite oxidation by Fe$^{3+}$ is much higher than the oxidation by O$_2$ and water. Due to the production of H$^+$ ions the pH of the whole system drops drastically and becomes highly acidic. If the pH of the system remains over 3.5-4.0 standard units, Fe$^{2+}$ precipitates in the form of Fe(OH)$_3$. The yellow-orange colored precipitation of iron hydroxide is known as “yellow boy.”

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \quad [\text{iv}]$$

The overall stoichiometric pyrite oxidation reaction can be written as (Stumm and Morgan, 1981):

$$\text{FeS}_2 + 3.75 \text{O}_2 + 3.5 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ + \text{heat} \quad [\text{v}]$$

Due to high acidity, the mobility of the metals in the environment increases significantly. Extensively acidic pH (as low as 2-4 standard units) coupled with metals toxicity can elicit severe impacts on aquatic biodiversity (Soucek et al. 2000; Hansen et al. 2002; Schmidt et al. 2002; Gergardt et al. 2004; Martin and Goldblatt 2007; Jennings et al. 2008; Trout Unlimited 2011). Abandoned mine sites often accelerate the AMD generation process and may require decades of proper management practices to reclaim. The adverse environmental impacts of AMD can exist forever if not addressed. The current number of abandoned mines in the US is estimated to be more than 557,000 (U.S. Forest Service, 2005); many of which are active sources of AMD. Approximately 15,000 to 23,000 kilometers of streams are currently impacted by AMD in the US (Kim et al. 1982; U.S. Forest Service 1993; USEPA 1994; Benner et al. 1997; Jennings et al. 2008; USEPA, 2011), which also represents a direct threat to human
health. Due to its complex nature and wide array of consequences, AMD is termed a “multiheaded beast” (U.S. Forest Service, 2005), and taming this beast is a challenging task. According the US Forest Service (2005), the estimated cost of cleaning up AMD impacted sites on National Forest System (NFS) land is around $4 billion. Between the years 1998 and 2003 around $310 million was spent on AMD impacted NFS land clean-up services (U.S. Forest Service, 2005). Currently several AMD prevention and remediation technologies are in effect at various AMD impacted sites. The objective of this paper is to review the commonly used AMD treatment technologies based on their working principles and efficiency.

1.2 AMD Treatment Technologies

AMD treatment technologies can be divided into two major categories: 1) prevention or source control techniques and 2) remediation techniques. While the former focuses on prevention of AMD generation and migration by controlling its source, the later focuses more on the mitigational measurements of produced AMD.

1.2.1 Prevention or Source Control Technologies

Safe disposal and storage of post-mining overburdens and tailings play a vital role in AMD control. Several source controlling techniques are available to prevent AMD formation. As pyrite-bearing mine wastes produce AMD in the presence of water and oxygen, one way to prevent AMD production is the exclusion of either one or both of them from the system. Co-disposal of pyritic materials along with some benign material (waste rock, limestone) is the most common practice to reduce AMD
production from mine waste (Kuyuck, 1999; Skousen et al., 2000; Johnson and Hallberg, 2005). The mixing of large waste rocks with fine tailings is practiced sometimes which possesses higher moisture content and hence reduce oxygen penetration through mine wastes (Kuyuck, 1999). Depending upon the Neutralization Potential (NP) of the soil type, pyritic wastes are mixed with alkaline amendments such as limestone to reduce acidity of the overall system (Brady et al., 1990; Perry and Brady, 1995; Mehling et al., 1997; Skousen et al., 2000). Besides limestone, materials such as Fluidized Bed Combustion (FBC) ash and Kiln dust with higher NP (20-70%) are also used as alkaline amendments. In addition to their ability to increase the net alkalinity of the system, these materials also transform into a cement-like hard substance which acts as a barrier and stabilization material (Rich and Hutchinson, 1994; Stehouwer et al., 1995; Skousen et al., 1997; Skousen et al., 2000). Flooding/sealing of underground mines (Johnson and Hallberg, 2005), underwater storage of mine tailings, and land based storage in sealed waste heaps are some of the commonly used techniques to prevent AMD migration to local water bodies (Li et al., 1997). The diversion of surface and groundwater from acid producing pyritic waste piles is another important AMD prevention approach. Diversion ditches, grout barriers, and slurry walls are some of the techniques used to control water migration through mine spoils (Gabr et al., 1994; Kuyuck, 1999; Skousen et al., 2000). Encapsulation, capping, and sealing of sulfidic mine sites with non- sulfidic topsoil layer (Kuyuck, 1999; Bell, 2001) are often used to reduce water penetration (rainfall and runoff) through mine spoils. Single- (for semi-arid regions) or multi-layer (for high rainfall
regions) soil covers are used for encapsulation. The capping materials consist of a clay layer to prevent oxygen penetration and an alkaline layer to provide a hard capsulated barrier to prevent water from reaching the waste piles. A coarse layer is often present to drain the infiltrated water ((Yanful and Nicholson, 1991; Skousen et al., 2000). A vegetative top layer provides stabilization to the overall system and retains moisture (Dollhopf, 1998; Semalulu et al., 1998; Miekle et al., 1999; Johnson and Hallberg, 2005). As sulfur oxidizing bacteria play a vital role in the AMD generation process, the use of bactericides such as anionic surfactants is also a common practice. The bactericides, which are often applied as liquid amendment or spray, can control the AMD formation only for a limited time period (Skousen et al., 2000; Johnson and Hallberg, 2005). The major disadvantage of these expensive preventive technologies is their ineffectiveness in the long-term. Most of these techniques have failed to protect the environment against long and persistent AMD pollution.

1.2.2 Remediation Technologies

AMD remediation technologies can be divided into two categories: active treatment and passive treatment.

1.2.2.1 Active Treatment Technology

The responsibility to clean-up abandoned mine sites is borne by both private operators and government agencies. A number of federal and state laws such as the National Historic Preservation Act of 1966, the Clean Air Act of 1972, the Endangered Species Act of 1973, and the Surface Mining Control and Reclamation Act
of 1977 are currently in effect in the US to regulate the standards of the post-mining water discharges into the surrounding ecosystems (Skousen et al., 2000; U.S. Forest Service, 2005). The US Forest Service even has the authority to administer the Comprehensive Environmental Response Compensation and Liability Act of 1980 on National Forest System lands through an Executive Order (No. 12580) passed in 1987 (U.S. Forest Service, 2005). The addition of various acid neutralizing and metal precipitating chemical agents into AMD water is a common practice to meet the effluent discharge limits within a short time span. A wide range of chemical agents such as limestone (CaCO$_3$), hydrated lime (Ca(OH)$_2$), caustic soda (NaOH), soda ash (Na$_2$CO$_3$), calcium oxide (CaO), anhydrous ammonia (NH$_3$), magnesium oxide (MgO), and magnesium hydroxide (Mg(OH)$_2$) are being used during the active treatment of AMD water worldwide (Skousen et al., 2000; Johnson and Hallberg, 2005). The efficiency of each of the chemicals depends on factors such as the site specificity (seasonal variation), daily AMD load, and metal concentration. Hence, the selection of appropriate chemical agent is very important for the success of the treatment process.

One of the major advantages of the active treatment process is that unlike the passive treatment facilities it does not require any additional space or construction. Furthermore, the active treatment process is fast and effective in removing acidity and metals. The other advantage of the active treatment technique is the lower cost associated with handling and disposal of sludge in comparison to passive treatment techniques (Coulton et al., 2003). Although the active treatment process has several advantages, it is not favored due to its limitations. The major disadvantage of the
active treatment process is that it requires a continuous supply of chemicals and energy
to perform efficiently. Costly chemicals and engaging sufficient manpower to
maintain the system increases the overall cost of this technology significantly. The
efficiency of these systems is completely dependent on its regular maintenance and
chemical supply, which makes it difficult to control for most of the remotely located
abandoned mine sites. The efficiency and cost of the systems also vary with the type of
neutralizing agent used. Limestone is inexpensive but less soluble in water and hence
less effective than the other chemical agents. Chemicals such as hydrated lime are
also inexpensive but ineffective if higher pH (~9) is required for precipitation of metals
like Mn (Skousen et al., 2000; Skousen and Ziemkiewicz, 1996). Although NaOH is
approximately 1.5 times more effective than lime, NaOH is almost 9 times more
expensive (Johnson and Hallberg, 2005). Due to their extremely hazardous nature,
chemical agents such as NaOH and anhydrous ammonia need special attention during
handling. Also, the use of excessive ammonia can create problems such as nitrification
and denitrification in receiving water bodies (Hilton, 1990; Skousen et al., 2000).

1.2.2.2 Passive Treatment Technology

Passive AMD treatment technologies can be classified into two groups:
Conventional and Emerging technologies. The conventional passive treatment
technologies such as constructed wetlands and anaerobic sulfate reducing
bioreactors have been used for a long time. Emerging technologies such as
phytoremediation are also being investigated for efficient AMD remediation.
1.2.2.2.1 Conventional Passive Treatment Technology

1.2.2.2.1.1 Constructed Wetlands

Constructed wetlands are one of the most commonly used passive AMD treatment technologies. There are two types of wetlands: aerobic and anaerobic. Aerobic wetlands are shallow water bodies (<30 cm in depth), which provide sufficient retention time to oxidize and precipitate subsequent metal hydroxides. Wetland plants such as *Typha sp.*, *Juncus sp.*, and *Scirpus sp.* regulate the water flow, stabilize and accumulate the metal precipitates, maintain the microbial population, and increase the aesthetic value of the contaminated site (Johnson and Hallberg, 2005; Skousen and Ziemkiewicz, 2005). Wetland plants involve two major mechanisms to remove heavy metals from AMD: phytoextraction and rhizofiltration. In phytoextraction, metal-hyperaccumulating plants uptake metals from wetland substrate and store them in their root and/or shoot. In rhizofiltration, plants absorb, adsorb or precipitate metals in the root zones (rhizosphere) (Baker and Brooks, 1989; Salt et al., 1995; Cunningham et al., 1997; Tordoff et al., 2000; Karathanasis and Johnson, 2003; Padmavathiamma and Li, 2007). The studies often reported that the amount of metal retention inside the wetland cells is higher than the metal uptake in the plant tissues (Karathanasis and Johnson, 2003; Nyquist and Greger, 2009). Plants such as *Typha latifolia*, *Scirpus validus*, *Phragmites australis*, and *Oryza sativa* form plaques in their root epidermis by producing metal oxide and hydroxide precipitates that prevent the translocation of metals in the plant tissues (Snowden and Wheeler, 1995; Batty et al., 2000; Hansel et al., 2001; Karathanasis and Johnson, 2003). Although formation of Fe-oxide and
hydroxide plaques in plant root zones is more common, Al and Mn plaques are also reported by researchers (Batty et al., 2000; Karathanasis and Johnson, 2003). Aerobic wetlands are more efficient in removing Fe, Al and Mn in comparison to other metals. The Fe retention rate in aerobic wetlands can vary from 0.13-96% of the initial Fe load (Barton and Karathanasis, 1999; Karathanasis and Johnson, 2003; Sheoran, 2006; Nyquist and Greger, 2009). Wetland plants such as *Typha latifolia, Lemna minor, Nuphar variegatum* and *Potamogeton epihydrus* can remove 29-56% of the initial Al load (Goulet et al., 2005). High Mn retention (~76%) is also demonstrated by plants such as *Desmostachya bipinata* (Sheoran, 2006). Both Al and Fe are mainly stored in the root zone, but the distribution of Mn is often noticed in the entire plant body. High acidity removal (43%) and an increase of the pH from 2.9 to 7.1 are also observed inside the aerobic wetlands (Hellier et al., 1994; Sheoran, 2006). The efficiency of wetlands in treating AMD depends on factors such as seasonal variations, acidity and metal load, and the dissolve or soluble metal concentration gradient (Mitchell and Karathanasis, 1995; Qian et al., 1999; Karathanasis and Johnson, 2003; Nyquist and Greger, 2009).

Cost-effectiveness is one of the major advantages of aerobic wetlands. The cost of aerobic wetlands ranges from $23- $7,000/t/year in terms of removal of 0.1 to 27t/year of acidity over a 20 year life span (Skousen and Ziemkiewicz, 2005). The amount of metal retention is always higher than metal extraction in aerobic wetlands. Studies showed that aerobic wetlands possess high retention capacity for different metals such as 69 kg Al/year, 8089 kg Fe/year and 130 kg Mn/year (Barton and Karathanasis, 1999;
Karathanasis and Johnson, 2003). The efficiency of the aerobic wetland systems decrease if the influent water has a pH<5. Hence, aerobic wetlands are always associated with other passive treatment systems such as Anoxic limestone drains (ALDs) or Vertical flow wetlands (VFWs) and receive net alkaline AMD water from them (Hellier et al., 1994; Qian et al., 1999; Johnson and Hallberg, 2005; Skousen and Ziemkiewicz, 2005). Aerobic wetlands cannot remove sulfate (Nyquist and Greger, 2009) and are less effective when metal concentrations are very high in the system (Karathanasis and Johnson, 2003; Nyquist and Greger, 2009).

Anaerobic wetlands are built with organic-rich substrates, which provide reducing conditions and neutralizing agents such as limestone. Often anaerobic wetlands are constructed underground and are devoid of vegetation. In this kind of a system, net acidity of AMD water is removed by the dissolution of limestone and the metabolism of iron and sulfate-reducing bacteria. The organic rich substrates are prepared by mixing of biodegradable products such as manure with straw, peat, and sawdust. This mixture serves as a long-term food source for the indigenous anaerobic iron and sulfate-reducing bacteria due to their slow biodegradation rates. A variety of manures such as chicken, cow and horse litter, and mushroom compost are used as substrates for the microbial community (Wieder, 1992; Gross et al., 1993; Skousen et al., 2000; Johnson and Hallberg, 2005). Sometimes, the anaerobic wetlands are engineered as the reducing and alkalinity producing system (RAPS) (Younger et al., 2003) or as the successive alkalinity producing system (SAPS) (where multiple RAPS are used) (Kepler and McCleary, 1994). In this type of system, AMD first flows
downward through a compost layer, which removes dissolve oxygen (DO) and facilitates iron and sulfate reduction. Subsequently, the AMD passes through a limestone and gravel bed, which adds alkalinity. To precipitate and retain the iron hydroxides, water from the RAPS system is channeled through a settling pond or aerobic wetland. In anaerobic wetlands, the sorption of metals occurs on the organic substrates through exchangeable or complexation reactions. Initially, 50-80% of metal removal from the AMD inside the anaerobic wetland system takes place due to sorption, which decreases over time due to the substrate saturation (Brodie et al., 1988; Skousen et al., 2000). The retention of metals as of oxides, hydroxides, carbonates, and sulfides precipitates also occurs in anaerobic wetlands. Unlike sorption reactions, precipitation of metals is not time-limited, and depends on the density and volume of the wetland cells. The total Fe removed from AMD water by anaerobic wetland systems is dominated by Fe-hydroxides (~50-70%), and Fe-sulfides (~30%). Iron-hydroxide often reduces to Fe$^{2+}$ by anaerobic iron-reducing bacteria, and this reaction increases the pH of the system.

$$\text{Fe(OH)}_3 + 0.5\text{H}_2 \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2\text{O} \quad [\text{vi}]$$

Anaerobic sulfate reducing bacteria produce iron mono and disulfides while reducing the sulfate present in the AMD water. The reduction of sulfate also increases the pH of the system (Henrot and Wieder, 1990; McIntyre and Edenborn, 1990; Calabrese et al., 1991; Wieder, 1992; Skousen et al., 2000).

Anaerobic wetlands can remove approximately 0-67.9 t/year of net acidity, and costs between $341 and $4762/t/year (Skousen and Ziemkiewicz, 2005). The
removal of sulfate and increase in pH are some of the major advantages of the anaerobic wetlands. The anaerobic wetlands can also reduce the acidity and Fe concentration of the AMD water by 3-76% and 62-80%, respectively (Faulkner and Skousen, 1994). The major disadvantage of the anaerobic wetlands is the decrease of its efficiency over time. The saturation of substrates occurs within a span of 1-7 months as most of the available exchangeable and complexation sites become saturated with metals. Sometimes, the addition of organic matter is required to revive the filtering efficiency of the wetland (Eger and Melchert, 1992; Haffner, 1992; Stark et al., 1995; Skousen et al., 2000). The efficiency of the anaerobic wetlands also changes with seasonal variation, and wetland-age (Wieder, 1992; Skousen et al., 2000). The lifetime of the system can be severely affected if the plants above the ground penetrate the system’s protective cover through their roots and introduce oxygen to the anaerobic layers (Johnson and Hallberg, 2005).

A pilot passive treatment plant was constructed in 1994 at Wheal Jane Mine in Cornwall, England, for long-term AMD treatment. The project was unique because it employed both aerobic and anaerobic wetland facilities. After appropriate lime dosing, AMD water was allowed to pass through serious of anoxic cell, anoxic limestone drain, five aerobic cells, anaerobic cell and rock filter. Data show that this kind of hybrid system is capable of removing Fe and sulfate between 55% and 92%, and 3% and 38% respectively. This system can also remove other metals such as Cd, Cu, and Zn depending on the pretreatment and flow rate of the AMD (Whitehead, 2005).
1.2.2.1.2 Anaerobic Sulfate Reducing Bioreactors

Anaerobic sulfate reducing bioreactors are another type of widely used passive treatment technology, which involves sulfate reducing bacteria to remediate AMD. Sulfate reducing bacteria are a group of chemoorganotrophic and strictly anaerobic bacteria, which is primarily represented by the genera of *Desulfovibrio*, *Desulfomicrobium*, *Desulfobacter* and *Desulfotomaculum*.

Anaerobic sulfate reducing bioreactors are made up of a thick layer of organic rich materials mixed with limestone. An additional thin layer of limestone is also used under the organic layer, which provides the additional alkalinity and also supports the underlying drainage channels. The AMD passes vertically through the organic layer and limestone bed and is discharged through the drainage system. The organic layer serves as the substrate of sulfate reducing bacteria. In this layer, sulfate reducing bacteria reduce $\text{SO}_4^{2-}$ to $\text{H}_2\text{S}$ and oxidize organic matter ($\text{CH}_2\text{O}$) to bicarbonate ions ($\text{HCO}_3^-$) (Widdel, 1988). Sulfate reducing bacteria use the energy produced in this reaction for their growth and development.

$$\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- \quad [\text{vii}]$$

The reaction of AMD with limestone causes limestone dissolution and produces $\text{HCO}_3^-$ and $\text{Ca}^{2+}$.

$$\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad [\text{viii}]$$
The produced HCO$_3^-$ further reacts with H$^+$ ions and produces CO$_2$ and water. Hence, the consumption of the H$^+$ ions results in the increase of the pH of the overall AMD water. At high pH, metals start to precipitate in the form of metal sulfides, oxides, hydroxides, and carbonates.

In the anaerobic sulfate reducing system, the most common form is metal sulfide precipitation (Watzlaf et al., 2004).

$$\text{HS}^- + \text{M}^{2+} \rightarrow \text{MS} + \text{H}^+ \quad \text{[ix]}$$

In reaction [ix], M$^{2+}$ represents divalent metals such as Fe$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, Zn$^{2+}$; and MS represents the produced metal sulfide. Metals can also precipitate in the form of hydroxide or carbonate (Watzlaf et al., 2004).

$$\text{Fe}^{2+} + \text{HCO}_3^- \rightarrow \text{FeCO}_3 + \text{H}^+ \quad \text{[x]}$$

$$\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \quad \text{[xi]}$$

$$\text{Mn}^{2+} + \text{HCO}_3^- \rightarrow \text{MnCO}_3 + \text{H}^+ \quad \text{[xii]}$$

Thus, sulfate reducing bioreactors help in reducing acidity, metal and sulfate concentration of AMD water and improve the overall water quality. The efficiency of an anaerobic sulfate reducing bioreactor depends on various factors. The amount of sulfate removed is dependent on the available surface area and hydraulic retention time (HRT), while the rate of sulfate removal is dependent on the initial sulfate concentration in AMD (Neculita et al., 2007). Studies have been conducted to test the efficiency of sulfate reducing bacteria under various pHs. Researchers found that pH in the range of
5-8 is best for optimum activity of the sulfate reducing bacteria, as the inhibition of sulfate reduction and the increase in the solubility of metal sulfides occur at low pH (Dvorak et al., 1992; Elliott et al., 1998; Willow and Cohen, 2003; Neculita et al., 2007). Some studies also found that although at low pH (2.8-3.5), sulfate reducing bacteria can survive due to their acid tolerance, their sulfate removal efficiency dropped to 14-35% (Elliott et al., 1998; Segid, 2010). Several studies have been conducted to characterize the sulfate-reducing bacterial community. Researchers found that the type of sulfate reducing bacterial community change through time depending on the nature of the wastewater and the type of the food sources. Species such as *Desulfovibrio desulfuricans* and *Desulfobulbus rhabdoformis* are dominant in a sulfate reducing bioreactor (Luptakova and Kusnierova, 2005; Martins et al., 2009). Change of dominant bacterial community from iron oxidizing *Betaproteobacteria* in pre-treated AMD water to sulfur-oxidizing *Epsilonproteobacteria* and complex carbon degrading *Bacteroidetes* and *Firmicutes* phylums in post-treated water is also observed (Burns et al., 2012).

Studies have been conducted to evaluate the efficiency of the sulfate reducing bioreactors. It is observed that the efficiency varies from 39-82% removal of the initial SO$_4^{2-}$ load (900-2981 mg/L) (Jong and Parry, 2003; Tsukamoto et al., 2004; Segid, 2010; Behum et al., 2011). Sulfate reducing bioreactors exhibit a high metal removal ability, and they can remove 98-99% of initial Cu (Luptakova and Kusnierova, 2005; Martins et al., 2009), 85-90% of initial Fe (Neculita et al., 2008; Martins et al., 2009; Segid, 2010), and 95-99% of initial Al (Martins et al., 2009; Segid, 2010) load from the AMD water. A net decrease in acidity and increase in pH of the influent AMD
water can also be achieved through the bioreactors (Elliott et al., 1998; Segid, 2010; Behum et al., 2011; Burns et al., 2012).

The activity of sulfate reducing bacteria is the rate-limiting factor of the anaerobic sulfate reducing bioreactors. A near neutral pH, reducing environment, continuous supply of organic carbon and sulfate, solid support for microbial attachment, and the formation and retention capacity of precipitated metal sulfides are some of the key factors of an efficient sulfate reducing bioreactor. Extremely low pH (below 3.5) severely impacts the efficiency of the sulfate reducing bacteria (Elliott et al., 1998). Low temperature also impacts the acclimatization of the sulfate reducing bacteria significantly, but after acclimatization they can be active and functional even in the cold climates (1-16°C). A decrease in overall efficiency of sulfate reducing bioreactors has been observed during the winter seasons (Zaluski et al., 2003; Neculita et al., 2007). Despite their higher sulfate and metal removal efficiency, the sulfate reducing bioreactors often fail to perform over long-term mainly due to the exhaustion of the substrates required for sustaining the sulfate reducing bacterial community.

1.2.2.2.3 Other commonly used Passive Treatment Techniques

Anoxic limestone drains (ALD) are one of the commonly used passive AMD treatment systems. ALDs are typically 30 m long, 1.5 m deep and 0.6-20 m wide underground systems filled with limestone. Only anoxic water is introduced in the ALDs, which are impervious to air and water. In ALD, limestone reacts with AMD water and produces CO2 which cannot escape from the system and raises the overall
alkalinity (Watzlaf et al., 2004). Due to the anoxic condition, the iron remains in the reduced form inside the ALDs, and the formation and precipitation of iron hydroxide does not occur. The optimal performance of the ALD can be attained if the AMD channeled through it contains no ferric iron, aluminum, or DO. The pH of ALD systems needs to be 6.0, because under more acidic conditions metals like Fe and Al precipitate as hydroxides and form coats or armors on limestone (Johnson and Hallberg, 2005). Thus, iron hydroxide precipitation severely impacts the efficiency of the ALDs. ALDs can produces up to 275mg/L of net alkalinity in comparison to 50-60 mg/L of net alkalinity produced by an open system in equilibrium (Kleinmann et al., 1998). A decrease of acidity by 50-80% can be achieved through ALDs (Gross et al., 1993; Skousen et al., 2000). The major drawback of ALD is its longevity. The presence of ferric iron and Al in AMD water can form hydroxide precipitates which reduce the permeability and efficiency of the ALD systems (Evangelou, 1998). Typically, ALDs are used as a part of the hybrid passive treatment system in corporation with the aerobic and anaerobic wetlands (Kleinmann et al., 1998; Skousen et al., 2000; Johnson and Hallberg, 2005).

Vertical flow wetlands (VFW) or Permeable reactive barriers (PRB) are another type of passive AMD treatment system. In a VFW or PRB, AMD water flows through an organic rich layer followed by a limestone bed before discharging through a drainage system. The VFW systems reduce ferric to ferrous iron and decrease the amount of DO. Sulfate reduction and Fe sulfide precipitation can take place in this system. A series of drainage pipes placed below the limestone layer carry the water to
aerobic ponds where ferrous ions oxidize and precipitate (Younger et al., 2003; Johnson and Hallberg, 2005).

Limestone leach beds (LSB), Slag leach beds (SLB), and Open limestone channels (OLC) play a significant role in various AMD passive treatment systems. LSBs are ponds constructed to receive waters with little or no alkalinity and dissolved metals. These ponds are packed with limestone and designed to have retention time of at least 12 hours. The limestone layer can be replenished when necessary. Alkalinity in this system can reach 75mg/L (Skousen and Ziemkiewicz, 2005). In SLB ponds, a bed of steel slag fines are used to remediate AMD water, which need be devoid of metals such as Fe, Al and Mn. This system can produce alkalinity up to 2,000mg/L and the overall system is easy to replenish (Skousen and Ziemkiewicz, 2005). OLCs are open channels or trenches lined with limestone. In OLCs, limestone coated with Fe and Al hydroxides are used to decrease the limestone dissolution over time. The performances of the OLCs are dependent on different variables such as slopes, pH, flow velocity, thickness of the coating of limestone (Skousen and Ziemkiewicz, 2005). OLCs can remove 4-69% of acidity, 72% of Fe, and 20% of Mn and Al from AMD water (Ziemkiewicz et al., 1997; Skousen et al., 2000; Skousen and Ziemkiewicz, 2005). OLCs are generally constructed with the combination of other passive treatment systems. The major advantage of OLC is its low-cost as it does not require any maintenance once constructed properly (Skousen et al., 2000).
The construction of the passive treatment technologies depends on several factors such as characteristics of waste, flow rate, size of the construction area, local topography, and environment. Fig. 1-1 provides a decision making tree for passive treatment systems based on the characteristics of the influent AMD water. Most of the time, the adaptation of a hybrid system is necessary to achieve the regulatory standards before discharging the AMD water into the local water bodies. The installation costs of the conventional passive treatment technologies are very expensive, and these systems also require a periodic monitoring and maintenance (Gusek, 2013). The passive treatment facilities also generate a considerable amount of sludge, and the removal and disposal cost of the sludge is also very high.
Figure 1-1. Decision making tree for the design of passive treatment system [Redrawn after Hedin et al., 1994; Skousen and Ziemkiewicz, 2005; Zipper et al., 2011; Gusek, 2013].
1.2.2.2 Emerging Passive Treatment Technology: Phytoremediation

Phytoremediation is an emerging passive AMD treatment technology. Researchers and remediation practitioners are evaluating phytoremediation-based alternatives because of the higher costs associated with conventional AMD remediation approaches. Phytoremediation can be applied to both AMD impacted soil and water. As eroded AMD impacted soils generally end up in surrounding water bodies and elevate the risk, remediation of both soil and water is very important. Phytoremediation of contaminated mine sites mainly involves two mechanisms: phytoextraction and phytostabilization. In the phytoextraction process, plants extract heavy metals from the contaminated sites and store the extracted metals in their biomass. On the other hand, phytostabilization provides a vegetative cover to highly erosion prone and heavily contaminated acid sulfate soils (Baker and Brooks, 1989; Salt et al., 1995; Cunningham et al., 1997; Tordoff et al., 2000; Padmavathamma and Li, 2007). Sometimes, due to the presence of heavy metals in high concentration, complete metal removal cannot be possible. In such conditions, phytostabilization immobilizes the metals and traps them in plant root zones, which minimizes the metal exposure to the surrounding ecosystems. The extensive root systems of the plants also protect the soils against erosion and leaching.

Several metal tolerant plant species have been used to remediate contaminated mine sites. Success of phytoremediation depends on the proper selection of the metal-hyperaccumulator plants. Hyperaccumulator plants generally accumulate metals in their aboveground biomass at a concentration that is 100-fold greater than the non
hyperaccumulator plants. Generally, these plants accumulate up to or more than 0.1% of metals such as Cu, Pb, Cd, Cr, Ni, and Co; or 1% of metals such as Zn and Mn in their dry biomass (Baker and Brooks, 1989). The high accumulation factor (AF) and translocation factor (TF) are also some of the hyperaccumulation characteristics. More than 400 hyperaccumulator plant species belonging to families such as Brassicaceae, Asteraceae, and Poaceae exist, which can be used in metal contaminated mine sites (Baker and Brooks, 1989; Baker et al., 1994; Padmavathiamma and Li, 2007). Table 1-1 presents some of the most commonly used plants for remediation of AMD impacted sites.
Table 1-1. Plant species used for phytoremediation of AMD-impacted sites

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Family</th>
<th>Metals of Concern</th>
<th>Advantage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Atriplex halimus</em> L.</td>
<td>Amaranthaceae</td>
<td>Cd, Zn</td>
<td>Drought tolerant, Soil erosion prevention.</td>
<td>(Lutts et al., 2004)</td>
</tr>
<tr>
<td><em>Cichorium intybus</em></td>
<td>Asteraceae</td>
<td>Pb</td>
<td>Accumulation of Pb in biomass.</td>
<td>(Gonzalez and Gonzalez-Chavez, 2006)</td>
</tr>
<tr>
<td><em>Cynodon dactylon</em></td>
<td>Poaceae</td>
<td>Cd, Cu, Pb, Zn</td>
<td>Metal accumulation, Vegetative cover.</td>
<td>(Archer and Caldwell, 2004; Gonzalez and Gonzalez-Chavez, 2006)</td>
</tr>
<tr>
<td><em>Cyperus alternifolius</em></td>
<td>Cyperaceae</td>
<td>Cd, Cu, Mn, Pb, Zn</td>
<td>Acid tolerant.</td>
<td>(Shu, 2003)</td>
</tr>
<tr>
<td><em>Thlaspi caerulescens</em></td>
<td>Brassicaceae</td>
<td>Cd, Zn</td>
<td>Hyperaccumulator for Cd and Zn.</td>
<td>(Baker et al., 1994; Knight et al., 1997)</td>
</tr>
<tr>
<td><em>Vetiveria zizanioides</em> or <em>Chrysopogon zizanioides</em></td>
<td>Poaceae</td>
<td>Al, As, Cd, Cu, Fe, Hg, Mn, Pb, Zn</td>
<td>Metal hyperaccumulator, Acid tolerant, Soil erosion prevention, Soil stabilization.</td>
<td>(Du and Truong, 2003; Shu, 2003; Truong et al., 2003; Roongtanakiat et al., 2007; Roongtanakiat et al., 2008)</td>
</tr>
</tbody>
</table>

In China, a wide range of plant species (*Chrysopogon zizanioides*, *Sesbania rostrata*, *Phragmites australis*, *Cyperus alternifolius*, *Leucaena leucocephala*, *Panicum repens*, *Gynura crepidiodes*, *Alocasia macrorrhiza* and *Chrysopogon aciculatus*) have
been used to phytoremediate AMD water highly contaminated with Zn, Pb, SO$_4^{2-}$ (Yang et al., 1997; Shu, 2003; Wong, 2003). Plants like Cyperus alternifolius and Chrysopogon zizanioides possess very high acid tolerance characteristics. An increase of pH from 2.4 to 7.5, and 80% removal of its initial sulfate concentration are also noticed during the study (Shu, 2003). In Australia, plant species like Juncus usitatus, Lomandra longifolia, Cynodon dactylon, Pteridium esculentum, Acacia decurrens and Melaleuca alternifolia are used for remediation of metals such as Fe, As, Cd, Cu, Pb and Zn from both AMD impacted soil and water (Archer and Caldwell, 2004). All of the plant species thrived well under the acidic conditions (pH ranged from 2.9-5.6), and species like Cynodon dactylon can accumulate metals like Cd (14 mg/kg), Pb (658 mg/kg) and Zn (828 mg/kg) in its biomass. Species like Juncus usitatus, Lomandra longifolia can also accumulate significant amount of Cd in their biomass (26 and 21 mg/kg respectively). Another potential plant species for remediation of Cd and Zn contaminated mine sites is Thlaspi caerulescens. Studies reported that Thlaspi caerulescens can accumulate as high as 50-250 mg/kg Cd and 13,000-19,000 mg/kg Zn while growing in AMD contaminated sites (Baker et al., 1994; Knight et al., 1997). Due to the low biomass production, Thlaspi caerulescens is not an ideal plant for phytoremediation. On the other hand, plants like Cichorium intybus L. and Cynodon dactylon are potential phytoremediation candidates for Pb contaminated mine sites. Cichorium intybus and Cynodon dactylon can accumulate as high as 800-1500 mg/kg and 400-1200 mg/kg Pb in their biomass respectively (Gonzalez and Gonzalez-Chavez, 2006). In a similar study, it is observed that Atriplex halimus L. can accumulate 830 and
440 mg/kg of Cd and Zn respectively in its biomass while growing on mine tailing under greenhouse condition (Lutts et al., 2004). Another commonly used plant species for mine site remediation is Chrysopogon zizanioides, commonly known as vetiver grass. Due to their physiological characteristics and high tolerance of metals such as Al, Mn, Fe, and Zn (Roongtanakiat et al., 2007; Roongtanakiat et al., 2008), and heavy metals such as As, Pb, Hg, and Cd, vetiver can be used efficiently to restore metal contaminated sites (Truong and Baker, 1998). Vetiver can tolerate Fe concentrations even up to 63,920 mg/kg (Roongtanakiat et al., 2008). Vetiver can remediate iron ore tailings contaminated with high concentration of metals such as Fe, Zn, Mn and Cu, and can accumulate as high as 545-1,197 mg/kg Fe, 302-531 mg/kg Zn, 415-648 mg/kg Mn and 13-66 mg/kg Cu in its root and shoot. High mean translocation factors for Mn (0.86), Fe (0.71), Zn (0.69) and Cu (0.55) can be observed in vetiver’s tissue (Roongtanakiat et al., 2008). Use of soil amendments like DTPA (diethylenetriamine pentaacetic acid) and compost mixture increases the metal uptake ability of vetiver. Vetiver possesses a massive root system, which can stabilize the erosion prone acid sulfate soil. So, planting vetiver on metal contaminated mine soils can stabilize the soil and improve the overall soil quality (Wong, 2003; Roongtanakiat et al., 2008). Once established, vetiver grass can grow on the acidic soils with continuous acidity production by sulfidic minerals (Truong et al., 2003). In a study conducted in Queensland Australia, it was found that vetiver systems are able to control bank erosion while growing on acid sulfate soil (Truong et al., 2003). The study showed that the planting vetiver stabilized the edges of the channel, and also promoted the
establishment of other plants on the steep slopes, helping to prevent erosion and preventing the collapse of the highly acidic soil into the channel streams. Vetiver can trap sediments and pollutants from runoff water, which improves the overall water quality. The increase of pH and decrease of Fe concentration in water were also observed during the study (Truong et al., 2003).

Phytoremediation of AMD impacted soil and water has shown positive results, and fueled extensive research in this field worldwide. The major advantages of phytoremediation are that it is cost-effective and environment-friendly. The success of phytoremediation is primarily dependent on the plant-availability of the metals. Due to factors such as soil properties, metal species, loading level and soil-ageing, the amount of plant available metal varies significantly. Several chemical agents and soil amendments such as EDTA (Ethylenediaminetetraacetic acid), EDDS (Ethylenediamine-N,N'-disuccinic acid), compost, DTPA have been applied to increase the plant available metal fraction in the soil. Most of the phytoremediation studies were performed in either under greenhouse conditions, or in the field on a pilot scale. Hence, more extensive field based research is required to optimize this emerging technique.

1.3 Summary

Remediation of AMD is a challenging proposition that is dependent on several factors such as the daily AMD load, flow rate, net acidity, and metal concentration. The pre-mining analysis of the neutralization potential (NP) of soil through acid base
accounting (ABA) helps to predict the nature of AMD, and to adapt best AMD-management practices. A number of AMD prevention and remediation technologies are being used worldwide to prevent AMD pollution in both active and abandoned mines. Long-term monitoring of the constructed systems is necessary as AMD pollution can exists for decades. Most of the conventional passive AMD remediation technologies are ineffective and/or expensive for long-term and persistent AMD load. Hence, a search for an effective, viable, and sustainable AMD remediation technology is ongoing. Emerging passive treatment technologies such as phytoremediation have the potential to be successful, and are attractive because of sustainability and cost-effective aspects of their implementation. However, most of the research in this area so far has been limited to greenhouse or pilot-scale field studies. Further long-term research is needed in order for this promising technology to be widely implemented in AMD-impacted areas.

1.4 Objective of the Dissertation

The main objective of this dissertation was to develop and optimize a novel, cost-effective, efficient and “green” technology for the remediation of acid mine drainage (AMD)-impacted soil and water. Two efficient and environment-friendly remediation agents: drinking-water treatment residuals (WTRs) and vetiver grass (*Chrysopogon zizanioides* L.) were used to achieve the proposed research aims. This study utilized the metal binding and acid-neutralizing potential of WTRs to improve the quality of AMD-
impacted soil and water collected from the Tab Simco mine in Carbondale, IL. This study also used vetiver grass to lower erosion potential of acid sulfate soil.

1.4.1 Central Hypotheses

The entire study was based on the following central hypotheses:

- Co-application of aluminum based (Al-WTR) and lime based (Ca-WTR)-WTR in a granular filter bed will help to increase pH and reduce the concentration of metals from AMD-impacted water.

- Co-application of Al-WTR and Ca-WTR as soil amendment will help to immobilize and irreversibly remove metals from AMD-impacted soil and will increase soil pH.

- Use of vetiver grass will help to improve erosion potential of AMD-impacted soil.

Use of WTR-vetiver model will help to reduce metal leaching and soil erosion potential of AMD-impacted soil.

To test the above mentioned hypotheses the overall project was divided into following specific aims:

- Specific aim 1: Quality assessment of soil and water collected from the Tab Simco mine.

- Specific aim 2: Testing and optimization of WTR application rate for remediation of AMD-impacted water.

- Specific aim 3: Development of a field scale WTR-filter media for remediation of AMD-impacted water.
Specific aim 4: Testing and optimization of WTR application rate for remediation of AMD-impacted soil.

Specific aim 5: Development of a WTR-vetiver model to improve the quality of AMD-impacted soil.

1.5 Organization of the Dissertation

All the above mentioned objectives were tested and the results are presented in this dissertation in the form of the following chapters:

- Chapter 2 entitled “Assessment of Soil and Water Contamination from Acid Mine Drainage: A Case Study from Tab Simco Mine” discusses the extent of AMD contamination at Tab-Simco. This chapter explains why the AMD contamination scenario at Tab-Simco is unique in comparison to other AMD sites.

- Chapter 3 entitled “Developing a “Green” Remediation Technology for Acid Mine Drainage (AMD)-Impacted Water” documents the preparation of WTR-filter media from laboratory scale to its optimized field scale form. This chapter presented the results from laboratory batch sorption studies (using different AMD-water: WTR ratios), laboratory scale WTR-filter experiments (using different sand: WTR ratios), and field-scale WTR-filter media study.

- Chapter 4 entitled “Removal of Acidity and Metal Concentrations from Acid Mine Drainage-Impacted Soils Amended with Drinking-Water Treatment Residuals: Soil Incubation Study” documents the results from a 60 days soil-WTR incubation study. This study showed how WTRs amendment was effectively
increased soil pH and immobilized the metals from AMD-impacted soil.

- Chapter 5 entitled “Control of Erosion and Metal Leaching from Acid Mine Drainage (AMD)-Impacted Soil using Drinking-Water Treatment Residuals and Vetiver Grass” documents results from a greenhouse column study and a simulated field study using WTR-vetiver model. This study shows that the use of WTRs amendment and vetiver grass was able to increase soil pH and reduce metal leachability and erosion-potential of AMD-impacted soil.
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CHAPTER 2
Assessment of Soil and Water Contamination from Acid Mine Drainage: A Case Study from Tab Simco Coal Mine

[This chapter has been accepted for publication in Mine Water and the Environment]

Abstract

Acid Mine Drainage (AMD) pollution is one of the largest environmental problems associated with mining activities. Due to the complex nature of AMD, and the wide array of environmental consequences it causes, reclamation of AMD impacted soil and water is always a challenge. Site characterization is the first step towards developing an appropriate remediation or reclamation approach. This study focused on characterizing the current state of pollution in the Tab-Simco site, an abandoned coal mine located 10 km southeast of Carbondale, Illinois. In 1996, the Tab-Simco site was reported as one of the highly contaminated AMD sites in the mid-continent region. In 2007, a sulfate reducing bioreactor was constructed in Tab-Simco, but the system failed in 2011. In order to characterize the current extent of AMD pollution, a suite of AMD impacted soil and water samples were collected from various locations in the Tab-Simco site following standard USEPA protocols, and were analyzed for pH, electrical conductivity, the eight metals monitored by RCRA (Resource Conservation and Recovery Act), and total Al, Fe, Cu, Ni, Mn concentrations. Water samples were also analyzed for total SO$_4^{2-}$ concentration. In addition, soil samples were analyzed for their total sulfur content, and an Acid Base Accounting (ABA) was performed. Results showed that the Tab-Simco site
is severely impacted by AMD. Mean pH of soil and water samples were found to be 2.69 and 2.07, respectively. Net Neutralization Potential (NNP) of soil samples ranged between -22.1 and -6.75 kg CaCO$_3$/ton of material. Mean sulfur content of the soil samples was 0.5%. The AMD impacted soils contained high concentrations of metals, such as Fe, Zn, Ni, Cr, Cu, Pb, and As. The AMD impacted water also contained high concentrations of metals, including Fe, As, Zn, Pb, Cr, Al, Cd, Cu, and Ni, as well as SO$_4^{2-}$, all of which were significantly above their USEPA permissible limits for surface water. This study provides a detailed insight into the current extent of the decades long AMD pollution at the Tab-Simco mine site.

**Keywords:** Acid base accounting; RCRA 8 metals; Reclamation; Sulfate Reducing Bioreactor; Surface mining.
2.1 Introduction

2.1.1 AMD Pollution: Cause and its Impact

Surface mining is an important revenue generating industry throughout the world. A major environmental concern associated with this industry is the generation of acid mine drainage (AMD) and acid sulfate soil, which are responsible for habitat deterioration of the surrounding ecosystem (Ferguson and Erickson 1988; U.S. Forest Service 1993; USEPA 1994a).

During the AMD generation process, the pH of the system drops significantly which increases the mobility of metals in the environment. Exposure to high levels of AMD results in the degradation of adjacent surface water quality, which becomes unsuitable for sustaining biodiversity. In addition, the acid sulfate soils are structurally unstable and highly prone to erosion. Former mine sites require the implementation of proper management practices, sometimes for decades, to minimize the overall environmental impact. If unattended, the environmental damage could persist forever (U.S. Forest Service 2005). According to the U.S. Forest Service (2005), the current number of abandoned hardrock mines in the US is 557,000; many of which are active sources of AMD generation. In the eastern US, more than 7,000 km of streams are currently impacted by AMD, and in the western US, the number is between 8,000 and 16,000 km (Kim et al. 1982; U.S. Forest Service 1993; USEPA 1994a; Benner et al. 1997; Jennings et al. 2008; USEPA, 2011). Severe impact of AMD on aquatic biodiversity in contaminated regions has been reported by many researchers (Soucek et
al. 2000; Hansen et al. 2002; Schmidt et al. 2002; Gergardt et al. 2004; Martin and

2.1.2 The Study Site

Tab-Simco is an abandoned coal mine located 9.7 km southeast of Carbondale, IL
(Fig. 2-1). The area is “horseshoe” shaped, and is approximately 37 m higher in elevation
than its surrounding lowland (Smith 2002; Behum et al. 2011). A part of the
Pennsylvania bedrock system, the shallow bedrock of Tab-Simco consists of shale,
sandstone, siltstone and limestone. Two layers of coal: Murphysboro Coal layer and
Mount Rorah Coal layer were located within the Spoon formation in this region. Both
coal layers were separated by a 3-8 m thick layer of shale and capped by a 10 m thick
layer of pyritic sandstone (Smith 2002; Segid 2010; Behum et al. 2011; Behum et al.
2012; Behum et al. 2013). Between 1890 and 1955, underground mining in this region
targeted the lower approximately 2.5 m thick continuous Murphysboro Coal layer, and
the upper 0-1.5 m thick discontinuous patchy Mount Rorah Coal layer (Smith 2002;
Behum et al. 2012; Behum et al. 2013). After the end of decades long underground
mining, the area was sealed off by water inflows which eventually became the source of
AMD generation. Later, the area underwent surface mining in the 1960’s and 1970’s.
Stripping operations were responsible for several break-ins to the previously sealed
underground structure. The mine pool of this region contains an estimated 40,000 to
77,000 m$^3$ of severely contaminated water (Smith 2002; Behum et al. 2012; Behum et al.
2013). Currently, an average of 150 m$^3$ AMD is being generated per day, which is
coming out through the fractured zones and contaminating the surrounding ecosystem.
(Smith 2002). AMD deposition on the floodplain has created an approximately 36,421 m² “kill zone” on its way to the adjacent Sycamore Creek (Fig. 2-2), a stream flowing towards the North. More than 3 km of the Sycamore Creek has been heavily contaminated by AMD (Smith 2002; Segid 2010; Behum et al. 2011; Behum et al. 2012; Behum et al. 2013). In 1996, the Tab-Simco site was reported as one of the most highly contaminated AMD sites in the mid-continent region (Smith 2002; Segid 2010).

Figure 2-1a. Location of the Tab-Simco site (RoyChowdhury et al., Accepted).
Figure 2-1b. Google Earth image of the Tab-Simco site (Taken on 10-14-14).

Figure 2-2. AMD impacted Sycamore Creek at Tab-Simco.
2.1.3 Background Information about the SRB and its Fate

In 2007, a 3000 m$^2$ sulfate reducing bioreactor (SRB) was constructed in the Tab-Simco site to assist in managing the AMD. The bioreactor consisted of 0.3 m thick limestone layer, 2 m thick organic layer and 0.3 m water impoundment from bottom to top. The organic layer was composed of woodchips, ground limestone, straw mulch, and compost (Behum et al., 2010; Segid 2010; Behum et al., 2011; Behum et al. 2012; Burns et al. 2012; Behum et al. 2013). The operation of the constructed SRB was started in early 2008 (Lewis 2008; Segid 2010). The performance of Tab-Simco SRB in terms of removal of acidity, metals and sulfate from AMD water is presented in Table 2-1.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before Treatment</th>
<th>After Treatment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.8-3.9</td>
<td>6.2-6.5</td>
<td>Behum et al. 2010; Segid 2010; Behum et al. 2011; Behum et al. 2012; Burns et al. 2012.</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>450.6-884</td>
<td>1.8-6.7</td>
<td>Behum et al. 2010; Segid 2010; Behum et al. 2011; Behum et al. 2012.</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>113-173</td>
<td>0.2-0.4</td>
<td>Behum et al. 2010; Segid 2010; Behum et al. 2011; Behum et al. 2012.</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>35.7-40</td>
<td>21.3-28.8</td>
<td>Behum et al. 2010; Segid 2010; Behum et al. 2011; Behum et al. 2012.</td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>2.2</td>
<td>0.1</td>
<td>Behum et al. 2010; Behum et al. 2012.</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>2.6-2.9</td>
<td>0.2-0.3</td>
<td>Behum et al. 2010; Behum et al. 2012.</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>2981-4589</td>
<td>1153-2214</td>
<td>Behum et al. 2010; Segid 2010; Behum et al. 2011; Behum et al. 2012; Burns et al. 2012.</td>
</tr>
</tbody>
</table>
The SRB system failed in 2011 (Behum et al. 2013), and the bioreactor is currently filled with AMD water (Fig. 2-3).

Figure 2-3. Non-functional SRB filled with AMD at Tab-Simco.

2.1.4 Objective of this Study

The main objective of this study was to collect and characterize AMD impacted soil and water from the Tab-Simco site to better understand the current extent of the problem. No data was available about the Tab-Simco site since failure of the SRB, and this study was aiming to fill up that gap.
2.2 Materials and Methods

2.2.1 Sample Collection

Soil samples were collected from the impacted areas around the SRB (S1, and S2), and from three different locations (S3, S4, and S5) within the “kill zone” (Fig. 2-4). At each sampling location, composite soil samples were collected. Composite samples were the mixture of soils from four different spots within that sampling point. The 1981 EPA/CE-81-1 protocol was followed during sample handling (Plumb 1981). Water samples were collected from three different locations (W1, W2, and W3) of the currently non-functional SRB pond, plus two other locations (W4, and W5) from the AMD impacted portion of the Sycamore Creek (Fig. 4). Sampling zones were selected so as to cover the entire AMD impacted areas of the Tab-Simco site. Sampling was conducted in October, 2014. All samples were transported back to Montclair State University, NJ for characterization.
Figure 2-4. Map of the Tab-Simco Showing Sampling Points. (Original Map was taken from Segid 2010; Behum et al. 2011; Behum et al. 2012; Behum et al. 2013, and modified accordingly).

2.2.2 Characterization of the Soil Samples

Collected soil samples were dried, ground and sieved through 1-2 mm mesh. Fractions < 2 mm were used for the following soil characterization protocols.
2.2.2.1 Acid-Base Accounting (ABA)

ABA is a commonly used test for measuring the acid producing potential and alkalinity producing potential of overburden in a mining area. It is the most preferred method for prediction of post-mining long-term water quality. Developed by Smith et al. in the 1970s, the ABA method comprises of two measurements, Maximum Potential Acidity (MPA), and Neutralization Potential (NP) (Smith et al. 1974; Smith et al. 1976; Sobek et al. 1978; Skousen et al. 1990; Perry 1998; Skousen et al. 2002, Fey 2003).

For this study, MPA was determined by multiplying % of total sulfur (S) with a constant, 31.25 (Perry 1998; Skousen et al. 2002). NP was estimated by following the Sobek Method (Sobek et al. 1978). “Fizz” ratings for each sample were determined by adding a few drops of 1:3 Hydrochloric acid (HCl). Based on the result of the “fizz-test,” soil samples were digested with 20 mL (for fizz-rating 0), or 40 mL (for fizz-rating 1) of 0.1N HCl, and solutions were titrated with 0.1N NaOH up to pH 7.0.

2.2.2.2 Soil pH

Soil samples were mixed with deionized water at 1:1 ratio. The solutions were stirred for 5 sec, and allowed to stand for 10 min (Sobek et al. 1978; Page et al. 1982; Mills 2014). pH measurements were recorded in triplicate using an Oakton ion 510 series pH meter.
2.2.2.3 Electrical Conductivity (EC)

Soil samples were mixed with 0.01 M KCl solution at 1:5 solid: solution ratio. The solutions were stirred and allowed to stand for 4 hrs (Sparks 1996). EC measurements were conducted in triplicate using an Orion conductivity meter.

2.2.2.4 Soil texture

Soil texture (% clay, silt and sand) was determined by a Malvern Mastersizer 2000 laser particle size analyzer. Analysis was done in triplicate.

2.2.2.5 Total C, H, N and S content

Total C, H, N and S concentrations in soil samples were analyzed by an Elementer Vario EL-III CHNS analyzer. Dried soil samples were sieved through a 0.5 mm sieve and the fine sized samples were used for this analysis. Analysis was done in triplicate.

2.2.2.6 Metal concentration

Concentrations of different metals in the soil samples were determined by USEPA 3050B soil digestion method (USEPA 1996), using a Linx wireless digestion system. Digested samples were filtered using 0.45 µm nylon syringe filter, and analyzed for total RCRA 8 metals (Ag, As, Ba, Cd, Cr, Hg, Pb, Se) plus Fe, Al, Ni, Cu, and Mn concentrations by a Inductively coupled plasma mass spectrometer (ICP-MS, X-series, Thermo Scientific).
2.2.3 Characterization of the Water Samples

2.2.3.1 pH and Electrical Conductivity

pH and EC of the water samples were measured using an Oakton ion 510 series pH meter and an Orion conductivity meter respectively. Measurements were made on-site, and were validated in the laboratory. All measurements were made in triplicates.

2.2.3.2 Metal concentration

Water samples were filtered using a 0.45 µm syringe filter, the filtered samples were diluted 100 fold, and analyzed for total-recoverable RCRA 8 metals plus total Fe, Al, Ni, Cu, and Mn by ICP-MS.

2.2.3.3 Total sulfate concentration

Water samples were filtered using a 25 µm syringe filter. Filtered samples were diluted by 50 times and were analyzed for the total sulfate ($SO_4^{2-}$) concentration by a Dionex Ion Chromatograph.

2.2.3.4 Mineral acidity and Total acidity

Mineral and total acidity of the water samples were measured by USEPA 305.1 titration method using 1N NaOH solution (USEPA 1994b). Mineral acidity (methyl orange acidity) was measured by titration to a pH of 3.7, the methyl orange end point. Titration to the phenolphthalein end point (pH 8.3) measures both mineral acidity plus acidity due to weak acids, as weak acids are neutralized by titration to pH 8.3. This total acidity is also called phenolphthalein acidity. 50 mL water sample was used for the titration. Analysis was done in triplicate.
The following equations were used to calculate the mineral and total acidity:

Mineral acidity\(\left(\frac{mg}{L}CaCO_3\right)\) = \(\frac{\text{Volume of NaOH to raise pH to 3.7} \times \text{Normality of NaOH} \times 50 \times 1000}{\text{Volume of sample taken}}\) \hspace{1cm} (1)

Total acidity\(\left(\frac{mg}{L}CaCO_3\right)\) = \(\frac{\text{Volume of NaOH to raise pH to 8.3} \times \text{Normality of NaOH} \times 50 \times 1000}{\text{Volume of sample taken}}\) \hspace{1cm} (2)

2.2.4 Quality Assurance or Quality Control (QA/QC)

All measurements were carried out in triplicates. Established QA/QC protocols of the Environmental Geochemistry Laboratory of Montclair State University were followed. External standards were used. Spike recoveries of ±10% were considered acceptable for ICP-MS analyses. Continuing calibration verifications were performed at 10 sample intervals.

2.3 Results and Discussions

2.3.1 Soil Characterization

Table 2-2 presents selected physico-chemical properties of Tab-Simco soils. Results showed that soils from the entire sampling area were highly acidic, with a mean pH of 2.69± 0.05. Mean EC was 2.35± 0.14 mS/cm. Soil texture analysis demonstrated that the soil was comprised mostly of silt (53.5%) and sand (36.8%), followed by clay (9.7%). Total S content of the soil was 0.54%, which places the Tab-Simco soil in the potential acid producing category (Miller and Murray 1988; Brady and Hornberger 1990; Perry 1998). Results also showed that the soil contained an average of 7.8% total nitrogen, and 0.08% total carbon.
Table 2-2. Physico-chemical Properties of the Tab-Simco Soil Samples. Data show soil properties for individual sampling sites (n=3) along with the mean (n=5) value for the entire area.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH</th>
<th>EC (ms/cm)</th>
<th>Total C (%)</th>
<th>Total H (%)</th>
<th>Total N (%)</th>
<th>Total S (%)</th>
<th>Soil Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Clay (%)</td>
</tr>
<tr>
<td>S1</td>
<td>2.69</td>
<td>2.25</td>
<td>0.08</td>
<td>1.62</td>
<td>7.9</td>
<td>0.54</td>
<td>9.7</td>
</tr>
<tr>
<td>S2</td>
<td>2.76</td>
<td>2.47</td>
<td>0.09</td>
<td>1.59</td>
<td>7.8</td>
<td>0.59</td>
<td>9.7</td>
</tr>
<tr>
<td>S3</td>
<td>2.74</td>
<td>2.52</td>
<td>0.07</td>
<td>1.69</td>
<td>7.8</td>
<td>0.53</td>
<td>9.8</td>
</tr>
<tr>
<td>S4</td>
<td>2.65</td>
<td>2.35</td>
<td>0.07</td>
<td>1.65</td>
<td>7.8</td>
<td>0.5</td>
<td>9.7</td>
</tr>
<tr>
<td>S5</td>
<td>2.64</td>
<td>2.15</td>
<td>0.08</td>
<td>1.55</td>
<td>7.9</td>
<td>0.56</td>
<td>9.7</td>
</tr>
<tr>
<td>Mean</td>
<td>2.69 ±</td>
<td>0.05</td>
<td>0.08 ± 0.01</td>
<td>1.64 ± 0.05</td>
<td>7.8 ± 0.06</td>
<td>0.54 ± 0.03</td>
<td>9.7 ± 0.3</td>
</tr>
</tbody>
</table>

Results of ABA tests are presented in Table 2-3. Four out of five soil samples (S1, S3, S4, and S5) produced a “0” fizz-rating (Sobek et al. 1978), which indicated that these soils are potentially acid producing (Perry 1998; Fey 2003). The S2 sample produced a fizz-rating of “1”. Based on the average total S content (Table 1), MPA was calculated for the soil samples, which ranged between 15.6 and 18.4 kg CaCO₃ equivalent/ton of material. NP of the soil samples ranged between -6.75 and 11.69 kg CaCO₃ equivalent/ton of material. NNP for each soil sample was calculated between -22.1 and -6.75 kg CaCO₃ equivalent/ton of material. According to the literature, soils with less than -20 kg CaCO₃ equivalent/tons of material of NNP are acid producing (USEPA 1994a; Perry 1998; Fey 2003), and three (S1, S4, and S5) out of the five soil samples fell in this category (Table 2). The remaining two soil samples (S2 and S3) were
in the potentially acid producing zone (-20 to 20 kg CaCO\textsubscript{3} equivalent/tons of material) (Fey 2003). Sampling site S2 was located in the area where the SRB and oxidation ponds were constructed in 2007 and that could be a reason behind the slightly higher acid neutralizing capacity of this soil compared to the rest of the Tab-Simco soil samples. Although this study used total S value for calculating MPA following methods of Perry (1998) and Skousen et al. (2002), other researchers have pointed out that use of total S concentration can sometime overestimate MPA value, particularly when a majority of MPA is contributed by non-acid producing organic sulfur (Sahoo et al., 2014). Still, MPA value, calculated based on total S concentration, could be a good indicator of acid producing nature of specific soil types (Perry, 1998) which is applicable to the Tab-Simco site.

Table 2-3. Acid-Base Accounting of the Tab-Simco Soil.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Fizz-Rating</th>
<th>NP</th>
<th>MPA</th>
<th>NNP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>------kg CaCO\textsubscript{3} equivalent/ tons of material------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>0 (No-fizzing)</td>
<td>-6.75</td>
<td>15.6</td>
<td>-22.1</td>
</tr>
<tr>
<td>S2</td>
<td>1 (Slight-fizzing)</td>
<td>11.69</td>
<td>18.44</td>
<td>-6.75</td>
</tr>
<tr>
<td>S3</td>
<td>0 (No-fizzing)</td>
<td>3.99</td>
<td>16.56</td>
<td>-12.57</td>
</tr>
<tr>
<td>S4</td>
<td>0 (No-fizzing)</td>
<td>-6.51</td>
<td>15.63</td>
<td>-22.1</td>
</tr>
<tr>
<td>S5</td>
<td>0 (No-fizzing)</td>
<td>-4.4</td>
<td>17.5</td>
<td>-21.9</td>
</tr>
</tbody>
</table>

Physico-chemical characterization of the Tab-Simco soil revealed its acidic nature. Due to this high acidity, mobility of the metals in the soil are likely to increase,
and the metals are likely to become more soluble and bioavailable. Only those metals that were found in high concentrations in Tab-Simco soil after acid digestion are listed in Table 2-4. High concentration of Fe (41,012 ± 10 mg/ kg) was reported in all soil samples. High concentrations of Zn (419 ± 63 mg/ kg), Ni (175 ± 5.9 mg/ kg), Cr (152 ± 15 mg/ kg), Cu (148 ± 2.1 mg/ kg), Pb (145 ± 25 mg/ kg), As (127 ± 16 mg/ kg), Cd (4 ± 0.5 mg/ kg), and Hg (3.7 ± 0.2 mg/ kg) were also reported in the soil samples.

Table 2-4. Metal Concentrations in the Tab-Simco Soil Samples. Data show metal concentrations at individual sampling sites (n=3) along with the mean (n=5) value for the entire area.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>As (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Fe (mg/kg)</th>
<th>Hg (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Zn (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>125</td>
<td>4</td>
<td>160.7</td>
<td>148</td>
<td>41005</td>
<td>3.8</td>
<td>174</td>
<td>146</td>
<td>526</td>
</tr>
<tr>
<td>S2</td>
<td>116</td>
<td>3.3</td>
<td>125.9</td>
<td>145</td>
<td>41002</td>
<td>3.3</td>
<td>165</td>
<td>103</td>
<td>409</td>
</tr>
<tr>
<td>S3</td>
<td>109</td>
<td>4.5</td>
<td>152.9</td>
<td>151</td>
<td>41029</td>
<td>3.5</td>
<td>176</td>
<td>148</td>
<td>410</td>
</tr>
<tr>
<td>S4</td>
<td>149</td>
<td>3.7</td>
<td>161.7</td>
<td>148</td>
<td>41015</td>
<td>3.9</td>
<td>181</td>
<td>157</td>
<td>362</td>
</tr>
<tr>
<td>S5</td>
<td>137</td>
<td>4.5</td>
<td>162.1</td>
<td>148</td>
<td>41012</td>
<td>3.8</td>
<td>177</td>
<td>169</td>
<td>386</td>
</tr>
<tr>
<td>Mean</td>
<td>127 ± 16</td>
<td>4 ± 0.5</td>
<td>152 ± 15</td>
<td>148 ± 2.1</td>
<td>41012 ± 10</td>
<td>3.7 ± 0.2</td>
<td>175 ± 5.9</td>
<td>145 ± 25</td>
<td>419 ± 63</td>
</tr>
</tbody>
</table>

2.3.2 Water Characterization

The impact of AMD on Tab-Simco water samples was apparent from the characterization data (Table 2-5). Samples collected from the SRB (W1, W2, and W3) verified that the SRB is not functional (Behum et al., 2013), and reflected the characteristic properties of AMD impacted water. Samples collected from the Sycamore Creek (W4, and W5) also showed that the stream is heavily impacted by AMD. Results
indicated extremely acidic nature of the water samples with a mean pH of 2.07 ± 0.02. The mean EC was 3.94 ± 0.03 mS/cm. Mineral and total acidity of the water samples was 467 ± 50 mg/L CaCO₃ and 1089 ± 60 mg/L CaCO₃ respectively. This extremely low pH and high acidity indicate that AMD generated in Tab-Simco mine is negatively impacting the surrounding water bodies, making them potentially unsustainable in terms of aquatic population and biodiversity.

Table 2-5. Characterization of the Tab-Simco Water Samples. Data show characteristics for individual sampling sites (n=3) along with the mean (n=5) value for the entire area.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH</th>
<th>EC (ms/cm)</th>
<th>Mineral Acidity (mg/L CaCO₃)</th>
<th>Total Acidity (mg/L CaCO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>2.06</td>
<td>3.94</td>
<td>480</td>
<td>1100</td>
</tr>
<tr>
<td>W2</td>
<td>2.07</td>
<td>3.92</td>
<td>520</td>
<td>1170</td>
</tr>
<tr>
<td>W3</td>
<td>2.06</td>
<td>3.92</td>
<td>400</td>
<td>1000</td>
</tr>
<tr>
<td>W4</td>
<td>2.11</td>
<td>3.99</td>
<td>430</td>
<td>1089</td>
</tr>
<tr>
<td>W5</td>
<td>2.09</td>
<td>3.95</td>
<td>500</td>
<td>1090</td>
</tr>
<tr>
<td>Mean</td>
<td>2.07 ± 0.02</td>
<td>3.94 ± 0.03</td>
<td>467 ± 50</td>
<td>1089 ± 60</td>
</tr>
</tbody>
</table>

High concentrations of metals were reported in the Tab-Simco water samples (Table 2-6). Water contained 137 (± 5) ppm of Fe, which was more than 100 times higher than the USEPA permissible limit of Fe (1 ppm) in surface water (USEPA, 1994c; NCAC, 2003). Among toxic metals, high concentrations of As (4 ± 0.01 ppm), Zn (11 ± 0.9 ppm), Pb (7 ± 1.2 ppm), and Cr (1 ± 0.04 ppm) were found in the water samples at levels well above the USEPA permissible limits (0.05 ppm, 0.5 ppm, 0.25 ppm, 0.5 ppm, respectively) (USEPA, 1994c; NCAC, 2003). Other metals, such as Al (80 ± 15 ppm), Cu (4 ± 0.05 ppm), Cd (1 ± 0.01 ppm), and Ni (3 ± 0.25 ppm) were also present in the water,
along with high SO$_4^{2-}$ concentrations (2481 ± 50 ppm). These results clearly demonstrated the negative impact of AMD pollution on Tab-Simco water bodies. Researchers have reported presence of metals like Fe, Al and Mn in most AMD contaminated sites in states, such as Alabama, Indiana, Kentucky, Maryland, Ohio, Tennessee, and West Virginia (Skousen and Ziemkiewicz, 2005). What makes the Tab-Simco mine site unique is the presence of a wide range of metals beside Fe, Al and Mn in significantly higher amounts than reported in other AMLs. Although exploring the specific sources of these metals was beyond the scope of this study, it can however, be stated with certainty that this very low pH system makes these metals soluble, hence, mobile in the surrounding ecosystem, thus exposing the living organisms to high bioavailable metal concentrations.
Table 2-6. Metal and Sulfate Concentrations in the Tab-Simco Water Samples. Data show metal concentrations at individual sampling sites (n=3) along with the mean (n=5) value for the entire area.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Al</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>90</td>
<td>4</td>
<td>1.06</td>
<td>1.09</td>
<td>4</td>
<td>135</td>
<td>3.5</td>
<td>8.7</td>
<td>11.8</td>
<td>2515</td>
</tr>
<tr>
<td>W2</td>
<td>95</td>
<td>4</td>
<td>1.05</td>
<td>1.01</td>
<td>4</td>
<td>136</td>
<td>3.4</td>
<td>8.1</td>
<td>11.5</td>
<td>2516</td>
</tr>
<tr>
<td>W3</td>
<td>87</td>
<td>4</td>
<td>1.04</td>
<td>1</td>
<td>4</td>
<td>135</td>
<td>3.1</td>
<td>8.3</td>
<td>11.1</td>
<td>2525</td>
</tr>
<tr>
<td>W4</td>
<td>61</td>
<td>3.96</td>
<td>1.01</td>
<td>1</td>
<td>3.88</td>
<td>132</td>
<td>2.9</td>
<td>6.05</td>
<td>9.6</td>
<td>2420</td>
</tr>
<tr>
<td>W5</td>
<td>69</td>
<td>3.99</td>
<td>1.05</td>
<td>1</td>
<td>3.97</td>
<td>145</td>
<td>3</td>
<td>6.34</td>
<td>11.7</td>
<td>2433</td>
</tr>
<tr>
<td>Mean</td>
<td>80</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>137</td>
<td>3</td>
<td>7</td>
<td>11</td>
<td>2481</td>
</tr>
</tbody>
</table>

2.4 Conclusions

The objective of this study was to evaluate the current extent of AMD pollution in the Tab-Simco mine site after failure of the SRB in 2011. The results clearly showed that both soil and water in the study area were heavily impacted by AMD. Very low pH and strongly negative NNP values were indicative of the acid producing nature of Tab-Simco soils. High concentrations of metals, such as Fe, Zn, Ni, Cr, Cu, Pb, and As were found in the soil samples, which are very likely mobile in the highly acidic environment. Tab-Simco water samples were also characterized by their very low pH, and high mineral and total acidity, indicative of active AMD pollution. Water samples were reported to contain high concentrations of metals, such as Fe, As, Zn, Pb, Cr, Al, Cd, Cu, and Ni as a direct consequence of AMD pollution. The water samples possessed very high SO$_4^{2-}$.
concentration as well, indicating the current non-functional state of the SRB, which is filled with AMD water. Samples collected from the Sycamore Creek indicated severe AMD impact on this stream. Given that the last mining activity in the Tab-Simco site was reported in the 1970’s, this study reveals the extent of AMD pollution that can persist in an abandoned mine site decades after the cessation of mining operation, and the necessity of developing proper remedial and/or management plans to protect the surrounding ecosystem from AMD pollution.
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CHAPTER 3

Developing a “Green” Remediation Technology for Acid Mine Drainage (AMD)-impacted Water

[This chapter has been submitted to a journal]

Abstract

One of the biggest environmental impacts associated with mining industries is generation of Acid Mine Drainage (AMD). In absence of proper post-mining management practices, AMD-pollution can wipe out local biodiversity. Current AMD management practices often fail to meet the expectations in terms of cost, efficiency and environment-friendliness. The objective of this study was to use the metal binding and acid-neutralizing capacity of an industrial by-product, namely drinking water treatment residuals (WTRs), to treat AMD water collected from Tab-Simco coal mine in Carbondale, Illinois. AMD water of Tab-Simco was extremely acidic (pH 2.27) and contaminated with high concentration of metals (Fe, As, Pb, Zn, Al and Mn) and SO$_4^{2-}$. The ultimate objective of this study was to design a filter media using locally generated aluminum (Al) and calcium (Ca)-based WTRs to remove metals and SO$_4^{2-}$ from AMD-impacted water. Initially, laboratory batch equilibrium studies using a series of WTR (Al and Ca): AMD-water ratios were performed, and metal adsorption capacity of WTRs was tested. These tests were followed by preparation of laboratory scale WTR filter bed columns. An optimized WTR to sand ratio of 1:6 was selected to increase the permeability of the filter media. Al- and Ca-WTRs were mixed at a 1:1 ratio. After obtaining satisfactory results from lab scale studies, a field scale WTR-based filter was
designed and tested. The results showed that the WTR filter media removed more than 99\% of the initial Fe (137mg/L), Al (80mg/L), Zn (11mg/L), Pb (7mg/L), As (4mg/L), Mn (33mg/L), and 44\% of the initial $\text{SO}_4^{2-}$ (2481mg/L) concentration from Tab-Simco AMD water. pH of effluent water was considerably higher (7.8±0.05). Our study demonstrated that this “green” (recycling of a waste product), inexpensive (raw materials obtained free-of-charge), and ecologically sustainable (no adverse effect on ecosystem) technology can effectively treat AMD-impacted water.

**Keywords:** Acid Mine Drainage, Water Treatment Residuals, Tab-Simco mine, Green remediation, Filter media.
3.1 Introduction

3.1.1 AMD and its impact on ecosystem

Production of acid mine drainage (AMD) is one of the most concerning environmental impacts associated with mining operations. Oxidation of pyrite (FeS$_2$), in presence of oxygen and water, is responsible for the generation of a metal-rich and highly acidic AMD solution. The overall pyrite oxidation reaction can be expressed as (Stumm and Morgan, 1981):

$$\text{FeS}_2 + 3.75 \text{O}_2 + 3.5 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ + \text{heat}$$

The pH of AMD is often reported as low as 2-4, which eventually increases mobility of the metals in the system. Adverse impact of AMD pollution on local biodiversity such as impact on trout, shrimp, and mosquitofish populations were reported extensively by many researchers (Soucek et al., 2000; Hansen et al., 2002; Schmidt et al., 2002; Gerhardt et al., 2004; Martin and Goldblatt, 2007; Jennings et al., 2008; Trout Unlimited, 2011). Without proper management practices, abandoned mine sites can accelerate the AMD generation process. Currently more than 557,000 abandoned mines exist in the US (US Forest Service, 2005). AMD impacted streams in the US range from 15,000 to 23,000 km (Kim et al., 1982; U.S. Forest Service, 1993; USEPA, 1994a; Benner et al., 1997; Jennings et al. 2008). Current AMD remediation techniques such as aerobic wetlands, anaerobic wetlands, and sulfate-reducing bioreactors are expensive, require proper maintenance, and often failed to contain the AMD problem over a
prolonged period. Hence, the search for an efficient AMD remediation technology is ongoing.

3.1.2 Study Site

The proposed study site, Tab-Simco, is an abandoned coal mine located in Carbondale, Illinois. Between 1890 and 1955, this area underwent underground coal mining, which was followed by surface coal mining in the 1960’s and 1970’s. The area currently contains 40,000 to 77,000 m$^3$ of severely contaminated mine pool. Currently, this area produces an average of 150 m$^3$ AMD per day which is severely impacting the local biodiversity (Smith, 2002; Behum et al., 2012; Behum et al., 2013). Due to the contour difference, AMD flows northward and finally discharges into a nearby stream known as Sycamore Creek. This continuous AMD discharge has created a 36,421 m$^2$ area, devoid of vegetation and biodiversity, in AMD’s flow path to the Sycamore Creek. Over 3 km of the Sycamore Creek is also heavily impacted by acid water and metal precipitates (Smith, 2002; Behum et al., 2011; Segid, 2010; Behum et al., 2012; Behum et al., 2013). Tab-Simco was reported as one of the most highly AMD impacted areas in the mid-continent region in 1996 (Smith, 2002; Segid, 2010). In 2007, a sulfate reducing bioreactor (SRB) was constructed in the Tab-Simco site, but the system failed in 2011 (Behum et al., 2013). The bioreactor is currently filled with AMD water (Figures 3-1 and 3-2).
Figure 3-1. Google Earth image of the Tab-Simco site (Taken on 10-14-14).

Figure 3-2. Non-functional SRB pond at Tab-Simco (October, 2014).
3.1.3 Role of WTRs as AMD remediation agent

Drinking water treatment residuals (WTRs) are by products of the drinking water treatment process. To settle out the particulate matters from the water, generally alum, iron salts, or lime is used as a flocculation and coagulation agent. Depending on the type of flocculating or coagulating agent (alum, iron salt or lime), the Al-WTR, Fe-WTR or Ca-WTR is produced. More than 2 mega tons of WTRs are generated from the water treatment facilities in the US every day (Prakash and Sengupta, 2003) and are mostly landfilled. Al- and Fe-WTRs are primarily made of amorphous oxides and hydroxides of aluminum and iron which provide the reaction sites for the adsorption of different heavy metals like Cu, Pb, and Zn. WTRs also have high affinity for a wide range of environmental contaminants like perchlorate, phosphate, dichromate, and arsenate (Makris et al., 2004; Makris et al., 2006a; Makris et al., 2006b, Hardy et al., 2007). WTRs have a small particle size distribution and an extensive micro-porous network, giving them a high relative surface area. Several studies have also shown that the WTRs are not toxic and not harmful to the environment. Toxicity Characteristic Leaching Protocol (TCLP) studies proved that after binding, leaching out potential of bound metals from WTRs are well under the USEPA prescribed limit (Sarkar et al., 2007). The unique characteristics of Al-WTR could be used for removal of toxic metals from AMD-impacted water. Also, Ca-WTR could be used as a liming agent to increase the pH of AMD-impacted water.
3.1.4 Objective of the study

This study aimed to develop a cost-effective and efficient remediation technology for AMD-impacted water collected from the Tab-Simco mine. The main objective of this study was to prepare a WTR-based gravity flow filter media in order to decrease the acidity and metal concentration from AMD water.

3.2 Materials and Methods

3.2.1 Sample Collection and Characterization

AMD-impacted water samples were collected from the currently non-functional SRB pond in October, 2014. All samples were brought back to Montclair State University, NJ and used for this study. Water samples were tested for pH (using Oakton ion 510 series pH meter) and Electrical Conductivity (using Orion conductivity meter). Water samples were filtered (using 0.45 µm syringe filter) and tested for Resource Conservation Recovery Act (RCRA) 8 metals plus Fe, Al, Mn, Cu and Ni using an ICP-MS (Thermo-scientific X-series). Filtered water samples were also tested for total sulfate (SO$_4^{2-}$) using a Dionex IC. All analyses were done in triplicate.

3.2.2 Collection and Characterization of WTRs

Al-WTR was collected from City of Carbondale water treatment plant, IL, and Ca-WTR was collected from Saline Valley water treatment plant, IL. WTR samples were air-dried, ground and sieved through a 1-mm sieve and were used for all experiments. pH and EC of Al-WTR and Ca-WTR were measured following standard protocols (Klute, 1996; Sparks, 1996). Organic matter content of WTRs was calculated using Loss on
Ignition (LOI) method (Klute, 1996). Total C and N content of Al-WTR and Ca-WTR was analyzed following dry combustion process using an Elementer Vario EL-III CHNS analyzer. Total Fe and Al concentrations of Al-WTR and Ca-WTR were analyzed by ICP-MS following USEPA 3050B digestion method (USEPA, 1996). Oxalate extractable Fe and Al concentrations of Al-WTR and Ca-WTR were determined by ICP-MS following ammonium oxalate extraction method (McKeague et al., 1971). Following the USEPA 1311 method, the Toxicity Characteristics Leaching Protocol (TCLP) test was used for WTRs, to test if they are non-hazardous and safe to use. All analyses were done in triplicate.

### 3.2.3 Laboratory Batch Sorption Experiments

Metal sorption by Al-WTR and Ca-WTRs were investigated as a function of solid: solution ratio and contact time. All the batch experiments were carried out in triplicate. The analysis of metals was carried out using ICP-MS. Only the metals that were present at higher concentrations in Tab-Simco AMD water were analyzed for these experiments.

#### 3.2.3.1 Effect of solid: solution ratio

Six different solid: solution (g: mL) ratios of WTR to AMD-water were used in this study (1:10, 1:25, 1:50, 1:100, 1:125, and 1:150 respectively). Specific solid: solution ratios were prepared by adding WTR in AMD water in 50 mL polypropylene centrifuge tubes. All of those above mentioned solid: solution ratios were prepared separately for Al-WTR and Ca-WTR. The effect of co-application of Al-WTR and Ca-WTR was tested
by mixing them at a 1:1, 1:2 and 2:1 ratio respectively. Another batch of solid: solution ratios of WTR to AMD water was prepared only for higher dilutions (1:100, 1:125 and 1:150) using these WTR mixtures (Al-WTR to Ca-WTR at 1:1, 1:2 and 2:1). The results from co-application of Al-WTR and Ca-WTR could explain if fewer amounts of WTRs could be used while remediating AMD water. A total of 21 different treatments were used in this study. No pH control was imposed for any of these treatments. However, pH of all the treatments was checked before and after the sorption experiment. The suspensions in the test tubes were shaken end-over-end on a reciprocating shaker at 250 rpm for 24 h. Following the shaking period, the samples were centrifuged (4000 g), filtered and analyzed for metals. The optimum solid: solution ratio determined by this step was used for rest of the study.

3.2.3.2 Effect of contact time

Different time intervals ranging from 1 minute to 24 h (1 min, 2 min, 3 min, 5 min, 10 min, 15 min, 30 min, 1 h, 2 h, 6 h, 10 h, and 24 h) were examined to determine the effect of contact time on sorption of metal onto the WTR surface. WTRs were added in to AMD water to make up the optimum solid: solution ratio determined by the previous section (3.2.3.1). Treatments were shaken on a reciprocating shaker at 250 rpm for 24 h, followed by centrifugation (4000 g), filtration, and metal analysis. Analysis was done in triplicate.

After the sorption experiment, desorption studies were performed on the metal containing WTR samples for 48 hours. Supernatant from each tube was decanted, and WTR containing pellets were air dried and weighed. Then DI water was added to the
tubes so as to bring back the desired solid: solution ratio. Samples were shaken at 250 rpm on a reciprocating shaker until desorption equilibrium was reached. At specific time intervals (1 h, 6 h, 12 h, 24 h, 40 h, and 48 h), the samples were withdrawn, filtered, and analyzed for metals.

3.2.4 Development of laboratory scale WTR-filter bed column

WTR-filter bed-columns were prepared using 30 cm × 2.54 cm clear PVC pipes. Each end of the pipe was fitted with 2.54 cm dome shaped caps. Each of these caps was drilled to install inlet/outlet tubing. Glass wool and filter membranes were installed in the bottom caps to prevent the leaching of the filter media. Finally, these columns were connected with a Cole-Parmer’s Ismatec 4 channel peristaltic pump that delivers water into the columns (Figure 3-3).

![Figure 3-3. Schematic design of the laboratory scale WTR-filter bed column.](image-url)
WTRs are relatively impermeable, and to increase the porosity of the overall granular filter bed, WTRs were mixed with sand in ten different ratios: 1:1 to 1:10 respectively. Sand was thoroughly washed with DI water and dried before mixing with WTRs. Based on the results of the previous experiments, a 1:1 mixture of Al-WTR to Ca-WTR was used for this study. Hydraulic tests were conducted using DI water to select best WTR: sand ratio. The height and volume of the filter bed were measured as 10 cm and 53 mL respectively. The time required to cross one bed volume was measured for each column. Pressure of the water table above the filter media always controls the final flow rate. Therefore, the impact of height of water table, seating on top of the filter media, on output flow rate was measured for each treatment column by accumulating ten different water heights (1 cm to 10 cm) above the media.
Based on the test results, optimized WTR to sand ratio was selected to ensure an acceptable hydraulic condition and was used for rest of the study. Finally, AMD water was channeled through the WTR-filter bed media, and representative samples were collected from each bed volume up to 50 bed volumes. Collected samples were filtered and analyzed for total RCRA 8 metals plus Fe, Al, Mn, Cu and Ni (using ICP-MS), and $\text{SO}_4^{2-}$ concentration (using IC). pH measurement was also carried out for all the samples. All measurements were done in triplicate.
3.2.5 Development of field scale 208 Liter (55 gallon) drum filter

Based on the previous laboratory scale WTR filter column studies, a field scale 208 L (55 gallon) drum filter was designed (Figure 3-5). 90 kg of filter media was loaded inside the filter, which was equipped with an outlet pipe at the bottom. Inside the drum, a membrane filter was installed to prevent the leaching of filter media. Two different types of “green” filter media (1 and 2) were prepared to test the effluent flow rate. The filter media 1 was prepared by mixing sand and WTRs at a 1:6 ratio while keeping a 1:1 ratio of Al-WTR and Ca-WTR. The filter media was initially saturated with water, and after draining, 378 L (100 gallons) AMD-water, collected from Tab-Simco SRB pond, was channelled through it. During this entire process, a gravity-induced flow of AMD water, without applying any additional energy, was maintained. Filtered AMD water was collected through the outlet. To increase the flow rate of the filter media, some carbon materials were added to the sand-WTR mixture. A specific amount of carbon material was placed at the bottom of filter 2, and sand-WTR mixture was placed on top of that layer. The rest of the process was similar to filter media 1. Effluent collected from both filter media 1 and 2 was analyzed for total RCRA 8 metals plus Fe, Al, Mn, Cu and Ni (using ICP-MS), and SO$_4^{2-}$ concentration (using IC). pH measurement was also carried out for all the samples. Flow rate measurement was conducted for both the filters. All measurements were done in triplicate.
3.3 Results and Discussions

3.3.1 Characterization of Tab-Simco AMD water

Table 3-1 presents characterization data of Tab-Simco AMD water. Water samples were extremely acidic with a mean pH of 2.27± 0.2. The mean EC of the water samples was measured as 3.9± 0.03 mS/cm. Presence of a wide range of metals was found in the Tab-Simco AMD water samples. Fe concentration in the water samples was measured as 137± 5 mg/L, which exceeded USEPA permissible limit of Fe (1 mg/L) in surface water by more than 100 times (USEPA, 1994c; NCAC, 2003). Among RCRA8
metals, concentration of As (4± 0.01 mg/L), Pb (7± 1.2 mg/L), and Cr (1± 0.04 mg/L) were significantly higher than their USEPA permissible limit (0.05 ppm, 0.25 ppm, 0.5 ppm, respectively) (USEPA, 1994b; NCAC, 2003). Concentration of Zn (11± 0.9 mg/L) was also reported higher than its USEPA permissible limit (0.5 mg/L). High concentration of Al (80± 15 mg/L), Cu (4± 0.05 mg/L), Cd (1± 0.01 mg/L), Mn (33± 2.4 mg/L) and Ni (3± 0.25 mg/L) was also found in water samples. Concentration of SO_4^{2-} (2481± 50 mg/L) was also high in water samples.

Table 3-1. Physico-chemical and metal characterization of Tab-Simco water samples (n=3 for each measurement).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH</th>
<th>EC (mS/cm)</th>
<th>Al</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>SO_4^{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMD water</td>
<td>2.2</td>
<td>3.9± 0.03</td>
<td>80± 15</td>
<td>4± 0.01</td>
<td>1± 0.01</td>
<td>1± 0.04</td>
<td>4± 0.05</td>
<td>137± 5</td>
<td>33± 2.4</td>
<td>3± 0.25</td>
<td>7± 1.2</td>
<td>11± 0.9</td>
<td>2481± 50</td>
</tr>
</tbody>
</table>

3.3.2 Characterization of WTRs

Physico-chemical characterization of both Al-WTR and Ca-WTR is presented in Table 3-2. pH of Al-WTR was 5.9± 0.06, where Ca-WTR had alkaline pH (9.4± 0.3). It was clear from the result that Ca-WTR has the potential to neutralize acidity of AMD water. EC of Al-WTR and Ca-WTR was measured as 1,615± 10.2 µS/cm and 1,552± 2.7 µS/cm respectively. Al-WTR had 6.78% organic matter content, where Ca-WTR had even lower organic matter content of 0.49%. C: N ratio of Al-WTR and Ca-WTR was measured as 21 and 17 respectively. Al-WTR had 35,691 (± 114) mg/kg and 15.1 (±1.7)
mg/kg of total Al and Fe content respectively, and among them 79% Al and 45% Fe was oxalate-extractable. Total Al and Fe content of Ca-WTR were 191 (± 2.5) mg/kg and 1,200 (±8.3) mg/kg with a 46% oxalate-extractable Al and 45% oxalate-extractable Fe fraction.

Table 3-2. Physico-chemical properties of Al-WTR and Ca-WTR (n=3 for each measurement).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>OM (%)</th>
<th>C(%)</th>
<th>N(%)</th>
<th>Total Al (mg/kg)</th>
<th>Total Fe (mg/kg)</th>
<th>Oxalate Al (%)</th>
<th>Oxalate Fe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-WTR</td>
<td>5.9 ± 0.06</td>
<td>1,615 ± 10.2</td>
<td>6.78 ± 0.21</td>
<td>21.3 ± 0.83</td>
<td>0.97 ± 0.02</td>
<td>35,691 ± 114</td>
<td>15.1 ± 1.7</td>
<td>28,552 ± 93</td>
<td>6.8 ± 0.3</td>
</tr>
<tr>
<td>Ca-WTR</td>
<td>9.4 ± 0.3</td>
<td>1,552 ± 2.7</td>
<td>0.49 ± 0.01</td>
<td>10.4 ± 0.41</td>
<td>0.61 ± 0.05</td>
<td>191 ± 2.5</td>
<td>1,200 ± 8.3</td>
<td>89 ± 5.2</td>
<td>540 ± 9.1</td>
</tr>
</tbody>
</table>

Table 3-3 presents TCLP results for RCRA8 metals and Al and Fe. All RCRA8 metals were well under their corresponding allowable USEPA limit indicating that both Al-WTR and Ca-WTR can be classified as non-hazardous materials; hence can be reused. TCLP results for Al and Fe also showed that none of our WTRs were leaching any significant amount of Al and Fe.
Table 3-3. Toxicity Characteristic Leaching Protocol (TCLP) results of WTRs (n=3 for each measurement).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Cr</th>
<th>Pb</th>
<th>Hg</th>
<th>Se</th>
<th>Ag</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-WTR</td>
<td>BDL</td>
<td>0.07</td>
<td>0.006</td>
<td>0.07</td>
<td>0.06</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>166</td>
<td>1.8</td>
</tr>
<tr>
<td>Ca-WTR</td>
<td>0.005</td>
<td>BDL</td>
<td>0.002</td>
<td>0.09</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>1.03</td>
<td>16.6</td>
</tr>
<tr>
<td>EPA Limit</td>
<td>5.0</td>
<td>100</td>
<td>1.0</td>
<td>5.0</td>
<td>5.0</td>
<td>0.2</td>
<td>1.0</td>
<td>5.0</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

BDL= Below method detection limit; NR= Not regulated

3.3.3 Batch sorption experiments

3.3.3.1 Effect of solid: solution ratio on pH

Figure 3-6 presents effect of solid: solution ratio of WTR to AMD water on system pH. For Al-WTR treatments, final pH after 24h of shaking ranged from 4.73 to 3.32, which clearly showed that higher dilutions had very low impact on improving pH of AMD water. For Ca-WTR treatments, final pH ranged from 6.32 to 6.11 indicating that Ca-WTR was significantly increasing pH of AMD water. Co-application of Al-WTR and Ca-WTR increased pH of AMD water significantly for higher dilutions (1:100-1:150). pH of 6.8 and 6.6 were measured for 1:100 solid: solution ratio where Al-WTR and Ca-WTR were mixed at 1:2 and 1:1 ratio respectively. This result clearly indicated that co-application of Al- and Ca-WTR reduces the overall amount of WTRs required to treat AMD water.
3.3.3.2 Effect of solid: solution ratio on metal adsorption onto WTR surface

Adsorption data for only those metals (Fe, As, Pb, Cd, and Zn) that were present beyond their USEPA limit in Tab-Simco AMD samples are presented in this section. Effect of solid: solution ratio on Fe-adsorption onto WTR surface is presented in Figure 3-7. Final Fe concentration after 24h shaking for Al-WTR treatments ranged between 1.04 mg/L (for 1:10 dilution) and 4.77 mg/L (for 1:150 dilution), where for Ca-WTR treatments it varied between 0.3 mg/L (for 1:25 dilution) and 0.8 mg/L (for 1:150 dilution). Co-application of Al-WTR and Ca-WTR further reduced the initial Fe concentration of AMD water (137 mg/L) to 0.5 mg/L (1:100 WTR: AMD where Al-WTR and Ca-WTR were used at 1:1 ratio). All treatments containing both Al-WTR and Ca-WTR were able to reduce final Fe concentration well under the USEPA limit for Fe in surface water (1 mg/L).
Effect of solid: solution ratio on As adsorption onto WTRs surface is presented in Figure 3-8. Arsenic (As) concentration after 24h shaking for Al-WTR treatments was ranged between 0.11 mg/L (1:10 dilution) and 1.46 mg/L (1:150 dilution). As concentration for Ca-WTR treatments was ranged between 0.13 mg/L (1:25 dilution) and 0.73 mg/L (1:150 dilution). The lowest As concentration among the co-application treatments was registered by 1:100 solid: solution ratio with 1:1 Al-WTR and Ca-WTR in it, and was 0.21 mg/L.
Effect of solid: solution ratio on As-adsorption onto WTRs surface.

Figure 3-8. Effect of solid: solution ratio on As-adsorption onto WTRs surface.

Effect of solid: solution ratio on Pb-adsorption is presented in Figure 3-9. Pb concentration after 24h shaking ranged from 0.02 mg/L to 1.66 mg/L and from 0.18 mg/L to 1.81 mg/L for Al-WTR and Ca-WTR treatments respectively. Pb concentration ranged between 0.47 mg/L and 2.17 mg/L for the treatments where both WTRs were used together.
Figure 3-9. Effect of solid: solution ratio on Pb-adsorption onto WTRs surface.

Figure 3-10 presents effect of solid: solution ratio on Cr-adsorption onto WTR surface. Cr concentration after 24h shaking was ranged between 0.04 mg/L and 0.24 mg/L for all Al-WTR and Ca-WTR treatments. Cr concentration was ranged from 0.06 mg/L to 0.23 mg/L for all treatments with Al- and Ca-WTR mixture.
Figure 3-10. Effect of solid: solution ratio on Cr-adsorption onto WTRs surface.

Effect of solid: solution ratio on Zn-adsorption onto WTR surface is presented in Figure 3-11. Zn concentration after 24 h shaking was measured between 0.09 mg/L and 3.87 mg/L for Al-WTR treatments, and from 0.11 mg/L and 0.3 mg/L for Ca-WTR treatments. Again, it was found that co-application of Al-WTR and Ca-WTR could significantly reduce Zn concentration for higher dilutions.
All results from this section showed that WTRs were able to significantly remove acidity and metal concentration from AMD water. It was further incurred from the results that co-application of Al-WTR and Ca-WTR was able to reduce acidity and metal concentration from AMD water even for higher dilutions. A dilution of 1:100 WTR: AMD water with a 1:1 ratio of Al-WTR to Ca-WTR was selected for the next part of our study.

**3.3.3.3 Effect of contact time**

Within the first 3 min of adsorption, pseudo-equilibrium was achieved for all metals (Figure 3-12). Total 99%, 100%, 97%, 100% and 95% of initial Fe, As, Pb, Cr, and Zn content of AMD water got adsorbed onto WTR surface respectively. Mean pH of all treatments was recorded as 6.9± 0.2.
Result of desorption study, initiated right after the adsorption study, is presented in Figure 3-13. It was noticed that metals were strongly bound on WTR surface and the binding was irreversible. There was no significant impact of contact time (0-48 h) on desorption of metals from WTR particles using DI water. The percentage of metal desorption was always <5% of their previously adsorbed amount.

Figure 3-12. Adsorption of (a) Fe, (b) As, (c) Pb, (d) Cr, and (e) Zn on WTRs, as a function of contact time.
Figure 3-13. Metal(s) desorption from WTR particles using DI water, as a function of desorption time

3.3.4 Laboratory scale WTR-filter bed column.

Batch sorption experiments showed that Al-WTR and Ca-WTR could be used as AMD remediation agents. A 1:1 ratio of Al-WTR to Ca-WTR was selected for further scaled up studies. 30 cm x 2.54 cm clear PVC pipes were used to build WTR-filter bed columns. As WTRs are impermeable to water, they were mixed with sand at ten different ratios. A bed volume of 53 mL was used for our study which was equivalent to 10 cm bed height. A series of hydraulic tests were performed to select best WTR: sand ratio in terms of producing best hydraulic condition and AMD remediation at a same time. Results of selected hydraulic tests are presented in Figures 3-14 and 3-15. Time taken to cross one bed volume ranged from 6.18 min to 1.35 min for different WTR: sand ratios (Figure 14). It was seen that sand-WTR mixtures with higher WTR fraction were resulted in lower effluent flow rate. A ratio of 1:6 WTR to sand was selected for the next phase of
study as it was providing a desirable outlet flow rate (15mL/min) while having 10 cm water accumulation on the top of it (Figure 3-15).

![Bar chart showing time taken to cross one bed volume at different WTR to sand ratios.]

Figure 3-14. Time taken to cross one bed volume at different WTR to sand ratios.
After optimizing the filter bed composition, AMD water was channeled through the filter at a flow rate of 15 mL/min. Effluents were periodically collected at different bed volumes and the result is presented in Table 3-4. It was noticed that for up to 20 bed volumes, the filter media significantly removed acidity and metal concentrations, but after that its overall performance dropped. The result indicated that after treating 20 bed volume equivalent of AMD water the filter materials were exhausted. Rust formation inside the filter media during the treatment can be seen in Figure 3-16, which indicated the removal of Fe from AMD water. pH of filtered AMD water was recorded as high as 6.15 (at 1 bed volume). During the study, significant metal removal was observed from the AMD water. A maximum 36% removal of sulfate was noticed during the study.
Table 3-4. Metal and Sulfate removal by WTR filter bed column over time (n=3 for each measurement).

<table>
<thead>
<tr>
<th>Name</th>
<th>pH</th>
<th>Al (ppm)</th>
<th>As (ppm)</th>
<th>Cu (ppm)</th>
<th>Fe (ppm)</th>
<th>Ni (ppm)</th>
<th>Pb (ppm)</th>
<th>Zn (ppm)</th>
<th>Mn (ppm)</th>
<th>SO(_4^{2-}) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1BV</td>
<td>6.15</td>
<td>0.21</td>
<td>BDL</td>
<td>0.03</td>
<td>0.36</td>
<td>0.6</td>
<td>0.21</td>
<td>0.45</td>
<td>0.1</td>
<td>1661</td>
</tr>
<tr>
<td>2BV</td>
<td>6.12</td>
<td>BDL</td>
<td>0.08</td>
<td>0.07</td>
<td>0.41</td>
<td>0.79</td>
<td>0.04</td>
<td>0.72</td>
<td>0.1</td>
<td>1718</td>
</tr>
<tr>
<td>5BV</td>
<td>6.13</td>
<td>0.7</td>
<td>BDL</td>
<td>0.1</td>
<td>0.39</td>
<td>0.67</td>
<td>0.23</td>
<td>0.94</td>
<td>0.1</td>
<td>1675</td>
</tr>
<tr>
<td>10BV</td>
<td>5.73</td>
<td>1.3</td>
<td>BDL</td>
<td>0.1</td>
<td>0.54</td>
<td>0.97</td>
<td>BDL</td>
<td>1.34</td>
<td>0.1</td>
<td>1602</td>
</tr>
<tr>
<td>15BV</td>
<td>5.81</td>
<td>1.4</td>
<td>0.03</td>
<td>0.1</td>
<td>0.5</td>
<td>0.79</td>
<td>0.07</td>
<td>1.17</td>
<td>0.1</td>
<td>1580</td>
</tr>
<tr>
<td>20BV</td>
<td>5.92</td>
<td>3</td>
<td>0.03</td>
<td>0.33</td>
<td>0.74</td>
<td>0.44</td>
<td>0.69</td>
<td>1</td>
<td>0.2</td>
<td>1587</td>
</tr>
<tr>
<td>25BV</td>
<td>4.09</td>
<td>34</td>
<td>0.82</td>
<td>0.33</td>
<td>1.04</td>
<td>0.25</td>
<td>0.42</td>
<td>1.65</td>
<td>0.2</td>
<td>1573</td>
</tr>
<tr>
<td>40BV</td>
<td>4.14</td>
<td>23.7</td>
<td>0.55</td>
<td>0.28</td>
<td>0.95</td>
<td>1.28</td>
<td>0.85</td>
<td>1.55</td>
<td>0.2</td>
<td>1672</td>
</tr>
<tr>
<td>50BV</td>
<td>4.32</td>
<td>9</td>
<td>0.16</td>
<td>0.36</td>
<td>0.74</td>
<td>1.05</td>
<td>1.2</td>
<td>1.4</td>
<td>0.3</td>
<td>1624</td>
</tr>
<tr>
<td>Raw AMD</td>
<td>2.27</td>
<td>80</td>
<td>4</td>
<td>137</td>
<td>3</td>
<td>7</td>
<td>11</td>
<td>33.19</td>
<td>2481</td>
<td></td>
</tr>
<tr>
<td>Max Removal% achieved</td>
<td>100</td>
<td>100</td>
<td>99.3</td>
<td>99.7</td>
<td>91.6</td>
<td>100</td>
<td>95.9</td>
<td>99.7</td>
<td>36.3</td>
<td></td>
</tr>
</tbody>
</table>

BDL= Below method detection limit; BV= Bed Volume
3.3.5 Field scale WTR-based drum filter

Both filter media 1 and 2 resulted in similar chemical treatment in terms of removal of acidity and metal concentrations from AMD water (Table 3-5). Only difference between both the media was observed in their effluent flow rate. The flow rate of filter media 1 was measured as 3.78 L/min (1 gallon/min), while the flow rate of filter media 2 was over 15 L/min (4 gallons/min). Both the filter media 1 and 2 improved the AMD pH significantly, and measured as 7.1± 0.03 and 7.8± 0.05 respectively. Concentration of metals such as Fe, As, Cr, Pb and Zn were found to be well under their USEPA permissible limits in all effluent samples. Filter media 1 and 2 removed 20% and 44% of the initial $SO_4^{2-}$ concentration respectively. A visual comparison of AMD samples before and after filtration is presented in Figure 3-17.
Table 3-5. Characterization of Tab-Simco AMD before and after filtration (n=3 for each measurement).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw AMD from Tab-Simco</th>
<th>Filtered AMD</th>
<th>Filter Media 1</th>
<th>Filter Media 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.27± 0.2</td>
<td>7.1± 0.03</td>
<td>7.8± 0.05</td>
<td></td>
</tr>
<tr>
<td>EC (ms/cm)</td>
<td>3.9± 0.03</td>
<td>2.3± 0.01</td>
<td>2.5± 0.01</td>
<td></td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>137± 5</td>
<td>0.04± 0.001</td>
<td>0.06± 0.003</td>
<td></td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>80± 15</td>
<td>0.5± 0.03</td>
<td>0.7± 0.01</td>
<td></td>
</tr>
<tr>
<td>Ni (mg/L)</td>
<td>3± 0.25</td>
<td>0.04± 0.001</td>
<td>0.04± 0.001</td>
<td></td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>11± 0.9</td>
<td>0.01± 0.001</td>
<td>0.01± 0.001</td>
<td></td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>7± 1.2</td>
<td>BDL</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>As (mg/L)</td>
<td>4± 0.01</td>
<td>BDL</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>Cr (mg/L)</td>
<td>1± 0.04</td>
<td>BDL</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>4± 0.05</td>
<td>BDL</td>
<td>BDL</td>
<td></td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>33.19± 0.38</td>
<td>0.3± 0.01</td>
<td>0.2± 0.01</td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>2481± 50</td>
<td>1984± 15</td>
<td>1370± 8</td>
<td></td>
</tr>
</tbody>
</table>

BDL = Below method detection limit
Figure 3-17. Visual Comparison of AMD water before and after filtration through WTR-based filter media.

No gypsum saturation was visibly noticed inside the filter media after the AMD filtration process. All experimental parameters were also inserted in the Visual MINTEQ (version 3.1) software to check whether gypsum saturation is likely to occur inside the filter media. MINTEQ results also confirmed that gypsum saturation is unlikely to happen as saturation index was always negative.

3.4 Conclusions

This study demonstrated that Al-and Ca-WTR-based filters have the potential for remediation of AMD-impacted water. Co-application of Al-WTR and Ca-WTR has demonstrated the acid neutralization and metal removal capabilities of the filter media while treating AMD water. The field scale 208 Liter drum filter was able to significantly
remove acidity and metal concentration from Tab-Simco AMD water, and has proved the efficiency of this technique. As we have discussed earlier, WTRs are primarily landfilled. This study showed that a second life could be given to this waste product, which makes the whole technology “green”. There is no cost associated with obtaining WTRs (except the transportation cost from drinking water treatment plant to lab), which significantly lowered the overall expense of the entire technology. Also, this whole technique is environmentally sustainable as WTRs don’t have any adverse impact on environment. Hence, the study showed that WTR-based filter could effectively and cost-efficiently remediate AMD-impacted water.
3.5 References


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CHAPTER 4

Removal of Acidity and Metal Concentrations from Acid Mine Drainage (AMD)-Impacted Soils Amended with Drinking-Water Treatment Residuals: Soil Incubation Study

[This chapter has been submitted to a journal]

Abstract

Mining industries are responsible for a wide range of environmental concerns and generation of acid mine drainage (AMD), and acid sulfate soils are definitely the most common and concerning among them. Due to their acidic pH and high metal concentrations, both AMD and acid sulfate soils can completely destroy the local ecosystem. Proper post-mining management practices can control AMD-pollution. Current AMD-impacted soil treatment technologies are time-intensive and very expensive. This study evaluated the potential of a cost-effective and environment-friendly technology in treating AMD-impacted soils that utilizes the metal binding and acid-neutralizing capacity of an industrial by-product, namely drinking water treatment residuals (WTRs). Two types of locally generated WTRs: Al-WTR and Ca-WTR were used for this study. AMD-impacted soils were collected from the Tab-Simco coal mine in Carbondale, IL. Soils collected from the Tab-Simco mine were highly acidic and possessed high concentration of metals such as Fe (41,018 mg/kg), Ni (178 mg/kg), and As (131 mg/kg). A 60 day laboratory soil incubation study was performed by mixing AMD soils with WTRs at different rates (2.5%, 5% and 10% w/w respectively). Results
showed that due to WTRs amendment, soil pH was increased from 2.68 to 6.86. Results also showed that due to WTRs amendment, 94% soluble Fe-fraction, and 85% exchangeable Fe-fraction was decreased over time. This study clearly showed that WTRs amendment on AMD-impacted soil can significantly reduce acidity and soluble and exchangeable metal fractions (hence, metal leachability and bioavailability). The study demonstrated the high potential of success of this innovative, cost-effective, and ecologically sustainable technology in remediating AMD-impacted soils.

**Keywords:** Acid mine drainage, acid sulfate soil, drinking-water treatment residuals, soil amendment, soil remediation.
4.1 Introduction

A series of negative environmental consequences are directly associated with mining activities worldwide and generation of acid mine drainage (AMD), and acid sulfate soils are one the most concerning problems among them. AMD, an extremely acidic and metal-rich solution, is produced when pyrite oxidizes in the presence of oxygen and water. Soils exposed to AMD become highly erosion prone, and known as acid sulfate soils. Due to the low pH (2-4), metals present in soils become more soluble and bioavailable; hence, acid sulfate soils eventually become unsuitable to support biodiversity (Stumm and Morgan, 1981; Ferguson and Erickson, 1988; U.S. Forest Service 1993; USEPA, 1994). Adaptation of proper post-mining management practices plays an important role in controlling AMD-pollution. Although federal regulations such as the Surface Mining Control and Reclamation Act (SMCRA) of 1977 have imposed strict regulations for reclaiming mine land, still more than 557,000 abandoned mines exist in the US, many of which are actively generating AMD (U.S. Forest Service, 2005). A detailed discussion about current AMD management practices and their pros and cons was presented in one of our recent publications (RoyChowdhury et al., 2015). The search for more affordable and efficient AMD remediation technology is ongoing.

4.1.1 Study Site

Our study area, the Tab-Simco site, is an abandoned coal mine located approximately 10 km southeast of Carbondale, Illinois (Figure 4-1). This area underwent extensive underground coal mining (1890-1955) and surface coal mining (1960’s and
1970’s) for decades. More than 40,000 m³ of contaminated underground mine pool is currently present in this area and is coming out through the fractures and cracks (Smith, 2002; Behum et al., 2012; Behum et al., 2013). Many studies have reported that approximately 150 m³ of AMD is being produced in this area each day (Smith, 2002). Approximately a 36,421 m² area, devoid of any plantation, has been created due to the AMD pollution, which is often termed as “kill zone” (Figures 4-2 and 4-3) (Smith, 2002; Segid, 2010; Behum et al., 2011; Behum et al., 2012; Behum et al., 2013). In 1996, the Tab-Simco site was named as one of the highest AMD contaminated areas in the mid-continent region (Smith, 2002; Segid, 2010). In 2007, an anaerobic sulfate reducing bioreactor (SRB) was constructed at this site (Behum et al., 2010; Segid, 2010; Behum et al., 2011; Behum et al., 2012; Burns et al., 2012; Behum et al., 2013), but it failed in 2011 (Behum et al., 2013). The failure of the SRB might have happened due to the death of the bacterial culture.
Figure 4-1. Location of Tab-Simco site (RoyChowdhury et al., Accepted).

Figure 4-2. Google Earth image of Tab-Simco site (captured on 10/14/14).
4.1.2 Water Treatment Residuals (WTRs)

Drinking water treatment processes generate a waste byproduct commonly known as drinking water treatment residuals (WTRs). One of three different kinds of WTRs: Al-WTR, Fe-WTR or Ca-WTR is produced depending on the nature of the added flocculation and coagulation agents (alum, iron salts or lime). Approximately 2 mega tons of WTRs are produced in the US daily and end up in landfill sites (Prakash and Sengupta, 2003). Al-WTR, Fe-WTR, and Ca-WTR are primarily composed of amorphous aluminum oxides and hydroxides, iron oxides and hydroxides and calcium carbonate respectively. Due to their unique composition, WTRs are able to readily adsorb a number
of heavy metals such as Cu, Pb, and Zn and other environmental contaminants such as perchlorate, phosphate, and arsenate (Makris et al., 2004; Makris et al., 2006a; Makris et al., 2006b, Hardy et al., 2007; Hardy, 2008). WTRs typically have small particle size and extensive micropore networks, giving them high specific surface. Numerous studies have shown that the WTRs can be used as soil amendments and are not toxic or harmful to the environment (Sarkar et al., 2007). WTRs can be obtained free of charge from drinking water treatment plants and have great potential for reuse.

4.1.3 Objective of the study

This main objective of this study was to evaluate the potential of WTRs as a soil amendment for AMD-impacted soils. This study was designed to test and optimize the application rate of Al-WTR and Ca-WTR for reduction of acidity and metal concentration from AMD-impacted soils.

4.2 Materials and Methods

4.2.1 Soil collection and characterization

Our previous study characterized soil and water samples from entire Tab-Simco area (RoyChowdhury et al., accepted). Soil samples collected from different locations of “kill-zone” were used for this study. Soils were collected at a depth of 0-15 cm and were mixed thoroughly following established USEPA protocols (Plumb, 1981). Sample collection was conducted in Fall, 2014. Collected soils were air dried, ground and sieved (2 mm). Soil pH and EC measurements were conducted following standard protocols.
using an Oakton ion 510 series pH meter and an Orion conductivity meter respectively (Sparks, 1996). Soil samples were digested following USEPA 3050B soil digestion method (USEPA, 1996) using a Linx wireless digestion system. Total concentrations of RCRA8 (Resource Conservation and Recovery Act) metals (Ag, As, Ba, Cd, Cr, Hg, Pb, and Se), Fe, Al, Ni, Cu and Mn in digested samples were analyzed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, X-series, Thermo Scientific).

4.2.2 WTR collection and characterization

Two locally generated WTRs were used for this study: Al-WTR from City of Carbondale water treatment plant, IL, and Ca-WTR from Saline Valley water treatment plant, IL. WTRs were air-dried, ground and sieved. pH, EC, and organic matter content of both WTRs were analyzed following standard methods (Klute, 1996; Sparks, 1996). Total C and N concentration of both WTRs were analyzed using an Elementer Vario EL-III CHNS analyzer. Oxalate extractable Al, and Fe concentrations of both WTRs were measured following ammonium oxalate extraction method (McKeague et al., 1971). Total Al and Fe concentrations of both WTRs were measured using USEPA 3050B acid digestion method (USEPA 1996). Toxicity Characteristic Leaching Protocol (TCLP) of these WTRs was conducted following USEPA Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846).

4.2.3 Soil incubation study

100 gram of soil was placed in each polythene bags (Fig 4-4). For one set of treatment, soils were thoroughly mixed with three rates of Al-WTR: 2.5%, 5% and 10%
(maximum land application rate) w/w. For another set of treatments, Al-WTR and Ca-WTR were first mixed at 1:1 ratio, and then soil samples were amended with this WTR mix at 2.5%, 5% and 10% application rate w/w. All bags were maintained at 70% of soil’s water holding capacity. All analyses were done in triplicate. Incubation study was conducted for 60 days. Periodic samplings were carried out on 0, 30, and 60 days. Samples were again air-dried, ground, and analyzed for pH.

4.2.3.1 Sequential Extraction

Sequential extraction of metals were performed for all periodically collected soil samples following methods reported by Chunguo and Zihui (1988) with some modifications proposed by Datta and Sarkar (2004). The extraction method was used to determine the following operationally defined metal fractions: water soluble phase (DI-water extractable), exchangeable phase (NH₄Cl extractable), Al/Fe bound phase (NaOH extractable), Ca/Mg bound phase (H₂SO₄ extractable), organic matter bound phase (H₂O₂ extractable), and residual phase (conc. HNO₃ extractable). Extracts were filtered and analyzed for metals using an ICP-MS. All analyses were done in triplicate.
4.3 Results and Discussion

The characterization result of Tab-Simco soil is presented in Table 4-1. The soil was highly acidic with a mean pH of 2.68 ± 0.05. Electrical conductivity of soil was 2.34 ± 0.18 ms/cm. A detailed characterization result of Tab-Simco soil was reported previously (RoyChowdhury et al., accepted). Fe concentration was very high in Tab-Simco soil (41,018 ± 9 mg/kg). High concentrations of Ni (178 ± 2.6 mg/kg) and As (131 ± 20 mg/kg) were also measured. Metals that were found in higher concentrations in Tab-Simco soil are only reported here.
Table 4-1. Selected physico-chemical property and metal concentrations of Tab-Simco soil samples (n=3).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH</th>
<th>EC (ms/cm)</th>
<th>Fe (mg/kg)</th>
<th>As (mg/kg)</th>
<th>Ni (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMD-Soil</td>
<td>2.68 ± 0.05</td>
<td>2.34 ± 0.18</td>
<td>41,018 ± 9</td>
<td>131 ± 20</td>
<td>178 ± 2.6</td>
</tr>
</tbody>
</table>

Results from Al-WTR and Ca-WTR characterization tests are presented in Table 4-2. Ca-WTR had a pH of 9.4, which indicated that it could be used as a liming agent. pH of Al-WTR was measured as 5.9. EC measurements were 1,615 and 1,552 µS/cm for Al-WTR and Ca-WTR respectively. Organic matter content of Al-WTR and Ca-WTR was 6.78% and 0.49% respectively. Both WTRs had C: N ratio at a range between 17 and 21, which indicates that both WTRs possessed a significant pool of N, which is available for plant uptake (Makris, 2004). Al-WTR had 28,552 mg/kg oxalate extractable Al and 6.8 mg/kg oxalate extractable Fe, which is 79% of its total Al content and 45% of its total Fe content respectively. Approximately 45% of total Al and Fe content of Ca-WTR was oxalate extractable. Higher oxalate extractable Al and Fe fractions are an indication of the amorphous nature of WTR (Makris, 2004).
Table 4-2. Selected physico-chemical properties of Al-WTR and Ca-WTR (n=3).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>OM (%)</th>
<th>C(%)</th>
<th>N(%)</th>
<th>Total Al (mg/kg)</th>
<th>Total Fe (mg/kg)</th>
<th>Oxalate Al (mg/kg)</th>
<th>Oxalate Fe (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-WTR</td>
<td>5.9 ±0.06</td>
<td>1,615 ±10.2</td>
<td>6.78 ±0.21</td>
<td>21.3 ±0.83</td>
<td>0.97 ±0.02</td>
<td>35,691 ±114</td>
<td>15.1 ±1.7</td>
<td>28,552 ±93</td>
<td>6.8 ±0.3</td>
</tr>
<tr>
<td>Ca-WTR</td>
<td>9.4 ±0.3</td>
<td>1,552 ±2.7</td>
<td>0.49 ±0.01</td>
<td>10.4 ±0.41</td>
<td>0.61 ±0.05</td>
<td>191 ±2.5</td>
<td>1,200 ±8.3</td>
<td>89 ±5.2</td>
<td>540 ±9.1</td>
</tr>
</tbody>
</table>

Results from the TCLP test for Al-WTR and Ca-WTR are presented in Table 4-3. TCLP results showed that both Al-WTR and Ca-WTR can be safely land-applied because metal leaching under normal precipitation conditions were well below EPA limits. Noticeably, none of the WTRs were leaching any significant amount of Al and Fe during the TCLP test.
Table 4-3. Results from TCLP test for Al-WTR and Ca-WTR.

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Cr</th>
<th>Pb</th>
<th>Hg</th>
<th>Se</th>
<th>Ag</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BDL</strong></td>
<td>0.07</td>
<td>0.06</td>
<td>0.07</td>
<td>0.06</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>166</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Ca-WTR</td>
<td>0.005</td>
<td>BDL</td>
<td>0.002</td>
<td>0.09</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>1.03</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>EPA Limit</td>
<td>5.0</td>
<td>100</td>
<td>1.0</td>
<td>5.0</td>
<td>5.0</td>
<td>0.2</td>
<td>1.0</td>
<td>5.0</td>
<td>NR</td>
<td>NR</td>
</tr>
</tbody>
</table>

BDL= Below Method Detection Limit; NR= Not Regulated.

Change of pH for all treatments over 60 days incubation period is presented in figure 4-5. It was clearly visible from the results that soil pH increased significantly for all treatments amended with Al- and Ca-WTR mixture in compare to control. Although mean pH for all treatments (excluding control) was 4.3± 1.6 and 4.5± 1.69 after 30 and 60 days respectively, mean pH for treatments with WTR mix (1:1 Al and Ca) was 5.6± 1.2 and 5.84± 1.3 after 30 and 60 days respectively. Soil incubation study showed that in 60 days, best soil pH was measured for 5% WTR [1:1 Al and Ca] and 10% WTR [1:1 Al and Ca] treatment, which was 6.35± 0.4 and 6.86± 0.2 respectively.
Since the concentration of Fe was very high in Tab-Simco acid sulfate soil, only the sequential extraction results for soil Fe fractionation are presented in figure 4-6. Results showed that the majority of the Fe present in unamended Tab-Simco soil (control) was in the form of soluble (25%) and exchangeable (33%) fractions. Fe/Al-bound, Ca/Mg-bound, organic matter bound, and residual Fe fractions were measured as 30%, 6%, 2.5%, and 3% respectively in unamended Tab-Simco soil (control) at time zero. Application of WTRs significantly decreased the soluble and exchangeable Fe fractions. It was found that 68% and 80% reduction of soluble fraction was achieved for the 5% Al-WTR amendment at day 30 and at day 60 respectively. 10% Al-WTR amendment decreased the soluble fraction by 60% and 68% at day 30 and day 60 respectively. A similar thing was also noticed for the exchangeable fraction. Over 60 days, the exchangeable fraction was decreased by 76% and 38% with 5% Al-WTR and
10% Al-WTR amendment respectively. The best result was achieved by 5% WTR [1:1 Al and Ca] amendment, where 94% of soluble fraction and 85% of exchangeable fraction was decreased over 60 days. With the decrease of soluble and exchangeable fractions, an increase of Fe/Al-bound and Ca/Mg-bound fractions were also noticed. The highest Fe/Al-bound fraction (70%) was found in 5% Al-WTR amendment at day 60. A 25% Ca/Mg-bound fraction was found in both 5% WTR [1:1 Al and Ca] and 10% WTR [1:1 Al and Ca] at day 60. It was clear from the results that soluble and exchangeable fractions were getting adsorbed on WTR surfaces; hence, an increase in Fe/Al-bound and Ca/Mg-bound fractions was observed over time. Soluble fraction of metal is subjected to surface run-off or leaching very easily. Furthermore, soluble and exchangeable metal fractions are considered as bioavailable fraction; hence, they are toxic to living organisms. Our study showed that WTR amendment can significantly decrease soluble and exchangeable metal fractions and can convert those to Fe/Al-bound and Ca/Mg-bound fractions, which are stable and non-toxic to living organisms. WTR amendments such as 5% WTR [1:1 Al and Ca] and 10% WTR [1:1 Al and Ca] reduced the soluble and exchangeable fractions below 10% level.
Figure 4-6. Effect of WTR on soil iron fractionation in Tab-Simco acid sulfate soil at (a) Day 0, (b) Day 30, and (c) Day 60. Control soil had no WTR amendment. (n=3).
4.4 Conclusions

The study showed that co-application of Al-WTR and Ca-WTR can effectively increase pH and decrease metal availability (hence, leachability) in acid sulfate soils. Soluble and exchangeable fractions of metals are readily available for plant uptake; hence, increase the potential of metal toxicity in organisms. Our study showed that Al- and Ca-WTRs significantly lowered the soluble and exchangeable fractions of metals; hence, the WTRs were able to lower metal toxicity in acid sulfate soils. As we mentioned earlier, there is no cost associated with obtaining WTRs from drinking-water treatment plants, and our study showed that a second life can be provided to this industrial waste byproduct. Results of this study showed that 5% and 10% WTR application rate with a 1:1 mix of Al-WTR and Ca-WTR in it can significantly reduce acidity and metal toxicity from AMD-impacted soil. This study clearly showed that low cost WTR amendment has the potential to improve the quality of AMD-impacted soil.
4.5 References


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CHAPTER 5

Control of Erosion and Metal Leaching from Acid Mine Drainage (AMD)-Impacted soil using drinking-water treatment residuals and Vetiver grass

[This chapter has been submitted to a journal]

Abstract

Mining activities create a number of negative environmental consequences and most concerning among them are the generation of acid mine drainage (AMD) and acid sulfate soils. Local ecosystems become severely impacted due to the AMD pollution. It is very important to implement appropriate post-mining AMD management practices to minimize environmental impacts such as high soil acidity, soil erosion, and metal leachability. The objective of this study was to develop a cost-effective and environment-friendly “green” technology for the treatment of AMD-impacted soils. This study utilized the metal binding and acid-neutralizing capacity of an industrial by-product, namely drinking water treatment residuals (WTRs), and the extensive root system of a metal hyper-accumulating, fast-growing, non-invasive, high biomass perennial grass, vetiver (Chrysopogon zizanioides L.) to prevent soil erosion. Aluminum (Al)-based and calcium (Ca)-based WTRs were used to treat AMD-impacted soil collected from the Tab-Simco coal mine in Carbondale, IL. Tab-Simco is an abandoned coal mine, and soil collected this area was highly acidic and possessed a number of metals such as Fe, Ni, Zn, Pb, and As at high concentrations. A greenhouse column study was performed over four months
using 5% and 10% w/w WTR application rates. Vetiver grass was grown on the soil-WTR mixed media. Turbidity and Total suspended solids (TSS) analysis of leachates showed that soil erosion decreased in the soil-WTR-Vetiver system over time. Difference in pH of leachate samples collected from control (3.06) and treatment (6.71) columns at day 120 indicated high acidity removal potential of this technology. A scaled up simulated field study was performed using 5% WTR application rate and Vetiver. Soil pH increased from 2.69 to 7.2, and soil erosion indicators such as turbidity (99%) and TSS (95%) in leachates were significantly reduced. Results from the study showed that this “green” remediation technique has the potential to effectively treat AMD–impacted soils.

**Keywords:** Acid Mine Drainage, Acid Sulfate Soil, Drinking-Water Treatment Residuals, Vetiver grass, Green Remediation.
5.1 Introduction

Pyrite (FeS$_2$), in the presence of oxygen and water, oxidizes and generates a metal-rich acid solution: acid mine drainage (AMD). Acid sulfate soils result during this process as well. Both AMD and acid sulfate soils can severely impact the surrounding ecosystem and can wipe out the local biodiversity. Acid sulfate soils can be characterized as structurally unstable soils that are extremely erosion prone (Ferguson and Erickson, 1988; U.S. Forest Service, 1993; USEPA, 1994). Implementation of effective post-mining management practices is very important as abandoned mine sites can significantly accelerate the production of AMD. Currently, a number of federal regulations such as the Surface Mining Control and Reclamation Act (SMCRA) of 1977 are in effect to oversee the post-mining land reclamation processes. According to the US Forest Service (2005), more than 557,000 abandoned mines are still present in the US, and many of these mines are active sources of AMD. A number of AMD management practices are available (RoyChowdhury et al., 2015), but they are either very costly or ineffective for controlling AMD over a long period of time. Hence, it is necessary to develop more effective, sustainable, and affordable AMD treatment processes.

5.1.1 Study Site

The Tab-Simco coal mine was selected as the area of study. Tab-Simco is a heavily AMD-impacted abandoned mine located in Carbondale, IL. The area was extensively mined between 1890 and 1955 (underground mining) and again in the 1960’s and 1970’s (surface mining). AMD from the mine, with its low pH, high metals, and
sulfate concentration, still discharges at a rate of approximately 150 m$^3$/day, and has significantly impacted the surrounding ecosystem. The AMD discharge has created a 36,421 m$^2$ “kill zone”-devoid of vegetation and biodiversity-in its path (Fig 5-1) (Smith, 2002; Segid, 2010; Behum et al., 2011; Behum et al., 2012; Behum et al., 2013). Due to the severity of the contamination, in 1996, the Tab-Simco site was declared as one of the highest AMD-contaminated locations in the mid-continent region (Smith, 2002; Segid, 2010). Although an anaerobic sulfate reducing bioreactor (SRB) was built at the Tab-Simco site in 2007 (Behum et al., 2010; Segid, 2010; Behum et al., 2011; Behum et al., 2012; Burns et al., 2012; Behum et al., 2013), the SRB failed in 2011 because of the death of the sulfate-reducing bacterial culture (Behum et al., 2013).

Figure 5-1. Google Earth image of Tab-Simco site (captured on 10/14/14)
5.1.2 Drinking-Water Treatment Residuals (WTRs)

Drinking-water treatment residuals (WTRs), a waste by-product, are generated in the drinking-water treatment facilities. Different types of flocculating and coagulating agents such as alum, iron salts, and lime are added to water during the drinking-water treatment process to settle out the larger particles. Depending upon the type of the applied flocculation and coagulation agent, aluminum-based (Al-WTR), iron-based (Fe-WTR), or calcium-based (Ca-WTR) WTR is generated. Daily WTR production in different drinking-water treatment facilities all over the US is over 2 mega tons (Prakash and Sengupta, 2003). WTRs are mostly sent for landfilling. WTRs are composed of amorphous Al- or Ca- or Fe-oxides/hydroxides, have very small particle sizes (nM to mM), and extensive microporous structures. Studies have shown that WTRs are good adsorbent for a number of heavy metals (Hardy et al., 2007; Hardy, 2008). Sustainable use of WTRs as soil amendment without causing any harm to the environment is also well documented (Sarkar et al., 2007; Nagar et al., 2014; Nagar et al., 2015).

5.1.3 Vetiver Grass

Vetiver (Chrysopogon zizanioides L.) is a high biomass, fast-growing, perennial grass, which possesses a large (3-4 m), deep, penetrating, massive and complex root system. Vetiver was first promoted by the World Bank for soil and water conservation in India in the mid-1980s (Dalton et al., 1996). As vetiver grass does not produce seeds and stolons, it is considered as noninvasive species. Vetiver has been grown in Louisiana for well over 100 years without showing any signs of invasiveness (Truong, 2000). Vetiver
has been applied widely for applications such as mine dump rehabilitation, slope stabilization, wind and water barriers, seepage control, production of essential oils, and water treatment throughout the world (Du and Truong, 2003; Truong et al., 2003; Roongtanakiat et al., 2007). Vetiver’s ability to tolerate high acidity, metal concentrations, and different environmental parameters is presented in Table 5-1. Use of Vetiver on AMD-impacted soil can be extremely useful for preventing soil erosion.

**Table 5-1. Summary of vetiver grass’s ability to tolerate different environmental parameters and heavy metal concentrations (Du and Truong, 2003; Truong and Hart, 2001; Roongtanakiat et al., 2007; Shu, 2003).**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tolerance Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>2.5–10.5</td>
</tr>
<tr>
<td>Acidity Tolerance Index</td>
<td>90.75%</td>
</tr>
<tr>
<td>Arsenic (mg/kg)</td>
<td>100–250</td>
</tr>
<tr>
<td>Copper (mg/kg)</td>
<td>35–190</td>
</tr>
<tr>
<td>Chromium (mg/kg)</td>
<td>200–600</td>
</tr>
<tr>
<td>Nickel (mg/kg)</td>
<td>50–100</td>
</tr>
<tr>
<td>Mercury (mg/kg)</td>
<td>&gt; 6</td>
</tr>
<tr>
<td>Lead (mg/kg)</td>
<td>1500–3125</td>
</tr>
<tr>
<td>Selenium (mg/kg)</td>
<td>&gt; 75</td>
</tr>
<tr>
<td>Iron (mg/kg)</td>
<td>683–63920</td>
</tr>
<tr>
<td>Zinc (mg/kg)</td>
<td>750–3400</td>
</tr>
<tr>
<td>Manganese (mg/kg)</td>
<td>3220</td>
</tr>
<tr>
<td>Altitude</td>
<td>2800 m</td>
</tr>
<tr>
<td>Frost (ground temperature)</td>
<td>~10°F (-14°C)</td>
</tr>
<tr>
<td>Heat</td>
<td>&gt;110°F (43°C)</td>
</tr>
<tr>
<td>Drought (w/o effective rain)</td>
<td>15 months</td>
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</tbody>
</table>
5.1.4 Objective of the study

The main objective of this study was to improve the quality of the AMD-impacted soil of Tab-Simco by removing acidity, metal leaching, and erosion potential using a combination of Al- and Ca-WTR and vetiver grass.

5.2 Materials and Methods

5.2.1 Soil collection and characterization

Soil samples were collected from various locations of the “kill-zone” in Fall, 2014. Samples were collected from 0-15 cm depth and were mixed together. All samples were completely air-dried, ground, and sieved (2 mm). pH and EC of soil samples were analyzed following standard protocols (Sparks, 1996). Soil samples were digested following USEPA 3050B acid digestion method (USEPA, 1996), and digests were filtered and analyzed for total concentrations of RCRA8 (Resource Conservation and Recovery Act) metals (Ag, As, Ba, Cd, Cr, Hg, Pb, and Se), plus Fe, Al, Ni, Cu, and Mn using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). A detailed characterization result of the Tab-Simco soils was documented previously (RoyChowdhury et al., accepted).

5.2.2 WTR collection and characterization

Locally produced aluminum (Al-WTR) and calcium-based (Ca-WTR) WTRs were used for this study. Al-WTR was collected from the City of Carbondale water treatment plant, IL, and Ca-WTR was collected from the Saline Valley water treatment
plant, IL. WTRs were air-dried, ground, and sieved (2 mm). Toxicity Characteristic Leaching Protocol (TCLP) test following USEPA 1311 Method was performed for WTR samples. A detailed characterization result for WTR samples was also discussed earlier.

5.2.3 Greenhouse column study

Greenhouse columns were prepared using 45 cm × 15 cm PVC pipes. Each column was fitted with a drainage outlet at the bottom that was connected to a leachate collection bottle. Each column was filled with 15 cm of soil-WTR mix over a 25 cm of play sand and 2.5 cm of marbles (Fig 5-2). Results from our previous soil incubation study showed that 5% and 10% WTR amendment rates can effectively improve the quality of Tab-Simco soil. One batch of treatment was prepared by mixing Tab-Simco soils with Al-WTR at 5% and 10% w/w application rate. For another batch of treatment, first Al-WTR and Ca-WTR were mixed together at a 1:1 ratio, and then Tab-Simco soil was amended with this mixture at 5% and 10% application rate. Soil-WTR mixture was allowed to equilibrate for one month. Following one month of soil-WTR equilibrium period, vetiver and Fescue (control plant) grasses were planted on top of the soil layer. One set of control with no WTR amendment and plantation was used. Another set of control with no WTR amendment but with vetiver grass was also used. Columns were maintained at 70% water holding capacity. The greenhouse study was conducted for four months. Each treatment was used in triplicates, and a total of 30 greenhouse columns were used for this study. Periodic leaching of the columns by overwatering them was performed twice (at day 30: before grass plantation, and at day 120), and leachate
samples were collected and analyzed for pH, turbidity, total suspended solids (TSS), and total metals. Plants were harvested at the end of the study and were thoroughly washed with tap water. Plant samples were digested following USEPA 3050B method, and digests were filtered and analyzed for Fe using ICP-MS. Soil samples were analyzed for pH at the beginning (day 0) and at the end (day 120) of the experiment.

![Diagram of greenhouse column](image)

**Figure 5-2.** Schematic design of the greenhouse column (the diagram is modified from Andra, 2008).

### 5.2.4 Simulated field study

Two 4.0 ft. × 3.0 ft. × 1.0 ft. custom-made wooden platforms were set up outside the greenhouse facility, open to natural elements. Each panel was equipped with leachate and surface run-off collection systems. The panels were loaded with 5 inches of play sand and 5 inches of AMD soil. In treatment panel soil was mixed with WTRs (Al- and Ca-WTR mixed at 1:1 ratio) at 5% w/w application rate. Vetiver grasses were planted on top
of that WTR amended AMD soil. One control panel with no WTR and Vetiver was also used. Periodic leachate and surface run-off samples were collected from both the panels after major rainfall events. Samples were analyzed for pH, turbidity, TSS, and metals. The study was performed for four months. Soil samples were collected at the end of the study and were analyzed for pH. During this study, it was also noticed that some amount of sedimentation took place inside the surface run-off collection pipes. The soils were collected by washing the pipes (both control and treatment panels) at the end of the study and were tested for total suspended sediment concentration. Total suspended sediment concentration was measured using the following equation:

$$\text{Total Suspended Sediment conc. (mg/L)} = \frac{(A-B)}{C} \quad [i]$$

Where, 

$$A = \text{Weight of clean dried container (mg)}$$

$$B = \text{Weight of container and residue (mg)}$$

$$C = \text{Volume of water (L)}$$

Plants were harvested at the end of the study, and biomass was measured. Root and shoot samples were thoroughly washed with tap water and were digested following USEPA 3050B method. Plant digests were filtered and analyzed for total Fe using an ICP-MS.
5.3 Results and Discussions

5.3.1 Soil and WTR characterization

Results from soil characterization tests are presented in Table 5-2. Tab-Simco soil was acidic in nature with a pH of 2.68 ± 0.05. EC was measured as 2.34 ± 0.18 ms/cm. It was found that the concentration of Fe (41,018 ± 9 mg/kg) was very high in soil samples. Other metals such as, Ni (178 ± 2.6 mg/kg), As (131 ± 20 mg/kg), Pb (158 ± 10 mg/kg), Cr (159 ± 5 mg/kg), and Zn (386 ± 24 mg/kg) were also found in high concentrations in Tab-Simco soil samples.

Table 5-2. Physico-chemical characterization and metal concentrations in Tab-Simco soil samples (n= 3 for each measurements).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH (±)</th>
<th>EC (ms/cm)</th>
<th>Fe (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>As (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Zn (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tab-Simco Soil</td>
<td>2.68 ± 0.05</td>
<td>2.34 ± 0.18</td>
<td>41,018 ± 9</td>
<td>131 ± 20</td>
<td>178 ± 2.6</td>
<td>158 ± 10</td>
<td>159 ± 5</td>
<td>386 ± 24</td>
</tr>
</tbody>
</table>

The TCLP test results for both Al-WTR and Ca-WTR are presented in Table 5-3. Results showed that concentrations of all RCRA8 metals for both WTRs were well below their USEPA permissible limit. This result indicated that both WTRs can be safely used as soil amendment. Furthermore, the TCLP result showed that no significant Al and Fe leaching was occurring from any of the WTRs. A detailed discussion of both WTRs was presented in our previous study.
Table 5-3. TCLP test result for Al-WTR and Ca-WTR.

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Ba</th>
<th>Cd</th>
<th>Cr</th>
<th>Pb</th>
<th>Hg</th>
<th>Se</th>
<th>Ag</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDL</td>
<td>0.07</td>
<td>0.006</td>
<td>0.07</td>
<td>0.06</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>166</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>BDL</td>
<td>0.005</td>
<td>BDL</td>
<td>0.002</td>
<td>0.09</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>1.03</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>100</td>
<td>1.0</td>
<td>5.0</td>
<td>5.0</td>
<td>0.2</td>
<td>1.0</td>
<td>5.0</td>
<td>NR</td>
<td>NR</td>
<td></td>
</tr>
</tbody>
</table>

BDL = Below Method Detection Limit; NR = Not Regulated.

5.3.2 Greenhouse column study

Soil pH for all the treatments at the end of the greenhouse study is presented in Figure 5-3. It was noticed that irrespective of the type of grass (vetiver or control), all WTR amendments improved the soil pH during the four month long greenhouse study. The mean pH of all WTR treatments was 5.5 ± 1.2. It was also noticed that co-application of Al-WTR and Ca-WTR improved the soil pH even better than only Al-WTR application. The mean soil pH of all WTR co-application treatments was 6.6 ± 0.2. Soil pH of the control column with no-WTR and no-vetiver was measured as 2.89 ± 0.2, and soil pH of the control column with no-WTR but with vetiver was 2.99 ± 0.5. It was clear from the result that WTR amendment significantly reduced soil acidity.
The characterization result of leachate samples collected from the greenhouse study over time is presented in Table 5-4. Two sets of leachate samples were collected during the study: one at the end of the soil-WTR equilibrium period just before the grass plantation (at day 30) and another at the end of the study (at day 120). The mean pH of all leachate samples collected from WTR treatments at day 30 was 5.2±1.2. The mean pH of all leachate samples collected from WTR treatments at the end of the study was 5.5±1.1. The mean pH of all leachate samples collected from all WTR co-application treatments at day 120 was 6.5±0.1, which showed that co-application of both WTRs had a stronger effect on improving the acidity of leachates. pH of leachate samples collected from the control column without any WTR amendment or vetiver grass was 2.96±0.5 and 3.06±0.4 at day 30 and at day 120 respectively. In addition, pH of leachate samples collected
from the control column without any WTR amendment but with vetiver grass was 2.75±0.2 and 2.86±0.1 at day 30 and at day 120 respectively. It was observed from the study that WTR amendment reduced the acidity of leachates over time.

It was noticed from the study that soil erosion indicators such as turbidity of the leachate samples was improved by WTR amendment and vetiver plantation over time. After 30 days of soil-WTR equilibrium, turbidity of the leachate samples collected from 10% WTR [1:1 Al & Ca] treatment columns was reduced by 79% in comparison to the turbidity of control columns without any WTR amendment. It was also observed from the study that vegetative cover further reduced the turbidity of the leachate samples in comparison to the control columns during the study. The mean turbidity of leachate samples collected from all WTR treatments at the end of the study was 6.3±4.7, but the mean turbidity of leachate samples collected from all WTR treatments only with Vetiver was 3.4±2.9 at day 120. The best results were obtained from 5% and 10% WTR amendment with 1:1 Al & Ca in it (0.98±0.01 NTU and 0.93±0.02 NTU respectively), and leachate turbidity of these treatments were reduced by 97% in comparison to the unamended control column (41.5±5.7 NTU). It was also noticed that the control column with only vetiver grass but without any WTR amendment reduced the turbidity by 52% in compare to the control column without any WTR amendment or vetiver grass. Another soil erosion indicator, TSS of the leachate samples, was also improved by the proposed WTR-Vetiver model. The mean TSS of all leachate samples collected from WTR amended columns was 8.4±3.5 mg/L and 5.6±6.4 mg/L at day 30 and at day 120 respectively. It was noticed that WTR co-application was able to reduce TSS in leachate
samples at a higher rate in comparison to others, and a mean TSS of 2.4± 1.6 mg/L was measured for all WTR co-application treatments. Again, the best results were obtained from 5% and 10% WTR amendment with 1:1 Al & Ca in it (1.32± 0.02 mg/L and 1.3± 0.4 mg/L respectively), where leachate TSS was reduced by 93% in comparison to the unamended control column (20.18± 0.6 mg/L). A clear difference was observed in TSS measurements between the control columns with and without vetiver cover. Leachate samples collected from control columns with vetiver cover (8.5± 1.9 mg/L) had 57% less TSS in it in comparison to the control columns without any WTR amendment or vetiver grass (20.18±0.6 mg/L) at day 120, which indicates that the massive root system of vetiver was playing a big role in the prevention of soil erosion. It was clearly noticed from the study that the proposed WTR-vetiver model was able to reduce the erosion potential of AMD-soil significantly.

Only Fe and As were found in the leachate samples collected from the greenhouse study. It was found that the mean Fe concentration in leachate samples collected from all WTR amended treatments was 6.9 µg/L and 3.5 µg/L at day 30 and at day 120 respectively. Fe concentration in leachate samples collected from the control columns without any WTR and vetiver was measured as 39.19± 2.1 µg/L and 45.71±3.9 µg/L at day 30 and at day 120 respectively, indicating that significant Fe leaching was going on in absence of WTR amendment and plant cover. The lowest Fe concentration was found in the day-120-leachate samples collected from treatments with 5% (0.3± 0.001 ppb) and 10% (0.35±0.1 ppb) WTR amendment (with 1:1 Al & Ca in it) and vetiver grass, which was 96% lower than the Fe concentration of control leachates. A similar trend was
noticed for leachate As concentration. The mean As concentration in leachate samples collected from all WTR amended treatments was 5.1 µg/L and 3.2 µg/L at day 30 and at day 120 respectively, which was 9.54 µg/L (at day 30) and 7.76 µg/L (at day 120) for the control treatment without WTR and vetiver. The lowest As concentration was found in the 10% WTR amendment rate (with 1:1 Al & Ca) with vetiver (0.07 µg/L), which was 99% lower than the As concentration measured in control (no WTR, no vetiver) leachate (7.76 µg/L) at day 120. The results showed that the proposed WTR-vetiver model was able to reduce the metal leachability of AMD-soil.
Table 5-4. Properties of Leachate samples collected from Greenhouse Column Study at day 30 (after soil-WTR equilibrium and before plantation) and at day 120 (n=3 for each measurement).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>TSS (mg/L)</th>
<th>Fe (ppb)</th>
<th>As (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day-30</td>
<td>Day-120</td>
<td>Day-30</td>
<td>Day-120</td>
<td>Day-30</td>
</tr>
<tr>
<td>5% Al-WTR &amp; Vetiver</td>
<td>3.93±0.4</td>
<td>4.09±0.5</td>
<td>25.05±1.1</td>
<td>5.36±0.5</td>
<td>10.59±1.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Al-WTR &amp; Control Grass</td>
<td>3.89±0.2</td>
<td>4.21±0.3</td>
<td>26.97±2.6</td>
<td>15.04±0.9</td>
<td>11.35±0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% WTR [1:1] &amp; Vetiver</td>
<td>6.35±0.3</td>
<td>6.57±0.3</td>
<td>28.46±0.7</td>
<td>0.98±0.1</td>
<td>11.90±0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% WTR [1:1] &amp; Control Grass</td>
<td>6.21±0.5</td>
<td>6.35±0.7</td>
<td>29.18±0.5</td>
<td>10.14±0.2</td>
<td>12.17±1.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Al-WTR &amp; Vetiver</td>
<td>4.41±0.15</td>
<td>4.81±0.5</td>
<td>15.17±0.01</td>
<td>6.48±0.6</td>
<td>6.78±0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Al-WTR &amp; Control Grass</td>
<td>4.29±0.5</td>
<td>4.76±0.7</td>
<td>15.91±0.2</td>
<td>7.84±0.3</td>
<td>7.06±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% WTR [1:1] &amp; Vetiver</td>
<td>6.56±0.7</td>
<td>6.71±0.5</td>
<td>6±0.6</td>
<td>0.93±0.02</td>
<td>3.25±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% WTR [1:1] &amp; Control Grass</td>
<td>6.48±0.3</td>
<td>6.51±0.1</td>
<td>8.39±0.05</td>
<td>3.5±0.19</td>
<td>4.17±0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control-No WTR, no Vetiver</td>
<td>2.96±0.5</td>
<td>3.06±0.4</td>
<td>32.71±0.5</td>
<td>41.5±5.7</td>
<td>15.2±0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control-No WTR, with Vetiver</td>
<td>2.75±0.2</td>
<td>2.86±0.1</td>
<td>35.97±1.2</td>
<td>19.83±0.5</td>
<td>14.9±2.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


Plant samples were collected at the end of the greenhouse study and were analyzed for metals. The results are presented in Table 5-5. Only Fe was found in the roots and shoots of vetiver. No significant metal concentration was found in the control grass; hence, the data for control grass are not presented here. It was found that the translocation factor was always <0.1 for all the WTR treatments indicating that vetiver was mainly accumulating Fe in their roots. The translocation factor in control vetiver was higher than the rest (0.09) indicating that in absence of WTR amendment, a higher soluble and exchangeable Fe-fraction is available for plant uptake, which was also found during the previous soil incubation study. Hence, more Fe concentration was found in the roots (500± 37 mg/kg) of control vetiver. This study showed that vetiver was contributing more towards the prevention of soil erosion in comparison to the metal uptake.

Table 5-5. Metal concentration in Vetiver root and shoot (n=3 for each measurement).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Fe (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vetiver Root</td>
</tr>
<tr>
<td>5% Al-WTR</td>
<td>401± 12</td>
</tr>
<tr>
<td>5% WTR [1:1 Al &amp; Ca]</td>
<td>371± 14</td>
</tr>
<tr>
<td>10% Al-WTR</td>
<td>372± 10</td>
</tr>
<tr>
<td>10% WTR [1:1 Al &amp; Ca]</td>
<td>326± 23</td>
</tr>
<tr>
<td>Control- No WTR, with Vetiver</td>
<td>500± 37</td>
</tr>
</tbody>
</table>
5.3.3 Simulated field study

Based on the results obtained from the greenhouse study, a simulated field study was conducted using 5% WTR [1:1 Al & Ca] application rate (w/w) and vetiver grass for 4 months (Fig 5-4). At the end of the four-month long study, soil pH increased from 2.65± 0.3 to 7.7± 0.1 in the treatment panel. Soil pH in the control panel was measured as 3.5± 0.4 at the end of the study. Periodic leachate samples were collected from both control and treatment panels, and the characterization results of those samples are presented in Table 5-6. The mean pH of leachate samples was 3.25± 0.7 and 7.5± 0.2 for the control and treatment panel respectively at day 120. The mean pH of surface runoff samples was 4.01± 0.3 and 8.14± 0.2 for the control and treatment panel respectively at day 120. Soil erosion indicators such as turbidity and TSS measurements also showed that erosion potential of Tab-Simco AMD-soil was significantly reduced by the proposed WTR-Vetiver model. Results showed that turbidity of surface runoff and leachate collected from the treatment panel was significantly lower than the control panel at day 120: 76% and 99% respectively. Results also showed that TSS of surface runoff and leachate collected from the treatment panel was 75% and 95% lower than the control panel at day 120 respectively. The results clearly showed that the proposed WTR-vetiver model significantly reduced the soil erosion potential of AMD-soil in field conditions. During the simulated field study, it was noticed that some amount of sedimentation took place inside the surface run-off collection pipe. The soils were washed away from the panels during the heavy rainfalls and deposited inside the pipe. It was found that total suspended sediment concentration of control and treatment panel was 200 mg/L and 6
mg/L respectively. It was also clear from this test that WTR-vetiver treatment reduced the sedimentation rate (hence, the soil erosion potential) by 97% in comparison to the control panel. WTR-vetiver system was tightly holding the soil and wasn’t allowing them to wash away with the rainfall. The soil in the control panel was structurally unstable and hence, was easily subjected to erode with heavy rainfall.

The concentration of metals found in the leachate and surface run-off samples collected from the control and treatment panel is presented in Table 5-6. Results showed that Fe concentration in surface runoff and leachate samples collected from the treatment panel was 93% and 97% lower than the control panel at day 120 respectively. It was found that Fe concentration in all surface runoff samples collected from the control panel was higher than 250 µg/L, indicating the presence of a higher soluble and exchangeable Fe-fraction in soil, which is easily subjected to runoff. Lower Fe concentration in both control and surface runoff samples collected from the treatment panel also suggested that most of the soluble and exchangeable soil Fe-fractions were either adsorbed on the WTR surface or taken up by the plant, which validated the previous soil incubation study results (chapter 4). It was also found that the treatment panel removed 100% As from both surface runoff and leachate samples in comparison to the control panel at day 120. Only a small amount of Al was found in all surface runoff samples collected from the treatment panel, but the Al concentration was always <30 µg/L, and hence, was non-toxic. The results showed that the metal leachability from AMD-soil was significantly reduced by the proposed WTR-vetiver model in field conditions.
Table 5-6. Properties of Leachate and Surface Runoff samples collected from simulated field study (n=3 for each measurement).

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>TSS (mg/L)</th>
<th>Fe (ppb)</th>
<th>As (ppb)</th>
<th>Al (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Day -30</td>
<td>Day -60</td>
<td>Day -120</td>
<td>Day -30</td>
<td>Day -60</td>
<td>Day -120</td>
</tr>
<tr>
<td>Control Panel - Leachate</td>
<td>3.41 ± 0.2</td>
<td>3.09 ± 0.5</td>
<td>3.25 ± 0.7</td>
<td>45.97 ± 1.92</td>
<td>52.16 ± 3.5</td>
<td>68.21 ± 5.7</td>
</tr>
<tr>
<td>Control Panel - Surface Runoff</td>
<td>4.28 ± 0.04</td>
<td>3.97 ± 0.1</td>
<td>4.01 ± 0.3</td>
<td>33.41 ± 1.2</td>
<td>25.98 ± 0.5</td>
<td>39.08 ± 0.5</td>
</tr>
<tr>
<td>Treatment Panel - Leachate</td>
<td>7.37 ± 0.15</td>
<td>7.77 ± 0.2</td>
<td>7.5 ± 0.2</td>
<td>0.35 ± 0.01</td>
<td>0.19 ± 0.01</td>
<td>0.15 ± 0.05</td>
</tr>
<tr>
<td>Treatment Panel - Surface Runoff</td>
<td>8.16 ± 0.7</td>
<td>8.32 ± 0.5</td>
<td>8.14 ± 0.2</td>
<td>16 ± 0.6</td>
<td>11.83 ± 0.2</td>
<td>9.03 ± 0.1</td>
</tr>
</tbody>
</table>

BDL = Below Method Detection Limit.
Figure 5-4. Control panel and WTR-Vetiver treatment panel at (a) day 0 and (b) day 90.
Plants were harvested at the end of the study and were analyzed for metals. Only Fe was found in the root and shoot of vetiver. A mass balance for Fe was conducted at the end of the study using the amount of Fe present in the soil, amount of Fe present in the leachate and surface runoff, and amount of Fe present in the plant tissues. According to the mass balance equation:

\[
\text{Total Fe present in the soil at time zero} = (\text{Fe present in the soil at day 120}) + (\text{Fe present in the leachate and surface runoff}) + (\text{Fe present in the plant tissues}).
\]

A total of 100 kg of AMD-soil was used in this study; hence, based on the soil-Fe concentration, it can be assumed that a total of 4,101 kg Fe was present in the treatment panel at time zero. The volume of leachate and surface runoff collected throughout the study was always measured, and based on the Fe concentration reported in leachate and surface runoff samples (Table 5-6), it was found that a total of 544.5 mg of Fe exited the treatment panel during the study. The mean Fe concentration in vetiver roots and shoots was measured as 400± 17 mg/kg and 30± 11 mg/kg respectively. After measuring the plant biomass and concentration of Fe in individual plant tissues, it was found that approximately 1.2 kg of Fe was accumulated in Vetiver tissues. The mean soil Fe concentration at the end of the study was 40,755 mg/kg, indicating 4,075 kg of Fe was present in the soil at the end of the study. Total Fe concentration calculated by adding all of the Fe values was 4,076 kg which was very close to our time zero Fe value (4,101 kg).

Results from this study showed that although a high amount of Fe was still present in the treatment panel, the majority of it was not leaching, indicating the higher
adsorption of Fe on WTR surface. A similar trend was noticed during the previous soil incubation study. Hence, both the greenhouse and field study showed that WTR amendment can lower the risk of metal leachability from the AMD-soil. Although metal uptake by vetiver grass was low, the decrease of soil erosion indicators such as turbidity and TSS indicated that vetiver grass was able to reduce the soil erosion potential of AMD-soil. A low Fe-uptake by vetiver grass also indicated that less bioavailable Fe-fraction was present in the soil after WTR amendment.

5.4 Conclusions

Both the greenhouse column study and simulated field study showed that WTR amendment can effectively increase soil pH and decrease metal leachability from AMD-soil. Low metal concentrations in leachate samples collected from the simulated field study indicated that the majority of the metals were adsorbed on WTR surface; hence, the metal leachability and bioavailability were decreased significantly. The study also showed that vetiver grass significantly lowered erosion potential of AMD-soils in both greenhouse column study and simulated field study. The results demonstrated the high potential of success of this innovative, “green,” cost-effective, and ecologically sustainable technology in remediating AMD-impacted soil.
5.5 References


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Appendix-I

Limitation of this study

Although this study showed that the proposed field scale WTR-based filter media can significantly lower acidity and concentration of metals from AMD-water, only up to 44% of initial sulfate concentration was removed (by filter media 2) during the filtration process. Sulfate concentration in the filtered water was considerably higher (1370 mg/l) than acceptable values, which requires further treatment. Figure-AI presents the schematic design of a proposed “green” treatment process that can be used for removal of sulfate from the filtered water using vetiver grass (*Chryosopogon zizanioides* L.), which has been used extensively for mine site reclamation (as discussed in Chapter 5).

![Figure-AI](image_url)  
**Figure-AI.** Schematic design of the sulfate removal process from filtered AMD-water.
AMD-water can be channeled through the WTR-filter media and stored in a holding tank prior to discharge to the environment. Vetiver grass can be used in a floating platform setup as shown in Figure-AI. Vetiver’s ability to remove a number of environmental contaminants, including sulfate is well documented, and the use of floating vetiver platform will be able to remove the remaining sulfate from the filtered AMD-water.
Appendix-II

Life expectancy of the field scale WTR-filter

From the performance of the laboratory scale WTR-filter, an estimation on life expectancy of the field scale WTR-filter can be made.

Height and width of the filter media was 4” and 1” for laboratory scale WTR-filter. Hence the media volume was 3.14 inch$^3$ or 0.002 ft$^3$.

Height and width of filter media was 25” and 22” for filed scale WTR-filter. Hence, the media volume was 5.5 ft$^3$.

The assumption is, if 0.002 ft$^3$ media volume can filter 20 bed volume of AMD-water, then 5.5 ft$^3$ media volume can filter 55,000 bed volume of AMD-water.

Hence, it can be assumed that the field scale WTR-filter can filter 55 gallons $\times$ 55,000 = 3,025,000 gallons of AMD-water.
Appendix-III

Cost-benefit analysis of the field scale WTR-filter

Table-AI presents the estimated manufacturing and maintenance cost for the field scale WTR-filter. Manufacturing cost includes the cost of obtaining and preparing the 55 gallon drum (including sand and/or carbon material), and transporting Al-WTR and Ca-WTR from their respective water treatment plants to the Tab-Simco site. The distance of City of Carbondale water treatment plant and Saline Valley water treatment plant from the Tab-Simco site is 5 km and 75 km respectively. Transport allocation is estimated as a function of mass (tons) of materials transported and transport distances (km) from their source to the Tab-Simco site. Personnel cost is estimated based on the hours of involvement of two workers for transportation of WTRs, loading the filter media inside the drum filter, emplacing the drum filter onsite, and collection of periodic water samples for laboratory analysis (twice a year), a total of 50 hours. The cost of chemical analysis of periodic water samples is calculated based on the standard analytical rates of commercial laboratories. The spent sorbent can be regenerated and reused. Hence, disposal cost has not been included in the estimate.
Table-A1. Estimated cost of the field scale 55 gallon drum filter.

<table>
<thead>
<tr>
<th>Item</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>55 gallon drum filter (including sand)</td>
<td>$500</td>
</tr>
<tr>
<td>Transportation</td>
<td>$150</td>
</tr>
<tr>
<td>Personnel (50hrs at $20/hr. rate)</td>
<td>$1000</td>
</tr>
<tr>
<td>Laboratory analysis</td>
<td>$600</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>$2,250</strong></td>
</tr>
</tbody>
</table>

Hence, the estimated cost to treat 3,025,000 gallons of AMD water using the field scale 55 gallon drum filter is $2,250. According to the CNN.com (August 13, 2015), USEPA crew accidentally spilled 3 million gallons of AMD water from the abandoned Gold King Mine, Colorado to nearby Animas River, Colorado on August 6, 2015, and the estimated cost to treat that AMD-spill is around $3 million to $16 billion (The Daily Caller News Foundation, August 18, 2015). Reports show that the construction cost for some of the commonly used passive AMD treatment technologies (such as lime bioreactors) ranges between $690,000 and $1 million. Operation and maintenance cost for these facilities to treat 7.2 million gallons to 13 million gallons of AMD water ranges between $700,000 and $1.22 million. Hence, the overall AMD treatment cost for commonly used passive treatment technologies range between $1.4 million and $2.2 million (Gusek et al., 2013; Mayer et al., 2013). It is clear that the field scale 55 gallon drum filter can treat AMD water efficiently and cost-effectively in comparison to the other commonly used AMD treatment technologies.
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