Understanding Iron Oxide Mineralogy to Enhance Sorption: Sustainable Environmental and Economic Reuse of Mine Drainage Treatment Solids

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1 Executive Summary

Sustainable reclamation design must consider the full life cycle impacts and costs of any selected remedy – and in the case of mine water treatment, that includes the ultimate disposition, disposal, or reuse of accumulated water treatment solids. The chemical composition of iron oxide solids is based on the untreated mine water and the specific treatment mechanisms resulting in solids retention. The resulting chemical composition, along with environmental conditions and time, drives the mineralogy of these solids. It is well-established that iron oxides have substantial surface area per unit mass and considerable sorption capacity. By properly understanding iron oxide mineralogy and its effect on sorption capacity, sustainable environmental reuse of mine drainage treatment solids may present an opportunity to offset perpetual water treatment and solids disposal costs, thus further stretching reclamation dollars. The overall goal of this project was to develop a thorough understanding of the relationships between mineralogy and sorption capacity in mine-drainage derived iron oxides, especially with respect to source water chemical composition and age.

The following determinations were made. First, mine drainage water chemical composition had a discernible impact on the resulting iron oxide precipitate chemistry and mineralogy, especially on surface morphology and chemical properties such as the point of zero net charge, a critical parameter with regard to sorption capacity. Although the iron oxides collected from multiple sites were all predominantly goethite, they differed greatly in surface morphology and metals concentrations. Second, despite the physical and chemical differences in iron oxides collected from different sites and within individual sites, all iron oxides analyzed for phosphorus sorption capacity showed a high affinity for phosphate and were viable as sorbents. Third, although iron oxides had a high affinity for phosphate, solids with greater metals concentrations showed an increased desorption of metals at greater phosphorus concentrations. Additional research is required to examine the competing relationships and mechanisms between ions in iron oxides produced in natural environments. Fourth, fresh (recently precipitated) iron oxides showed smaller particles and increased surface area whereas aged (precipitated years ago) iron oxides were largely aggregated particles and showed lesser specific surface area. The considerable difference in surface morphology indicates distinctive differences in mineralogy, potentially affecting sorption capacity. Fifth, reuse and recycling of mine drainage derived iron oxides produced in passive treatment systems represents an economically viable approach to solids management.

The following hypotheses were supported. Mine drainage chemical composition in which the solids form influences the physicochemical and mineralogical characteristics of resulting iron oxides. This marked difference affects phosphorus sorption capacity of iron oxides and, as they age, their mineralogical, physical, and chemical properties change, also affecting their sorption capacity. Despite these differences in chemical, physical, and mineralogical properties over time and space, reusing iron oxides as phosphorus sorbents appears to be economically favorable compared to traditional disposal methods.

2 Introduction

Sustainable reclamation design must consider the full life cycle impacts and costs of any selected remedy – and in the case of mine water treatment, that includes the ultimate disposition, disposal, or reuse of accumulated treatment solids. Solids disposal represents approximately 10% of global water treatment costs, with sludge disposal costing around $23-75 per ton depending on the solids content of the sludge and delivery distance (Zinck and Griffith 2013). At many active mines, the disposition of solids generated through active chemical treatment is addressed on-site through pond, pit lake, mine workings, or backfill disposal (Zinck 2006). In addition, mining companies, federal and state agencies, and non-profit organizations have designed and constructed hundreds of passive treatment systems throughout coal country (e.g., Skousen et al. 2017). In these cases, although funds for design and construction may be adequate, additional dollars for monitoring or maintenance are typically wholly lacking. Although these systems are often designed with initial lifetimes of two to three decades, they do require maintenance and principal among the needed tasks is the management of accumulated water treatment solids. These solids are often iron oxides. The chemical composition of the solids is based on the untreated mine water and the specific treatment mechanisms resulting in solids retention. The resulting chemical composition, along with environmental conditions and time, drives the mineralogy of these solids. It is well-established that iron oxides have substantial surface area per unit mass and considerable sorption capacity (Acero et al. 2006, Cornell and Schwertmann 2003; Dempsey and Jeon 2001; Fenton et al. 2009; Figueiredo and Silva 2011; Gagliano et al. 2004; Hedin 2012; Kairies 2003; Neely 2010; Ozeki and Inouye 1988; Rakotonimaro et al. 2017; Sibrell et al. 2015; Sibrell and Tucker 2012; Tang and Nairn 2020; Torrent et al. 1992; Zeng et al. 2004). By properly understanding iron oxide mineralogy and its effect on sorption capacity, sustainable environmental and economic reuse of mine drainage treatment solids may present an opportunity to offset perpetual water treatment and solids disposal costs, thus further stretching reclamation dollars.

2.1 Mine drainage treatment and associated solids

One of the main environmental problems associated with mining sites is the production of polluted mine drainage which degrades surface and groundwater quality (Johnson and Hallberg 2005; Nairn et al. 2009; Skousen et al. 2017; Taylor et al. 2005; Watzlaf et al. 2004; Younger et al. 2002). During mining, pyritic materials are oxidized by air and water forming mine drainage which often contains elevated concentrations of dissolved metals, sulfate, and acidity as shown in Reaction 2.1 (Younger et al. 2002).

$$FeS_2\,(s) + 3O_2\,(aq) + 2H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 4H^+ \qquad \text{Reaction 2.1}$$

Total acidity in mine drainage is caused by proton acidity (H^+), carbon dioxide acidity (H_2CO_3), and mineral acidity, due to the oxidation and hydrolysis of dissolved metals (Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}) which eventually produces proton acidity. If the water interacts with carbonate strata (e.g., $CaCO_3$ or $CaMg(CO_3)_2$) before discharging, enough alkalinity in the form of carbonate and bicarbonate may be present to buffer pH changes of the water upon metal hydrolysis (Watzlaf et al. 2004; Younger et al. 2002). Whether net-acidic or net-alkaline, the elevated concentrations of metals in mine drainage are serious environmental problems that can have long-term watershed-scale impacts if left untreated (Nairn et al. 2009; Taylor et al. 2005; Watzlaf et al. 2004; Younger et al. 2002).

Mine drainage treatment is generally classified into two main types: active treatment and passive treatment. Active treatment requires continuous inputs of resources including labor, chemicals, and energy. Although active treatment can be efficient and cost-effective for active mining operations, it is typically not feasible for abandoned mine sites (Johnson and Hallberg 2005; Watzlaf et al. 2004; Younger et al. 2002). In contrast, passive treatment systems are ecologically engineered to utilize biogeochemical and physical processes and renewable energy to treat mine drainage, thus eliminating the need for daily operation and maintenance. This makes passive treatment more favorable for remote and abandoned mine sites (Johnson and Hallberg 2005; Nairn et al. 2009; Skousen et al. 2017; Watzlaf et al. 2004; Younger et al. 2002).

Active treatment using chemical neutralizing agents is one of the most common and traditional technologies to address mine drainage. Highly alkaline chemicals such as lime (CaO) or hydrated lime ($Ca(OH)_2$), calcium carbonate ($CaCO_3$) or sodium hydroxide ($NaOH$) are added to acidic mine waters to raise the pH and accelerate the oxidation, hydrolysis, and precipitation of ferrous iron and other dissolved metals (Johnson and Hallberg 2005). In many cases, the sludge produced is either disposed of in a low-density sludge system or a portion is recycled in a high-density sludge system. The low-density sludge system produces sludge with a low solids content (<5% wt.) whereas the high-density sludge system produces denser sludges (>20% wt.) (Johnson and Hallberg 2005; Taylor et al. 2005). Although the sludge produced varies based on the quality of the water being treated and the type of treatment used, generally it is composed of Fe, Al, Mn, Ca and Mg oxides and hydroxides. However, other metal and metalloid species may be present depending on the composition of the untreated mine drainage (Johnson and Hallberg 2005; Taylor et al. 2005).

Passive treatment utilizes naturally occurring biogeochemical and microbiological processes to improve water quality through multiple process units, which may take the form of ponds, wetlands, bioreactors, or geochemical reactors. Dominant treatment mechanisms include alkalinity generation via limestone dissolution, metal oxidation and hydrolysis, bacterial sulfate reduction to form metal sulfides, and reaeration and ecological polishing of the water before it is discharged (Johnson and Hallberg 2005; Nairn et al. 2009; Skousen et al. 2017; Taylor et al. 2005; Watzlaf et al. 2004; Younger et al. 2002). In either naturally or induced (e.g., via anoxic limestone drains) net-alkaline waters, oxidation ponds and aerobic wetlands are used to aerate the water and oxidize, hydrolyze, precipitate, and settle metals as oxides or oxyhydroxides. They are often designed with Fe removal rates of 10 to 20 g Fe m^{-2} day^{-1} (Hedin et al. 1994; Watzlaf et al. 2004; Younger et al. 2002). The sludge produced from these units typically has a solids content higher than 25% and is mainly composed of iron oxyhydroxides (Taylor et al. 2005).

Regardless of the type of sludge, residual solids management represents a large and costly challenge to mine drainage treatment (Dempsey and Jeon 2001; Hedin 2012; Rakotonimaro et al. 2017; Zinck and Griffith 2013). The produced sludges often have relatively low solids content and chemical and physical stability and thus may need to be conditioned before disposal (Dempsey and Jeon 2001). A survey of mine operations around the world showed that, on average, each site produced on average 9,500 dry tons of sludge per year. Dredging the sludge can cost between \$5-20/m^3 amounting to \$1M or more in annual costs for many sites. That cost does not consider the expense related to conditioning the sludge for disposal. It is estimated that sludge management costs account for 5-20% of operational water treatment cost (Zinck and Griffith 2013). Given the costs associated with sludge management and disposal, more research into the recovery and reuse of produced mine drainage treatment solids is necessary to help alleviate expenses.

2.2 Iron oxide mineralogy

There are 16 identified iron oxide mineral species consisting of iron oxides, hydroxides, oxide-hydroxides, and hydroxysulfates that are collectively referred to as iron oxides (Cornell and Schwertmann 2003). In most iron oxide compounds, iron is in the trivalent state (Fe^{3+} or Fe(III)) and consists of close-packed arrays of anions that differ primarily in the way basic structural units are arranged in space. The degree of structural order and crystal size of iron oxides depends on the age of the mineral, pH, the chemical composition of the water in which it formed, and the temperature to which the mineral is exposed (Cornell and Schwertmann 2003). Almost all iron oxides display crystallinity except for ferrihydrite and schwertmannite which are poorly crystalline (Cornell and Schwertmann 2003). Iron oxides typically found in mine drainage include schwertmannite ($Fe_{16}O_{16}(OH)_y(SO_4)_z \bullet nH_2O$), ferrihydrite ($Fe_5HO_8 \bullet 4H_2O$), jarosite ($KFe^{3+}_3(SO_4)_2(OH)_6$) and goethite ($\alpha$-FeOOH) (Acero et al 2006; Gagliano et al. 2004; Kairies et al. 2003; Murad and Rojík 2005). Although goethite and hematite are the most thermodynamically stable, less stable iron oxides are found in the environment because their formation is kinetically favored. The precipitation, dissolution and reprecipitation of iron oxides in the environment depend on many factors such as pH, oxidation-reduction potential, temperature, and presence of inhibitors and accelerating agents (Schwertmann and Cornell 1991).

Schwertmannite is a common oxidation product found in many mine discharges and treatment systems with pH values ranging from 3.0 to 4.5 and elevated sulfate concentrations (Acero et al. 2006; Cornell and Schwertmann 2003). Similarly, ferrihydrite is another mineral commonly found in iron precipitates from mine drainage with a pH greater than 5.0 (Murad and Rojík 2005). Both schwertmannite and ferrihydrite are nanocrystalline and metastable compared to other iron oxide minerals. Their small crystal structures allow schwertmannite and ferrihydrite to have large surface areas and thus often act as sinks for trace metals and anions, depending on environmental conditions (Acero et al. 2006; Gagliano et al. 2004; Murad and Rojík 2005). Schwertmannite and ferrihydrite have been shown to transform into more stable iron oxide minerals, such as goethite, on a timescale of weeks to years depending on pH, redox conditions, and chemical composition of the water (Acero et al. 2006; Gagliano et al. 2004; Murad and Rojík 2005). The transformation of ferrihydrite to goethite and hematite can take months to years at neutral pH but can take days if accelerated with organic reducing agents (Schwertmann and Cornell 1991; Paige et al. 1997). A summary of some of these characteristics is shown in Table 2.1 and a schematic representation of the formation and transformation pathways of common oxides is shown in Figure 2.1 (Schwertmann and Cornell 1991).

Table 2.1 Summary of characteristics for iron oxide minerals commonly found in mine drainage systems (after Cornell and Schwertmann 2003; Figueiredo and Silva 2011; Ozeki and Inouye 1988).

Iron Oxide Mineral	Formula	Color	Density (g cm^{-3})	Specific Surface Area (g m^{-2})
Schwertmannite	$Fe_{16}O_{16}(OH)_y(SO4)_z \bullet nH_2O$	Orange-Brown	≈ 3.8	125-320
Ferrihydrite	$Fe_5HO_8 \bullet 4H_2O$	Red-Brown	3.96	200-400
Jarosite	$KFe^{3+}{}_3(SO_4)_2(OH)_6$	Yellow-Brown	≈ 3.25	≈ 150
Goethite	α-FeOOH	Yellow-Brown	4.26	8-200
Hematite	α-Fe_2O_3	Blood- Red	5.26	5-200

Under certain conditions, schwertmannite will spontaneously transform into goethite releasing all its structural sulfate and releasing proton acidity as shown in Reaction 2.2 (Acero et al. 2006; Cornell and Schwertmann 2003).

$$Fe_8O_8(OH)_6SO_4 + 2\ H_2O \rightarrow 8\ FeOOH + H_2SO_4 \qquad \text{Reaction 2.2}$$

Initially, Fe is released into solution but the aqueous concentration then decreases as goethite forms. Typically, proton acidity produced by this transformation will be neutralized in natural settings, raising the pH of the solution, and increasing the rate of goethite formation (Cornell and Schwertmann 2003). For passive treatment systems addressing net-acidic mine drainage in Ohio, transformation rates of schwertmannite into goethite were found to range between 10 to 30 mol m^{-3} yr^{-1} (Gagliano et al. 2004).

Ferrihydrite forms in situations where Fe^{2+} is oxidized rapidly, hydrolyzes, nucleates, and forms small aggregates that form small nanocrystals. The formation of ferrihydrite is kinetically favored and is often a precursor to goethite and hematite development. However, ferrihydrite can be found in the environment where Fe^{2+} is oxidized rapidly and where crystallization inhibitors are present. Crystallization inhibitors include organics, silicate, and phosphate species that have a high affinity for the iron oxide surface. As these inhibitors co-precipitate and sorb onto the ferrihydrite crystal, the ferrihydrite crystals become more tightly bound, limiting the dissolution and rearrangement processes needed to crystallize to either goethite or hematite. This inhibition allows ferrihydrite to maintain a poorly crystalline structure and very small particle size which increases its surface area (Schwertmann and Cornell 1991; Cornell and Schwertmann 2003; Paige et al. 1997).

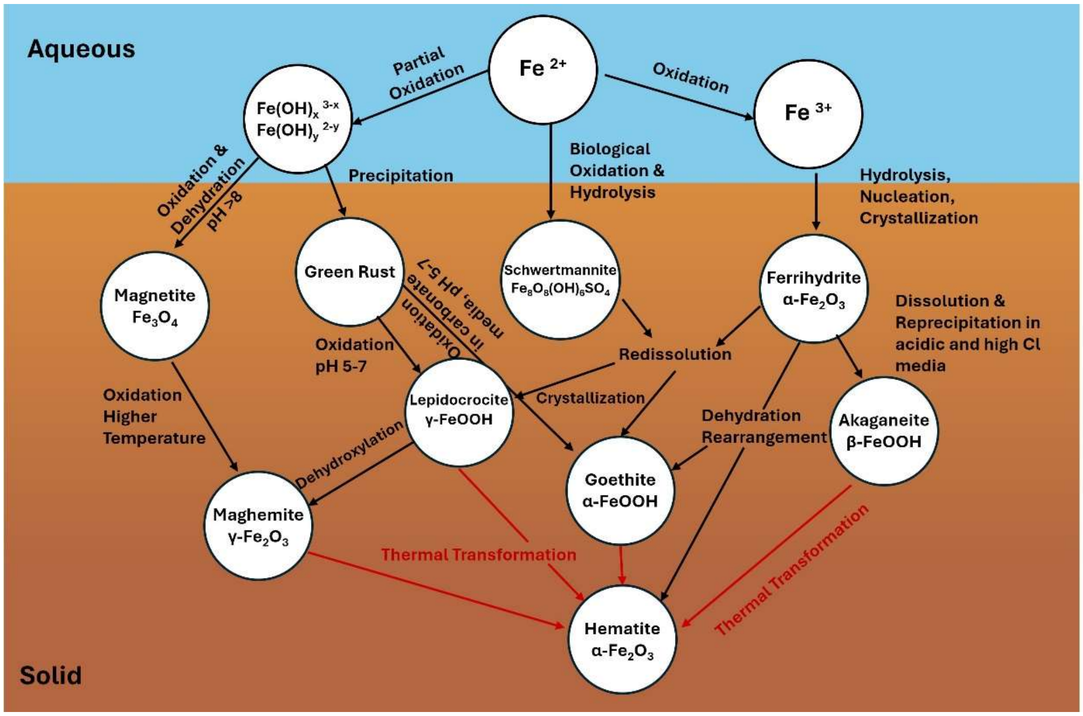

Figure 2.1 Schematic representation of the formation and transformation pathways of common iron oxides and the approximate transformation conditions

Like schwertmannite, ferrihydrite is metastable and will spontaneously transform into goethite or hematite over time. Goethite is formed by the dissolution of ferrihydrite that is then crystallized in bulk solutions. This process happens because ferrihydrite has a much higher solubility (pK_S 37-39) than goethite ($pK_S \geq 42$). Hematite forms within ferrihydrite particles by a dehydration and rearrangement mechanism and thus is favored at a pH near the point of zero charge (PZC) of ferrihydrite (pH 7-8) where the solubility of ferrihydrite is lowest and is favored at higher temperatures (Cornell and Schwertmann 2003). As the solution becomes more acidic or basic, more ferrihydrite is dissolved and goethite formed. However, at pH less than 4 or around 14, although the solubility of ferrihydrite remains high, the formation of hematite will be favored over goethite (Cornell and Schwertmann 2003).

Goethite is one of the most thermodynamically stable iron oxides to form and thus is often the final mineral formed after a series of transformations. Goethite is often used in industry as a pigment and thus it is often sought (Cornell and Schwertmann 2003). While goethite crystals can be on the nanometer scale, they are often larger than schwertmannite and ferrihydrite crystals, and thus easier to identify using X-ray diffraction (XRD) analyses even when present in minor amounts (Acero et al. 2006; Gagliano et al. 2004; Murad and Rojík 2005). Due to its stability, goethite is often the product of the transformation of other iron oxide minerals and thus is found in systems with a wide variety of pH values (Murad and Rojík 2005). While larger crystals allow goethite to be more easily identified, they also decrease the surface area of goethite which can potentially decrease the sorption capacity for metals and other ions to the mineral phase.

Jarosite is an iron-hydroxysulfate mineral that is commonly found in acidic (pH 2.0 - 3.0) and sulfate-rich environments such as mine drainage. Unlike schwertmannite and ferrihydrite, jarosite is relatively well crystallized and thus can be identified by XRD analyses even at lesser concentrations. Similar to ferrihydrite and schwertmannite, jarosite is metastable with respect to goethite and will transform into goethite within months to years (Murad and Rojík 2005).

Due to their high surface area and surface charge, iron oxides have been used as sorbents in a variety of water treatment applications (Cornell and Schwertmann 2003). Schwertmannite and ferrihydrite are preferred due to their low crystallinity and high surface area, yet all known iron oxide minerals exhibit relatively strong sorption capacities (Acero et al. 2006; Cornell and Schwertmann 2003; Gagliano et al. 2004). Given the variety of iron oxide minerals found in natural systems and the high sorption capacity of these solids, a deep understanding of the factors affecting their sorption capacity is necessary in order to sustainably use iron oxide-rich mine drainage residual solids as sorbents.

2.3 Factors affecting sorption capacity

Many factors can affect the sorption capacity of a given media including the minerology of the media, pH of the surrounding environment, species competing for binding sites, and the crystallinity and specific surface area of the media. The removal efficiency of contaminants onto iron oxides is greatly influenced by pH. The PZC is an essential characteristic of surface chemistry. It is the pH value related to zero electrical charge density of the sorbent surface (Rakotonimaro et al. 2017). The PZC values for iron oxides and hydroxides range from 8 to 9 (Cornell and Schwertmann 2003). If the pH is below the PZC, the surface of the iron oxide is positively charged and thus attracts anions whereas if the pH is above the PZC, the surface is negatively charged and attracts cations. The pH of the system is important not only because it affects the surface charge chemistry of the iron oxide solids, but because it can also influence the rate at which iron oxide minerals transform into more stable iron oxides, as discussed previously (Cornell and Schwertmann 2003; Gagliano et al. 2004; Murad and Rojík 2005).

In mixed systems where two or more adsorbates are present, either synergistic or competitive effects can operate (Cornell and Schwertmann 2003). Synergistic effects can be caused by ternary adsorption where the presence of anions and cations in solution can form mixed metal and ligand surface complexes that can enhance cation adsorption (Schindler 1990). The most common form of ternary adsorption observed for iron oxides is the case where a polydentate ligand bridges the adsorbed metal ion and the surface metal ion (Cornell and Schwertmann 2003). However, in many cases ions compete with one another for the limited reaction sites thus potentially limiting the sorption capacity for a targeted contaminant (Cornell and Schwertmann 2003). This relationship has been explored extensively for cations and anions alike, especially for trace metals and phosphate. Phosphate has been shown to suppress the adsorption of arsenate and selenite on goethite (Hingston et al. 1971), and to promote desorption of sulfate from goethite (Lui et al. 1999) and of silicate from goethite (Torrent et al. 1992).

While pH and the presence of other ions affect the sorption capacity of iron oxides, one of the most important characteristics of iron oxide sludge reuse is the surface area of the particles (Dempsey and Jeon 2001). The number of available sites per unit mass depends on the type of iron oxide and its surface area. The specific surface area of an iron oxide determines its reactivity, particularly its dissolution and dehydroxylation behavior, how it transforms through phases, its thermodynamic stability, and how it interacts with other chemical species (Cornell and Schwertmann 2003). A larger specific surface area allows for more sorption sites which allows for greater retention of contaminants. Hedin (2012) reported that the surface area of recovered iron oxides from the active treatment of mine drainage ranged from 23 to 114 m^2/g while solids recovered from passive treatment systems had surface areas ranging from 119 to 215 m^2/g. The relatively large range in surface areas for iron oxide minerals is because a particle's size and crystallinity are governed by the chemical environment experienced during crystal growth, and thus the surface area of an iron oxide is dependent upon the environment in which the oxide formed (Cornell and Schwertmann 2003).

Research has shown that iron oxide sediment columns in passive treatment systems are not static systems (Acero et al. 2006; Gagliano et al. 2004). Schwertmannite and ferrihydrite will transform over time into the more thermodynamically stable goethite mineral, as shown in Figure 2.1 (Acero et al. 2006; Cornell and Schwertmann 2003; Gagliano et al. 2004; Murad and Rojík 2005; Oxenford 2016). As the crystals grow and become increasingly crystalline, their surface area decreases. As the specific surface area decreases, the number of available sorption sites also decreases, decreasing the sorption capacity of the iron oxide solid (Figure 2.2). This issue is problematic because goethite is less likely to incorporate trace metals or oxyanions into its crystal structure or sorb them onto its surface, decreasing the sorption capacity of the iron oxide and potentially causing the desorption and remobilization of contaminants (Acero et al. 2006; Gagliano et al. 2004).

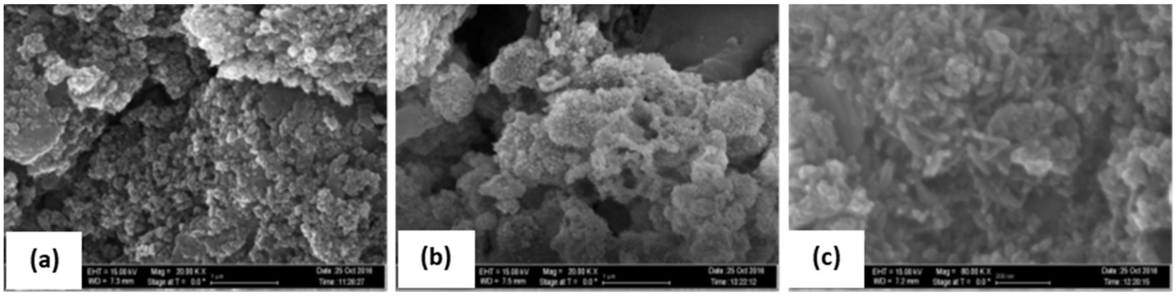

Figure 2.2 Scanning electron microscopy images of (a) nano-crystalline iron oxide (ferrihydrite) found in fresh surface samples, (b) crystallization of older samples, and (c) crystallized goethite found in older deeper samples collected from the Mayer Ranch passive treatment system oxidation pond, Ottawa County, OK (Oxenford 2016).

Given the great number of factors that can affect the sorption capacity of iron oxides, it is important to have a robust and deep understanding on how each of these factors interact and change over time and affect the sorption capacity of iron oxides in the long-term. Iron oxides may be able to be reused in a variety of water chemical compositions for a multitude of applications. Therefore, it is critical to understand the relationship between water chemical composition and iron oxide mineralogy and its effect on the sorption capacity to ensure the environmentally and economically sustainable reuse of iron oxide solids.

2.4 Phosphorus pollution and control

The release of phosphorus to surface waters is a global environmental concern. Phosphorus is often a limiting nutrient for the growth of photosynthetic organisms and thus is an important wastewater contaminant due to its role in eutrophication, which leads to oxygen depletion and aquatic toxicity in receiving surface water bodies (Rakotonimaro et al. 2017; Sibrell and Tucker 2012; Zeng et al. 2004). It has been known that iron and aluminum oxides have a strong affinity for phosphate and thus it is standard wastewater treatment to remove phosphorus with iron and aluminum salts (Sibrell and Tucker 2012). Due to the high reagent costs associated with manufactured iron and aluminum salts, research into the more cost-effective use of waste products has been explored (Fenton et al. 2009; Sibrell and Tucker 2012; Sibrell et al. 2015; Zeng et al. 2004).

Zeng et al. (2004) explored the adsorptive removal of phosphate from aqueous solutions using iron oxide mine tailings. The experiments showed that the use of tailings found from a mineral processing facility to remove phosphate was feasible. Initial benchtop sorption studies showed that initial adsorption of phosphate was rapid and that it decreased as pH increased, due to the PZC of the majority magnetite iron oxides found in the tailings. As the pH increased from 3.2 to 9.5, the magnetite crystals began to develop a negative surface charge which repelled the negatively charged phosphate ions. Similarly, phosphate desorption of 13-14% was observed indicating strong bonding between the phosphate ions and the iron oxide solids. Column flow-through tests were performed to confirm the findings of the small-scale experiments and the study concluded that these iron oxide tailings had the potential to be used as a cost-effective removal technology of phosphate in wastewater.

The use of iron oxides produced from mine drainage has been explored as a possible technology to remove phosphate from water. Studies evaluating the application of iron oxide solids in different treatment scenarios have been completed (Fenton et al. 2009; Sibrell and Tucker 2012; Sibrell et al. 2015). Sibrell and Tucker (2012) evaluated phosphorus removal using iron oxides derived from mine drainage in a fixed bed sorption system to investigate the effect that influent concentration, flow rate, and media particle size had on the removal of phosphorus. This study found optimal results with relatively small media particle size (0.028 cm) with 96% removal of phosphorus over 46 days of continuous operation. The study estimated that the phosphorus sorption capacity of their iron oxide media derived from mine drainage to be 10,000 mg/kg at an equilibrium solution concentration of 1.0 mg/L phosphorus, indicating that fixed bed sorption of phosphorus using mine drainage iron oxide solids was feasible.

Sibrell et al. (2015) further examined the practicality of using mine drainage iron oxides to remove phosphorus from agricultural wastewater. Three different mine drainage iron oxide samples from sources with different water chemical composition were collected and their ability to remove phosphorus from dairy farm effluent was compared. The mine drainage solids were collected from an active treatment system with influent mine drainage with a pH of 5-7 and treated with lime, an untreated discharge with pH of 3-6 and elevated concentrations of Fe and Mn, and from a passive treatment system receiving net-alkaline, elevated Fe mine drainage. All the solids decreased water-extractable phosphorus concentrations from 30-50 mg/L to 5 mg/L. The application of amending manure with mine drainage iron oxide solids was shown to feasibly decrease the amount of water-extractable phosphorus and to be economically more favorable than disposing of the iron solids. However, the acidic condition of one of the samples caused the release of manganese and nickel into the water column. A similar study evaluating the use of mine drainage from an abandoned copper-sulfur mine to remove phosphorus showed the mobilization of metals in distilled water, surface lake water, and agricultural wastewater batch experiments (Fenton et al. 2009). While reusing mine drainage iron oxide solids to remove phosphorus from wastewater is effective at phosphate uptake and possibly economically viable, the release of harmful metals, if present, may limit the reuse applicability of iron oxide solids.

3 Project Description

3.1 Purpose, goal and objectives

The overall goal of this project was to develop a thorough understanding of the relationships between mineralogy and sorption capacity in mine-drainage derived iron oxides with respect to phosphorus so that they can potentially be beneficially reused as a phosphorus sorbent. Beneficial reuse of mine water iron oxide solids not only decreases the environmental footprint of mine drainage treatment, but also alleviates the financial burdens of storing, treating, and disposing of such solids. Given the massive scope of the mine drainage problem and that today's reclamation budgets are severely limited, effective methods to decrease costs are both economically attractive and environmentally essential. The project specifically addressed the goal of OSMRE's Applied Science Projects program "to develop and demonstrate improved science-based technologies to address environmental and restoration topics related to the mining of coal", identified as High Priority Topic #8 in the OSMRE FY2020 Applied Science Projects Notice of Funding Opportunity.

The work was completed by personnel from the Center for Restoration of Ecosystems and Watersheds (CREW) at the University of Oklahoma (OU), which maintains a well-established research program (http://crew.ou.edu) focused on watershed biogeochemistry, ecological engineering, and nature-based solutions. In particular, CREW focuses on mine water biogeochemistry and the passive treatment of coal and metal mine waters using natural infrastructure. CREW maintains access to six state-of-the-art, full-scale passive treatment systems and multiple mine drainage discharges in the Mid-Continent Region. The CREW research team is multidisciplinary consisting of engineers and scientists with diverse areas of expertise and interests who together use their understanding of ecosystem biogeochemistry to develop sustainable solutions to complex mining-related environmental problems.

It was hypothesized that the chemical composition of mine drainage waters has a cumulative effect on resulting precipitate mineralogy and physicochemical characteristics affecting their initial sorption capacity. It was also hypothesized that as these iron oxides age they will become more crystalline, and their sorption capacity will decrease causing increased phosphorus and metals concentrations in solution. Lastly it was hypothesized that the reuse of mine drainage iron oxides as a sorbent is economically favorable to traditional solids disposal. The project utilized iron oxide solids from six field sites, four of which were included in the original proposal (Gowen discharge, Howe discharge, Leboskey passive treatment system (PTS) and Rock Island #7 PTS) and two (Mayer Ranch PTS and Southeast Commerce PTS) which were added to diversify the mine drainage chemistry analyzed and to address the loss of the Leboskey site, due to situations beyond the research team's control.

Three related objectives were pursued in completion of the project goal. Objective 1 was to comprehensively evaluate how water chemical composition affects the mineralogy of iron oxide mine drainage treatment solids and their sorption properties. Objective 2 was to evaluate iron oxide mineralogical changes over time and the resulting effects on ratios of adsorption/desorption. Although the methodology proposed to achieve this objective changed as the project proceeded, the objective was still met. Lastly, objective 3 was to estimate the economic benefit provided by using mine drainage treatment solids as sorbents.

3.2 Project tasks

Eight project work tasks were identified to address the project purpose, goal and objectives. They are reiterated here for clarity and references are provided to the appropriate portions of this draft final report where each task is addressed.

Task 1 focused on water quality characterization for each location. Comprehensive water quality sampling and analyses were completed at all study sites and included regular (quarterly) visits. Similarly, historical water quality data were incorporated into the analysis. Task 2 addressed the mineralogical, chemical and physical characteristics of different mine drainage treatment-derived solids from each site location. Task 3 focused on performance of laboratory scale phosphorus sorption studies to determine the solids initial phosphorus sorption capacity and potential for metals desorption. Task 4 evaluated the effect aging of the iron oxide solids had on their phosphorus sorption capacity and metals desorption potential. Task 5 was to create isotherms from data collected from Task 3 and 4 to compare the phosphorus sorption capacity of the iron oxides from different mine drainage chemical compositions and at different ages. Task 6 was to perform an initial economic analysis comparing the costs of recovering iron oxides and reusing them as phosphorus sorbents to traditional sludge management and disposal. Task 7 included data analysis and dissemination to end users. Task 8 was regular project reporting.

Tasks 1, 2, 3, 4, 5 and 6 are addressed in Section 4.0 Results and Discussion. Tasks 7 and 8 include previously submitted Quarterly Project Reports, this draft final report and associated deliverables. Additional publications, presentations and other project outputs are provided in Appendix A.

3.3 Study Sites

3.3.1 Gowen and Howe discharges

The untreated Rock Island Mine #40 (40 Gowen) discharge is located in the Gaines Creek watershed of Pittsburg and Latimer Counties, Oklahoma (Figure 3.1). Of the approximately 10-15 identified discharges in the watershed, waters emanating from the 40 Gowen site, a large volume (836 ± 94 liters per minute), low pH (3.2), metal-rich, and highly visible abandoned mine discharge, have the greatest impact on the receiving stream. The discharge is located near Gowen, Latimer County, Oklahoma and drains the abandoned Rock Island Improvement Company #40 and Kali-Inla Coal Company underground mines, which were mined in the early 1900s. This discharge was chosen for a pilot-scale passive treatment project in 1997, which operated from 1998 through 2003 and successfully retained metals and acidity at controlled flow rates. However, the system was closed after project completion and untreated mine waters now flow through roadside channels to Pit Creek, a tributary to Gaines Creek. These channels accumulate ample iron oxide solids, leading to maintenance issues (Nairn and Mercer 2000).

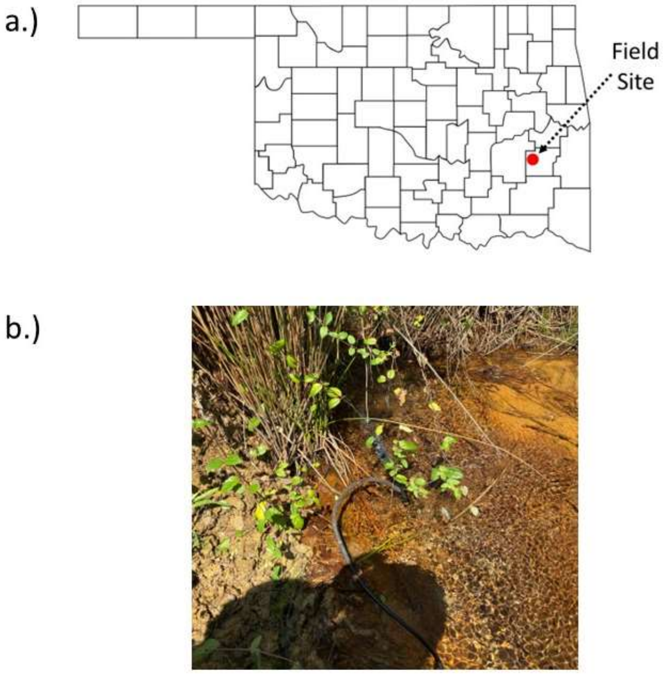

Figure 3.1 a) Location of the Gowen discharge in Latimer County, OK and b) photo of the artesian flowing Gowen discharge during a sampling event.

The untreated Howe discharge emanates from an abandoned underground mine approximately one mile southwest of the community of Howe, Oklahoma and five miles northwest of Heavener, Oklahoma in LeFlore County, OK (Figure 3.2). Like many mines in the Howe-Wilburton District, peak production occurred in the early 20th century after which the mine was abandoned. The artesian discharge flows into a channel before entering Coal Creek.

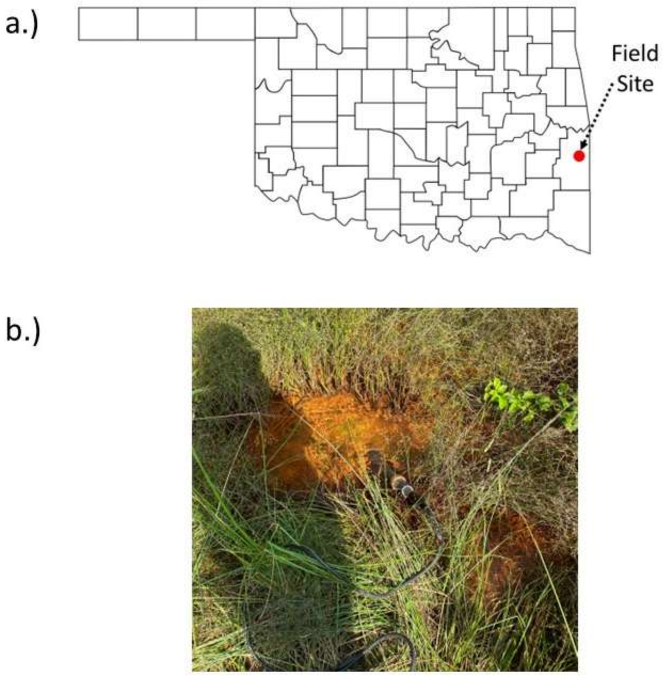

Figure 3.2 a) Location of the Howe discharge in LeFlore County, OK and b) photo of the Howe discharge during a sampling event.

3.3.2 Leboskey PTS and Rock Island #7 PTS

The Leboskey passive treatment system (2004 Clean Streams Reclamation Project 064) was a cooperative effort of OCC and OSMRE Mid-Continent Region (MCR). An artesian underground mine discharge approximately four miles west of Fanshawe, LeFlore County, Oklahoma was captured by an anoxic limestone drain (ALD), an oxidation pond, and a surface flow treatment wetland as shown in Figure 3.3 (Behum et al. 2006). Although initial sampling was completed at this site, landowner concerns and resulting access issues led to the site being deleted for any further analyses. The current status of the Leboskey passive treatment system is unknown.

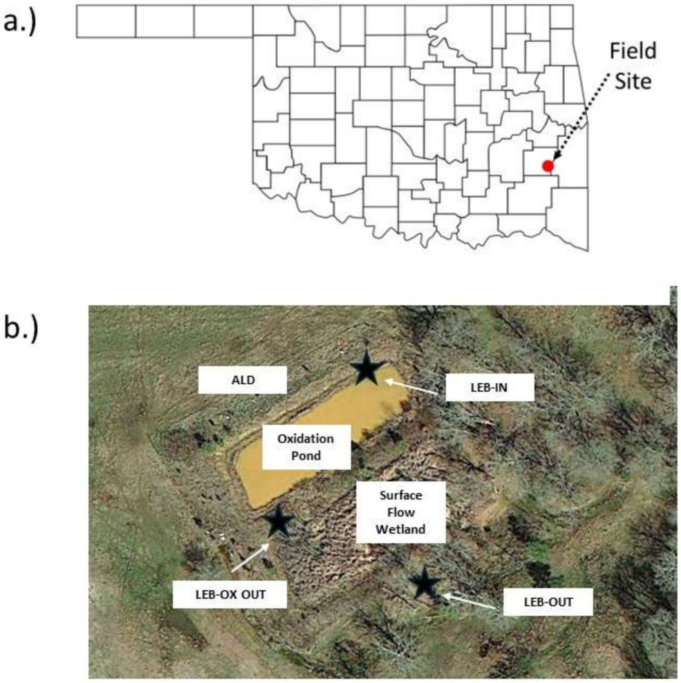

Figure 3.3 a) Location of the Leboskey PTS in LeFlore County, OK and b) aerial view of the system comprised of an anoxic limestone drain (ALD), oxidation pond and surface flow wetland showing the sampling locations.

The Rock Island #7 passive treatment system was constructed in 2005 through a cooperative effort of the OSMRE, Oklahoma Conservation Commission (OCC), Watershed Restoration Incorporated (WRI), and the University of Oklahoma to treat an abandoned (ca. 1930s) discharge from the Rock Island Coal Company #7 underground mine near the town of Hartshorne, Pittsburg County, OK (Figure 3.4). An abandoned fan shaft from which the water discharged was converted into a vertical anoxic limestone drain (VALD). A foundation of local dolomitic stone was placed in the shaft to provide stability, which was then covered by 22 m of calcite limestone (approximately 210 tons) to generate alkalinity. The water then enters the first oxidation pond through an effluent header pipe. The first oxidation pond (1215 m^2) was designed for iron retention via oxidation, hydrolysis, precipitation, and settling and includes three sub-cells separated by limestone reaeration structures. This cell discharges water to a vertical flow cell (650 m^2) that contains a spent mushroom substrate over limestone. The water then enters another oxidation pond, vertical flow cell, aerobic pond, and small polishing wetland before discharge to an existing pond (LaBar et al. 2008; LaBar and Nairn 2009). Water samples were collected from middle influent of the Rock Island #7 PTS (RI7-IN), the effluent of the initial oxidation pond (RI7-OX OUT) and effluent of entire system (RI7-OUT). Iron oxide solids were collected from the second sub-cell in the first oxidation pond of the system where there was sufficient iron oxide accumulation and minimal organic debris.

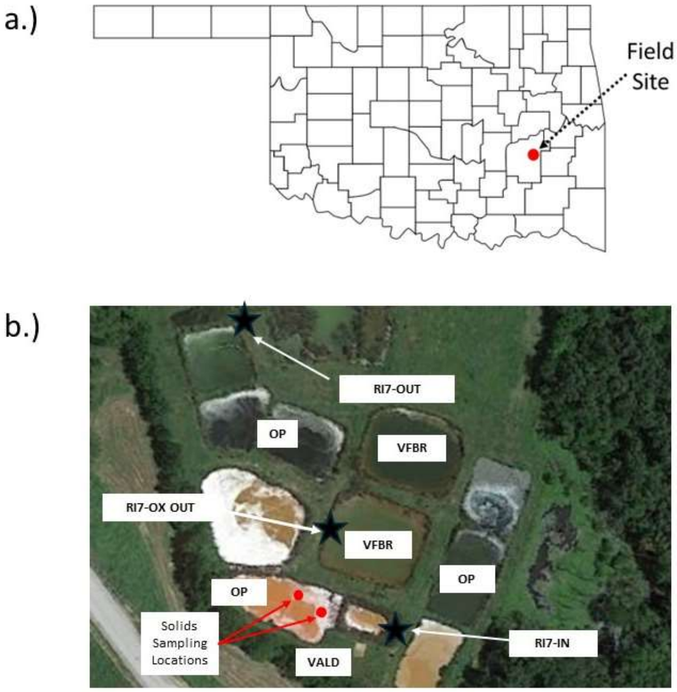

Figure 3.4 a) Location of the Rock Island #7 passive treatment system in Pittsburg County, OK and b) plan view of system showing process units (VALD = vertical anoxic limestone drain, OP = oxidation pond, VF = vertical flow bioreactor, and PW = polishing wetland) with water and solid sample locations.

3.3.3 Mayer Ranch and Southeast Commerce PTS

Sample collection and analyses at the Mayer Ranch and Southeast Commerce passive treatment systems were added as field sites because they increased the robustness of the overall project by providing a readily available source of unique mine drainage chemical composition and resulting novel iron oxide solids. Both systems were designed to treat abandoned mine drainage at the Tar Creek Superfund Site in Ottawa County, Oklahoma. The Tar Creek Superfund Site is located within the Tri-State Lead-Zinc Mining District of Kansas, Oklahoma and Missouri. The mine drainage is net-alkaline with a circumneutral pH and elevated concentrations of Fe, Zn, Pb and Cd.

The Mayer Ranch passive treatment system was constructed in 2008 and consists of an initial oxidation pond (4084 m^2) followed by parallel trains of surface flow wetlands, vertical flow bioreactors, re-aeration ponds, and horizontal flow limestone beds, and a single polishing unit before discharge into an unnamed tributary of Tar Creek. Figure 3.5 shows an aerial of the Mayer Ranch passive treatment system and the water and solids sampling locations.

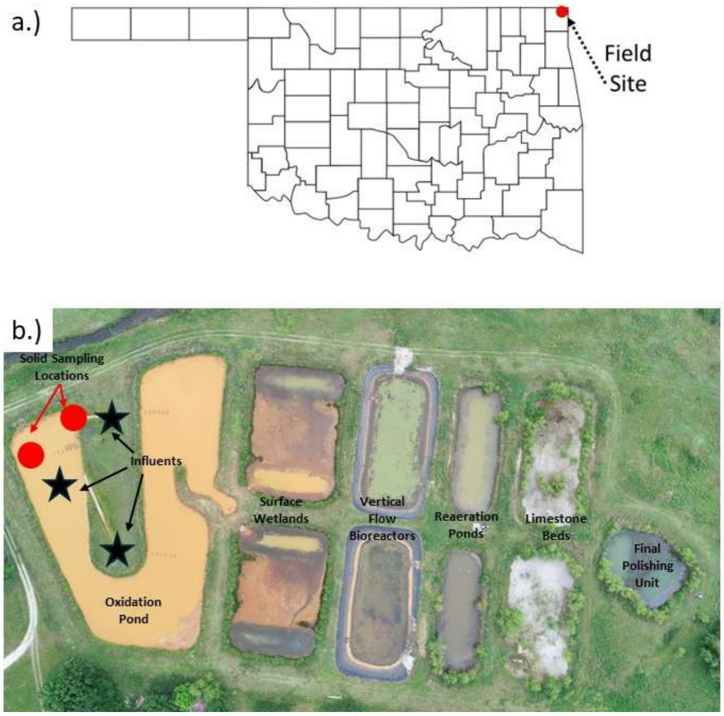

Figure 3.5 a) Location of the Mayer Ranch passive treatment system in Ottawa County, OK and b) aerial plan view of system showing process units: initial oxidation pond, followed by parallel surface-flow aerobic wetlands/ponds, vertical-flow bioreactors, re- aeration ponds, horizontal-flow limestone beds, and a single polishing pond/wetland with water and solids sampling locations marked.

The Southeast Commerce passive treatment system was constructed in 2017 and consists of four treatment cells. The first three treatment cells share a common water surface. The first unit is an oxidation pond (3315 m^2) that includes two solar-powered float-mix aerators that provide air into the water column to facilitate iron oxidation and retention. The water then flows into a surface flow wetland after following a serpentine flow path caused by directional baffle curtains installed to increase the hydraulic residence time. From the wetland, the water enters a vertical flow bioreactor consisting of a woodchip and spent mushroom compost media that promotes sulfate reduction and the production of metal sulfides before it enters a final polishing unit with two more float mix aerators that help add oxygen into the water before it is discharged into the unnamed tributary of Tar Creek (Figure 3.6).

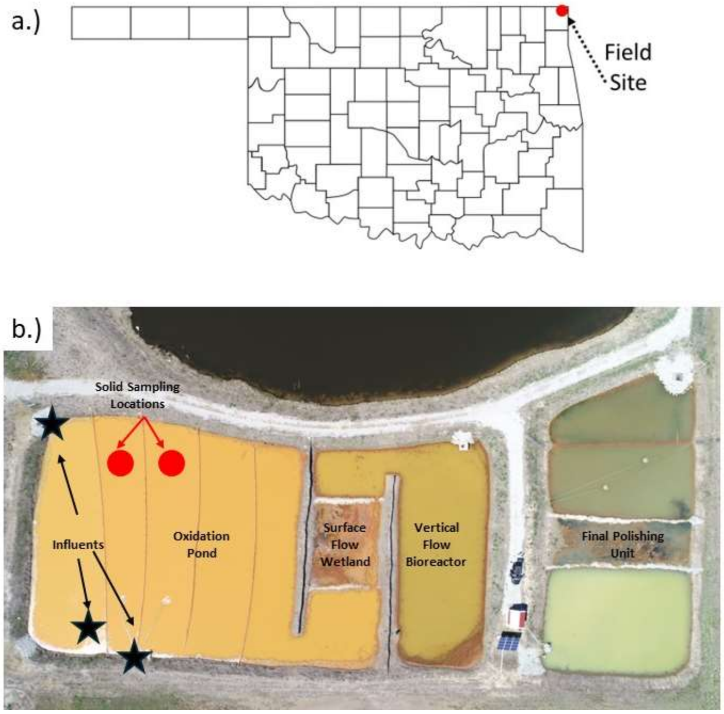

Figure 3.6 a) Location of the Southeast Commerce passive treatment system in Ottawa County, OK and b) aerial view of system showing process units: initial oxidation pond, followed by surface-flow aerobic wetlands vertical-flow bioreactor a final polishing unit with water and solids sampling locations marked.

3.4 Experimental and analytical procedures

3.4.1 Water quality sampling and analysis

Water quality sampling events were conducted on May 20, 2021, June 16, 2021, July 26, 2021, August 18, 2021, October 8, 2021, January 12, 2022, April 15, 2022, July 18, 2022, November 15, 2022 and April 15, 2023. During these sampling events, complete water quality characterizations were made at Howe discharge (HOWE), the untreated Rock Island Mine #40 Gowen discharge (GOWEN), the inlet of the Leboskey PTS (LEB-IN), the outlet of the Leboskey PTS oxidation pond (LEB-OX OUT), effluent of the Leboskey PTS (LEB-OUT), middle influent of the Rock Island #7 PTS (RI7-IN), the effluent of the Rock Island #7 PTS oxidation pond (RI7-OX OUT) and effluent of the Rock Island #7 PTS (RI7-OUT) when there was flow and access to the site. Regular water quality monitoring of the Mayer Ranch and Southeast Commerce passive treatment systems was conducted under a separate and distinct project from a different funding source.

These monitoring efforts included in-situ analyses and collecting water samples for further analysis in the laboratory. Measurements of pH, dissolved oxygen (as concentration and percent saturation), specific conductance, conductivity, resistivity, salinity, total dissolved solids, oxidation-reduction potential (ORP) and temperature were obtained in situ using a multi-parameter water quality instrument (YSI 600QS with 650MDS controller). Turbidity was determined on a portable Hach 2100P Ratio Turbidimeter. Total alkalinity was measured via Hach

Digital Titrator (Method 8203) with sulfuric acid cartridges of the appropriate normality and volumetric glassware. All field instruments were properly calibrated and maintained and appropriate Quality Assurance/Quality Control procedures were followed.

For each sampling event (location-date pair), samples were collected for analysis of total and dissolved metals (e.g., Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn) and anions (Cl^- ,NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}). Water samples were gathered in pre-cleaned 250-mL HDPE bottles at all sampling locations. Samples for total metals analyses were field-acidified with trace-metal grade HNO_3 to a pH <2 to prevent precipitation of dissolved metals. Another sample was field-filtered upon collection through a 0.45 µm in-line filter and field-acidified to pH < 2 for dissolved metals analyses. Samples for anions were left unpreserved with zero head space. All samples were placed on ice in insulated coolers and stored at 4°C upon collection. All samples were returned to the CREW laboratories at the University of Oklahoma for analysis.

Total and dissolved metals underwent a hot nitric acid digestion (EPA Method 3015 using a CEM MARS Xpress Digestion System) before being analyzed via inductively coupled plasma-optical emission spectroscopy (ICP-OES) (EPA Method 6010 using a Varian Vista-Pro simultaneous axial ICP-OES). Anion samples were analyzed using their respective EPA Methods on a Seal Analytical AQ 300 automated discrete analyzer.

3.4.2 Iron Oxide Solids Collection and Characterization

Iron oxide solids were initially collected as grab samples with a stainless-steel shovel from multiple surface locations at each site. The solids were stored in 1-L sealable LDPE bags and were placed on ice in insulated coolers and stored at 4°C upon collection. The stainless-steel shovel was thoroughly washed with deionized water between each sampling site. Once the samples arrived at the CREW laboratories at the University of Oklahoma, they were frozen and later freeze dried at a vacuum of 10 µm of mercury and a vessel temperature of -40°C with a Labconco benchtop freeze dry system. Freeze drying was utilized to avoid any phase transformations that could occur (especially with ferrihydrite) during conventional air or oven drying processes (Schwertmann and Cornell, 1991). After the solids were freeze-dried, they were sieved through a No. 60 sieve (250 µm) to remove organic debris.

The solids were analyzed for their moisture content and organic matter content following gravimetric water content (ASTM D-2216) and loss on ignition (ASTM D7348-21) methods, respectively. The total metals concentrations of the iron oxide solids were determined after hot nitric acid digestion (EPA Method 3051) via ICP-OES (EPA Method 6010). The percent crystallinity of the solids was determined using ammonium oxalate extractions (Schwertmann and Cornell 1991) which selectively removes nanocrystalline iron oxide minerals such as ferrihydrite and schwertmannite. All these analyses were run in triplicate to account for heterogeneity within samples.

The point of zero net charge (PZNC) was calculated for the solids from each location using the static point method and by the ion adsorption method (Appel et al. 2003). The static point method described in Ahmed and Maksimov (1968) involves measuring how the pH of the solid and solution changes over time and the number of protons or hydroxyl ions released by the solid is calculated. The ion adsorption method involves saturating the solid with salt solutions across a pH range and calculating the cation exchange capacity (CEC) and anion exchange capacity (AEC) for the solid. The CEC and AEC are plotted against pH and the pH at which the AEC and CEC cross is the PZNC.

The mineralogy of the solids was determined using powder X-ray diffraction (XRD) analyses using a Rigaku SmartLab diffractometer with a Cu X-ray source. The resulting XRD peaks and patterns were matched to an existing database using the Rigaku SmartLab Studio and JADE Pro software packages to determine the minerals present. Particle size and surface morphology and additional mineral identifications were determined using a Zeiss NEON Field-Emission Scanning Electron Microscope. Microscopy data collection was performed at the Samuel Roberts Noble Microscopy Laboratory, an OU core facility supported by the Vice President for Research and Partnerships. Micrographs of several magnifications were taken for each sample in order to capture the array of particle sizes that are present, while still allowing for the inspection of individual crystalline structures. Specific surface area analyses were performed by the Integrated Core Characterization Center laboratory at the University of Oklahoma by BET nitrogen gas adsorption using a Micrometrics TriStar II Plus surface area and porosity analyzer.

3.4.3 Static sorption studies

After characterizing the iron oxide solids from different sites, solids from Gowen, RI7 and MRPTS were selected for further analysis. These solids were used to represent the three main different mine drainage chemical compositions: untreated net-acidic coal mine discharges (Gowen), net-acidic coal mine drainage rendered net-alkaline via an anoxic limestone drain (RI7) and net-alkaline hard rock mine drainage (MRPTS). Ferrihydrite was synthesized in the laboratory and used as a positive control to examine what the optimum phosphorus sorption capacity could be and how the naturally derived iron oxide solids compared.

The sorption study was performed in a controlled environment using deionized water with phosphorus added to the water as anhydrous KH_2PO_4 salt with phosphorus concentrations ranging from 0 to 4,000 mg/L P. In each case, 0.5 g of freeze-dried sample and 100 mL of various phosphorus concentrations (0, 1, 5, 10, 50, 100, 250, 500, 1000, 2000, 3000 and 4000 mg/L P) were added into sealed 250-mL glass Erlenmeyer flasks. The pH of each sample was measured and then all the flasks were placed on an orbital shaker at 100 rpm for 24 hours. After mixing, the samples were analyzed for pH and then filtered through 0.45-µm syringe filters into clean sample bottles and analyzed for soluble reactive phosphorus via the SEAL Analytical AQ 300 automated discrete analyzer (EPA Methods 145-A and 146-A) and dissolved metals concentrations via ICP-OES (EPA Methods 3015 and 6010). Isotherms were created for each sample subset to track the phosphorus adsorption capacity and metal desorption capacity of the iron oxide solids.

3.4.4 Aging sorption studies

Sorption behavior is related to mineralogy, but mineralogy changes over time and space. To examine this phenomenon in a real-world setting, accumulated iron oxide core samples were collected from the RI7 and MRPTS sites to determine how the solids age in situ. The core samples were collected in 3.2 cm diameter polyacrylic tubes. The cores were taken to the CREW laboratories at the University of Oklahoma where they were frozen, then cut into 10 cm sections and freeze-dried. These solids were characterized physicochemically and mineralogically to determine their differences prior to sorption studies. These solids were analyzed mineralogically via XRD and SEM imaging and their charge capacity determined by measuring their SSA using the same instruments and methods stated before.

The age of the solids was estimated from mass loading rates and depth of the sample. The fresh samples were the top 10 cm of the core while the “aged” solids were considered the bottom 10 cm of the core depth. Once the “fresh” and “aged” solids were characterized, a series of static sorption studies were performed with a constant phosphorus concentration of 50 mg/L P and a range of mass (0.005 to 1.0 gram) of freeze dried “fresh” and “aged” solids from each site. The pH of each batch with differing iron oxide samples was measured before the vessels were shaken for 24 hours at 150 rpm. The pH of the solutions was then measured before the solution was decanted and filtered from the mixture and analyzed for ortho-phosphate concentrations and metals concentrations via methods described previously. Isotherms were created for each sample subset to track the phosphorus adsorption capacity and metal desorption capacity of the iron oxide solids. The phosphorus and metals isotherms were compared for the “fresh” and “aged” solids from each site to determine how age affects the sorption capacity of iron oxides.

3.4.5 Economic analysis

The cost related to managing mine drainage treatment solids is being estimated and compared to the storage and management costs associated with traditional disposal practices to evaluate the potential, economic advantage of reusing iron solids as sorbents. The oxidation pond and sludge removal estimates are being augmented with updated industry prices and incorporating as much of the characterization data collected as possible. Estimates for recovering, processing, and producing iron oxide solids from passive treatment systems are being compared to the costs of traditional sludge management such as landfills. In addition, the cost of the recovered iron and their sorption capacity is compared to other commercially available phosphate sorbents to determine their market competitiveness.

4 Results and Discussion

4.1 Mine drainage and solids characterization

Water quality sampling events at the Gowen discharge, Howe discharge, Leboskey PTS and RI7 PTS were conducted from May 2021 to April 2023, as previously described in Methods. The Leboskey PTS was not sampled after July 2022 due to the landowner's wishes to have the PTS removed. Table 4.1 provides a summary of the water quality physical parameters collected in the field at each location. A summary of the anion and total metals data collected from these sampling events and analyzed in the CREW laboratory are shown in Table 4.2 and Table 4.3, respectively.

Because the water quality data sets for the Mayer Ranch and the Southeast Commerce passive treatment systems are much more robust and complete than for the other sites, these data are summarized for the life of the systems, fifteen and six years, respectively, rather than for the shorter period of this study. The summary of physical parameters, anions and total metals data are shown in Tables 4.4, 4.5, and 4.6.

Table 4.1 Summary statistics for water quality physical parameter data (temperature, specific conductance, dissolved oxygen as percent saturation and concentration, oxidation-reduction potential, total alkalinity, and turbidity) for the sites sampled for this project. Sample sizes ranged from 6-10 depending on the presence of flow. "SE" refers to standard error of the mean; "Max." and "Min." refer to maximum and minimum values.

	Temp. (°C)	SC (mS/cm)	DO (%Sat)	DO (mg/L)	pH (su)	ORP (mV)	T. Alk. (mg/L $CaCO_3$)	Turb. (NTU)
GOWEN								
Mean	17.35	0.98	32.64	3.12	4.47	174.97	5.31	2.43
SE	0.04	0.03	6.90	0.66	0.11	48.57	1.84	0.71
Max.	17.52	1.09	87.60	8.36	4.92	519.50	14.45	6.51
Min.	17.17	0.84	12.50	1.20	3.96	-13.00	0	0.19
HOWE								
Mean	16.84	0.41	29.37	2.84	4.46	150.08	2.02	3.50
SE	0.06	0.01	7.95	0.77	0.11	39.84	0.88	1.49
Max.	17.09	0.48	92.80	8.94	5.01	317.20	6.45	14.30
Min.	16.39	0.36	5.90	0.57	3.73	-82.20	0	0.41
LEB-IN								
Mean	17.47	0.36	24.33	2.32	6.63	-53.26	182	7.66
SE	0.56	0.01	5.96	0.56	0.11	13.52	8.70	1.81
Max.	18.76	0.40	59.70	5.58	7.19	21.30	214	13.10
Min.	14.16	0.31	7.30	0.68	6.27	-82.40	135	0.47
LEB-OX OUT								
Mean	23.51	0.29	64.51	5.74	6.93	-5.90	130	27.79
SE	3.60	0.01	14.20	1.32	0.06	48.40	3.38	4.26
Max.	31.37	0.37	117	9.64	7.12	137.40	148	50
Min.	4.89	0.25	15.20	1.20	6.71	-221.50	121	118
LEB-OUT								
Mean	20.46	0.27	40.70	3.67	6.72	-39.07	161	10.15
SE	2.32	0.02	7.61	0.64	0.03	25.27	7.59	3.25
Max.	25.78	0.35	76.10	6.22	6.86	31.80	182	26.97
Min.	6.49	0.20	14.50	1.21	6.61	-135.90	136	2.20
RI7-IN								
Mean	20.11	3.07	39.71	3.57	6.41	-24.28	308	3.64
SE	0.39	0.64	6.91	0.62	0.09	61.23	6.98	0.57
Max.	20.86	5.47	80.80	7.18	6.97	400.20	331	6.35
Min.	17.98	0.08	17.30	1.60	6.17	-133.50	269	1.50
RI7- OX OUT								
Mean	23.59	3.94	111.73	9.43	6.48	91.25	78.92	82.21
SE	3.93	0.60	16.09	1.29	0.25	52.95	23.42	15.66
Max.	34.04	5.44	160	13.76	7.18	340.90	162	133
Min.	7.44	2.18	58.40	5.27	5.90	-1.40	26.50	32.93
RI7-OUT								
Mean	22.24	3.31	94.91	8.14	6.95	120.89	146	20.30
SE	2.57	0.47	16.45	1.29	0.28	52.29	28.04	11.02
Max.	31.51	4.96	175	13.56	7.74	430.90	298	96.53
Min.	7.93	0.47	55.70	4.37	5.26	-24.20	14.50	2.61

Table 4.2 Summary of anion concentrations for the sites sampled for this project. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit. "SD" and"SE" refer to the standard deviation and standard error of the mean.

	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)
GOWEN					
Mean	456	10.56	0.01	0.04	0.10
N	10	10	8	8	8
SD	129	2.91	0.00	0.06	0.04
SE					
HOWE					
Mean	164.80	3.81	0.01	0.07	0.09
N	10	10	9	9	8
SD	45.61	0.42	0.01	0.06	0.05
SE					
LEB-IN					
Mean	1010	4.18	0.04	0.54	0.14
N	8	8	8	3	6
SD	2472	1.35	0.02	0.80	0.03
SE					
LEB-OX OUT					
Mean	370.46	1.34	0.01	0.07	0.07
N	7	7	7	4	5
SD	766.56	0.27	0.01	0.12	0.05
SE	289.73	0.10	0.00	0.06	0.02
LEB-OUT					
Mean	262.34	0.99	0.01	0.06	0.10
N	7	7	7	3	5
SD	495.81	1.00	0.002	0.07	0.04
SE	187.40	0.38	0.001	0.04	0.02
RI7-IN					
Mean	3358.76	87.07	0.05	BDL	0.18
N	8	8	8		7
SD	5164.57	26.34	0.02		0.05
SE	1825.95	9.31	0.01		0.02
RI7- OX OUT					
Mean	1816.10	81.86	0.03	0.05	0.18
N	6	6	5	6	5
SD	875.14	25.59	0.01	0.05	0.07
SE	357.28	10.45	0.01	0.02	0.03
RI7-OUT					
Mean	1837.94	68.05	0.01	0.11	0.11
N	8	8	6	3	6
SD	842.38	38.14	0.01	0.13	0.02
SE	297.83	13.48	0.00	0.08	0.01

Table 4.3 Summary of total metals concentrations for the sites sampled during this project period. "BDL" refers to below detection limits. "SD" refers to the standard deviation. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit.

		Ag	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe
		--mg/L--									
GOWEN											
	Mean	0.004	14.88	BDL	0.01	51.80	0.01	0.10	0.004	0.002	124
	SD	0.001	5.14		0.001	5.51	0.002	0.04	0.002	0.001	17.59
	N	5	10		9	10	10	9	9	8	10
HOWE											
	Mean	0.003	2.19	BDL	0.01	16.81	0.005	0.07	0.002	0.004	35.86
	SD	0.0001	0.78		0.0008	1.00	0.002	0.02	-	0.003	10.10
	N	2	10		9	10	9	10	1	8	10
LEB-IN											
	Mean	0.003	0.10	BDL	0.01	48.46	0.004	0.003	BDL	0.003	30.75
	SD	0.002	0.18		0.00	3.92	0.001			0.002	3.86
	N	4	8		8	8	8	1		6	8
LEB-OX OUT											
	Mean	0.003	0.08	BDL	0.02	48.04	0.002	0.004	BDL	0.003	9.46
	SD	0.002	0.08		0.01	3.27	0.001	0.002		0.002	11.79
	N	3	7		7	7	3	2		3	7
LEB-OUT											
	Mean	0.003	0.05	BDL	0.02	50.64	BDL	BDL	BDL	0.004	1.69
	SD	0.0004	0.04		0.01	10.26				0.002	1.02
	N	3	8		8	8				5	8
RI7-IN											
	Mean	0.01	0.04	0.03	0.01	278.50	0.02	0.01	BDL	0.004	168.62
	SD	0.002	0.03	-	0.001	73.46	0.01	0.004		0.003	102.49
	N	8	8	1	7	8	7	3		7	8
RI7-OX OUT											
	Mean	0.01	0.04	BDL	0.01	293.74	0.01	0.003	BDL	0.01	49.88
	SD	0.003	0.03		0.005	96.13	0.005	-		0.002	48.93
	N	6	6		5	6	5	1		5	6
RI7-OUT											
	Mean	0.01	0.29	BDL	0.02	273.80	0.0006	BDL	0.01	0.01	1.40
	SD	0.003	0.34		0.01	108.65	0.0005		-	0.003	1.15
	N	8	8		7	8	2		1	7	8

Table 4.3 Continued Summary of total metals concentrations for the sites sampled during this project period. "BDL" refers to below detection limits. "SD" refers to the standard deviation. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit.

		K	Li	Mg	Mn	Na	Ni	Pb	Si	Zn
		mg/L								
GOWEN										
	Mean	6.70	0.10	34.04	6.01	16.50	0.27	0.19	18.49	0.46
	SD	0.47	0.01	2.59	2.26	2.67	0.05	0.03	2.81	0.16
	N	10	10	10	10	10	10	9	10	10
HOWE										
	Mean	1.90	0.07	17.60	2.76	4.07	0.16	0.06	10.37	0.27
	SD	0.23	0.01	2.32	1.04	0.58	0.03	0.02	0.88	0.06
	N	10	10	10	10	10	10	9	10	10
LEB-IN										
	Mean	2.47	0.04	6.20	1.09	4.55	0.03	0.05	9.91	0.01
	SD	0.25	0.01	0.54	0.11	0.59	0.02	0.01	0.83	0.003
	N	8	8	8	8	8	8	7	8	7
LEB-OX OUT										
	Mean	2.51	0.04	6.23	3.44	4.63	0.02	0.06	8.10	0.01
	SD	0.34	0.005	0.49	3.76	0.48	0.01	-	0.67	0.004
	N	7	7	7	7	7	7	1	7	6
LEB-OUT										
	Mean	1.88	0.04	6.53	1.64	4.15	0.02	0.04	8.39	0.01
	SD	0.91	0.01	1.03	1.06	1.20	0.01	0.05	1.97	0.001
	N	8	8	8	8	8	8	2	8	6
RI7-IN										
	Mean	24.20	0.21	79.19	3.24	471.96	0.05	0.29	20.86	0.02
	SD	7.50	0.05	31.23	2.01	238.04	0.03	0.17	1.17	0.01
	N	8	8	8	8	7	8	8	8	8
RI7-OX OUT										
	Mean	25.56	0.23	86.46	3.59	473.10	0.03	0.14	12.93	0.02
	SD	6.35	0.05	34.66	2.43	222.68	0.02	0.07	2.07	0.03
	N	6	6	6	6	6	6	4	6	5
RI7-OUT										
	Mean	22.74	0.18	71.84	2.19	406.32	0.02	0.02	8.18	0.01
	SD	7.98	0.08	30.82	3.44	186.11	0.02	0.01	3.12	0.02
	N	8	8	8	8	8	7	3	8	7

Table 4.4 Summary statistics for water quality physical parameter data (temperature, specific conductance, dissolved oxygen as percent saturation and concentration, oxidation-reduction potential, total alkalinity, and turbidity) for the lifespan of MRPTS and SECPTS. "SE" refers to standard error of the mean; "Max." and "Min." refer to maximum and minimum values.

	Temp. (°C)	SC (mS/cm)	DO (%Sat)	DO (mg/L)	pH (su)	ORP (mV)	T. Alk. (mg/L $CaCO_3$)	Turb. (NTU)
MRPTS (n=83)								
Mean	17.62	3.37	22.91	2.17	5.96	27.98	380	5.49
SE	0.02	0.003	0.26	0.03	0.002	1.42	0.38	0.12
Max.	18.19	3.63	105.60	9.88	6.60	349.40	424	72.75
Min.	6.26	2.47	2.60	0.24	4.91	-113.50	215	0.33
SECPTS (n=68)								
Mean	17.53	3.01	42.63	4.02	6.15	-80.92	349	3.82
SE	0.02	0.004	0.47	0.04	0.003	0.75	0.32	0.05
Max.	20.78	3.32	185.20	17.54	6.66	105.40	407	16.70
Min.	15.27	1.63	2.20	0.21	5.29	-160.50	287	0.54

Table 4.5 Summary of anion concentrations for the lifespan of MRPTS and SECPTS. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit. "SD" and"SE" refer to the standard deviation and standard error of the mean.

	SO_4^{2-} (mg/L)	Cl^- (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)
MRPTS					
Mean	2241.54	30.18	1.54	1.08	3.24
N	78	53	18	31	44
SD	304.32	6.08	2.75	0.65	1.87
SE	34.46	0.84	0.65	0.12	0.28
SECPTS					
Mean	1929.58	26.34	0.06	0.03	1.91
N	66	28	36	23	40
SD	251.02	2.44	0.29	0.02	2.28
SE	30.90	0.46	0.05	0.005	0.36

Table 4.6 Summary of total metals concentrations for the lifespan of MRPTS and SECPTS. "BDL" refers to below detection limits. "SD" refers to the standard deviation. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit.

		Ag	Al	As	Ba	Ca	Cd	Co	Cr	Cu	Fe
		mg/L									
MRPTS											
	Mean	0.01	0.12	0.06	0.02	706.51	0.02	0.04	0.004	0.003	165.10
	SD	0.001	0.14	0.01	0.01	43.55	0.01	0.02	0.003	0.002	23.69
	N	16	84	84	20	84	84	82	27	79	84
SECPTS											
	Mean	0.01	0.08	0.06	0.01	654.09	0.01	0.03	0.01	0.004	124.38
	SD	0.002	0.15	0.01	0.01	45.29	0.01	0.01	0.004	0.002	12.84
	N	42	51	65	52	67	65	66	17	63	67

		K	Li	Mg	Mn	Na	Ni	Pb	Si	Zn
		mg/L								
MRPTS										
	Mean	24.81	0.30	178.81	1.39	92.75	0.84	0.11	9.32	7.13
	SD	2.20	0.02	26.10	0.16	11.84	0.11	0.08	0.39	1.31
	N	85	20	85	85	85	85	85	20	85
SECPTS										
	Mean	22.84	0.25	120.83	1.82	79.33	0.47	0.19	18.47	6.24
	SD	1.77	0.02	14.61	0.16	10.59	0.05	0.07	1.67	0.73
	N	67	53	67	67	67	67	67	55	67

Solids produced by the mine drainage discharges and in the passive treatment systems were chemically and physically characterized. The resulting produced solids were mostly mineral iron oxides (Table 4.7). These precipitated solids are primarily in the goethite mineral phase with more amorphous goethite and ferrihydrite phases present in the iron oxides recently precipitated in passive treatment oxidation ponds with higher pH (Table 4.8). This result is perhaps because the PZNC for ferrihydrite is pH 7-8 which is when ferrihydrite is the least soluble and thus is less likely to dissolve and rearrange to form goethite. As the pH moves further away from the PZNC, the transformation rate of ferrihydrite to goethite increases causing a greater ratio of goethite to ferrihydrite (Cornell and Schwertmann 2003). Therefore, solids produced at GOWEN and HOWE which have a lower pH are slightly more crystalline as shown in Table 4.7 which decreases their specific surface area greatly compared to the other iron oxides (Table 4.8). Similarly, iron oxides formed in waters with greater metals concentrations have a greater resulting metal concentration (primarily Pb and Zn) in the solid phase and thus potentially can release more metals as they age or are reused as a sorbent (Figures 4.1-4.5).

Table 4.7 Mean and standard deviation of moisture content, organic matter content and crystallinity measured for iron oxides collected from each site (n=3 for each site).

	Moisture Content	Organic Matter Content	Crystallinity
	---------------------------------------	%	---------------------------------------
GOWEN	56 ± 17	17 ± 3.0	64 ± 5.2
HOWE	58 ± 17	11 ± 4.1	69 ± 4.1
LEB	89 ± 1.4	24 ± 2.8	52 ± 3.9
RI7	75 ± 8.1	14 ± 1.3	55 ± 8.4
MRPTS	81 ± 0.5	16 ± 0.3	56 ± 0.4
SECPTS	85 ± 1.3	14 ± 0.2	61 ± 11.8

Table 4.8 Selected characteristics of the iron oxide samples including predominant mineral phase, specific surface area, and point of zero net charge PZNC.

	Predominant Mineral Phase	Specific Surface Area (g/m^2)	PZNC
GOWEN	Goethite	18	5.55
HOWE	Goethite	40	4.24
LEB	Goethite	135	5.64
RI7	Goethite	167	5.76
MRPTS	Goethite and Ferrihydrite	115	7.11
SECPTS	Goethite	99	5.94

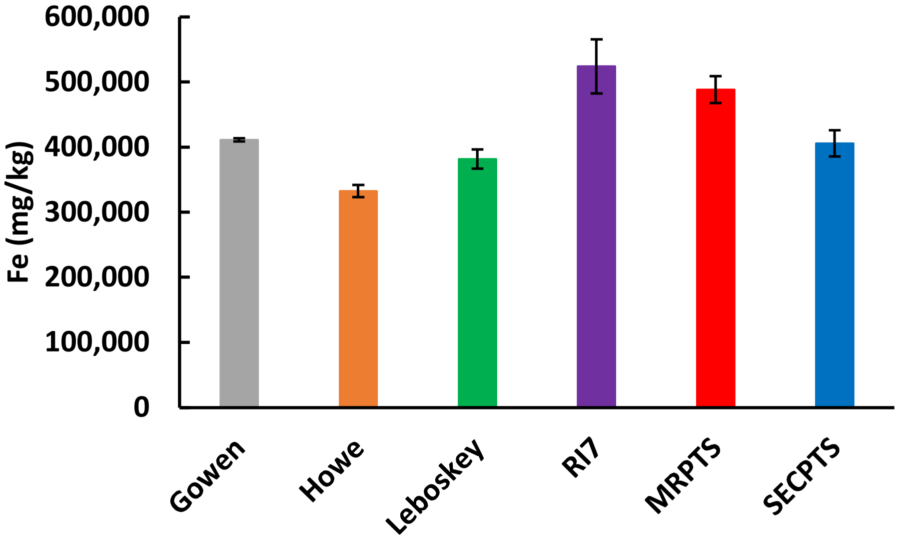

Figure 4.1 Iron concentrations (mean and standard deviation) of solid iron oxide samples collected from each site. The mean and standard deviation are based on n=3.

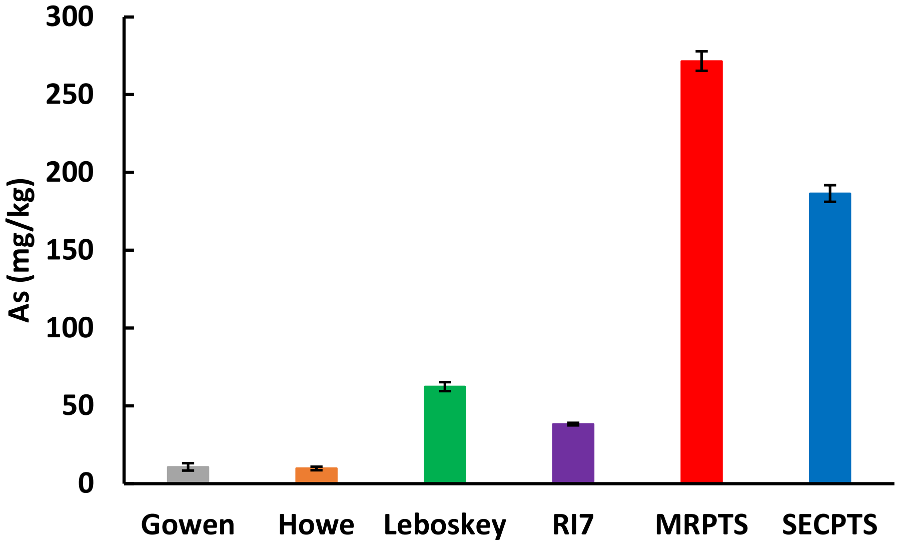

Figure 4.2 The mean and standard deviation of As concentration of solid iron oxide samples collected from each site. The mean and standard deviation are based on a n=3.

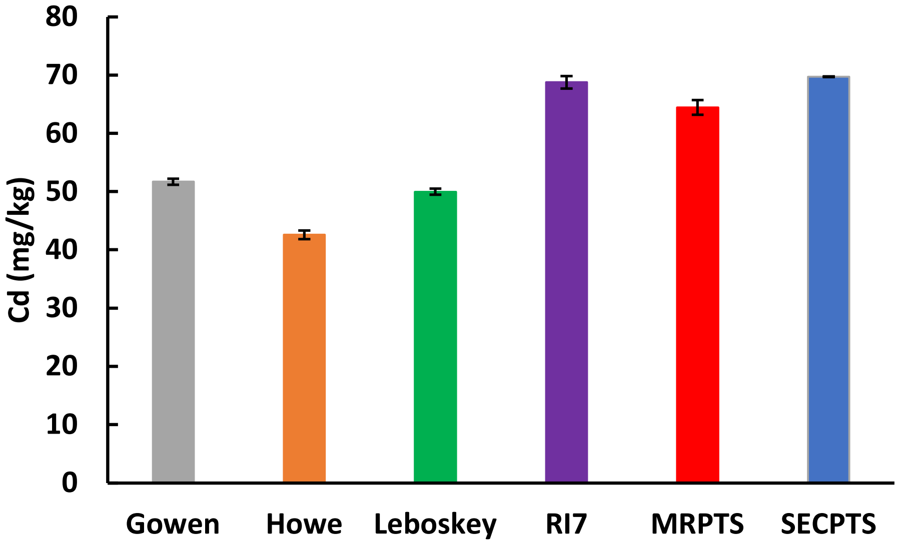

Figure 4.3 The mean and standard deviation of Cd concentration of solid iron oxide samples collected from each site. The mean and standard deviation are based on a n=3.

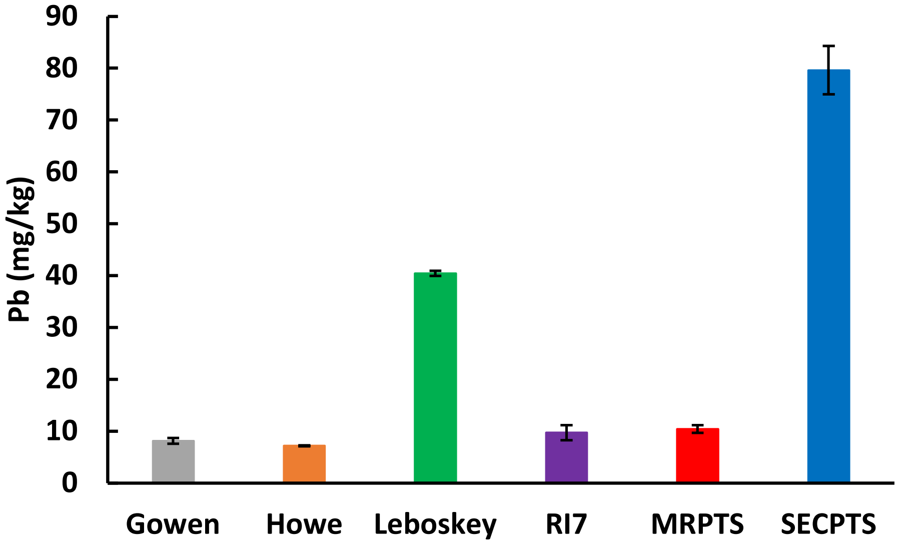

Figure 4.4 The mean and standard deviation of Pb concentration of solid iron oxide samples collected from each site. The mean and standard deviation are based on a n=3.

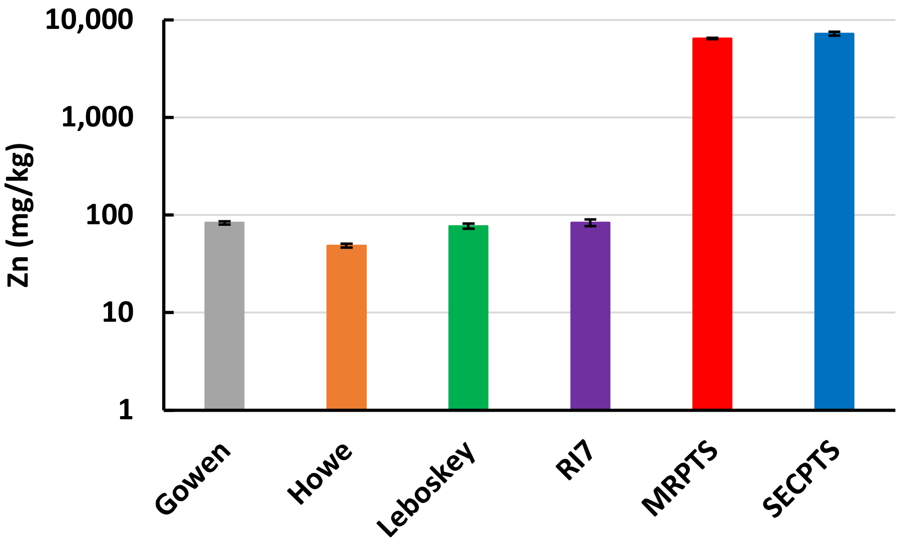

Figure 4.5 The mean and standard deviation of Zn concentration of solid iron oxide samples collected from each site on a logarithmic scale. The mean and standard deviation are based on a n=3.

Although the main mineral phase in all samples was goethite, each site had different mineral morphology and surface area as demonstrated by images captured from scanning electron microscopy (SEM) at a magnification of 5000X (Figure 4.6). The iron oxides from GOWEN and HOWE had a much lower specific surface area (18 and 40 m^2/g, respectively) compared to the iron oxides collected from all other locations which had specific surface areas ≥ 100 m^2/g (Table 4.8). The solids from LEB were larger (≈5 µm) and had a more globular morphology, perhaps exacerbated by the aggregation of smaller iron oxide particles onto larger iron oxide and clay particles. These samples were observed to have a higher clay content associated with them due to the shallow pond depth, presence of natural clay, and relatively low iron content of the source waters. The solids from the RI7 and MRPTS systems also had a globular morphology but were smaller in size (1-2 µm) and showed a smaller (<1 µm) spiky morphology on the surface indicating the aggregation of less amorphous ferrihydrite on their surface providing an even higher surface area for sorption mechanisms.

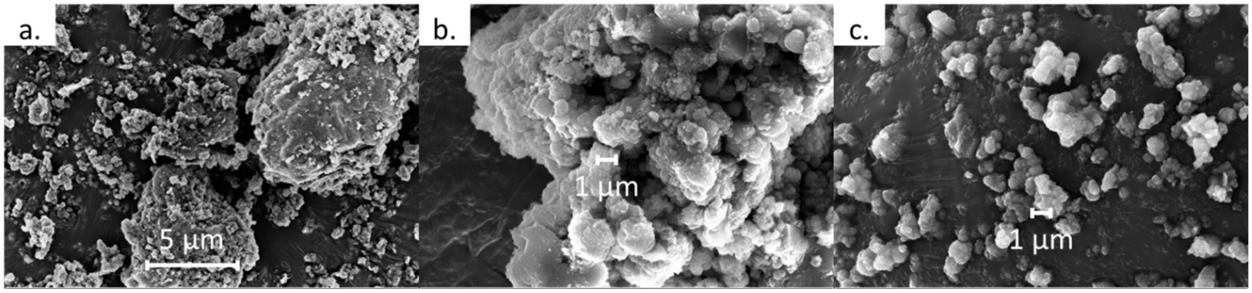

Figure 4.6 SEM photos at a magnification of 5000 of the surface morphology of iron oxides collected from a) the LEB site, b) the RI7 site and c) the MRPTS site.

4.2 Static sorption studies

To determine how mine drainage chemical composition affected the characteristics of the precipitated iron oxides and their initial sorption capacity, benchtop phosphorus sorption capacity experiments were performed. Previous literature has shown that iron oxides have a substantial sorption capacity potential for phosphorus, ranging as high as over 30 mg/g (Tang and Nairn, 2021). Therefore, initial sorption experiments performed for this study used 0.5 g of iron oxide solid with 100 mL of solution with phosphorus concentrations of 0, 1, 5, 10, 50, 100, 250, 500, 1,000 and 2,000 mg/L. However, initial data analyses showed that the sorption capacity of the solids was not reached so phosphorus concentration were increased to 3,000 mg/L and 4,000 mg/L to try to reach the sorption capacity maximum. For this part of the study, only solids collected from GOWEN, RI7, and MRPTS were analyzed. These three sites represent different mine drainage chemical compositions. Also, in order to compare their performance to laboratory-grade iron salts commonly used in industry, ferrihydrite was synthesized in the laboratory and used as a positive control. At least five trials were run with solids from each site in order to account for the heterogeneity of the solids. Figures 4.7-4.10 show the resulting sorption isotherms for laboratory synthesized ferrihydrite, Gowen, RI7 and MRPTS, respectively. There appear to be large standard deviations in the concentration of phosphorus sorbed (C_s) between trials, however, ANOVA showed that trials for each site were not significantly different.

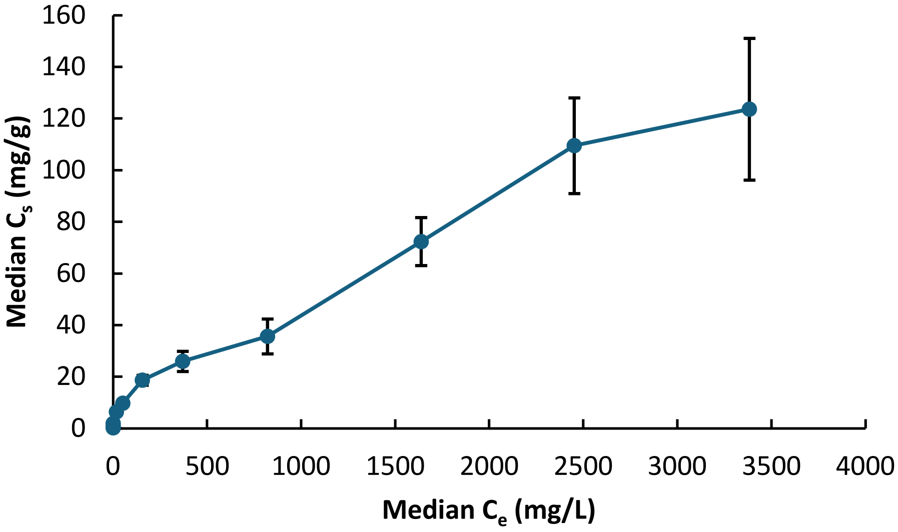

Figure 4.7 Phosphorus sorption isotherm for laboratory synthesized ferrihydrite with the median amount sorbed (C_S) on the y-axis and the amount remaining in solution (C_e) on the x-axis.

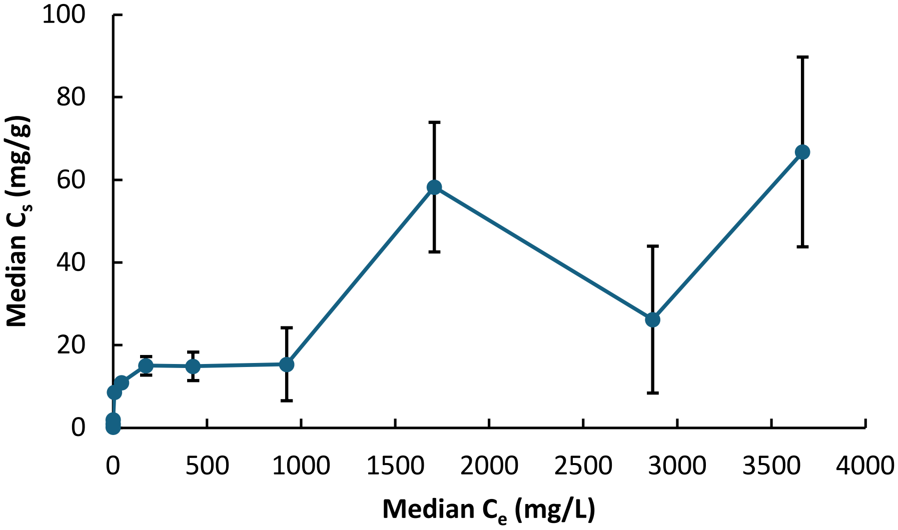

Figure 4.8 Phosphorus sorption isotherm for iron oxides collected from GOWEN with the median amount sorbed (C_S) on the y-axis and the amount remaining in solution (C_e) on the x-axis.

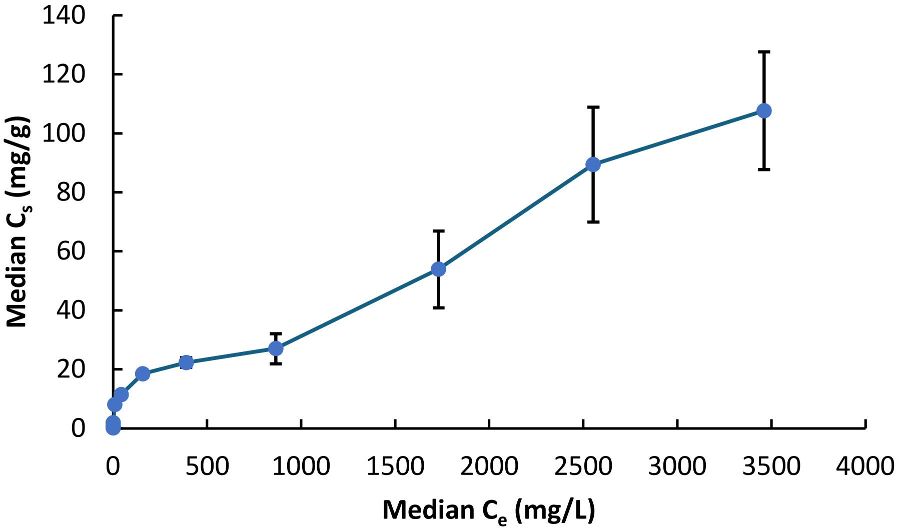

Figure 4.9 Phosphorus sorption isotherm for iron oxides collected from RI7 with the median amount sorbed (C_S) on the y-axis and the amount remaining in solution (C_e) on the x-axis.

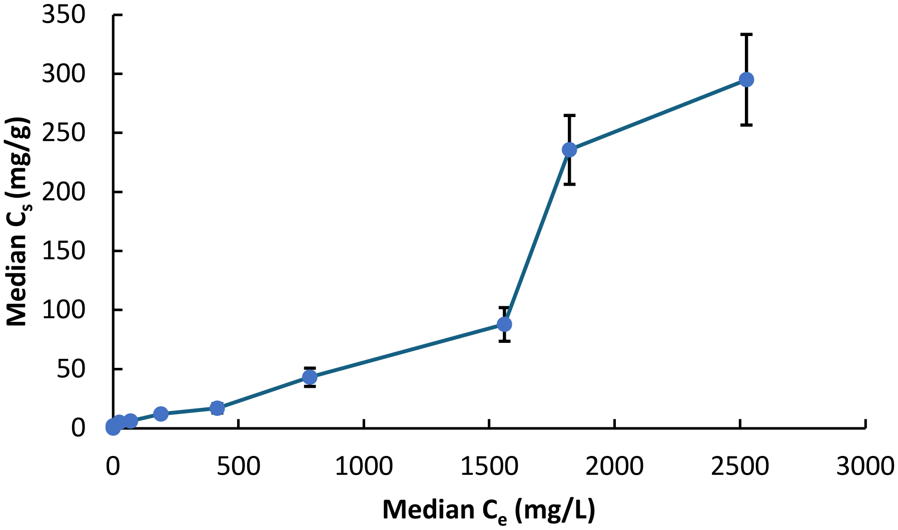

Figure 4.10 Phosphorus sorption isotherm for iron oxides collected from MRPTS with the median amount sorbed (C_S) on the y-axis and the amount remaining in solution (C_e) on the x-axis.

Iron oxides collected from MRPTS sorbed the most phosphorus with a median amount sorbed of 294 mg/g after 24 hours with an initial phosphorus concentration of 4,000 mg/L. This may be because the MRPTS solids have a much higher specific surface area than the GOWEN solids and because the MRPTS solids have a higher PZNC of 7.11 than the Gowen solids (5.55) and RI7 solids (5.76). When the pH of the solution is below the PZNC, the solid surface has a net positive charge and thus is more likely to attract and sorb anions such as phosphate. This result is further demonstrated in the change in pH before and after the sorption experiments in relation to the

PZNC. Figures 4.11-4.13 show the pre and post pH of the vessels for the given initial phosphorus concentration for each sample with respect to their PZNC.

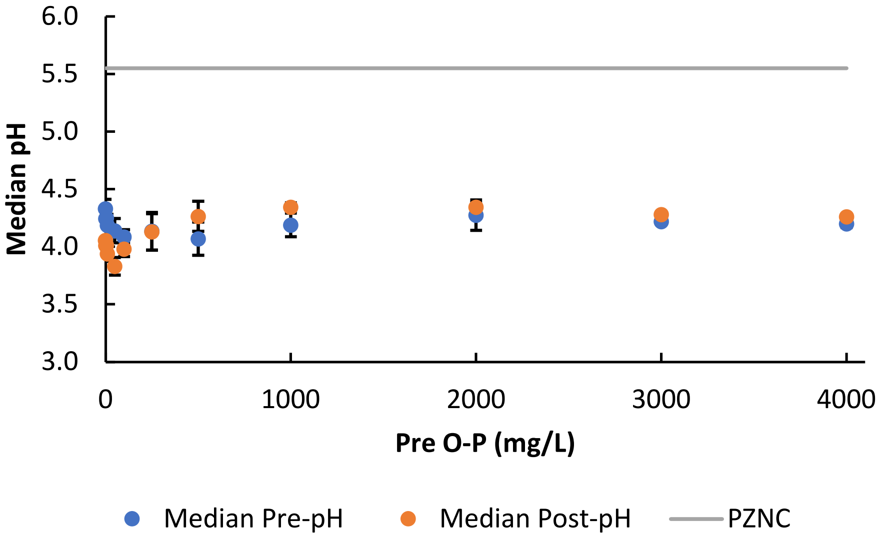

Figure 4.11 Median pH values pre and post 24-hour sorption study compared to the initial phosphorus concentration for GOWEN solids compared to the GOWEN solids PZNC.

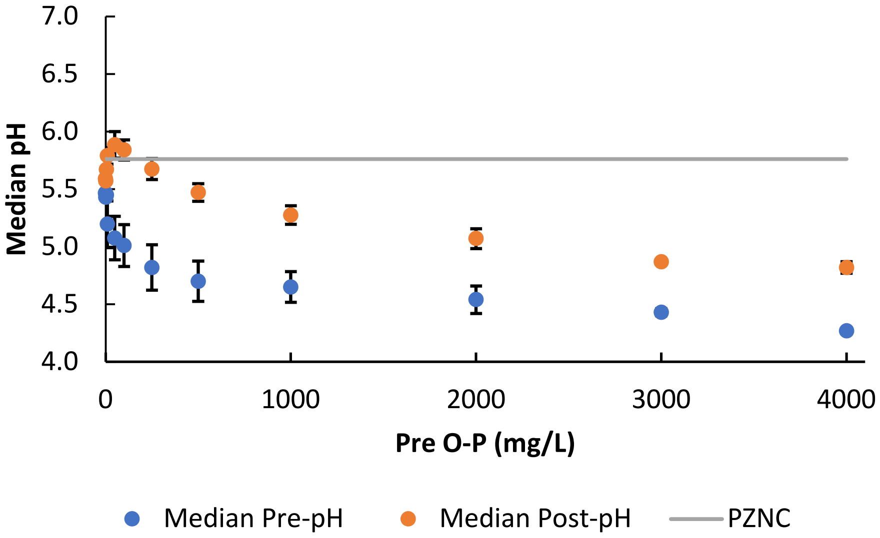

Figure 4.12 Median pH values pre and post 24-hour sorption study compared to the initial phosphorus concentration for RI7 solids compared to the RI7 solids PZNC.

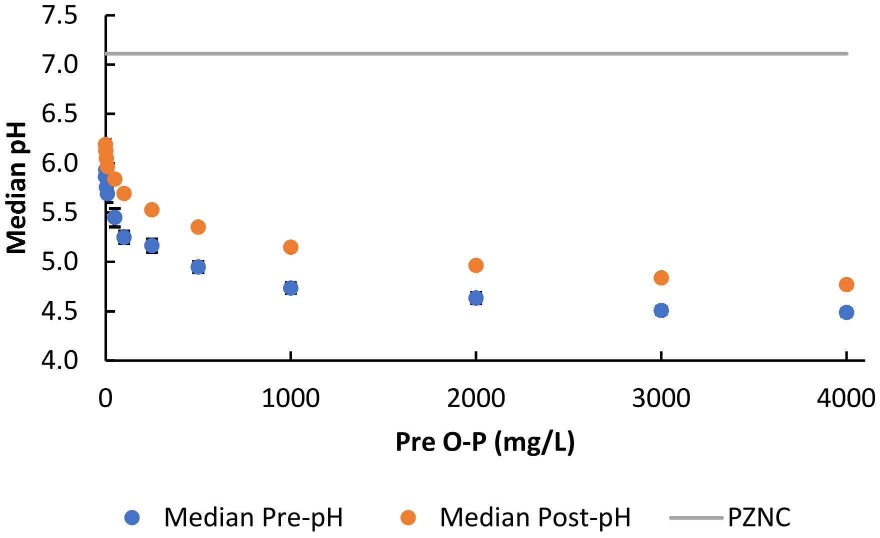

Figure 4.13 Median pH values pre and post 24-hour sorption study compared to the initial phosphorus concentration for MRPTS solids compared to the MRPTS solids PZNC.

The sorption data from the, GOWEN, RI7 and MRPTS trials fit a Freundlich isotherm model best as shown in Figure 4.14. The Freundlich equation is expressed as

$$q = KC^{1/n} \qquad \text{Equation 4.1}$$

where q is the mass of adsorbate adsorbed per unit mass of adsorbent after equilibrium (mg/g), C is the mass of adsorbate in the aqueous phase after equilibrium (mg/L), K is the Freundlich isotherm capacity parameter ((mg/g)(L/mg)$^{1/n}$) and 1/n is the Freundlich isotherm intensity parameter (unitless). For values of 1/n less than 1, the isotherm is considered favorable for sorption. The linearized form of the Freundlich equation (Equation 4.2) can be used to determine the Freundlich isotherm parameters. The corresponding Freundlich isotherm parameters for each iron oxide are shown in Table 4.9.

$$\log q = \log K + \left(\frac{1}{n}\right) \log C \qquad \text{Equation 4.2}$$

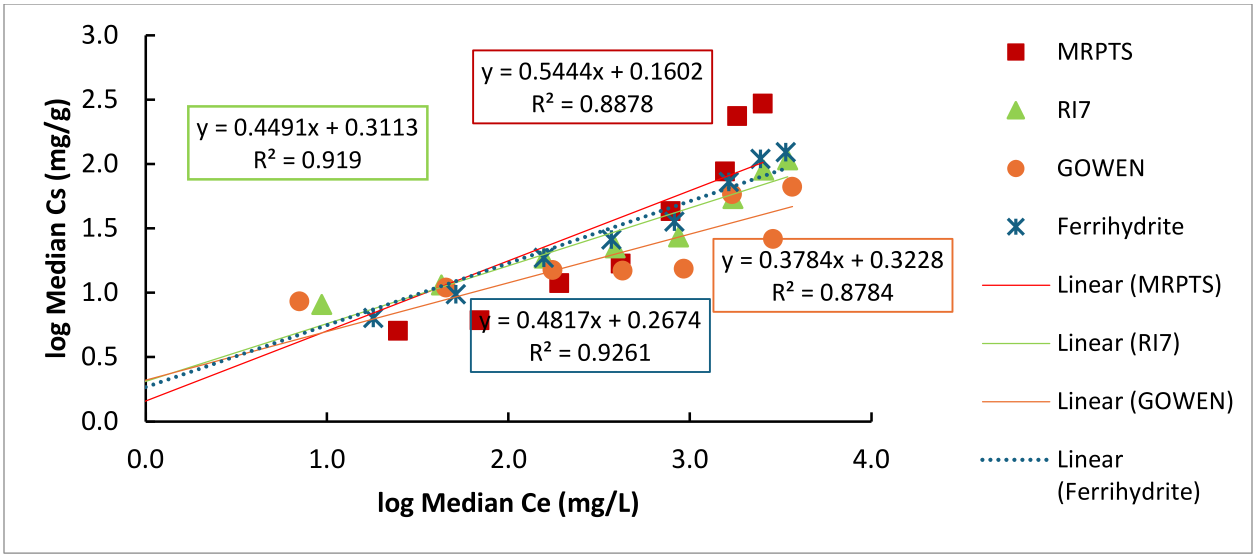

Figure 4.14 Linearized form of the Freundlich isotherm model for the median values of ferrihydrite, GOWEN, RI7 and MRPTS iron oxides.

Table 4.9 Freundlich isotherm parameters determined from experimental data for each set of iron oxide solids.

	K $((mg/g)(L/mg)^{1/n})$	1/n
Ferrihydrite	1.85	0.4817
GOWEN	2.10	0.3784
RI7	2.05	0.4491
MRPTS	1.45	0.5444

The application of the Freundlich model suggests that the surfaces of the iron oxide particles are heterogeneous which is confirmed in the SEM imagery in Figure 4.6. It also implies that the sorption of phosphorus occurs in the form of multilayers, thus determining an accurate phosphorus sorption capacity is impossible. However, the higher K values (>1) imply that the iron oxides can uptake phosphate ions easily and thus iron oxides produced from mine drainage have an equally high sorption capacity as laboratory-synthesized iron oxides.

However, one of the concerns with using iron oxides formed in mine drainage is their potential to release sorbed metals into the environment. Metals data were collected after each sorption trial to investigate whether iron oxides release metals as they uptake phosphorus. Figures 4.15-4.17 show the mean concentration of As, Ni and Zn after the 24-hour sorption study for each iron oxide. Most aqueous metals concentrations were below the detection limits and increased in concentration as the concentration of the phosphorus solution increased. This result may be due to the decrease in solution pH with increasing phosphorus concentrations which caused the surface charge of the iron oxides to become more positive and thus less attractive to metal cations. These elevated phosphorus concentrations are not commonly seen in the environment but were necessary to develop sorption isotherms and determine the ultimate sorption capacity of these solids. Therefore, they do not represent a real-world scenario in which these iron oxides would be used.

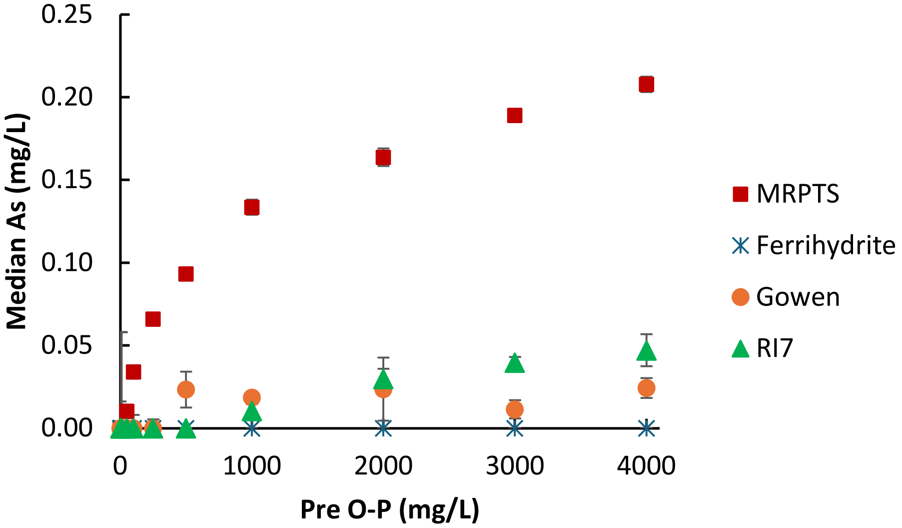

Figure 4.15 Median aqueous As concentrations after the 24-hour sorption study for each iron oxide and phosphorus concentration

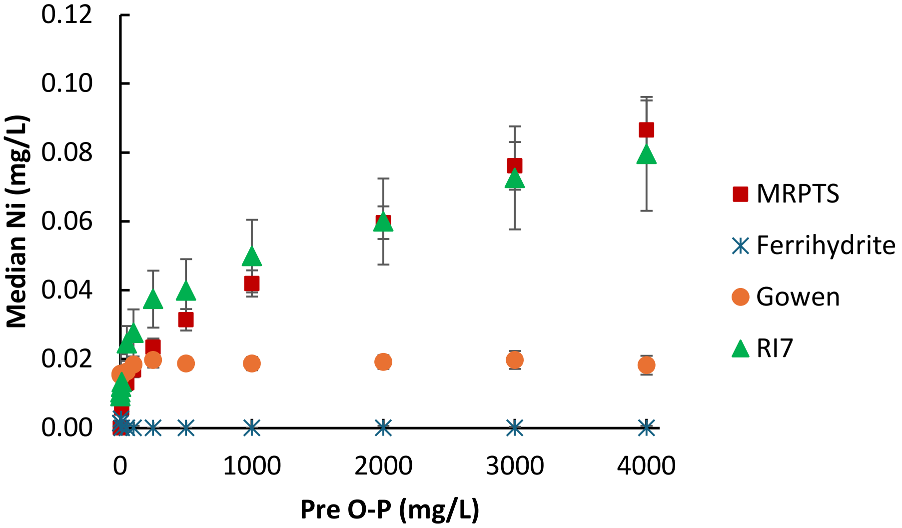

Figure 4.16 Median aqueous Ni concentrations after the 24-hour sorption study for each iron oxide and phosphorus concentration

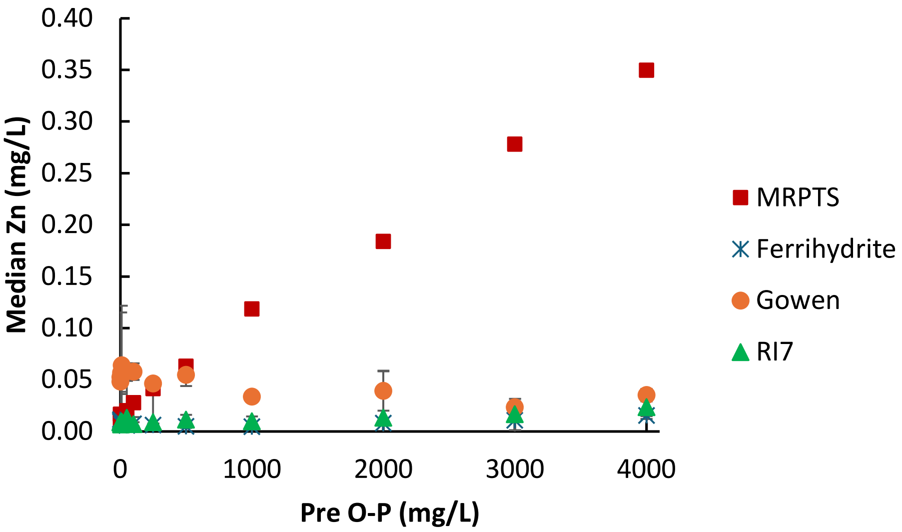

Figure 4.17 Median aqueous Zn concentrations after the 24-hour sorption study for each iron oxide and phosphorus concentration

4.3 Aged solids characterization and sorption study

The previous results have shown that iron oxides characteristics differ between different mine drainage chemical compositions and that they can display heterogeneity within the same site, especially as they are allowed to age in-situ for longer periods of time such as in passive treatment oxidation ponds. Figure 4.18 shows images captured from scanning electron microscopy (SEM) at a magnification of 5000X of the top 10 cm representing iron oxides formed within the past two years and bottom 10 cm of core collected from the MRPTS oxidation pond which formed 13-15 years ago. The top 0-10 cm show smaller particles (1-2 µm) with a spiky morphology showing an increased surface area whereas the bottom 80-90 cm have larger aggregated particles (10-15 µm) with a more platy and less globular morphology. This considerable difference in surface morphology is indicative of differences in mineralogy between the newly precipitated solids and the older deposited solids. This is corroborated by the difference in specific surface areas of iron oxides with depth and age as shown in Table 4.10 for RI7 and in Table 4.11 for MRPTS. The specific surface area of the iron oxides decreases with depth as the solids age and crystallize. The slight increase in specific surface area for MR 100-110 cm and MR 110-120 cm is probably due to the presence of native clay located at the bottom of the pond being captured in the core.

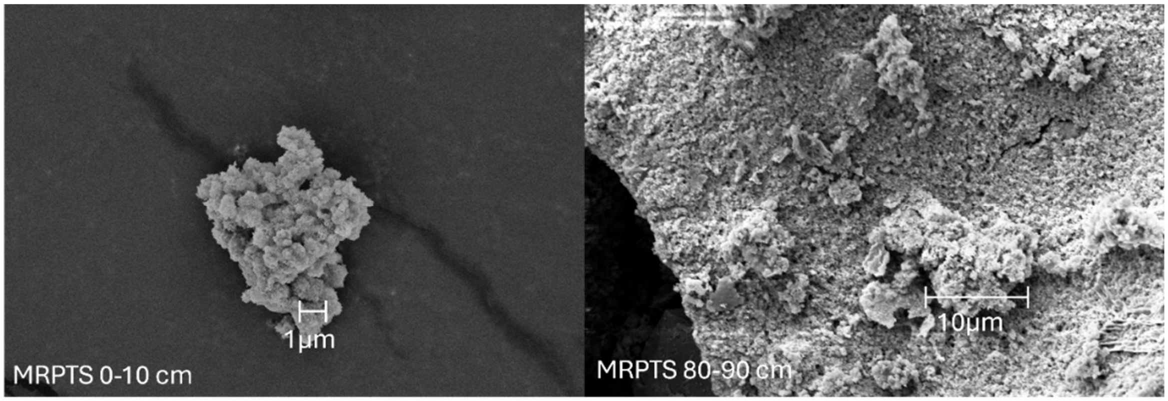

Figure 4.18 SEM photos at a magnification of 5000 of the surface morphology of the top 10 cm (left) and bottom 10 cm (right) of a core collected from the MRPTS oxidation pond.

Table 4.10 BET specific surface area for each 10 cm segment of the core collected from the RI7 passive treatment system oxidation pond.

Sample	Specific Surface Area g/m²
RI7 0-10 cm	149 ± 0.19
RI7 10-20 cm	140 ± 0.17
RI7 20-30 cm	124 ± 0.23
RI7 30-40 cm	128 ± 0.15
RI7 40-50 cm	109 ±0.12
RI7 50-60 cm	101 ± 0.14
RI7 60-70 cm	75 ± 0.16
RI7 70-80 cm	71 ± 0.09
RI7 80-90 cm	74 ± 0.08

Table 4.11 BET specific surface area for each 10 cm segment of the core collected from the MRPTS oxidation pond.

Sample	Specific Surface Area g/m^2
MRPTS 0-10 cm	157 ± 0.26
MRPTS 10-20 cm	136 ± 0.17
MRPTS 20-30 cm	117 ± 0.29
MRPTS 30-40 cm	127 ± 0.19
MRPTS 40-50 cm	108 ±0.14
MRPTS 50-60 cm	107 ± 0.14
MRPTS 60-70 cm	116 ± 0.16
MRPTS 70-80 cm	104 ± 0.13
MRPTS 80-90 cm	95 ± 0.13
MRPTS 90-100 cm	85 ± 0.12
MRPTS 100-110 cm	111 ± 0.15
MRPTS 110-120 cm	104 ± 0.18

The increase in crystallinity and reduction in specific surface area of the solids does impact the phosphorus sorption capacity of the solids as shown in the isotherms created for core samples collected from RI7 and MRPTS in Figures 4.19 and 4.20, respectively. The data were fitted to both a Freundlich and Langmuir isotherm model to determine which was a better fit to the data (Table 4.12). Both the Freundlich and Langmuir isotherms model the data well except for the older and deeper core samples in which the Langmuir isotherm better models their sorption behavior. The Langmuir isotherm assumes that the adsorbent surface is homogeneous and that there a definite number of sorption sites and monolayer coverage. As the iron oxides age, they become more crystalline and therefore the surface has become more homogeneous for monolayer sorption.

Both the Freundlich and Langmuir isotherms show that the newer and shallower iron oxides collected from each site have a greater affinity and sorption capacity for phosphate than the older and deeper iron oxides. The sorption capacity of a commercial iron oxide phosphate sorbent, Bayoxide® E33 P was tested and compared to the sorption capacity of iron oxides from each core to determine if the age greatly affects the marketability of the iron oxides as a phosphate sorbent. The isotherm data show that while Bayoxide® E33 P may have a slightly greater modeled sorption capacity (12.3 mg/g) than even the freshest iron oxide solids, the freshest iron oxides still have a sorption capacity of 9.42 mg/g and 10 .83mg/g for RI7 and MRPTS, respectively.

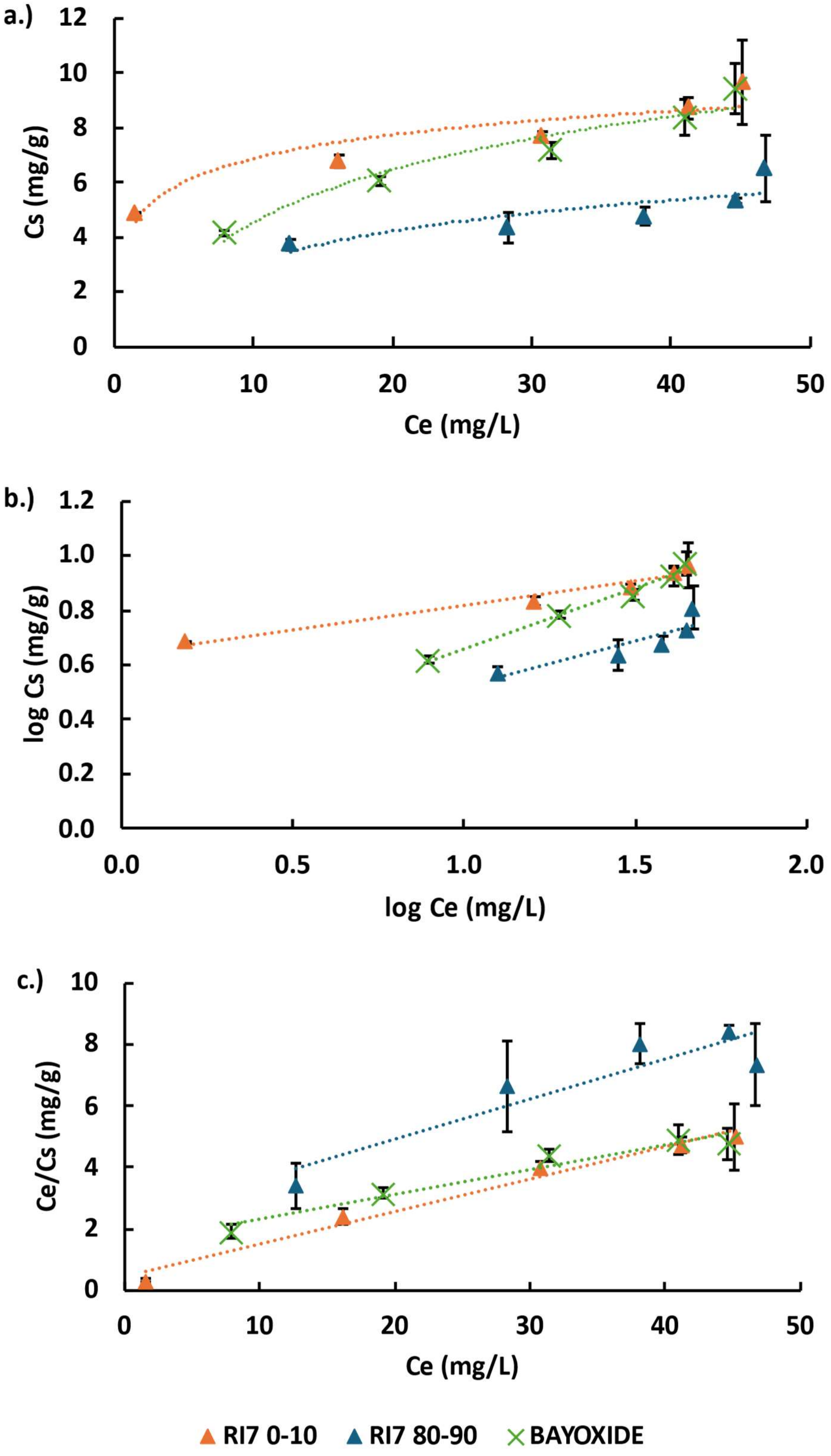

Figure 4.19 Comparison of the fresh top 10 cm and older bottom 10 cm of the RI7 iron oxides to Bayoxide® E33 P iron oxide with a.) sorption isotherm, b.) Freundlich sorption model and c.) Langmuir sorption model

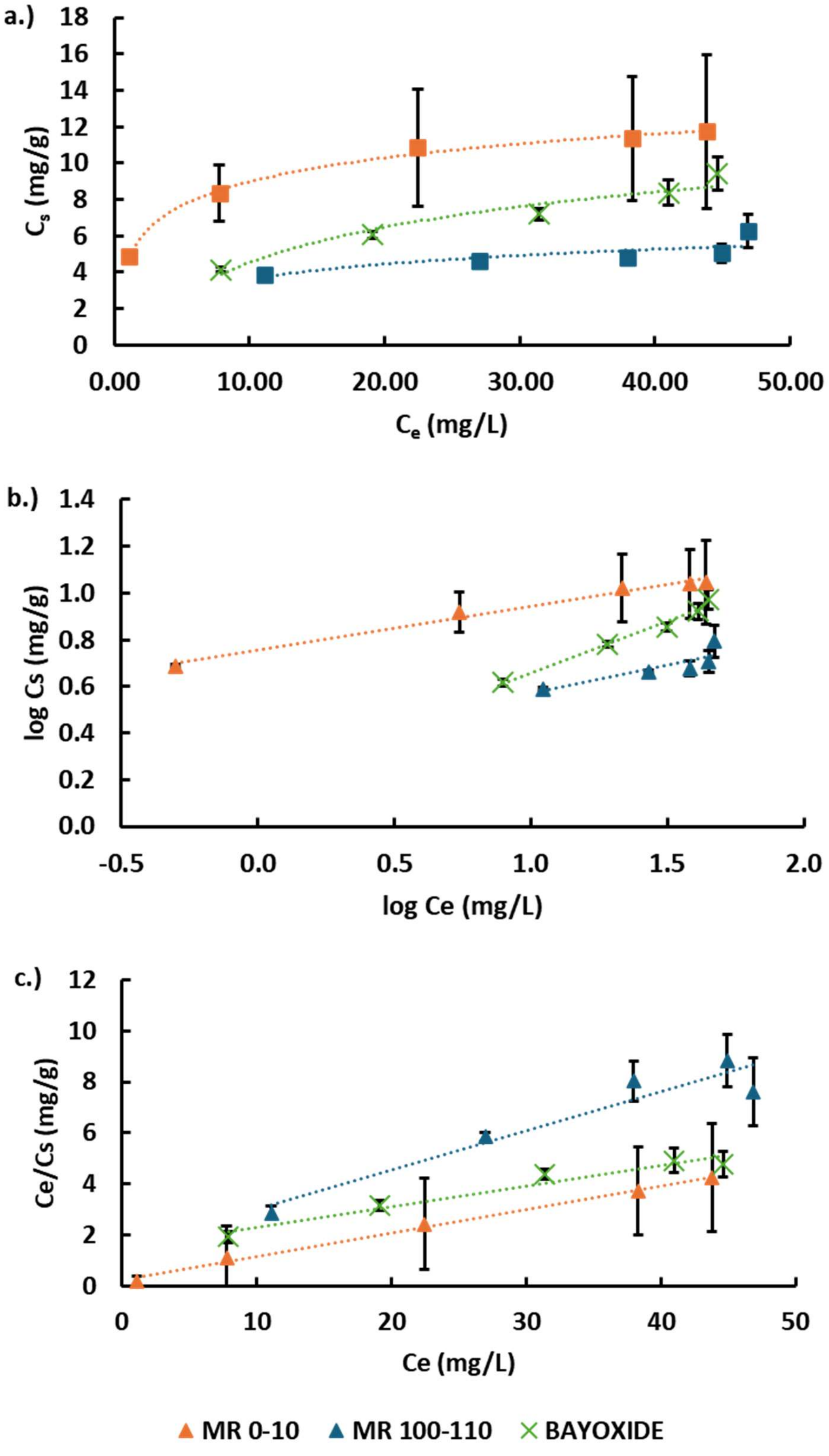

Figure 4.20 Comparison of the fresh top 10 cm and older bottom 10 cm of the RI7 iron oxides to Bayoxide® E33 P iron oxide with a.) sorption isotherm, b.) Freundlich sorption model and c.) Langmuir sorption model

Table 4.12 Freundlich and Langmuir isotherm parameters determined from experimental data for each set of iron oxide solids.

	Freundlich			Langmuir		
	K_F ((mg/g)(L/mg)$^{1/n}$)	1/n	R^2	K_L (L/mg)	Cs,max mg/g	R^2
RI7						
RI7 0-10 cm	4.38	0.18	0.9574	0.25	9.42	0.9809
RI7 80-90 cm	1.52	0.34	0.7712	0.06	7.64	0.8426
MRPTS						
MRPTS 0-10 cm	5.72	0.19	0.9858	0.40	10.83	0.9948
MRPTS 100-110cm	2.10	0.25	0.7500	0.10	6.51	0.9108
Bayoxide ® E33 P	1.63	0.44	0.9833	0.05	12.3	0.9531

4.4 Economic analysis

Management of sludge produced in treatment systems can be a substantial maintenance cost for mine drainage treatment systems. The cost of removing the iron oxide sludge from both the RI7 and MRPTS initial oxidation ponds was estimated. The cost estimates are broken down in three main cost categories including sludge pumping, dewatering and the eventual excavating and hauling. The cost was estimated for four different scenarios including dewatering with geotubes and hauling to a landfill, dewatering in a constructed dewatering basin and hauling to a landfill, dewatering with geotubes and being reused and dewatering in a dewatering basin and being reused. For this analysis, it was assumed that the dried iron oxides would stay on site and that the end-user or consumer would cover the hauling costs of the iron oxides to their facility.

For each system, it was assumed that the sludge layer was uniform throughout the oxidation pond and was one foot below the design water elevation to calculate the volume of sludge to be removed. This greatly overestimates the volume of sludge to be removed and represents a worst-case scenario since it has been shown that sludge accumulates in a wedge with a higher depth nearest the inflow and decreasing toward the outflow of the pond. Other input values and assumptions made include:

- The solids content of the solids was estimated from the average moisture content of the sludge measured in the laboratory. It assumes that the solids content is uniform with depth and throughout the sludge.
- The number of pump days was estimated assuming a pump rate of 250 gpm and an additional day for transportation. The pump rate and daily rental quote were provided from a local equipment rental company.
- The fuel costs associated with pumping were assumed to be negligible and not included in this analysis. The fuel costs associated with the excavator were assumed to be included in the hourly rate and mobilization/demobilization costs of the project.

- The available geotube sizes and prices were sourced from the AMDTreat software.
- The volume of the dewatering basin is based on the volume of sludge being removed from the oxidation pond plus an additional 10% to account for freeboard. The rate of $5.50 per cubic yard was sourced from the AMDTreat software.
- It was assumed that the geotubes and dewatering basin would dry the solids to a solids content of 45%, required to haul the material (Hedin 2016). The volume and mass to haul was recalculated assuming a 45% solids weight.
- For the RI7 system, the nearest landfill is Republic Services Alderson Regional Landfill, (201 N4120 Rd, Alderson, OK 74501) approximately 15-minute drive away. A 50-minute round trip was assumed for this cost analysis, utilizing five dump trucks with a capacity of 16 cubic yards.
- For the MRPTS system, the nearest landfill is the Central Mill Repository an approximately 10-minute drive away. A 35-minute roundtrip was assumed for this cost analysis, utilizing three dump trucks with a capacity of 16 cubic yards.
- A landfill tipping fee of $40 per ton was utilized in this cost analysis. This value was averaged from estimates provided by local landfills. It also matches the default value provided by the AMDTreat software.

Table 4.13 and 4.14 show the cost breakdown and comparison between scenarios for the RI7 and MRPTS systems. The cost to pump and dewater the solids ranged from $36-70 per mton of dried solid, which is comparable to values provide by Hedin (2016) of $99 per mton (2016 dollars) of dried solid. The slight discrepancies in values may be due to the fact additional labor and design costs were not included in the removal scenarios. It should be noted that the cost to dewater in a dewatering basin included the cost to excavate a basin, which is a one-time cost and thus the cost to pump and dewater in a dewatering basin will be even lower in future scenarios since the dewatering basin is reusable, unlike the geotubes. However, when the solids have to be hauled to a landfill, the cost to handle the solids increases to $171-190 per mton of dried solid. This estimate is largely dependent on the landfill tipping cost which accounts for over 50% of the cost.

Table 4.13 Cost analysis for removing iron oxide sludge from the RI7 oxidation pond using either geotubes or a dewatering basin and disposing in a landfill or storing on site for reuse

Cost Category	Item	Unit	Qnty	Unit Cost	Geotubes and Landfill	Drying Basin and Landfill	Geotubes and Reuse	Drying Basin and Reuse
1. Sludge Pumping	Pump rental	days	3	$325.00	$975.00	$975.00	$975.00	$975.00
	Excavator	hours	8	$250.00	$2,000	$2,000.00	$2,000.00	$2,000.00
2. Dewatering	1185 c.y. Geotube	LS	1	$10,000.00	$10,000	-	$10,000.00	-
	Drying Basin Excavation	c.y.	1000	$5.50	-	$5,500.00	-	$5,500.00
3. Excavating and Hauling	Excavator	hours	30	$250.00	$7,500.00	$7,500.00	-	-
	Trucks	hours	6	$150.00	$900.00	$900.00	-	-
	Landfill tipping fee	ton	619	$40.00	$24,756.49	$24,756.49	-	-
Mobilization/Demobilization (10% of cost)					$2,047.50	$1,597.50	$1,297.50	$847.50
				Total Cost	**$48,178.99**	**$43,228.99**	**$14,272.50**	**$9,322.50**
				Cost per kg of dried solid	**$0.19**	**$0.17**	**$0.06**	**$0.04**
				Cost per mton of solid	**$190.68**	**$171.09**	**$56.49**	**$36.90**

Table 4.14 Cost analysis for removing iron oxide sludge from the MRPTS oxidation pond using either geotubes or a dewatering basin and disposing in a landfill or storing on site for reuse

Cost Category	Item	Unit	Qnty	Unit Cost	Geotubes and Landfill	Drying Basin and Landfill	Geotubes and Reuse	Drying Basin and Reuse
1. Sludge Pumping	Pump rental	days	7	$ 325.00	$2,275.00	$2,275.00	$ 2,275.00	$ 2,275.00
	Excavator	hours	40	$ 250.00	$10,000.00	$ 10,000.00	$10,000.00	$ 10,000.00
2. Dewatering	950 c.y. Geotube	LS	4	$ 7,395.00	$ 29,580.00	-	$29,580.00	-
	465 c.y. Geotube	LS	1	$ 3,885.00	$ 3,885.00	-	$ 3,885.00	-
	Drying Basin Excavation	c.y.	4600	$ 5.50	-	$ 25,300.00	-	$ 25,300.00
3. Excavating and Hauling	Excavator	hours	19	$ 250.00	$ 4,750.00	$ 4,750.00	-	
	Trucks	hours	58	$150.00	$ 8,700.00	$ 8,700.00	-	
	Landfill tipping fee	ton	1758	$40.00	$ 70,339.79	$ 70,339.79	-	
Mobilization/Demobilization (10% of cost)					$ 5,049.00	$ 4,232.50	$ 4,574.00	$ 3,757.50
				Total Cost	**$ 134,578.79**	**$ 125,597.29**	**$ 50,314.00**	**$ 41,332.50**
				Cost per kg of dried solid	**$ 0.19**	**$ 0.17**	**$ 0.07**	**$ 0.06**
				Cost per mton of solid	**$ 187.47**	**$ 174.95**	**$ 70.09**	**$ 57.58**

Market research into the cost of Bayoxide® E33 P showed that the cost to purchase this commercial iron oxide is \$30-50 per kg, depending on supplier and shipping. In order to fairly compare the cost to use each material as a phosphate sorbent, the cost of iron oxide per gram of phosphorus sorbed was calculated using the unit price of each iron oxide and the phosphate sorption capacity for each material using a 50 mg/L P phosphate solution found during the aging study. The costs per gram of phosphate as P removed shown in Table X show that the cost of commercial phosphate sorbents can be 200-1,000 times more expensive than reusing naturally forming iron oxide formed in mine drainage treatment systems.

Table 4.15 Cost of each iron oxide depending on dewatering process normalized per gram of phosphorus removed based on their sorption capacity

	Bayoxide® E 33 P	RI7		MRPTS	
		Geotube and Reuse	Dewatering Basin and Reuse	Geotube and Reuse	Dewatering Basin and Reuse
Sorption Capacity, (mg P/g)	12.3	7.64-9.42	7.64-9.42	6.51-10.83	6.51-10.83
Cost per g P removed	\$2.43-4.07	\$0.006-0.007	\$0.004	\$0.006-0.011	\$0.005-0.009

5 Conclusions

Finding beneficial reuses for iron oxides produced in mine drainage environments is crucial for the environmental and economical sustainability of passive treatment. It is also important to find solutions to address the increasing eutrophication of waterways. This research examined how both problems facing the environment may be able to be solved by beneficially reusing iron oxides as phosphorus sorbents. It was hypothesized that the mine drainage in which the solids are formed influences the physicochemical and mineralogical characteristics of the produced iron oxides. It was also hypothesized that this difference in chemistry affects the phosphorus sorption capacity of these iron oxides and that as they age their mineralogical, physical, and chemical properties will change and also affect their sorption capacity. However, despite these differences in chemistries and properties over time and space, reusing iron oxides as phosphorus sorbents Is still hypothesized to be economically favorable compared to traditional disposal methods. Through a combination of water quality and solids sampling, characterizations, and benchtop sorption studies, this notion of reusing iron oxide solids as phosphorus sorbents was evaluated.

The overall evaluation of reusing iron oxide solids produced in mine drainage environments as phosphorus sorbents can be summarized as follows:

- The mine drainage water chemical composition has an impact on the resulting iron oxide precipitate chemistry and mineralogy, especially on surface morphology and chemical properties such as PZNC. Although the iron oxides collected from each site were all predominantly goethite, they differed greatly in surface morphology and metals concentrations.

- Despite the physical and chemical differences in iron oxides collected from different sites, all iron oxides analyzed for their phosphorus sorption capacity showed a high affinity for phosphate and were viable as sorbents.

- Although the iron oxides had a high affinity for phosphate, solids with greater metals concentrations showed an increased desorption of metals at greater phosphorus concentrations. This phenomenon has been documented by many researchers looking into using iron oxides as sorbents but the mechanisms and reasonings are still not well known. More research needs to look into the competing relationships and mechanisms between ions in iron oxides produced in natural environments.

- Fresh (recently precipitated) iron oxides showed smaller particles and increased surface area whereas aged (precipitated years to decades ago) iron oxides were largely aggregated particles and showed lesser specific surface area. The considerable difference in surface morphology indicates distinctive differences in mineralogy potentially affecting sorption capacity. Despite the increase in crystallinity and decrease in specific surface area with age, all iron oxides recovered had a high affinity for phosphate and still viable as sorbents.

- The cost to recover the iron oxides and store them on site is significantly less than the cost to haul and dispose of the solids in a landfill. The main factor affecting the cost of disposal is the landfill tipping fee. The use of a dewatering basin that can be reused multiple times is more cost-effective than geotubes and can decrease the cost of dewatering the iron oxide sludge. However, the dewatering costs can vary depending on criteria for the solids content of the sludge. Despite the cost to recover these iron oxides, iron oxides produced in mine drainage treatment systems are significantly less expensive than traditional phosphate sorbents.

6 Personnel Summary

A total of 28 research scientists, engineers and other interested individuals directly contributed to this project. The breakdown included two faculty members, three staff scientists or post-doctoral scholars, six doctoral students, 10 masters students, and seven undergraduates, two of whom completed related Honors Engineering Research Experience (HERE) projects supporting this project at no cost to the sponsor. Through University of Oklahoma formal classes (e.g., CEES 5363 Ecological Engineering Science, CEES 4324/5324 Environmental Biology and Ecology, BIOL

4970/5970 Wetlands Science and Management, and CEES 4970/5970 Engineering the Nature of Change), approximately another 200 students were exposed to the project.

7 Resulting Presentations and Publications

Thus far, the results of this project have been presented at two conferences and published in a refereed proceedings document. The appendix includes the published abstract and presentation from the 2023 American Society of Reclamation Sciences (ASRS) National Conference (Boise, Idaho) and the refereed publications and presentations from the 2023 and 2024 International Mine Water Association (IMWA) Conference (Newport, Wales, United Kingdom and Morgantown, West Virginia, USA). It is worthy to note that IMWA presentation by CREW PhD student Dayton M'Kenzie Dorman was recognized with a Best Student Oral Presentation Award. Although no refereed journal articles have been submitted as of yet, they will be in the future as data analyses continue.

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9 Appendices

Effect of Water Chemistry and Time on the Sustainable Reuse of Recovered Iron Oxides as Phosphate Sorbents[1]

D.M. Dorman* and R.W. Nairn[2]

Sustainable treatment of mine drainage must consider the economic and environmental impact of treatment processes including the ultimate fate of the mine drainage treatment residual solids. Disposition and disposal of these solids can be costly and have a large environmental footprint. Thus, finding ways to reuse these solids can help improve the economic and environmental sustainability of treatment systems. The surface chemistry and large surface area per unit mass of iron oxide solids make these materials an ideal sorbent for phosphate, possibly giving these treatment residuals a beneficial reuse. These materials and similar industrial byproducts (e.g., fly ash, cement kiln dust) have been evaluated for this purpose by several authors. However, limited research has been performed to analyze 1) how different mine drainage water chemistries affect the resulting iron oxide mineralogy and phosphate sorption capacity and 2) how these iron oxide solids change in situ over time and any resulting effects on phosphate sorption capacity and possible metals desorption. This research analyzed iron oxides from net-alkaline hard-rock mine drainage passive treatment systems (PTS) (Tar Creek Superfund Site, Oklahoma) and from net-acidic coal mine drainage discharges and net-alkaline coal mine drainage PTS (Arkoma Basin, Oklahoma). Preliminary data shows that more amorphous forms of iron oxides (ferrihydrite and poorly-ordered goethite) are found near discharges where precipitates were the freshest while more mature materials found in PTS demonstrated greater crystallinity. All samples have a large sorption capacity for phosphate (≈90 mg/g). Although the iron oxides from hard-rock mine drainage PTS had higher metals concentrations than iron oxides formed in coal mine drainage discharges, minimal desorption of metals was found over time in all samples. Management and disposal of these solids can be costly, however reuse of these solids as a phosphate sorbent may be an economically and environmentally sustainable alternative.

Additional Key Words: mineralogy, mine drainage residuals, passive treatment systems

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1. Oral paper presented at the 2023 National Meeting of the American Society of Reclamation Sciences, Boise, ID. June 4 - 7, 2023. Published by ASRS; 1305 Weathervane Dr., Champaign, IL61821.
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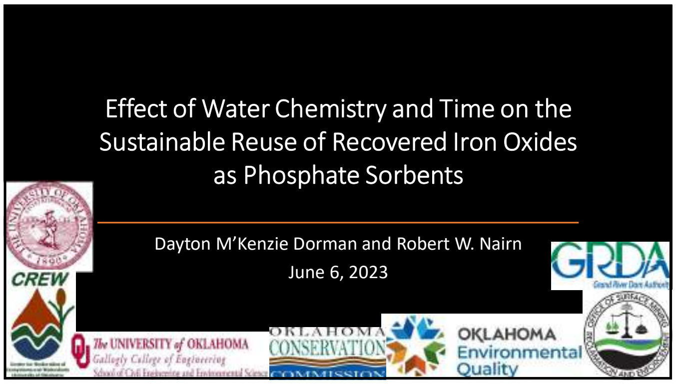
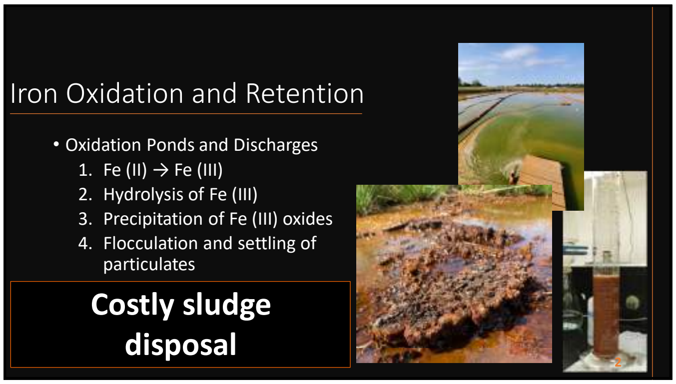


Effect of Water Chemistry and Time on the Sustainable Reuse of Recovered Iron Oxides as Phosphate Sorbents

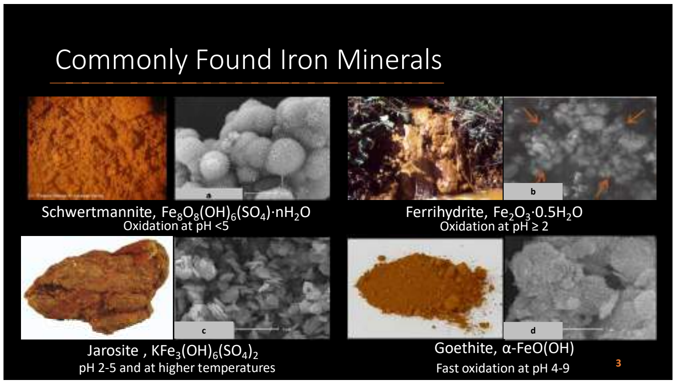
Dayton M'Kenzie Dorman and Robert W. Nairn
June 6, 2023



Iron Oxidation and Retention

- Oxidation Ponds and Discharges
  1. Fe (II) → Fe (III)
  2. Hydrolysis of Fe (III)
  3. Precipitation of Fe (III) oxides
  4. Flocculation and settling of particulates

Costly sludge disposal



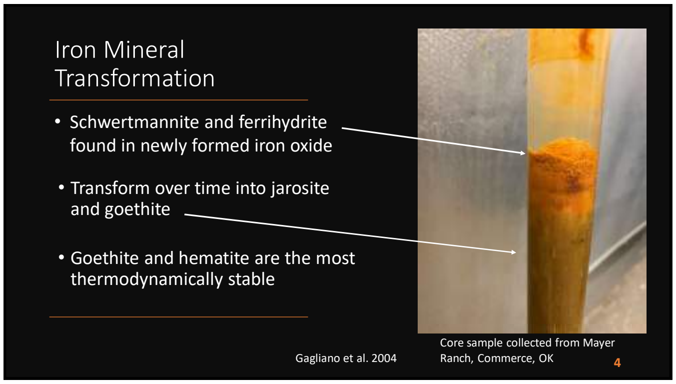
Commonly Found Iron Minerals

Schwertmannite, $Fe_8O_8(OH)_6(SO_4)\cdot nH_2O$
Oxidation at pH <5

Ferrihydrite, $Fe_2O_3\cdot 0.5H_2O$
Oxidation at pH ≥ 2

Jarosite , $KFe_3(OH)_6(SO_4)_2$
pH 2-5 and at higher temperatures

Goethite, α-FeO(OH)
Fast oxidation at pH 4-9

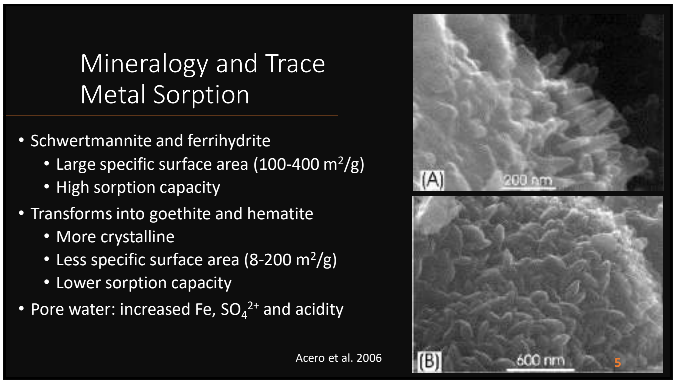


Iron Mineral Transformation

- Schwertmannite and ferrihydrite found in newly formed iron oxide
- Transform over time into jarosite and goethite
- Goethite and hematite are the most thermodynamically stable

Gagliano et al. 2004

Core sample collected from Mayer Ranch, Commerce, OK



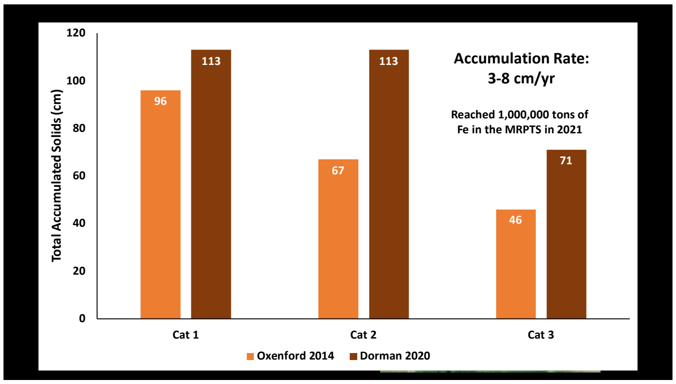
Mineralogy and Trace Metal Sorption

- Schwertmannite and ferrihydrite
  - Large specific surface area (100-400 m^2/g)
  - High sorption capacity
- Transforms into goethite and hematite
  - More crystalline
  - Less specific surface area (8-200 m^2/g)
  - Lower sorption capacity
- Pore water: increased Fe, SO_4^{2+} and acidity

Acero et al. 2006

Why It Matters

- Sinks become sources
- Affects PTS performance
- Affects disposal and beneficial reuse options for produced iron solids



Accumulation Rate:
3-8 cm/yr

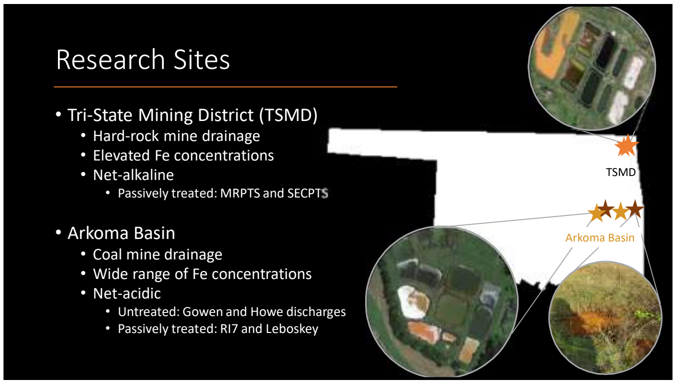
Reached 1,000,000 tons of Fe in the MRPTS in 2021

Challenges and Research Needs

- Most research performed in net-acidic coal mine drainage
  - Net-alkaline mine drainage → different mineralogy
  - Hard-rock mining drainage → elevated metal concentrations
- Relationship between iron mineralogy, pore water chemistry and time for different water chemistries

Hypotheses

1. Chemical composition of mine drainage waters (e.g., pH, total alkalinity, metals concentrations, anions concentrations, etc.) has significant cumulative effects on resulting precipitate mineralogy
2. The resulting mineralogy of iron oxides formed from different mine drainage water compositions affects their initial sorption capacity
3. As the mine drainage-derived solids age, they become more crystalline and thus sorption capacity decreases
4. Reuse of mine drainage treatment solids as sorption media is economically favorable to traditional solids disposal



Research Sites

- Tri-State Mining District (TSMD)
  - Hard-rock mine drainage
  - Elevated Fe concentrations
  - Net-alkaline
    - Passively treated: MRPTS and SECPTS
- Arkoma Basin
  - Coal mine drainage
  - Wide range of Fe concentrations
  - Net-acidic
    - Untreated: Gowen and Howe discharges
    - Passively treated: RI7 and Leboskey

Study 1: Characterization of Iron Oxides from Different Mine Water Chemistries

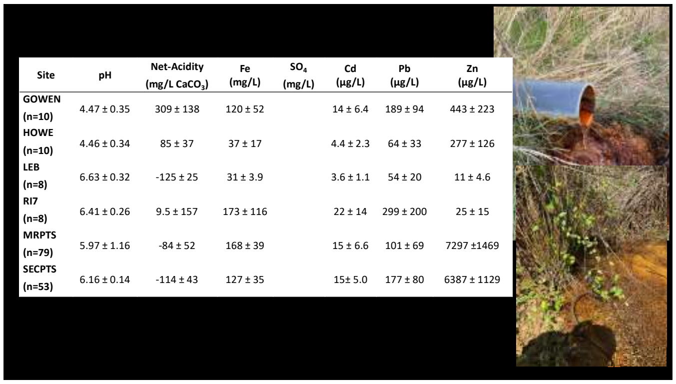
Water Quality Analyses

- Anions (Cl$^-$, NO$_3^-$, NO$_2^-$, PO$_4^{3-}$, SO$_4^{2-}$)
- Total and Dissolved Metals
- Physicochemical Parameters (pH, ORP, DO, Conductivity, etc.)
- Alkalinity
- Turbidity

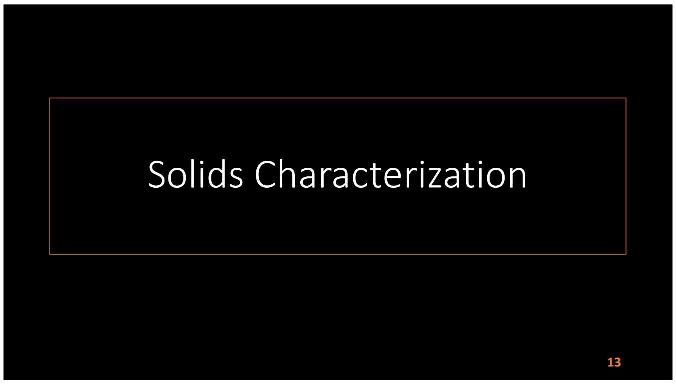
Solids Characterization

- Moisture Content
- Organic Matter Content
- Specific Surface Area
- Percent Crystallinity
- Total Metals Concentrations
- Mineralogy
  - X-ray Diffraction
  - Scanning Electron Microscopy
- Ion Exchange Capacity

Ongoing



Site	pH	Net-Acidity (mg/L CaCO$_3$)	Fe (mg/L)	SO$_4$ (mg/L)	Cd (µg/L)	Pb (µg/L)	Zn (µg/L)
GOWEN (n=10)	4.47 ± 0.35	309 ± 138	120 ± 52		14 ± 6.4	189 ± 94	443 ± 223
HOWE (n=10)	4.46 ± 0.34	85 ± 37	37 ± 17		4.4 ± 2.3	64 ± 33	277 ± 126
LEB (n=8)	6.63 ± 0.32	-125 ± 25	31 ± 3.9		3.6 ± 1.1	54 ± 20	11 ± 4.6
RI7 (n=8)	6.41 ± 0.26	9.5 ± 157	173 ± 116		22 ± 14	299 ± 200	25 ± 15
MRPTS (n=79)	5.97 ± 1.16	-84 ± 52	168 ± 39		15 ± 6.6	101 ± 69	7297 ±1469
SECPTS (n=53)	6.16 ± 0.14	-114 ± 43	127 ± 35		15± 5.0	177 ± 80	6387 ± 1129



Solids Characterization

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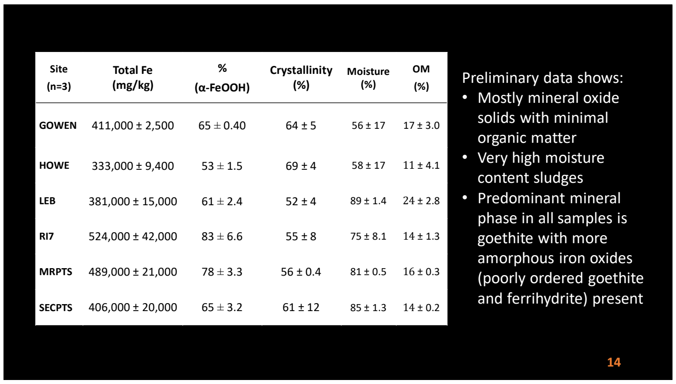

Site (n=3)	Total Fe (mg/kg)	% (α-FeOOH)	Crystallinity (%)	Moisture (%)	OM (%)
GOWEN	411,000 ± 2,500	65 ± 0.40	64 ± 5	56 ± 17	17 ± 3.0
HOWE	333,000 ± 9,400	53 ± 1.5	69 ± 4	58 ± 17	11 ± 4.1
LEB	381,000 ± 15,000	61 ± 2.4	52 ± 4	89 ± 1.4	24 ± 2.8
RI7	524,000 ± 42,000	83 ± 6.6	55 ± 8	75 ± 8.1	14 ± 1.3
MRPTS	489,000 ± 21,000	78 ± 3.3	56 ± 0.4	81 ± 0.5	16 ± 0.3
SECPTS	406,000 ± 20,000	65 ± 3.2	61 ± 12	85 ± 1.3	14 ± 0.2

Preliminary data shows:

- Mostly mineral oxide solids with minimal organic matter
- Very high moisture content sludges
- Predominant mineral phase in all samples is goethite with more amorphous iron oxides (poorly ordered goethite and ferrihydrite) present

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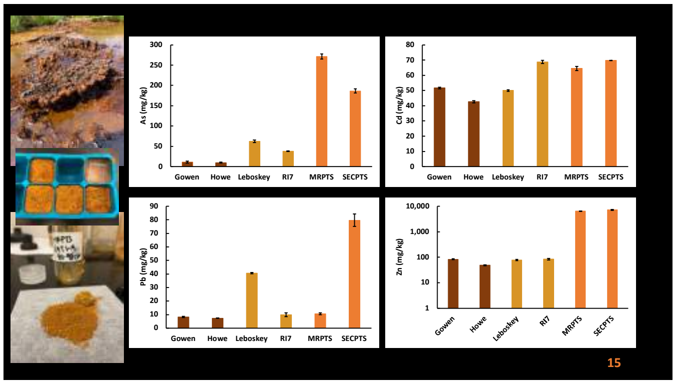

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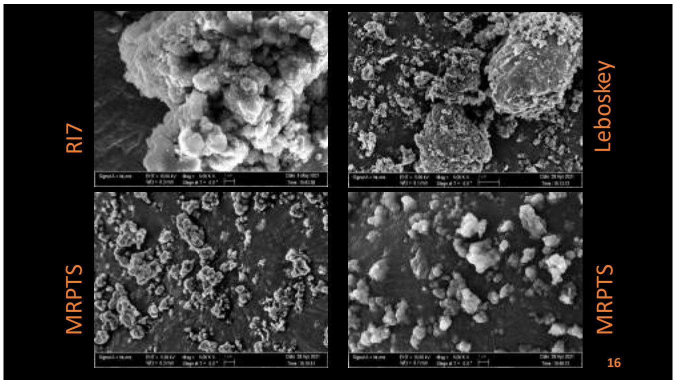

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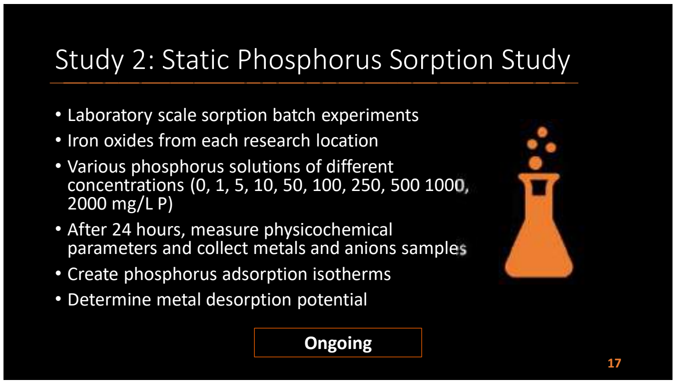

Study 2: Static Phosphorus Sorption Study

- Laboratory scale sorption batch experiments
- Iron oxides from each research location
- Various phosphorus solutions of different concentrations (0, 1, 5, 10, 50, 100, 250, 500 1000, 2000 mg/L P)
- After 24 hours, measure physicochemical parameters and collect metals and anions samples
- Create phosphorus adsorption isotherms
- Determine metal desorption potential

Ongoing

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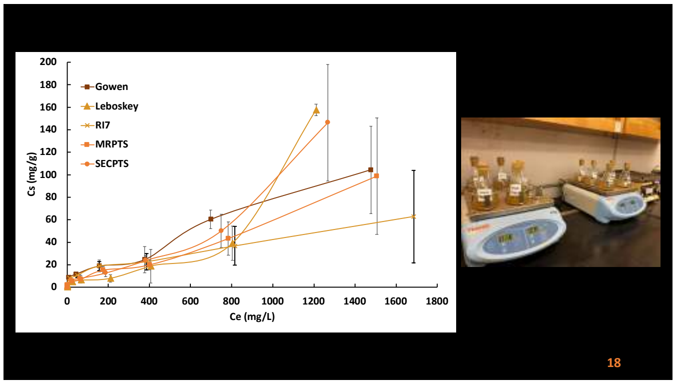

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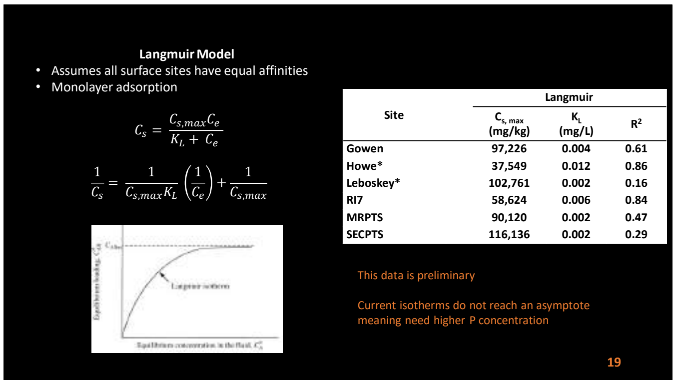


Langmuir Model

- Assumes all surface sites have equal affinities
- Monolayer adsorption

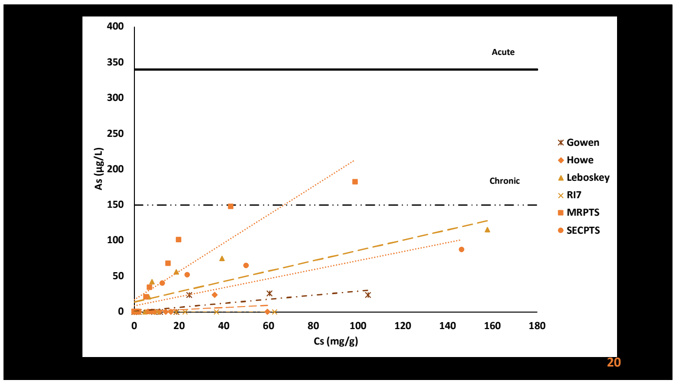
$$C_s = \frac{C_{s,max} C_e}{K_L + C_e}$$

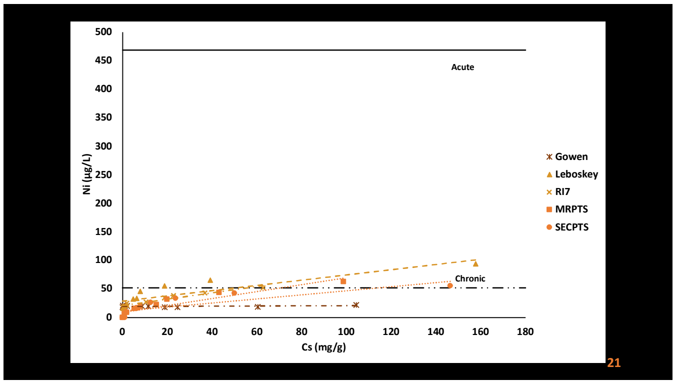
$$\frac{1}{C_s} = \frac{1}{C_{s,max} K_L}\left(\frac{1}{C_e}\right) + \frac{1}{C_{s,max}}$$

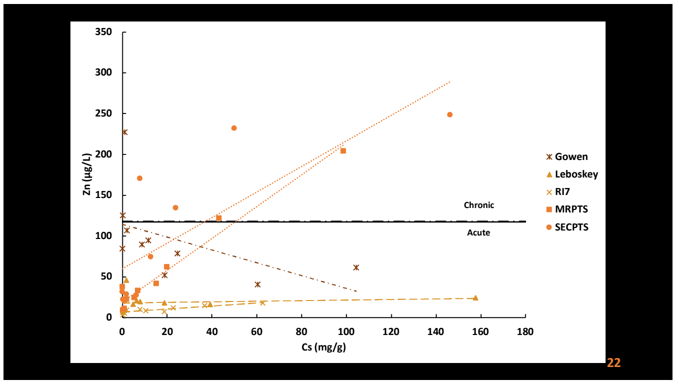
Site	Langmuir		
	$C_{s,\ max}$ (mg/kg)	K_L (mg/L)	R^2
Gowen	97,226	0.004	0.61
Howe*	37,549	0.012	0.86
Leboskey*	102,761	0.002	0.16
RI7	58,624	0.006	0.84
MRPTS	90,120	0.002	0.47
SECPTS	116,136	0.002	0.29

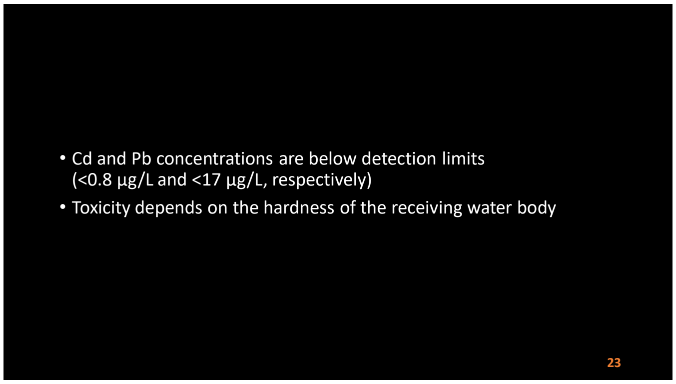
This data is preliminary

Current isotherms do not reach an asymptote meaning need higher P concentration

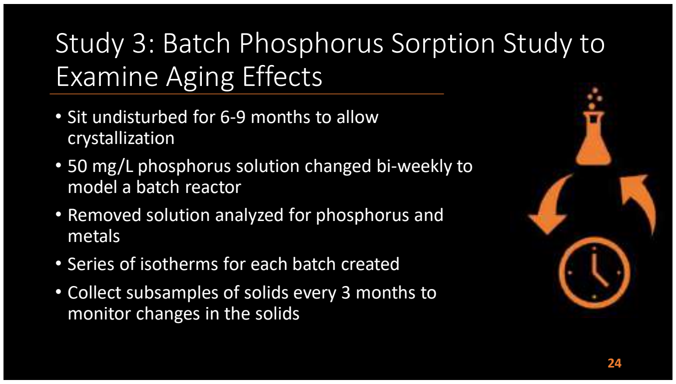






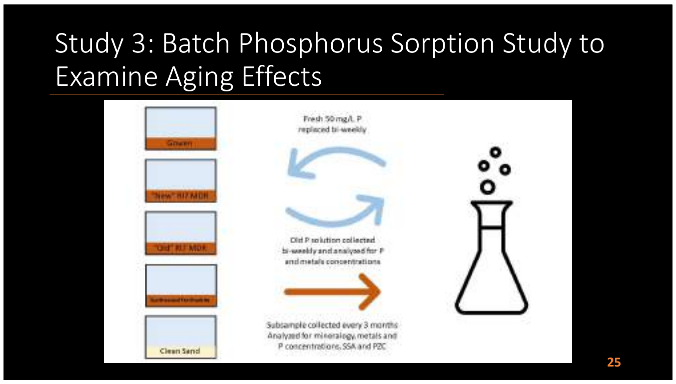


- Cd and Pb concentrations are below detection limits (<0.8 µg/L and <17 µg/L, respectively)
- Toxicity depends on the hardness of the receiving water body



Study 3: Batch Phosphorus Sorption Study to Examine Aging Effects

- Sit undisturbed for 6-9 months to allow crystallization
- 50 mg/L phosphorus solution changed bi-weekly to model a batch reactor
- Removed solution analyzed for phosphorus and metals
- Series of isotherms for each batch created
- Collect subsamples of solids every 3 months to monitor changes in the solids



Study 3: Batch Phosphorus Sorption Study to Examine Aging Effects

Fresh 50 mg/L P replaced bi-weekly

Old P solution collected bi-weekly and analyzed for P and metals concentrations

Subsample collected every 3 months Analyzed for mineralogy, metals and P concentrations, SSA and PZC

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Thank You!!

Any Questions?

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Effect of Time and Mineralogy on Sorption Capacity of Mine Drainage Passive Treatment Residuals: Is Sustainable Reuse Possible?

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Abstract

Sustainable reclamation design must consider the economic and environmental impact of the management of mine drainage treatment residuals. Iron-rich solids have substantial surface area and considerable sorption capacity for phosphorus. In this study, iron oxide solids were collected and analyzed from net-alkaline hard-rock mine drainage passive treatment systems (PTS), net-acidic coal mine drainage discharges and net-alkaline coal mine drainage PTS in Oklahoma, USA. These solids have a large sorption capacity for phosphorus (90 mg/g) and demonstrated minimal desorption of metals showing the sustainable reuse of these solids as a sorbent is possible.

Keywords: Iron Oxides, Mineralogy, Phosphorus, Sorption, Sustainable

Introduction

Sustainable reclamation design must consider the full life cycle impacts and costs of any selected remedy, including the ultimate disposition, disposal, or reuse of accumulated residual solids resulting from treatment of mine water containing elevated concentrations of metals. Solids disposal represents approximately 10% of global water treatment cost depending on the solids content of the sludge and the distance of delivery (Zinck and Griffith 2013). At many active mines, disposition of solids generated through active chemical treatment of mine waters is addressed on site through disposal to pond, pit lake, or mine workings, co-disposal with refuse or other wastes, or as backfill (Zinck 2006). In addition, mining companies, federal and state agencies, and non-profit organizations have designed and constructed hundreds of passive treatment systems throughout mining impacted regions (e.g., Skousen *et al*. 2017). In these cases, although funds for design and construction may be adequate, additional dollars for monitoring or maintenance are typically wholly lacking. Although these systems are often designed with operational lifetimes of two to three decades, they do require maintenance and principal among the needed tasks is management of accumulated water treatment solids. These solids are most often iron oxides. The chemical composition of the solids is based on the untreated mine water and the specific treatment mechanisms resulting in solids retention. The resulting chemical composition, along with environmental conditions and time, drives the mineralogy of these solids. It is well-established that iron oxides have substantial surface area per unit mass and considerable sorption capacity (Acero *et al*. 2006, Cornell and Schwertmann 2003; Dempsey and Jeon 2001; Fenton *et al*. 2009; Figueiredo and Silva 2011; Gagliano *et al*. 2004; Hedin 2012; Rakotonimaro *et al*. 2017; Sibrell *et al*. 2015; Sibrell and Tucker 2012; Tang and Nairn 2021; Zeng *et al*. 2004).

Initial forms of iron oxide typically produced in mine drainage systems are schwertmannite and ferrihydrite and more amorphous forms of goethite (Acero *et al*. 2006; Cornell and Schwertmann 2003; Gagliano *et al*. 2004; Murad and Rojík 2005). The small crystal structures of these minerals give these solids a large specific surface area facilitating them to act as sinks for trace metals and anions (Acero *et al*. 2006; Gagliano *et al*. 2004; Murad and Rojík 2005). However, these amorphous forms of iron oxide are metastable and will transform into more thermodynamically stable and crystalline forms of iron oxide such as goethite, hematite and jarosite. This transformation can occur on a timescale of weeks to years depending on pH, redox conditions and other physicochemical properties of the water (Acero *et al.* 2006; Gagliano *et al.* 2004; Murad and Rojík 2005). Although larger crystals allow goethite to be more easily identified, they also decrease the surface area of goethite which can potentially decrease the sorption capacity for metals and other ions to the mineral phase.

Due to their high surface area and surface charge, iron oxides have been used as sorbents in a variety of water treatment applications (Cornell and Schwertmann 2003). Schwertmannite and ferrihydrite are preferred due to their low crystallinity and high surface area, yet all known iron oxide minerals exhibit relatively strong sorption capacities (Acero *et al.* 2006; Cornell and Schwertmann 2003; Gagliano *et al.* 2004). One of these water treatment applications is phosphorus sorption. The release of phosphorus, most commonly found in the form of phosphate, to surface waters is an environmental concern. Phosphorus is often a limiting nutrient for growth of organisms and thus is an important wastewater contaminant due to its role in eutrophication which leads to oxygen depletion and aquatic toxicity in receiving surface water bodies (Rakotonimaro *et al.* 2017; Sibrell and Tucker 2012; Zeng *et al.* 2004). Iron and aluminum oxides have a strong affinity for phosphorus and thus it is standard in wastewater treatment to remove phosphorus with iron and aluminum salts (Sibrell and Tucker 2012). Due to the high reagent costs associated with manufactured iron and aluminum salts, research into the more cost-effective use of iron and aluminum waste products has been explored (Fenton *et al.* 2009; Sibrell and Tucker 2012; Sibrell *et al.* 2015; Zeng *et al.* 2004). Given the variety of iron oxide minerals found in natural systems, a thorough understanding of the factors affecting their sorption capacity is necessary to sustainably use residual iron oxides as sorbents.

Methods

This research examines iron oxide solids from six locations throughout Oklahoma, USA that represent different mine drainage chemistries (Figure 1). Two of the locations are the Mayer Ranch Passive Treatment System (MRPTS) and the Southeast Commerce Passive Treatment System (SECPTS) oxidation ponds treating naturally net-alkaline hard rock mine drainage in the north-eastern Oklahoma portion of the Tri-State Mining District. The other four locations are in the Arkoma Basin in south-eastern Oklahoma where Desmoinesian coal deposits were mined. Iron oxide solids were collected from the Leboskey (LEB) and Rock Island #7 (RI7) passive treatment systems where net-acidic coal mine drainage has been rendered alkaline by utilizing an anoxic limestone drain before the water reaches the surface. Similarly, iron oxide samples were collected from two untreated net-acidic mine drainage discharges (GOWEN and HOWE).

Water quality data were collected routinely to characterize the host mine drainage chemistry in which the iron oxides were produced. Water quality data include physicochemical parameters (pH, DO, temperature, specific conductance, ORP, alkalinity, turbidity), sulfate, chloride, and a suite of total and dissolved metals and base cations (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Si, Zn). Data for pH, alkalinity, and Fe, because they typically affect iron oxide mineralogy and Cd, Pb and Zn because desorption of ecotoxic metals is a concern regarding using these solids in the environment, will be explored in this paper.

Grab samples of iron oxide precipitates were collected at each location using a stainless-steel shovel. Samples were collected near the surface where the solids are typically fresher and have experienced less crystallization and are relatively free of organic debris. These samples were promptly frozen and freeze dried at a vacuum of 10 µm mercury and a vessel temperature of -40°C with a Labconco benchtop freeze drying system. Freeze drying was utilized to avoid any phase transformations that could occur (especially with ferrihydrite) during conventional air or oven drying

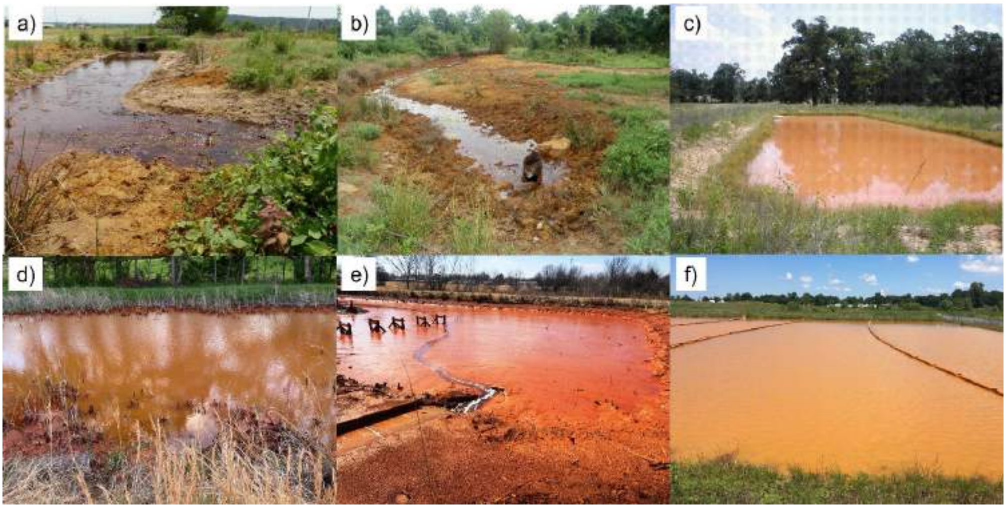

***Figure 1** Iron oxide deposits at untreated coal mine discharges a) Gowen and b) Howe; coal mine drainage passive treatment system oxidation ponds c) Leboskey and d) Hartshorne; and hard-rock mine passive treatment system oxidation ponds e) Mayer Ranch (during managed drawdown) and f) Southeast Commerce.*

***Table 1** Selected water quality data for the iron oxides collected at mine drainage discharges (GOWEN and HOWE) and PTS oxidation ponds (LEB, RI7, MRPTS and SECPTS)*

Site	pH	Net-Acidity (mg/L $CaCO_3$)	Fe (mg/L)	Cd (µg/L)	Pb (µg/L)	Zn (µg/L)
GOWEN (n=10)	4.47 ± 0.35	309 ± 138	120 ± 52	14 ± 6.4	189 ± 94	443 ± 223
HOWE (n=10)	4.46 ± 0.34	85 ± 37	37 ± 17	4.4 ± 2.3	64 ± 33	277 ± 126
LEB (n=8)	6.63 ± 0.32	-125 ± 25	31 ± 3.9	3.6 ± 1.1	54 ± 20	11 ± 4.6
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MRPTS (n=79)	5.97 ± 1.16	-84 ± 52	168 ± 39	15 ± 6.6	101 ± 69	7297 ±1469
SECPTS (n=53)	6.16 ± 0.14	-114 ± 43	127 ± 35	15± 5.0	177 ± 80	6387 ± 1129

processes (Schwertmann and Cornell 2003). The solids were then analyzed for their physical, chemical, and mineralogical characteristics including moisture content, organic matter content, total metals concentrations, percent crystallinity, and mineralogical make up. Center for Restoration of Ecosystems and Watersheds (CREW) standard operating procedures follow US Environmental Protection Agency (USEPA) methods for all analyses.

After the solids were characterized, phosphorus sorption capacity tests were performed. In each case, 0.5 g of freeze-dried sample and 100 mL of various phosphorus concentrations (0, 1, 5, 10, 50, 100, 250, 500, 1000, 2000, 3000 and 4000 mg/L) were added into sealed 250-mL glass Erlenmeyer flasks. All the flasks were placed on an orbital shaker at 100 rpm for 24 h. After mixing, the samples were analyzed for pH and then filtered through 0.45 µm syringe filters into clean sample bottles and analyzed for soluble reactive phosphorus and dissolved metals concentrations.

Results

A summary of the host water quality in which the iron oxide solids are produced is shown in Table 1. All the sites have elevated Fe concentrations and the sites receiving hard-rock mine drainage have higher concentrations of Cd, Pb and Zn. The resulting

Table 2 Selected characteristics of the iron oxide samples collected at each site (n=3)

Site	% (α-FeOOH)	Cd (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	% Crystallinity	Phosphorus Sorption Capacity (mg/kg)
GOWEN	65 ± 0.40	52 ± 0.5	8.17 ± 0.54	83 ± 2.9	64 ± 5.2	94785 ± 31684
HOWE	53 ± 1.5	43 ± 0.74	7.23 ± 0.10	49 ±2.2	69 ± 4.1	35828 ± 9080
LEB	61 ± 2.4	50 ± 0.53	40 ± 0.47	77 ± 4.4	52 ± 3.9	77561 ± 10710
RI7	83 ± 6.6	69 ± 1.1	9.8 ± 1.4	84 ± 6.7	55 ± 8.4	48977 ± 18161
MRPTS	78 ± 3.3	64 ± 1.3	10 ± 0.74	6448 ±91	56 ± 0.4	82568 ± 32426
SECPTS	65 ± 3.2	70 ± 0.07	80 ± 4.7	7256 ±315	56 ± 12	116231 ± 32693

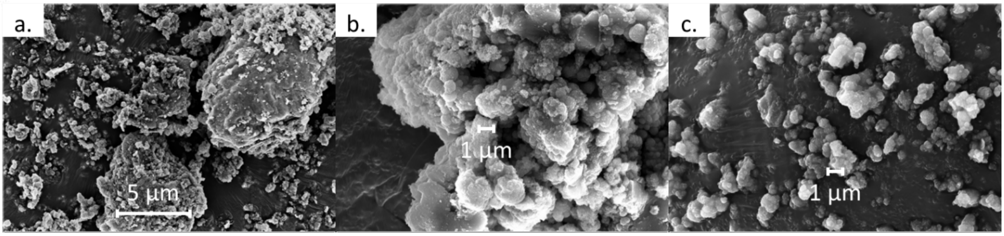

Figure 2 SEM photos at a magnification of 5000 of the surface morphology of iron oxides collected from a) the LEB site, b) the RI7 site and c) the MRPTS site

produced solids are mostly mineral (<20% organic) with a high moisture content (>60% moisture). These solids were also found to be mostly iron oxide with concentrations of metals including Cd, Pb and Zn associated with them (Table 2).

Initial characterization of these solids shows that the dominant mineral phase at all locations was goethite with more poorly-ordered goethite and amorphous ferrihydrite present. Although it was hypothesized that the net-acidic discharges would produce the less crystalline iron oxides, that was not the case. This result is perhaps due to the fact that these solids are produced in a shallow channel receiving mine drainage in which the increased oxic conditions and lower pH increased the transformation rate of ferrihydrite to goethite (Cornell and Schwertmann 2003). Despite the higher percent crystallinity of the solids, the phosphorus sorption capacity of the iron oxide solids recovered from mine drainage systems ranged from 35 mg/g from net-acidic coal mine drainage discharges to 116 mg/g from net-alkaline hard-rock mine drainage PTS (Table 2). The difference in sorption capacity is perhaps due to the difference in mineral morphology and surface area of the solids as demonstrated by images captured from scanning electron microscopy (SEM) at a magnification of 5000X (Figure 2). The solids from LEB are larger (≈5 µm) and have a more globular morphology, perhaps exacerbated by the aggregation of smaller iron oxide particles onto larger iron oxide particles and clay particles. These samples were observed to have a higher clay content associated with them due to the shallow pond depth, presence of natural clay and low iron content. The solids from the RI7 and MRPTS systems also have a globular morphology but are smaller in size (1-2 µm) and show a smaller (<1 µm) spiky morphology on the surface indicating the aggregation of less amorphous ferrihydrite on their surface providing an even higher surface area for phosphorus sorption mechanisms.

Despite the elevated metals concentrations associated with these solids, minimal desorption of metals was observed during the 24-h batch static sorption studies. Most aqueous metals concentrations were below the detection limits and increased in concentration as the concentration of the phosphorus solution increased. This may be due to the decrease in solution pH with increasing phosphorus concentrations which caused the surface charge of the iron oxides to become more positive and thus less attractive to metal cations. These elevated phosphorus concentrations are not commonly seen in the environment but were necessary to develop sorption isotherms and determine the ultimate sorption capacity of these solids. Therefore, they do not represent a real-world scenario in which these iron oxides would be used.

Conclusions

This research has shown that iron oxides recovered from mine drainage systems, especially PTS, are an effective and sustainable sorbent for phosphorus. All iron oxides studied had a high (>35 mg/g) sorption capacity for phosphorus and experienced minimal desorption of metals in the 24-h study. The primary factor affecting the sorption capacity of these solids is surface morphology and their subsequent surface area. More investigation is needed to explore how environmental conditions such as pH and cation/anion concentrations affect the formation of iron oxide precipitates and their sorption capacities. Ongoing research is also looking at how these solids age over time in a phosphorus solution and how the subsequent changes in mineralogy and morphology affect their sorption capacity for phosphorus and metals to help determine the long-term feasibility of reusing these iron oxides as sorbents in the environment.

Overall, this research has shown that iron oxides can be beneficially reused as a phosphorus sorbent which is economically and environmentally more sustainable than traditional management and disposal of these solids. Similarly, these iron oxides are less expensive than iron and aluminum salts typically used in water treatment processes to remove contaminants and excess nutrients.

Acknowledgements

This work was supported by the Oklahoma Department of Environmental Quality (Agreement PO2929019163), the Office of Surface Mining Reclamation and Enforcement (Agreement S21AC10011-00), and the U.S. Environmental Protection Agency (Agreement X7-97682001-0). Several private landowners provided access. The authors also wish to thank the Oklahoma Conservation Commission Abandoned Mine Lands Program for assistance.

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Effect of Time and Mineralogy on Sorption Capacity of Mine Drainage Passive Treatment Residuals: Is Sustainable Reuse Possible?

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Center for Restoration of Ecosystems and Watersheds,
University of Oklahoma, USA
July 20, 2023

The UNIVERSITY of OKLAHOMA
Gallogly College of Engineering
School of Civil Engineering and Environmental Science

CREW

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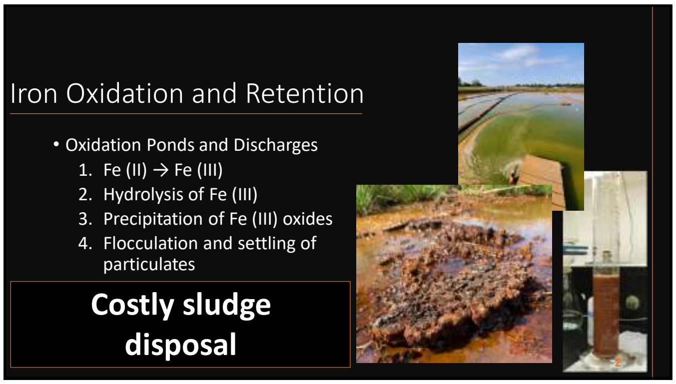
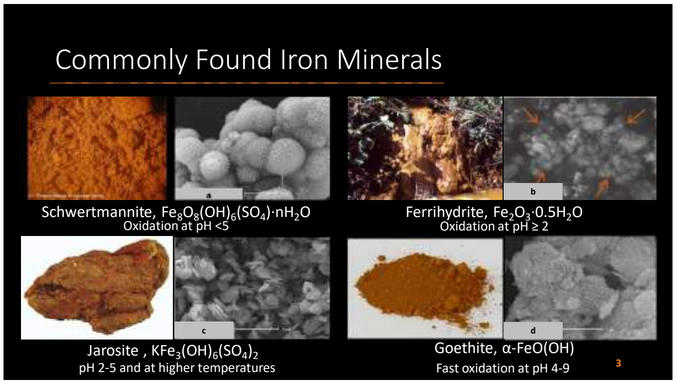


Iron Oxidation and Retention

- Oxidation Ponds and Discharges
  1. Fe (II) → Fe (III)
  2. Hydrolysis of Fe (III)
  3. Precipitation of Fe (III) oxides
  4. Flocculation and settling of particulates

Costly sludge disposal

2



Commonly Found Iron Minerals

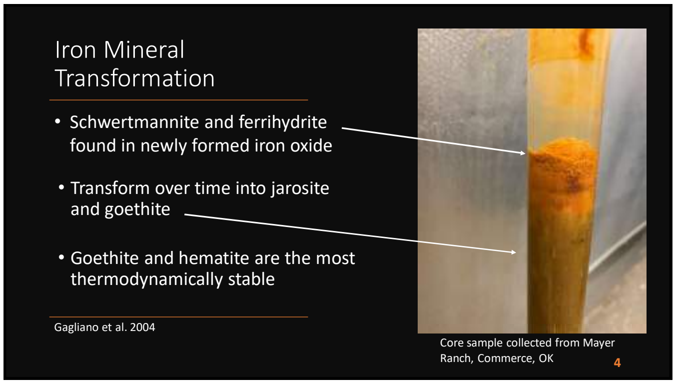
Schwertmannite, $Fe_8O_8(OH)_6(SO_4)·nH_2O$
Oxidation at pH <5

Ferrihydrite, $Fe_2O_3·0.5H_2O$
Oxidation at pH ≥ 2

Jarosite , $KFe_3(OH)_6(SO_4)_2$
pH 2-5 and at higher temperatures

Goethite, α-FeO(OH)
Fast oxidation at pH 4-9

3



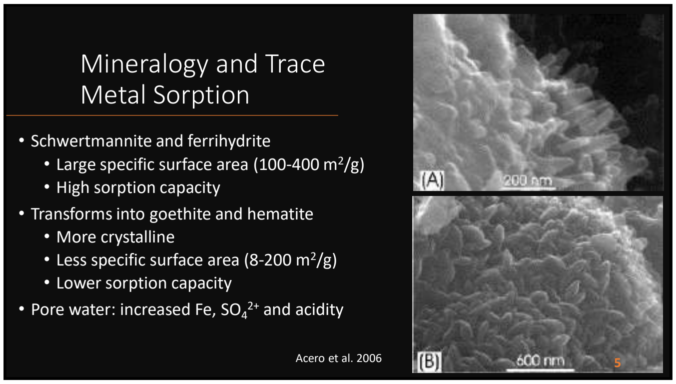
Iron Mineral Transformation

- Schwertmannite and ferrihydrite found in newly formed iron oxide
- Transform over time into jarosite and goethite
- Goethite and hematite are the most thermodynamically stable

Gagliano et al. 2004

Core sample collected from Mayer Ranch, Commerce, OK

4



Mineralogy and Trace Metal Sorption

- Schwertmannite and ferrihydrite
  - Large specific surface area (100-400 m^2/g)
  - High sorption capacity
- Transforms into goethite and hematite
  - More crystalline
  - Less specific surface area (8-200 m^2/g)
  - Lower sorption capacity
- Pore water: increased Fe, SO_4^{2+} and acidity

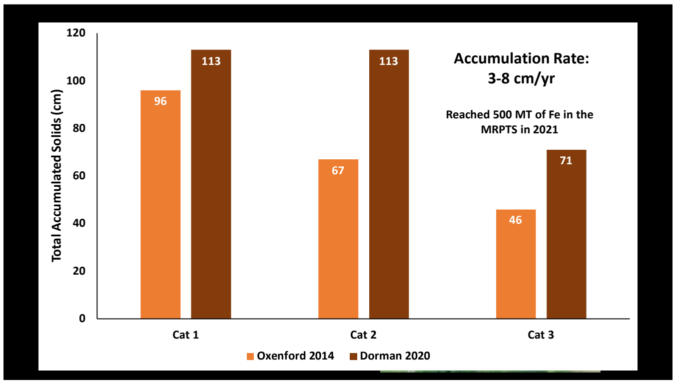
Acero et al. 2006

5

Why It Matters

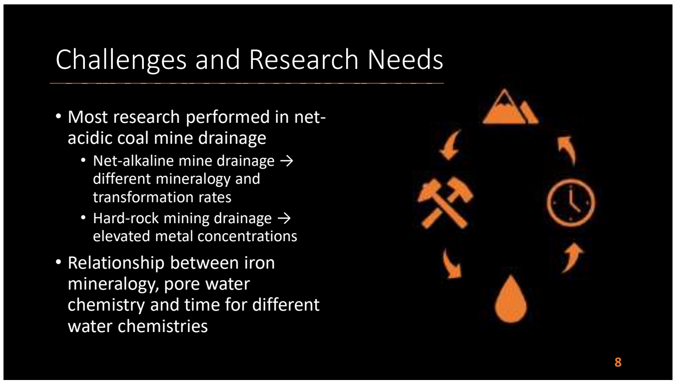
- Sinks become sources
- Affects PTS performance
- Affects disposal and beneficial reuse options for produced iron solids

6



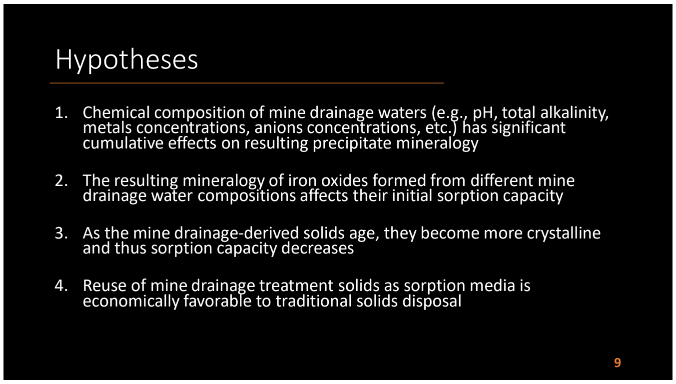
Accumulation Rate:
3-8 cm/yr

Reached 500 MT of Fe in the MRPTS in 2021



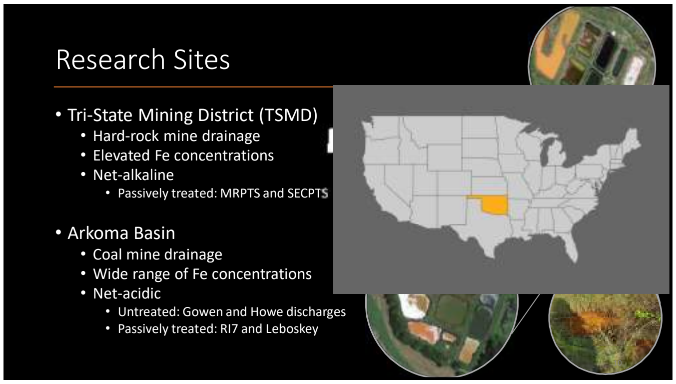
Challenges and Research Needs

- Most research performed in net-acidic coal mine drainage
  - Net-alkaline mine drainage → different mineralogy and transformation rates
  - Hard-rock mining drainage → elevated metal concentrations
- Relationship between iron mineralogy, pore water chemistry and time for different water chemistries



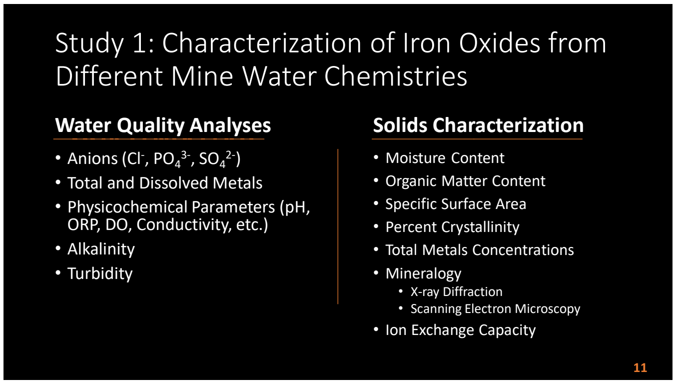
Hypotheses

1. Chemical composition of mine drainage waters (e.g., pH, total alkalinity, metals concentrations, anions concentrations, etc.) has significant cumulative effects on resulting precipitate mineralogy
2. The resulting mineralogy of iron oxides formed from different mine drainage water compositions affects their initial sorption capacity
3. As the mine drainage-derived solids age, they become more crystalline and thus sorption capacity decreases
4. Reuse of mine drainage treatment solids as sorption media is economically favorable to traditional solids disposal



Research Sites

- Tri-State Mining District (TSMD)
  - Hard-rock mine drainage
  - Elevated Fe concentrations
  - Net-alkaline
    - Passively treated: MRPTS and SECPTS
- Arkoma Basin
  - Coal mine drainage
  - Wide range of Fe concentrations
  - Net-acidic
    - Untreated: Gowen and Howe discharges
    - Passively treated: RI7 and Leboskey



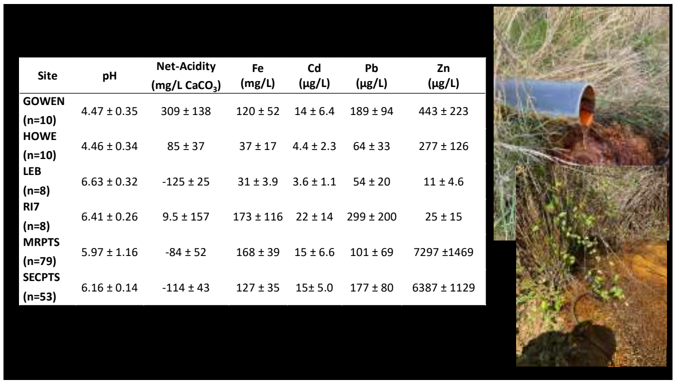
Study 1: Characterization of Iron Oxides from Different Mine Water Chemistries

Water Quality Analyses

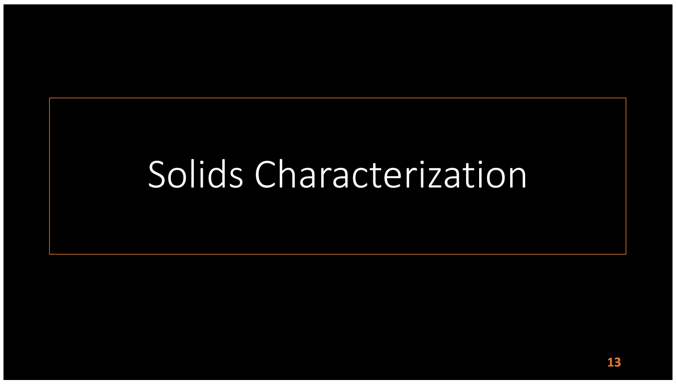
- Anions (Cl$^-$, PO$_4^{3-}$, SO$_4^{2-}$)
- Total and Dissolved Metals
- Physicochemical Parameters (pH, ORP, DO, Conductivity, etc.)
- Alkalinity
- Turbidity

Solids Characterization

- Moisture Content
- Organic Matter Content
- Specific Surface Area
- Percent Crystallinity
- Total Metals Concentrations
- Mineralogy
  - X-ray Diffraction
  - Scanning Electron Microscopy
- Ion Exchange Capacity



Site	pH	Net-Acidity (mg/L $CaCO_3$)	Fe (mg/L)	Cd (µg/L)	Pb (µg/L)	Zn (µg/L)
GOWEN (n=10)	4.47 ± 0.35	309 ± 138	120 ± 52	14 ± 6.4	189 ± 94	443 ± 223
HOWE (n=10)	4.46 ± 0.34	85 ± 37	37 ± 17	4.4 ± 2.3	64 ± 33	277 ± 126
LEB (n=8)	6.63 ± 0.32	-125 ± 25	31 ± 3.9	3.6 ± 1.1	54 ± 20	11 ± 4.6
RI7 (n=8)	6.41 ± 0.26	9.5 ± 157	173 ± 116	22 ± 14	299 ± 200	25 ± 15
MRPTS (n=79)	5.97 ± 1.16	-84 ± 52	168 ± 39	15 ± 6.6	101 ± 69	7297 ±1469
SECPTS (n=53)	6.16 ± 0.14	-114 ± 43	127 ± 35	15± 5.0	177 ± 80	6387 ± 1129



Solids Characterization

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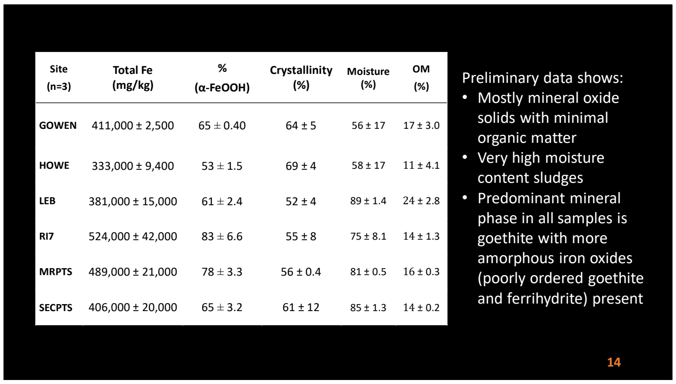

Site (n=3)	Total Fe (mg/kg)	% (α-FeOOH)	Crystallinity (%)	Moisture (%)	OM (%)
GOWEN	411,000 ± 2,500	65 ± 0.40	64 ± 5	56 ± 17	17 ± 3.0
HOWE	333,000 ± 9,400	53 ± 1.5	69 ± 4	58 ± 17	11 ± 4.1
LEB	381,000 ± 15,000	61 ± 2.4	52 ± 4	89 ± 1.4	24 ± 2.8
RI7	524,000 ± 42,000	83 ± 6.6	55 ± 8	75 ± 8.1	14 ± 1.3
MRPTS	489,000 ± 21,000	78 ± 3.3	56 ± 0.4	81 ± 0.5	16 ± 0.3
SECPTS	406,000 ± 20,000	65 ± 3.2	61 ± 12	85 ± 1.3	14 ± 0.2

Preliminary data shows:
- Mostly mineral oxide solids with minimal organic matter
- Very high moisture content sludges
- Predominant mineral phase in all samples is goethite with more amorphous iron oxides (poorly ordered goethite and ferrihydrite) present

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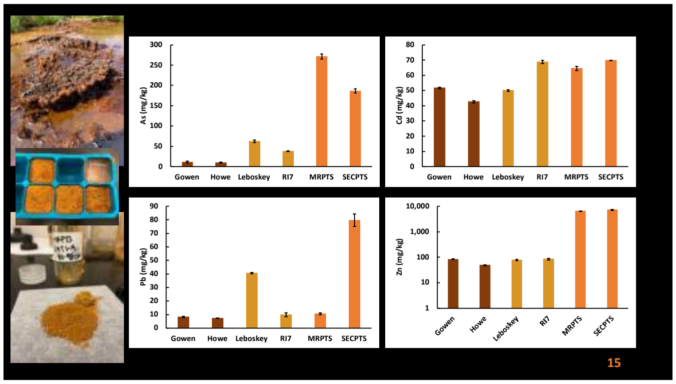

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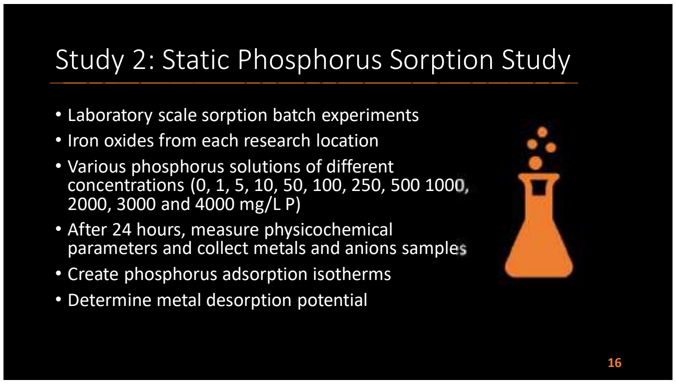

Study 2: Static Phosphorus Sorption Study

- Laboratory scale sorption batch experiments
- Iron oxides from each research location
- Various phosphorus solutions of different concentrations (0, 1, 5, 10, 50, 100, 250, 500 1000, 2000, 3000 and 4000 mg/L P)
- After 24 hours, measure physicochemical parameters and collect metals and anions samples
- Create phosphorus adsorption isotherms
- Determine metal desorption potential

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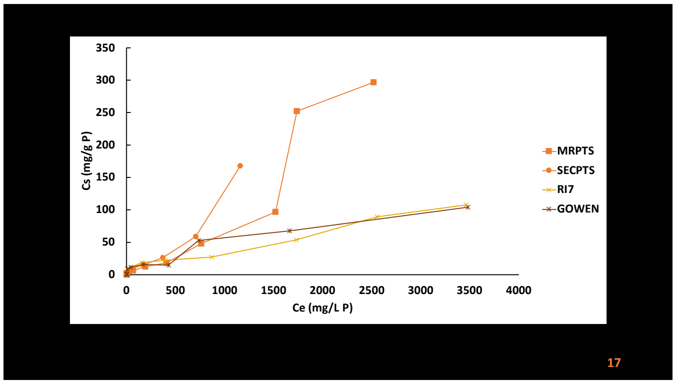

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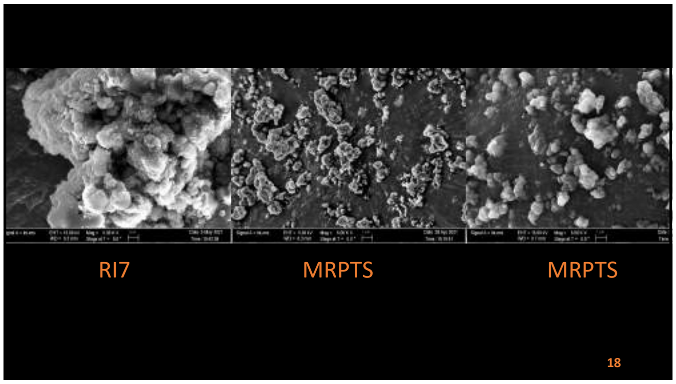

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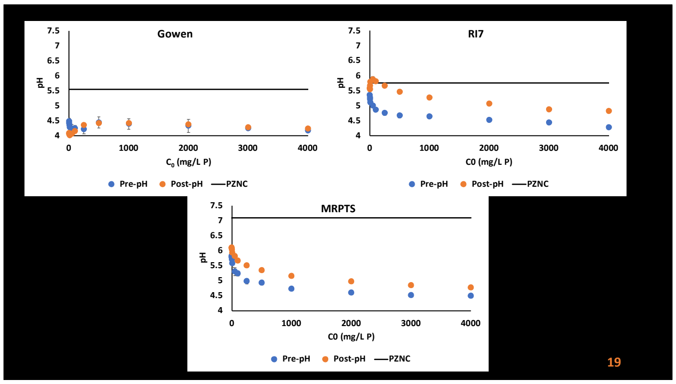
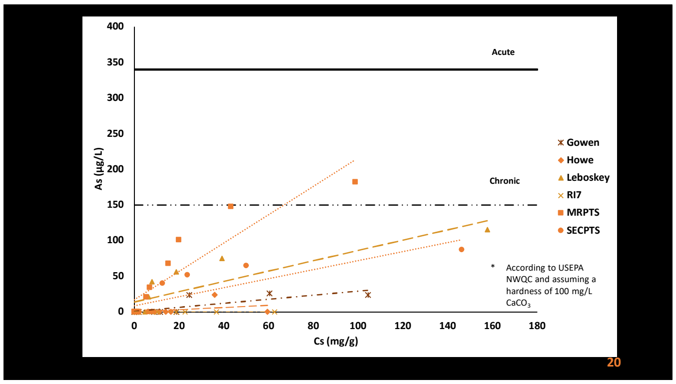
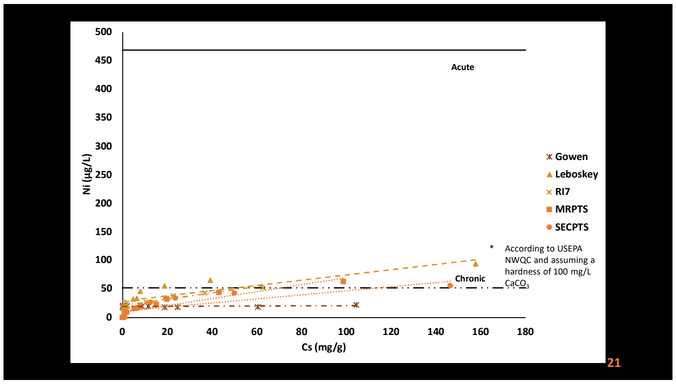




* According to USEPA NWQC and assuming a hardness of 100 mg/L $CaCO_3$



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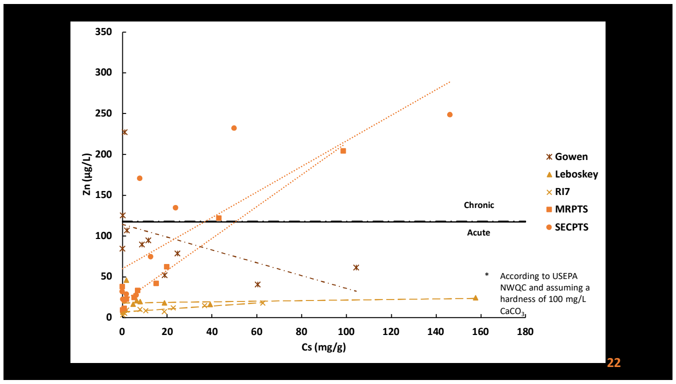
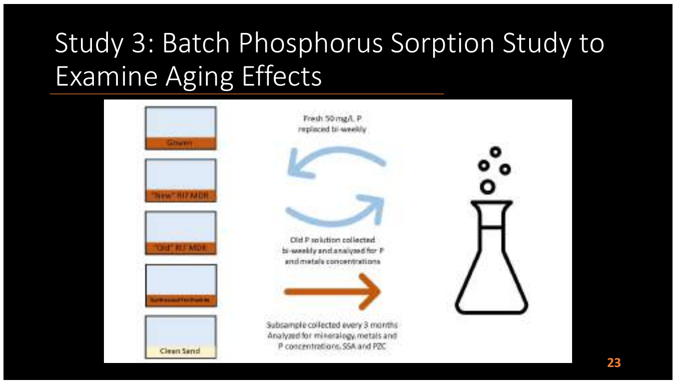


* According to USEPA NWQC and assuming a hardness of 100 mg/L $CaCO_3$

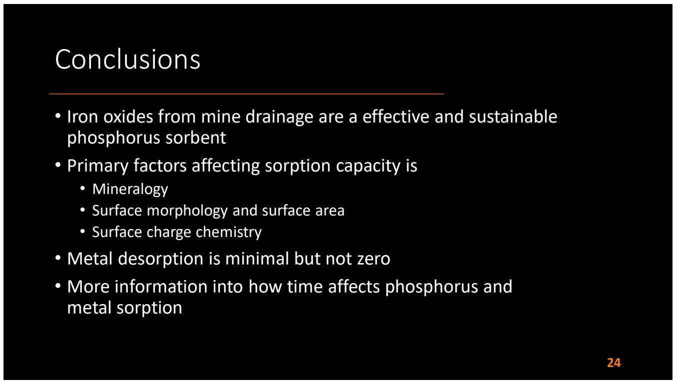


Study 3: Batch Phosphorus Sorption Study to Examine Aging Effects

Fresh 50 mg/L P replaced bi-weekly

Old P solution collected bi-weekly and analyzed for P and metals concentrations

Subsample collected every 3 months Analyzed for mineralogy, metals and P concentrations, SSA and PZC



Conclusions

- Iron oxides from mine drainage are a effective and sustainable phosphorus sorbent
- Primary factors affecting sorption capacity is
  - Mineralogy
  - Surface morphology and surface area
  - Surface charge chemistry
- Metal desorption is minimal but not zero
- More information into how time affects phosphorus and metal sorption

Acknowledgements

This work was supported by

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- Office of Surface Mining Reclamation and Enforcement (Agreement S21AC10011-00)
- U.S. Environmental Protection Agency (Agreement X7-97682001-0)
- Oklahoma Conservation Commission Abandoned Mine Land Program

Thank You!!

Any Questions?

Effect of source water chemical composition on the mineralogical and chemical properties of resulting iron oxide precipitates in coal and hard-rock mining influenced waters

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Abstract

Although most aerobic passive treatment systems (PTS) use similar processes to remediate mine drainage (MD) and create residual iron oxide precipitates, these solids greatly differ between sites. The purpose of this research was to study the effect that source MD chemical composition has on the mineralogical and chemical properties of formed iron oxides. The mineralogy and physicochemical properties of these solids can greatly affect reuse options such as phosphorus sorption. These analyses can help determine the potential beneficial reusability of these solids thus increasing the environmental and economic sustainability of PTS. A considerable data gap exists on the effect MD chemical composition has on the resulting physicochemical and mineralogical characteristics of formed iron oxide precipitates. In this study, MD water quality samples and iron oxide precipitates were collected and analyzed from six different and varied locations. Two of the locations were oxidation ponds in PTS located in the Tar Creek Superfund Site within the Tri-State Lead-Zinc Mining District, USA where the MD is net-alkaline and contains elevated concentrations of Fe, Pb, Zn, and Cd. Two of the locations were net-acidic coal MD discharges and two were oxidation ponds in net-alkaline coal MD PTS (where anoxic limestone drains generated alkalinity in net-acidic waters) in the Arkoma Basin, USA with a wide range of metal concentrations. The water samples were analyzed for total alkalinity, pH, total and dissolved metals, and anions. The solids were analyzed for total metals composition, point of zero net charge (PZNC), percent crystallinity, and their mineralogy via electron microscopy and x-ray diffraction. The solids from all locations were mostly crystalline with goethite as the major mineral phase. The iron oxides collected from net-alkaline hard rock MD systems had greater concentrations of As, Pb, and Zn associated with them and higher PZNC (7.1) compared to solids collected from the coal MD locations (PZNC 5.5). The higher PZNC of iron oxides from net-alkaline MDs provided a stronger affinity for anions such as phosphate, however, their increased metals concentrations may increase the likelihood of metal release as they age. This work comparing iron oxide compositions and characteristics from different MDs is especially important as PTS age and the produced iron oxide sludge needs to be removed. These analyses can help better determine effective beneficial reuse options for these solids rather than traditional disposal methods.

Keywords: Iron oxides, mineralogy, characterization, sustainable reuse

Introduction

Iron oxide minerals are ubiquitous in nature and are commonly found in mine drainage settings. Waters rich in Fe are exposed to the air and produce a wide range of iron precipitates such as schwertmannite and ferrihydrite which over time crystalize into more thermodynamically stable phases such as goethite and hematite (Acero et al. 2006; Cornell and Schwertmann 2003; Gagliano et al. 2004; Murad and Rojík 2005). The transformation pathways of these minerals and their resulting properties are directly influenced by the pH, temperature, redox conditions and presence of other ions in their host water (Cornell and Schwertmann

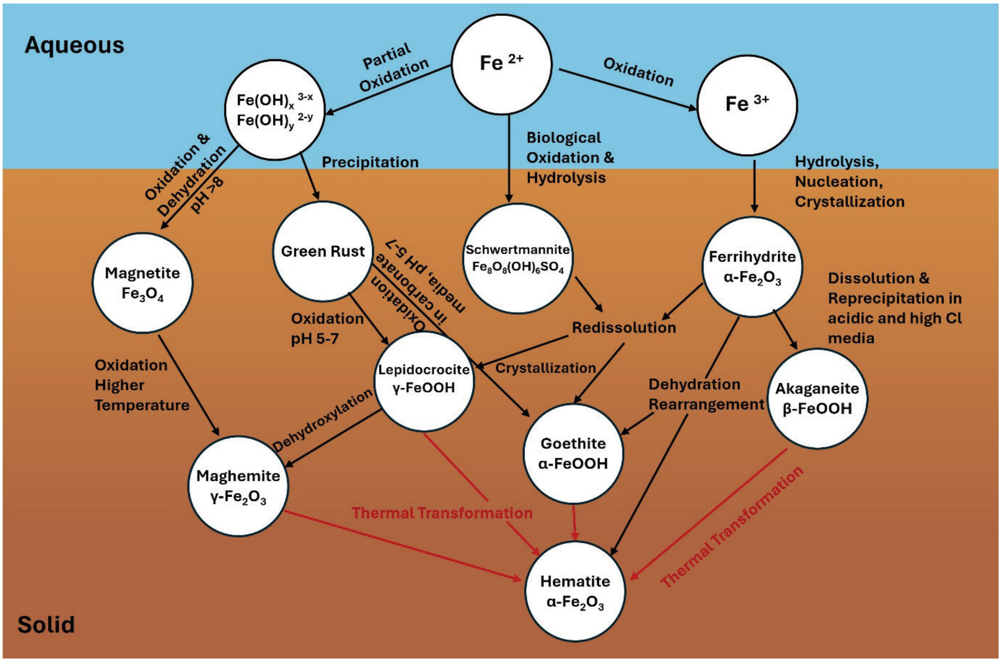

Figure 1 *Schematic showing the formation and transformation pathways of iron oxides*

2003; Murad and Rojík 2005; Yan et al. 2022; Zhang et al. 2018). Fig. 1 shows the different pathways and conditions for the formation and transformation of various iron oxides.

Understanding the physicochemical properties of the iron oxides and how they are affected by their host water quality is important. Initially formed iron oxides, such as schwertmannite and ferrihydrite, are nanocrystalline. The small crystal structures of these minerals give these solids a large specific surface area facilitating their potential role as sinks for trace metals and anions depending on their PZNC and the pH of the media (Acero et al. 2006; Gagliano et al. 2004; Murad and Rojík 2005). However, these amorphous forms of iron oxide are metastable and will transform into more thermodynamically stable and crystalline forms of iron oxide such as goethite, hematite and jarosite. This transformation can occur on a timescale of weeks to years depending on pH, redox conditions and other physicochemical properties of the water (Acero et al. 2006; Gagliano et al. 2004; Murad and Rojík 2005). A study performed by Gagliano et al. (2004) analyzed cores from a passive treatment wetland with iron oxide accumulation and showed that freshly precipitated iron oxides near the surface were schwertmannite with a high specific surface area. However, at depth, the older iron oxides had crystallized into goethite with larger crystal sizes and thus less specific surface area. Although larger crystals allow minerals to be more easily identified, the decrease in surface area can potentially decrease the sorption capacity for metals and other ions to the mineral phase.

The properties of the formed iron oxide precipitates are important not only from a scientific perspective but also from an applied management perspective. Disposal of solids from mine drainage sites, including passive treatment systems, can be costly and have a large environmental footprint. Beneficially reusing these solids can be more financially and environmentally sustainable. Iron oxides have long been researched and used as sorbents due to their high sorption capacity (Rakotonimaro et al. 2017; Sibrell and Tucker 2012; Zeng et al. 2004). Research into the more cost-effective use of iron and aluminium waste products instead of costly manufactured salts for water treatment has been explored (Sibrell

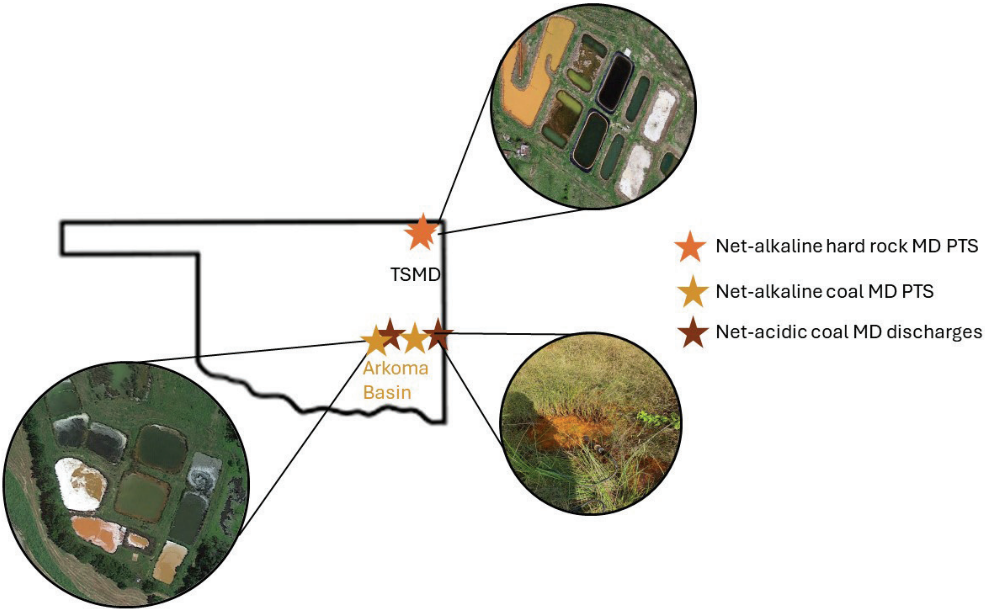

Figure 2 *Map of Oklahoma showing the relative locations of the sites investigated in this study including (from top right clockwise): MRPTS, HOWE discharge and RI7 PTS*

and Tucker 2012; Sibrell et al. 2015; Zeng et al. 2004). Given the variety of iron oxide minerals found in natural systems, a thorough understanding of the factors affecting their mineralogy and physicochemical properties is necessary to determine the sustainability of their reuse as sorbents.

Methods

This research examined the mine drainage water quality and iron oxide precipitates from six different locations throughout Oklahoma. Two of the locations are the Mayer Ranch Passive Treatment System (MRPTS) and the Southeast Commerce Passive Treatment System (SECPTS) oxidation ponds treating naturally net-alkaline hard rock mine drainage in the north-eastern Oklahoma portion of the Tri-State Mining District. The other four locations are in the Arkoma Basin in south-eastern Oklahoma where coal deposits were mined. Iron oxide solids were collected from the Leboskey (LEB) and Rock Island #7 (RI7) passive treatment systems where net-acidic coal mine drainage has been rendered alkaline by utilizing anoxic limestone drains before the water reaches the surface. Similarly, iron oxide samples were collected from two untreated net-acidic mine drainage discharges (GOWEN and HOWE). A map showing the relative locations of the sites in Oklahoma is shown in Fig. 2.

Water quality data were collected routinely to characterize the host mine drainage in which the iron oxides were produced. Water quality data included physicochemical parameters (pH, DO, temperature, specific conductance, ORP, alkalinity, turbidity), anions (Cl^-, SO_4^{2-}, NO_{2-}, NO_{3-}, PO_4^{3-}) and a suite of total and dissolved metals and base cations (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Si, Zn).

Grab samples of iron oxide precipitates were collected from each location. The grab samples were taken near the sediment surface where the solids have been freshly precipitated and deposited and are relatively free of organic matter. Similarly, a core sample was collected from the MRPTS oxidation pond to analyze how the solids have transformed and changed in-situ over time. The samples were then freeze dried to limit any phase transformations (Schwertmann and Cornell 1991). The solids were then analyzed for their physical, chemical, and mineralogical characteristics including total

Table 1 Selected water quality data for iron oxides collected at mine drainage discharges (GOWEN and HOWE) and PTS oxidation ponds (LEB, RI7, MRPTS and SECPTS)

Site	pH	Net-Acidity (mg/L $CaCO_3$)	Ionic Strength (M)	Fe (mg/L)	SO_4 (mg/L)
GOWEN (*n* = 10)	4.47 ± 0.35	309 ± 138	0.028 ± 0.003	124 ± 18	456 ± 129
HOWE (*n* = 10)	4.46 ± 0.34	85 ± 37	0.011 ± 0.001	36 ± 10	165 ± 46
LEB (*n* = 8)	6.63 ± 0.32	-125 ± 25	0.032 ± 0.05	31 ± 3.9	1010 ± 2472
RI7 (*n* = 8)	6.41 ± 0.26	9.5 ± 157	0.12 ± 0.11	169 ± 102	3359 ± 5165
MRPTS (*n* = 86)	5.97 ± 1.13	-84 ± 53	0.11 ± 0.2	165 ± 34	2241 ± 616
SECPTS (*n* = 71)	6.15 ± 0.17	-114 ± 59	0.10 ± 0.02	124 ± 31	1930 ± 343

metals composition, point of zero net charge (PZNC), percent crystallinity, and their mineralogy via electron microscopy and x-ray diffraction.

Results

A summary of the water quality data from host mine drainages in which the iron oxide solids are produced is shown in Table 1. All sites have elevated Fe and SO4 concentrations but vary in pH, net-acidity and ionic strength. The untreated coal mine drainages are net-acidic, with a pH of about 4.5 and a lower ionic strength than the net-alkaline hard rock mine drainage waters which have elevated alkalinity and concentrations of Cd, Pb and Zn.

The precipitate grab samples are mostly mineral (< 20% organic) iron oxides that are primarily in the goethite mineral phase. More amorphous goethite and ferrihydrite phases are present in the iron oxides recently precipitated in passive treatment oxidation ponds with a higher pH, perhaps because the PZNC for ferrihydrite is pH 7–8 at which ferrihydrite is the least soluble and thus is less likely to dissolve and rearrange to form goethite. As the pH moves farther away from the PZNC, the transformation rate of ferrihydrite to goethite increases causing a greater ratio of goethite to ferrihydrite (Cornell and Schwertmann 2003). Therefore, solids produced at GOWEN and HOWE which have a lower pH are slightly more crystalline as shown in Table 2. Similarly, iron oxides formed in waters with greater metals concentrations have a greater metal concentration (primarily Pb and Zn) and thus potentially can release more metals as they age or are reused as a sorbent.

While the main mineral in all samples is goethite, each site has different mineral morphology and surface area as demonstrated by images captured from scanning electron microscopy (SEM) at a magnification of 5000X (Fig. 2). The solids from LEB are larger (≈5 μm) and have a more globular morphology, perhaps exacerbated by the aggregation of smaller iron oxide particles onto larger iron oxide particles and clay particles. These samples were observed to have a higher clay content associated with them due to the shallow pond depth, presence of natural clay and low iron content. The solids from the RI7 and MRPTS systems also have a globular morphology but are smaller in size (1–2 μm) and show a smaller (< 1 μm) spiky morphology on the surface indicating the aggregation of less amorphous ferrihydrite on their surface providing an even higher surface area for sorption mechanisms.

While Fig. 2 shows how iron oxides can differ between sites, it is important to note that iron oxides can display heterogeneity within the same site. Fig. 3 shows images captured from scanning electron microscopy (SEM) at a magnification of 5000× of the top 10 cm representing iron oxides formed within the past two years and bottom 10 cm of core collected from the MRPTS

Table 2 Selected characteristics of the iron oxide samples collected at each site (n = 3)

Site	Fe (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Crystallinity %	PZNC
GOWEN	411000 ± 2400	52 ± 0.5	8.17 ± 0.54	83 ± 2.9	64 ± 5.2	5.55
HOWE	333000 ± 9400	43 ± 0.74	7.23 ± 0.10	49 ±2.2	69 ± 4.1	4.24
LEB	382000 ± 15000	50 ± 0.53	40 ± 0.47	77 ± 4.4	52 ± 3.9	5.64
RI7	524000 ± 42000	69 ± 1.1	9.8 ± 1.4	84 ± 6.7	55 ± 8.4	5.76
MRPTS	489000 ± 21000	64 ± 1.3	10 ± 0.74	6448 ±91	56 ± 0.4	7.11
SECPTS	406000 ± 20000	70 ± 0.07	80 ± 4.7	7256 ±315	56 ± 12	5.94

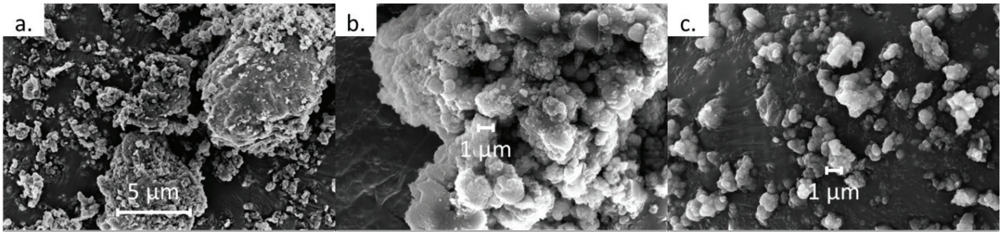

***Figure 2** SEM photos at a magnification of 5000 of the surface morphology of iron oxides collected from a) the LEB site, b) the RI7 site and c) the MRPTS site*

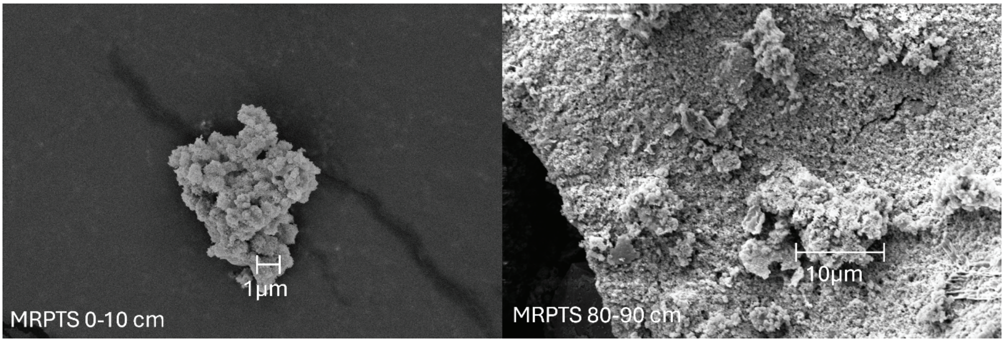

***Figure 3** SEM photos at a magnification of 5000 of the surface morphology of the top 10 cm (left) and bottom 10 cm (right) of a core collected from the MRPTS oxidation pond*

oxidation pond which formed 13 years ago. The top 0–10 cm show smaller particles (1–2 µm) with a spiky morphology showing an increased surface area whereas the bottom 80-90 cm have larger aggregated particles (10–15 µm) with a more platy and less globular morphology.

Conclusions

This work has found that source mine drainage water quality influences the mineralogical and physicochemical properties of the produced iron oxides. Iron oxides formed in net-acidic MD with a lower pH have lower PZNC and less ferrihydrite present compared to iron oxides formed in net-alkaline MD with higher pH. A lower PZNC makes these iron oxides less favourable for sorption of anions such as phosphate. However, these solids also have less metals accumulated within and sorbed onto their surface making them less likely to release metals as they age or are used a sorbent.

This research also showed that oxidation ponds are not static systems. The iron oxides accumulated within them will continue to change over time. Freshly precipitated iron oxides are smaller and less crystalline giving them a higher specific surface area. However, as they remain in-situ, they will transform over time into larger crystalline forms that will have a lower specific area. This can greatly affect the sorption capacity of these solids and therefore the potential reusability as a sorbent.

Overall, this work has shown that there is a great deal of heterogeneity of the iron oxides produced in different MD chemistries and within a single MD system. These differences are important to evaluate when considering reuse of produced iron oxides as a sustainable alternative to traditional salts typically used in water treatment processes.

Acknowledgements

This work was supported by the Oklahoma Department of Environmental Quality (Agreement PO2929019163), the Office of Surface Mining Reclamation and Enforcement (Agreement S21AC10011-00), and the U.S. Environmental Protection Agency (Agreement X7-97682001-0). Several private landowners provided access. The authors also wish to thank the Oklahoma Conservation Commission Abandoned Mine Lands Program for assistance.

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Effect of Source Water Chemical Composition on the Mineralogical and Chemical Properties of Resulting Iron Oxide Precipitates in Coal and Hard-rock Mining Influenced Waters

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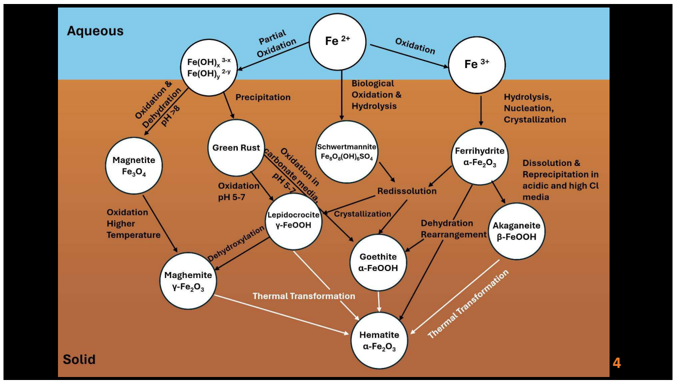
Center for Restoration of Ecosystems and Watersheds,
University of Oklahoma, USA
April 25, 2024

- Background
- Hypotheses
- Methods
- Results
- Key Takeaways

Iron Oxidation and Retention

- Oxidation Ponds and Discharges
  1. Fe (II) → Fe (III)
  2. Hydrolysis of Fe (III)
  3. Precipitation of Fe (III) oxides
  4. Flocculation and settling of particulates
- Residual management



Why It Matters

- Affects treatment performance
- Costly sludge disposal

Why It Matters

- Affects treatment performance
- Costly sludge disposal
- Turn "waste" into a resource
- Sustainable reuse

Welcome

environovida

Toxic mine pollution has turned Ohio rivers orange. Now it's being made into paint.

The Coal Authority

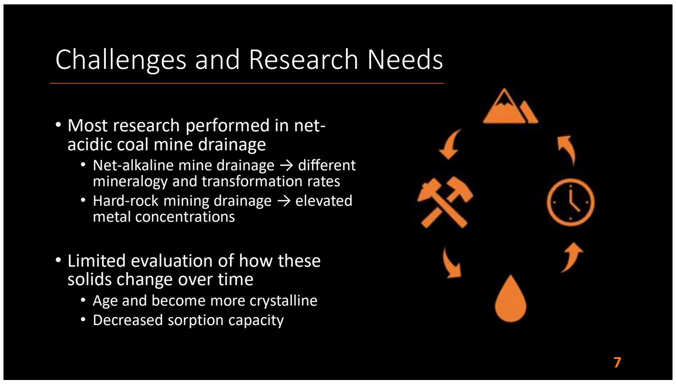
By April 2026 we will:

- Re-use or recycle 95% of the iron ochre and iron solids generated from our mine water treatment schemes to prevent disposal in landfill

By-Products
Opportunities Framework
2024 to 2027

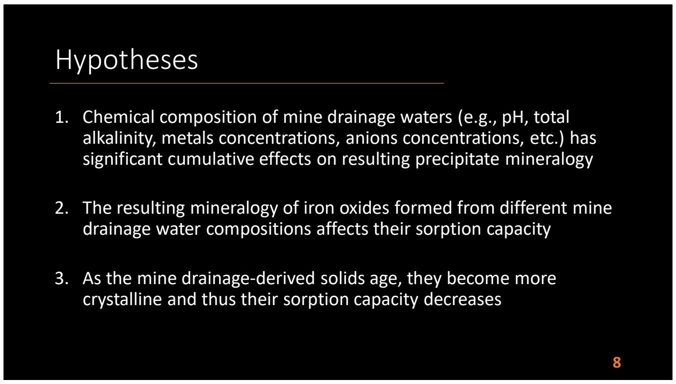
Remove and Reuse Phosphorus from Greenhouse and Plant Nursery Runoff

Megan Elizabeth Mary DeLaBarre Chase



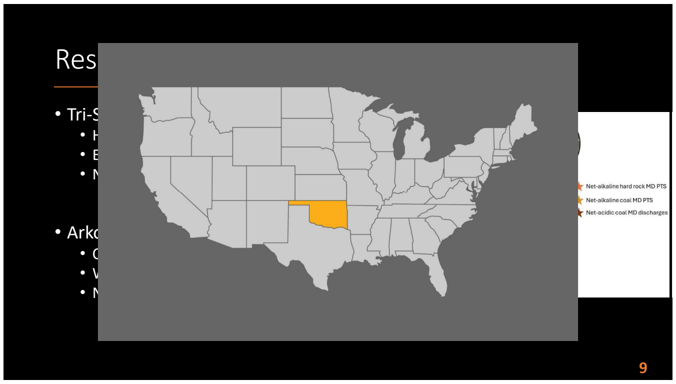
Challenges and Research Needs

- Most research performed in net-acidic coal mine drainage
  - Net-alkaline mine drainage → different mineralogy and transformation rates
  - Hard-rock mining drainage → elevated metal concentrations
- Limited evaluation of how these solids change over time
  - Age and become more crystalline
  - Decreased sorption capacity



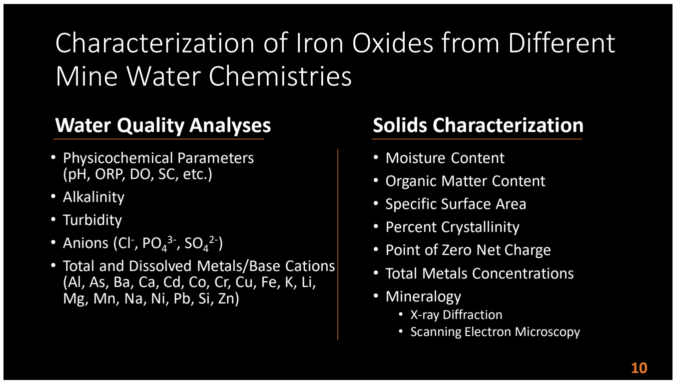
Hypotheses

1. Chemical composition of mine drainage waters (e.g., pH, total alkalinity, metals concentrations, anions concentrations, etc.) has significant cumulative effects on resulting precipitate mineralogy
2. The resulting mineralogy of iron oxides formed from different mine drainage water compositions affects their sorption capacity
3. As the mine drainage-derived solids age, they become more crystalline and thus their sorption capacity decreases



Res

- Tri-S
  - H
  - E
  - N
- Ark
  - C
  - V
  - N



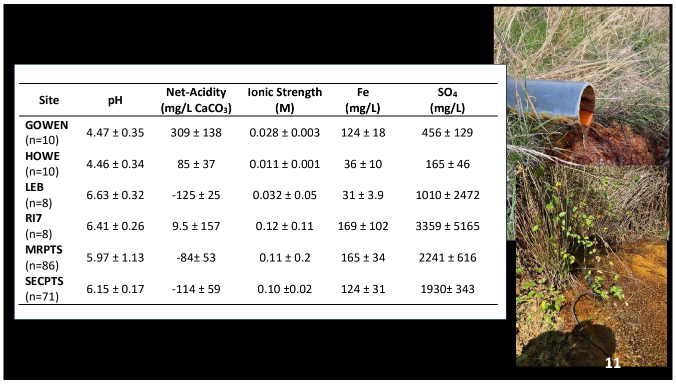
Characterization of Iron Oxides from Different Mine Water Chemistries

Water Quality Analyses

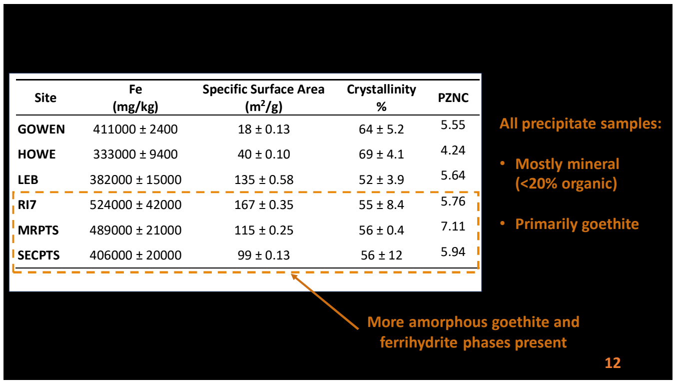
- Physicochemical Parameters (pH, ORP, DO, SC, etc.)
- Alkalinity
- Turbidity
- Anions (Cl^-, PO_4^{3-}, SO_4^{2-})
- Total and Dissolved Metals/Base Cations (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Si, Zn)

Solids Characterization

- Moisture Content
- Organic Matter Content
- Specific Surface Area
- Percent Crystallinity
- Point of Zero Net Charge
- Total Metals Concentrations
- Mineralogy
  - X-ray Diffraction
  - Scanning Electron Microscopy



Site	pH	Net-Acidity (mg/L $CaCO_3$)	Ionic Strength (M)	Fe (mg/L)	SO_4 (mg/L)
GOWEN (n=10)	4.47 ± 0.35	309 ± 138	0.028 ± 0.003	124 ± 18	456 ± 129
HOWE (n=10)	4.46 ± 0.34	85 ± 37	0.011 ± 0.001	36 ± 10	165 ± 46
LEB (n=8)	6.63 ± 0.32	-125 ± 25	0.032 ± 0.05	31 ± 3.9	1010 ± 2472
RI7 (n=8)	6.41 ± 0.26	9.5 ± 157	0.12 ± 0.11	169 ± 102	3359 ± 5165
MRPTS (n=86)	5.97 ± 1.13	-84± 53	0.11 ± 0.2	165 ± 34	2241 ± 616
SECPTS (n=71)	6.15 ± 0.17	-114 ± 59	0.10 ±0.02	124 ± 31	1930± 343

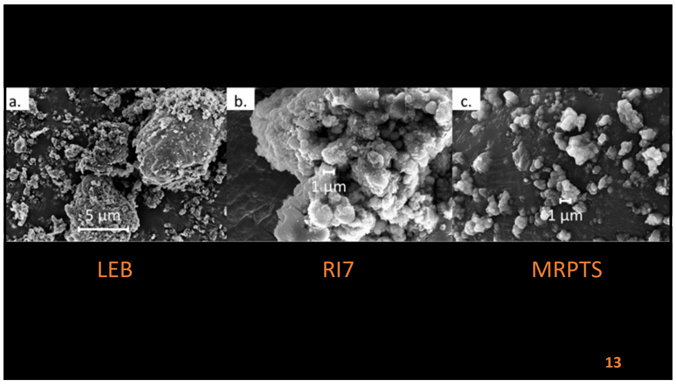


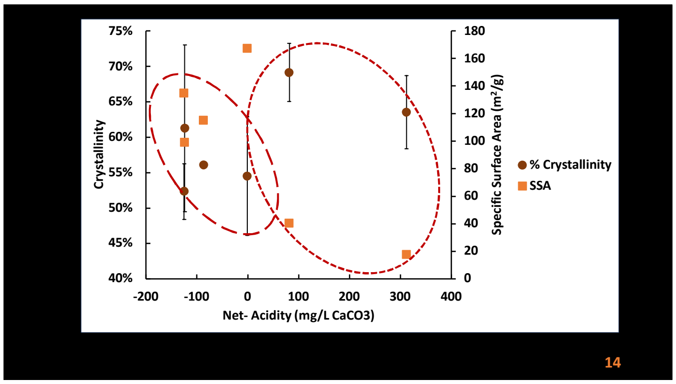
Site	Fe (mg/kg)	Specific Surface Area (m^2/g)	Crystallinity %	PZNC
GOWEN	411000 ± 2400	18 ± 0.13	64 ± 5.2	5.55
HOWE	333000 ± 9400	40 ± 0.10	69 ± 4.1	4.24
LEB	382000 ± 15000	135 ± 0.58	52 ± 3.9	5.64
RI7	524000 ± 42000	167 ± 0.35	55 ± 8.4	5.76
MRPTS	489000 ± 21000	115 ± 0.25	56 ± 0.4	7.11
SECPTS	406000 ± 20000	99 ± 0.13	56 ± 12	5.94

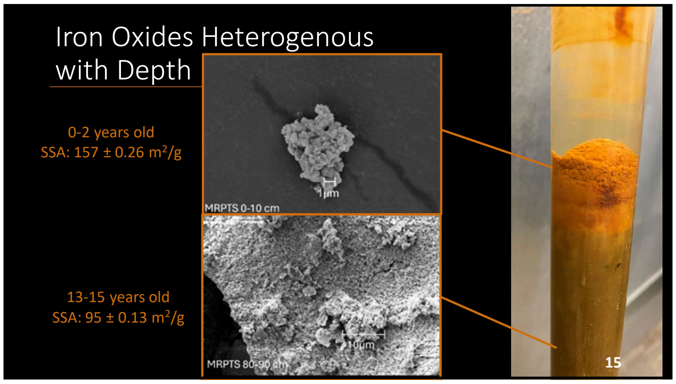
All precipitate samples:

- **Mostly mineral (<20% organic)**
- **Primarily goethite**

More amorphous goethite and ferrihydrite phases present







Iron Oxides Heterogenous with Depth

0-2 years old
SSA: 157 ± 0.26 m²/g

13-15 years old
SSA: 95 ± 0.13 m²/g

Key Takeaways

- Source mine drainage water quality influences the properties of iron oxide precipitates
  - Net-acidic pH → lower PZNC → higher crystallinity → lower SSA
  - Lower PZNC makes less favorable for anion sorption
  - Less metals sorbed less likely to release metals
- Oxidation ponds not static systems
  - Iron oxides continue to mineralize over time

Waste into Resource

Acknowledgements

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- Oklahoma Conservation Commission Abandoned Mine Land Program

Thank You!!

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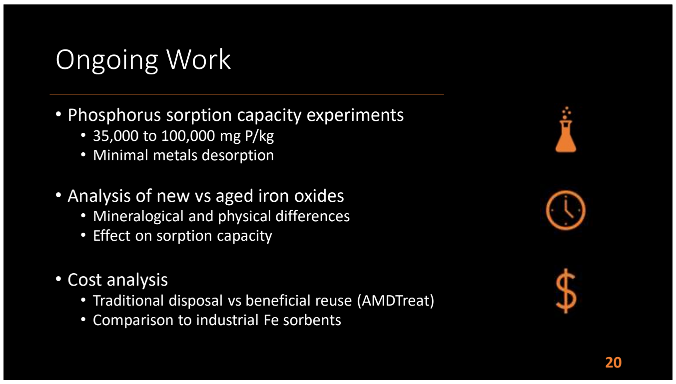

Ongoing Work

- Phosphorus sorption capacity experiments
  - 35,000 to 100,000 mg P/kg
  - Minimal metals desorption
- Analysis of new vs aged iron oxides
  - Mineralogical and physical differences
  - Effect on sorption capacity
- Cost analysis
  - Traditional disposal vs beneficial reuse (AMDTreat)
  - Comparison to industrial Fe sorbents