

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 Rojik 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 Rojik 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 Rojik 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 μ m 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

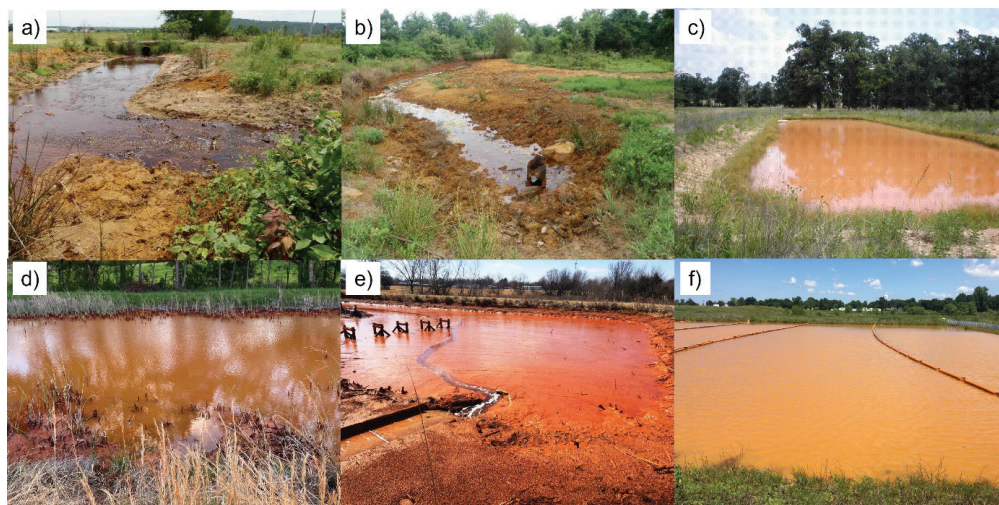


Figure 1 Iron oxide deposits at untreated coal mine discharges a) Gowen and b) Howe; coal mine drainage passive treatment system oxidation ponds c) Leboskey and d) Hartshorne; and hard-rock mine passive treatment system oxidation ponds e) Mayer Ranch (during managed drawdown) and f) Southeast Commerce.

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
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

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

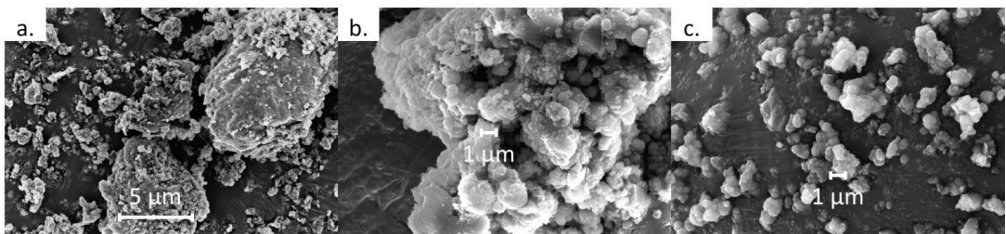
added into sealed 250-mL glass Erlenmeyer flasks. All the flasks were placed on an orbital shaker at 100 rpm for 24 h. After mixing, the samples were analyzed for pH and then filtered through 0.45 µm syringe filters into clean sample bottles and analyzed for soluble reactive phosphorus and dissolved 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 \pm 0.40	52 \pm 0.5	8.17 \pm 0.54	83 \pm 2.9	64 \pm 5.2	94785 \pm 31684
HOWE	53 \pm 1.5	43 \pm 0.74	7.23 \pm 0.10	49 \pm 2.2	69 \pm 4.1	35828 \pm 9080
LEB	61 \pm 2.4	50 \pm 0.53	40 \pm 0.47	77 \pm 4.4	52 \pm 3.9	77561 \pm 10710
RI7	83 \pm 6.6	69 \pm 1.1	9.8 \pm 1.4	84 \pm 6.7	55 \pm 8.4	48977 \pm 18161
MRPTS	78 \pm 3.3	64 \pm 1.3	10 \pm 0.74	6448 \pm 91	56 \pm 0.4	82568 \pm 32426
SECPTS	65 \pm 3.2	70 \pm 0.07	80 \pm 4.7	7256 \pm 315	56 \pm 12	116231 \pm 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 (\approx 5 μ m) 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 μ m) and show a smaller (<1 μ m) 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.

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