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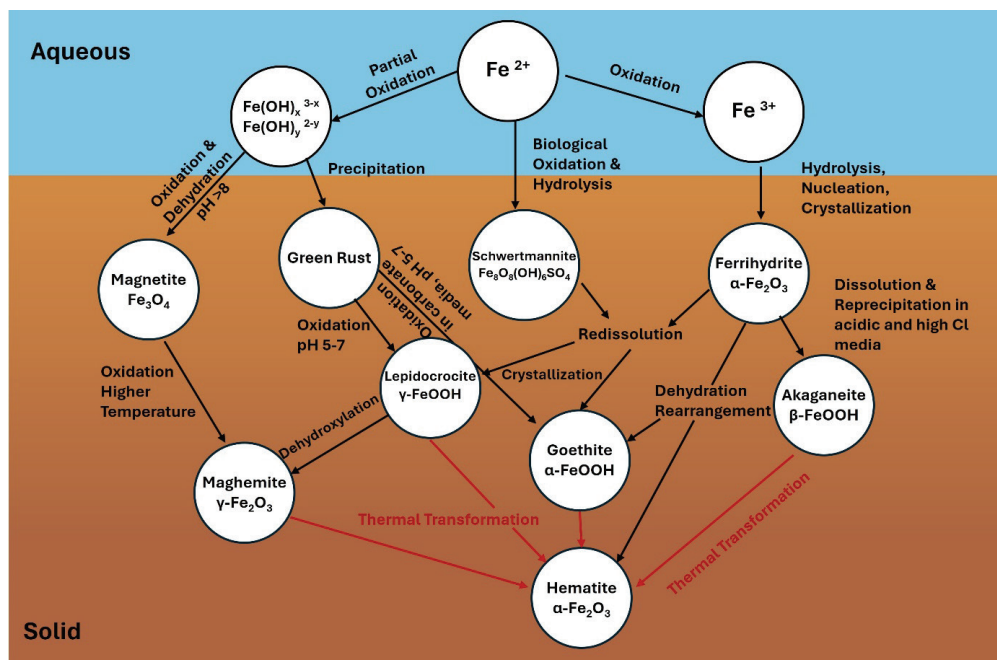
Figure 1 Schematic showing the formation and transformation pathways of iron oxides

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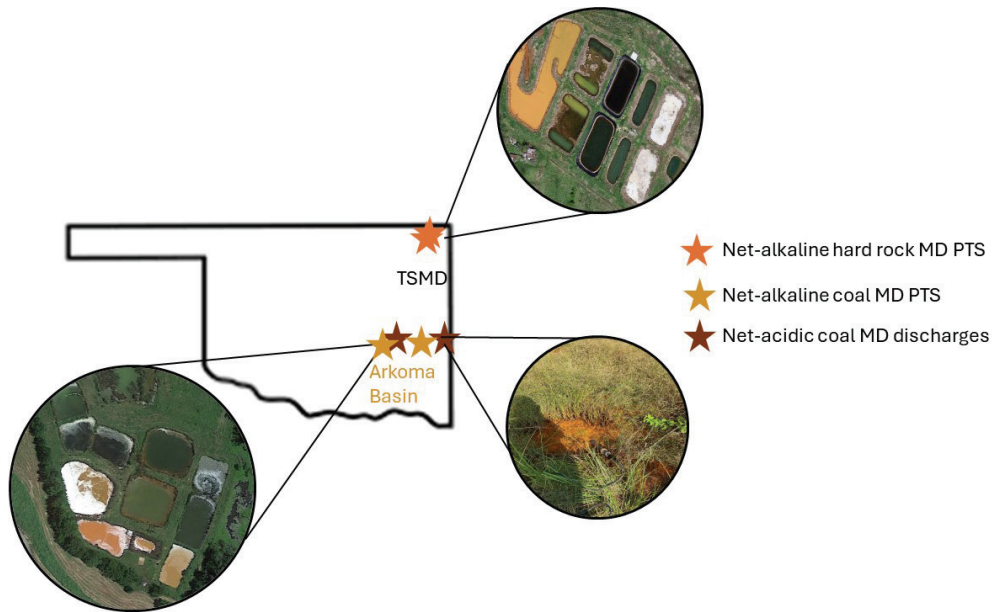
Figure 2 *Map of Oklahoma showing the relative locations of the sites investigated in this study including (from top right clockwise): MRPTS, HOWE discharge and RI7 PTS*

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 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.

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
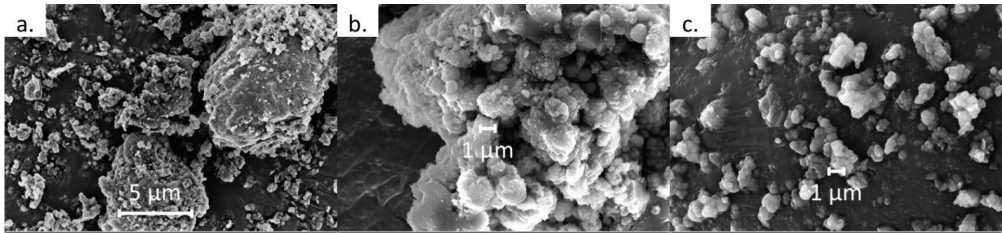
Figure 2 SEM photos at a magnification of 5000 of the surface morphology of iron oxides collected from a) the LEB site, b) the RI7 site and c) the MRPTS site
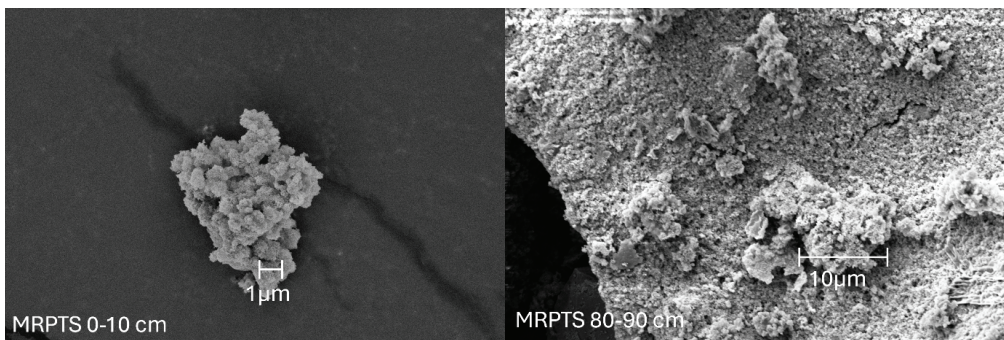
Figure 3 SEM photos at a magnification of 5000 of the surface morphology of the top 10 cm (left) and bottom 10 cm (right) of a core collected from the MRPTS oxidation pond

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

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