1 Accessible reactive surface area and abiotic redox reactivity of
2 iron oxyhydroxides in acidic brines

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ABSTRACT

The reactivity of iron oxyhydroxide nanoparticles in low pH and high ionic strength solutions was quantified to assess abiotic contributions to oxidation-reduction chemistry in acidic brine environments, such as mine groundwater seepage, lakes in Western Australia, and acid mine drainage settings, which are of global interest for their environmental impacts and unique geomicrobiology. Factors expected to influence accessible and reactive surface area, including Fe(II) adsorption and aggregate size, were measured as a function of pH and CaCl₂ concentration and related to the kinetics of redox reactions in aqueous suspensions of synthetic goethite (α -FeOOH), akaganeite (β -FeOOH), and ferrihydrite (Fe₁₀O₁₄(OH)₂) nanoparticles. Aqueous conditions and iron oxyhydroxides were chosen based on characterization of natural iron-rich mine microbial mats located in Soudan Underground Mine State Park, Minnesota, USA. Quinone species were used as redox sensors because they are well-defined probes and are present in natural organic matter. Fe(II) adsorption to the iron oxyhydroxide mineral surfaces from aqueous solution was measurable only at pH values above 4 and either decreased or was not affected by CaCl₂ concentration. Concentrations at or above 0.020 M CaCl₂ in acetate buffer (pH 4.5) induced particle aggregation. Assessment of Fe(II) adsorption and particle aggregation in acidic brine suggested that accessible reactive surface area may be limited in acidic brines. This was supported by observations of decreasing benzoquinone reduction rate by adsorbed Fe(II) at high CaCl₂ concentration. In contrast, the hydroquinone oxidation rate increased at high CaCl₂ concentrations, which may be due to suppressed adsorption of Fe(II) generated by the reaction. Results suggest that iron geochemical cycling in acidic brine environments will be substantially different than for iron oxyhydroxides in low-saline waters with circumneutral pH.

These findings have implications for acidic brine lakes and acid mine drainage locations that contain precipitated iron oxyhydroxides.

1. INTRODUCTION

Acidic brine environments form through rock alteration reactions in climates favoring evaporite deposition (Jones and Deocampo, 2003). Development of acidic conditions in these natural waters is strongly linked to iron geochemistry and the onset of oxidizing conditions. Specifically, high acidity develops through pyrite oxidation or, in sulfide-limited systems, through oxidation of Fe(II) and hydrolysis of Fe(III). Naturally formed acidic waters with brine or hypersaline ionic strength (as high as 300,000 mg/L salt content (Todd, 1980)) have been reported in northern Chile and Bolivia (Risacher and Fritz, 2009; Benison and Karmanocky, 2014), Western Australia (Burton et al., 2006; Benison and Bowen, 2013), and the United States (Johannesson et al., 1996). These acidic brines have been investigated for their environmental impacts as well as their potential to serve as Martian analogs of geology and microbiology (Jones and Deocampo, 2003; Benison and Karmanocky, 2014; Carter et al., 2015). Acidic brines also form in human-impacted settings, such as acid mine drainage and pit lakes of mines, which are of broad public concern and have been extensively studied (España, 2007; Zhu et al., 2012; Jacobs et al., 2014).

In some acidic brines, iron oxyhydroxide nanoparticles participate in the oxidation or reduction of organic contaminants or phenolic groups in natural organic matter through direct reaction with mineral surface sites or with adsorbed Fe(II) (Liu et al., 2014). Quinone moieties present in organic matter may also act as electron shuttles between iron oxyhydroxides and redox active bacteria, as has been observed using model quinone compounds in previous works (Orsetti

et al., 2013; Li et al., 2014). In human-impacted settings, such as polluted groundwater or acid mine drainage, the potential for iron oxyhydroxides to incorporate toxic metals can be exploited for remediation efforts (Maria Valente et al., 2011). Several studies have demonstrated that the accessible and reactive surface area of iron oxyhydroxides in aquatic systems depends on solution chemistry variables, such as ionic strength, pH, and concentration of reactive species (Baalousha, 2009; Hu et al., 2010), but extreme environments such as acidic brines have yet been fully explored. Ionic strength and acidity likely impact the reactivity of iron oxyhydroxide nanoparticles by affecting processes such as ion adsorption and aggregation, which in turn influence accessible and reactive surface area (Hayes and Leckie, 1987; Hayes et al., 1988; Antelo et al., 2005; Chekli et al., 2013).

Understanding abiotic iron cycling in acidic brines has the potential to elucidate fundamental processes in geochemistry as well as lead to improved remediation methods. A significant challenge, however, is the occurrence of both biological and abiotic influences. For example, some iron-rich saline and hypersaline microbial mats, such as those found in hydrothermal vents and solar salterns, are the subject of geomicrobial research (Wieland et al., 2005; Dickson and Giblin, 2009; Glazer and Rouxel, 2009; Toner et al., 2012). While the microbial reactivity in these iron-rich mats has been studied (Dichristina et al., 1989; Langley et al., 2009), the chemical behavior of the iron oxyhydroxides in high ionic strength and low pH conditions has not yet been evaluated, making it difficult to elucidate the mechanisms controlling iron redox cycling.

In this work, we assess the abiotic redox reactivity of iron oxyhydroxide nanoparticles in acidic brines. To model a natural environment, experiments were performed using solution chemistry similar to groundwater seepages found in the microbial mats of Soudan Underground

Mine, USA, which features an acidic brine environment with both microbial and abiotic contributions to iron cycling and where aqueous Fe(II) undergoes oxidation and hydrolysis upon exposure to the ambient air. Analysis of one location in the mine shaft with exposed groundwater seepage found three iron oxyhydroxide mineral phases present: goethite (α -FeOOH), akaganeite (β -FeOOH), and ferrihydrite ($\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$ (Michel et al., 2007)). In addition, the Fe(II) concentration was high, the pH acidic ($\sim$ pH 3), and the ionic strength high (> 2 M). Here, CaCl_2 was used to set ionic strength, and synthetic goethite, akaganeite, and ferrihydrite nanoparticles were prepared as model minerals.

The first objective of this work was to characterize accessible reactive surface area as a function of low pH and high ionic strength by quantifying adsorbed Fe(II) and assessing aggregation state. The second was to quantify rates of *p*-benzoquinone (referred to as benzoquinone hereafter) reduction via adsorbed Fe(II) or hydroquinone oxidation by iron oxyhydroxides as a function of increasing ionic strength at low pH. The results, along with consideration of thermodynamics, allow us to elucidate the relationship between surface redox reactions and acidic brine solution conditions due to the influence on accessible reactive surface area. These results offer a unique perspective on iron cycling in acidic brines, in which the abiotic redox reactions of iron oxyhydroxide minerals have yet to be described despite their occurrence in natural acidic brine environments and mine-impacted settings. Elucidation of abiotic redox reactions of iron oxyhydroxides will therefore enable a more complete understanding of iron cycling in acidic brines.

2. EXPERIMENTAL

2.1. Materials

Chemical sources and purities are listed in the supplementary material. All solutions were prepared in ultrapure water. For delivering aqueous Fe(II) to experiments, a stock solution of 200 mM Fe(II) was freshly prepared each day under anaerobic conditions by adding 1.1 mmol FeCl₂·4H₂O to 5 mL of water or 0.67 M CaCl₂ and 0.5 mL of 1 M HCl. When performing buffered experiments at pH 4.5, 40 mM acetate buffer was prepared by diluting glacial acetic acid with ultrapure water and adjusting the pH to 4.5 with 1 M NaOH.

2.2. Natural Soudan iron mats

Aqueous conditions and iron oxyhydroxides were chosen based on Soudan iron mats collected from the 27th Level West Drift, at a depth of 713.5 m below ground surface, of the Soudan Underground Mine State Park, Minnesota, USA. Sample collection and groundwater chemical analyses are described in the supplementary material. Soudan iron mat powders were gently ground using an agate mortar and pestle and applied to double-sided adhesive in thin layers. Samples were then analyzed at room temperature with no further processing.

Bulk Fe 1s extended X-ray absorption fine structure (EXAFS) spectra were collected at the Advanced Photon Source on beamline 20-BM in transmission mode. The monochromator energy was calibrated to 7110.75 eV (inflection point) using an Fe foil for each scan. The spectra were collected to a reciprocal space (k) value of greater than 15 (Å⁻¹). Individual scans were examined for changes in line-shape and peak position: no photon-induced sample damage was observed. Spectra were energy calibrated, averaged, and converted to k-space using the software Athena (Ravel and Newville, 2005). The spectra were compared to Fe EXAFS spectra for reference Fe-bearing minerals, and the minerals and their sources are listed in Table S2 (Hansel et al., 2003; Toner et al., 2009; Toner et al., 2012). Linear combination fitting of EXAFS spectra

using the reference spectra listed above was accomplished with custom software from Matthew Marcus in the k-range 2 to 11 Å⁻¹ (reflecting the shortest k-range of our reference spectra).

2.3. Nanoparticle synthesis and characterization

Details of the synthetic procedures summarized here are provided in the supplementary material. Goethite nanoparticles were synthesized using a modified version of the method from Anschutz and Penn (2005) by adding 0.48 M NaHCO₃ to 0.40 M Fe(NO₃)₃·9H₂O followed by aging and purification. Akaganeite nanoparticles were synthesized by aging 0.035 M FeCl₃·6H₂O in a hydrothermal bomb. Ferrihydrite nanoparticles were synthesized by forced hydrolysis and aging of a 0.20 M Fe(NO₃)₃·9H₂O solution as described in Schwertmann and Cornell (2000). The nanoparticles were stored as a suspension with known mass loadings in a Nalgene bottle at 5 °C to be delivered by volumetric pipette. Mass loading measurements were performed frequently to ensure accuracy. Considering ferrihydrite reactivity has been shown to change as a function of particle age, fresh ferrihydrite nanoparticles were prepared again after three weeks of use (Bligh and Waite, 2011). Particle composition, size, morphology, and surface area were determined by a combination of X-ray diffraction (XRD), transmission electron microscopy (TEM), and nitrogen sorption analysis (see supplementary material).

2.4. Iron adsorption

Iron adsorption was measured by quantifying the remaining Fe(II) in solution after filtration using the ferrozine colorimetric analysis (Stookey, 1970). In brief, nanoparticle suspensions were prepared in either 0 M or 0.67 M CaCl₂ at pH 3 – 7 and equilibrated for 21 h. Following equilibration, an aliquot was filtered, added to cuvettes containing ferrozine, and measured by UV-Vis spectroscopy. Details are provided in the supplementary material.

2.5. Aggregate size and zeta potential

Aggregate sizes and zeta potentials were collected by dynamic light scattering (DLS) as a function of CaCl_2 concentration using a ZetaPALS Zeta Potential Analyzer (Brookhaven) with the 90Plus/BI-MAS Multi Angle Particle Sizing Option installed. Goethite, akaganeite, or ferrihydrite samples (0.325 g/L) were prepared in 20 mL scintillation vials by volumetrically delivering particle stock suspension and 40 mM acetate buffer at pH 4.5 with either 0 or 0.67 M CaCl_2 so that the final CaCl_2 concentration ranged from 0 to ~ 0.67 M. The effect of added Fe(II) was examined by adding the Fe(II) stock solution so that the Fe(II) concentration was 0.342 mM. Aggregate sizes and standard errors were reported as mean number-based effective hydrodynamic diameters from 5 runs of 15 s each with a dust cut-off of 30 (instrumental parameter for filtering out rare intensity spikes most likely due to large dust particles). Average zeta potentials and standard errors were reported from 3 runs of 20 cycles. For monitoring aggregate size during reaction, a 3 mL sample from the reaction was measured using the same instrumental parameters.

2.6. Reaction kinetics

Benzoquinone reduction and hydroquinone oxidation experiments were run in 40 mM acetate buffer at pH 4.5 with either 0 or 0.67 M CaCl_2 . To 38 mL glass serum bottles, the appropriate iron oxyhydroxide suspension was volumetrically delivered so that the final mass loading was 0.325 g/L. When all three iron oxyhydroxides were added to one reactor, the total mass loading was either 0.325 or 0.975 g/L (equal mass ratios of each iron oxyhydroxide). Reactors were then transferred to an anaerobic chamber and diluted with 20 mL of 0 or 0.67 M CaCl_2 buffer. To vary the CaCl_2 concentration, appropriate ratios of the 0 and 0.67 M CaCl_2 buffers were added. For benzoquinone reduction, 0.342 mM Fe(II) was added using the Fe(II) stock solution. The reactors were then brought to a final volume of 35 mL with the appropriate

buffer, crimp capped, and sonicated for 20 min outside of the anaerobic chamber. Following sonication, the reactors were wrapped in aluminum foil to block light and magnetically stirred in the anaerobic chamber for 21 h of equilibration.

Reactors were spiked with benzoquinone or hydroquinone (0.1 mM) from a 10 mM stock solution prepared in the appropriate buffer solution. Samples (1 mL) were withdrawn using a plastic syringe and filtered into an amber glass HPLC vial. Benzoquinone and hydroquinone were quantified at 235 nm using an Agilent 1100 series HPLC (see supplementary material). Benzoquinone reduction was analyzed using a pseudo-first-order rate model, and hydroquinone oxidation was analyzed using the rate of benzoquinone production. The post-reaction suspensions were transferred to centrifuge tubes and collected using an Eppendorf 5804 centrifuge (6000 g for 3 min). Samples were washed three times with deoxygenated Milli-Q water (only opening when inside the anaerobic chamber). Collected solids were dried at room temperature in air, ground using mortar and pestle, and characterized by XRD in the same manner as the unreacted minerals.

3. RESULTS

3.1. Characterization

Groundwater emanating from exploratory boreholes on the 27th Level West Drift of the Soudan Mine is a chloride (1.40 M) brine with primarily calcium (0.408 M) and sodium (0.388 M) cations and minor contributions from magnesium (84.0 mM), strontium (5.08 mM), potassium (6.57 mM), and total dissolved Fe (1.80 mM). Complete geochemistry is described in the supplementary material (Table S1). The high calcium concentration makes this a uniquely terrestrial brine setting. To contrast the use of sodium chloride, which often simulates seawater, the ionic strength of kinetic experiments was set by adding calcium chloride (~ 0.7 M; nearly

two times the Ca^{2+} concentration of the Soudan Mine groundwater) in order to represent a terrestrial brine system with 1.4 M Cl^- . The groundwater has circumneutral pH and low redox potential. As the groundwater flows horizontally from diamond drill hole (DDH) 942, the waters are exposed to oxygen. As a result, dissolved Fe(II) undergoes oxidation to Fe(III), hydrolysis that reduces pH, and precipitation to form a variety of iron oxyhydroxide phases. The iron 1s EXAFS spectra for Soudan iron mats are displayed in Fig. 1 with reference spectra from iron oxyhydroxide phases goethite, akaganeite, and ferrihydrite (2-line). The Soudan iron mats are composed of Fe(III) oxyhydroxides with no evidence for mixed Fe(II)-Fe(III) phases such as green rust or Fe(II)-bearing minerals such as pyrite. The horizontal seeps of the 27th Level West Drift (samples SM03, SM04, SM05) all contain akaganeite with mole fractions ranging from 0.18 to 0.52 (± 0.10). Along the first 76.2 m of the flow path from DDH 942, the proportion of akaganeite, goethite, and ferrihydrite are similar within the estimated error of the linear combination fitting (Fig. 1). Given this natural setting as an example of an iron-rich acidic brine, experiments were designed to explore the abiotic reactivity of goethite, akaganeite, and ferrihydrite in an acidic calcium chloride brine.

For synthetic iron oxyhydroxides, TEM micrographs and XRD patterns are shown in the supplementary material (Fig. S1 and S2). The synthetic goethite particles have an acicular morphology with dimensions of 110 ± 41 nm in length and 12 ± 5 nm in width. The synthetic akaganeite nanoparticles are also acicular but smaller in size, with an average length of 36 ± 16 nm and width of 5 ± 2 nm. The synthetic ferrihydrite particles are 2 to 3 nm in diameter. No evidence of secondary phases was detected by XRD for any of the three samples. TEM surface area was determined to be $170 \text{ m}^2/\text{g}$, $230 \text{ m}^2/\text{g}$, and $510 \text{ m}^2/\text{g}$ for goethite, akaganeite, and ferrihydrite, respectively, using the assumption that goethite rods are prisms similar in shape as

described in previous work (Burrows et al., 2012), akaganeite rods are square cuboids (where $a = b \neq c$), and ferrihydrite dots are spheres. Densities used for goethite, akaganeite, and ferrihydrite were 4.26 g/cm^3 (Cornell and Schwertmann, 2003), 3.73 g/cm^3 (Song and Boily, 2011), and 3.96 g/cm^3 (Cornell and Schwertmann, 2003), respectively. Nitrogen sorption-BET analysis yielded a specific surface area of $140 \text{ m}^2/\text{g}$ for goethite, $278 \text{ m}^2/\text{g}$ for akaganeite, and $130 - 280 \text{ m}^2/\text{g}$ for ferrihydrite. The low and variable specific surface area measured for ferrihydrite by BET is consistent with considerable aggregation during drying, which would prevent condensation of N_2 on all mineral surfaces. For akaganeite, the higher specific surface area determined by BET analysis than by measurements from TEM images suggests that the square cuboid assumption may under-represent the akaganeite surface area. These akaganeite rods may be rounded at the ends or have a porous surface, similar to the more pronounced cigar-shape morphology and tunnel structure seen in larger akaganeite nanoparticles (Deliyanni et al., 2001).

3.2. Aggregation state vs. adsorbed Fe(II) and CaCl_2 concentration

Accessible surface area of iron oxyhydroxide nanoparticles in suspensions (buffered at pH 4.5) was monitored by DLS. Hydrodynamic diameter and zeta potential, which serve as proxies for aggregation state and surface charge, respectively, are shown in Fig. 2. In general, aggregate size increased with increasing CaCl_2 (Fig. 2a), with the largest changes in size observed at lower concentrations of CaCl_2 (below 0.1 M). The maximum quantitative size of this DLS instrument (3000 nm , provided in the manual, indicated by a dashed line in Fig. 2a) was observed for most suspensions below or at 0.1 M CaCl_2 . Additionally, suspensions prepared with and without Fe(II) were distinguishable at lower CaCl_2 concentrations but not statistically different above 0.1 M CaCl_2 . The observed decrease in zeta potential with increasing CaCl_2

concentration (Fig. 2b), approaching 0 mV in suspensions with 0.67 M CaCl₂, indicates decreasing surface repulsion of the particles.

3.3. Iron adsorption vs. pH and CaCl₂

To characterize the reactive surface area as a function of pH and ionic strength, Fe(II) adsorption edges (Fig. 3a-c) were collected and normalized to the number of reactive sites for each mineral (Fig. 3d and 3e, see supplementary material for calculations) (Hiemstra and van Riemsdijk, 2007; Hiemstra and Van Riemsdijk, 2009; Song and Boily, 2011). Fe(II) adsorption onto all three iron oxyhydroxides increased with increasing pH and measurable Fe(II) adsorption did not occur until pH values were greater than 4, consistent with previous works (Dixit and Hering, 2006; Jones et al., 2014). Generally speaking, the degree of adsorption was greatest on goethite and least on ferrihydrite when normalized to the total number of reactive sites. In the cases of goethite and ferrihydrite, Fe(II) adsorption decreased at high CaCl₂ concentration. In contrast, Fe(II) adsorption onto akaganeite was independent of CaCl₂ concentration, less than that observed for goethite, and greater than that observed for ferrihydrite.

3.4. Kinetics

Relevant one-electron transfer reduction reactions are summarized in Table 1, including the reduction potentials at pH 7 and pH 4.5. Thermochemical considerations of E_{H,pH 4.5} are necessary when comparing the relative reaction rates of each iron oxyhydroxide mineral in an acidic brine environment. Complexation of Fe(II) by chloride (i.e., Fe(II)Cl⁺) would also change reduction potentials in a consistent way for each equation involving Fe(II) concentrations (Brezonik and Arnold, 2011). It is not clear, however, if this will affect the sorption of Fe(II) on iron oxyhydroxides. Based strictly on thermodynamics, ferrihydrite is predicted to be the most

favorable iron oxyhydroxide for reductive dissolution. Goethite, on the other hand, is predicted to be the most favorable for oxidative growth.

Table 1: Reduction potentials of half reactions at pH 7 and pH 4.5 (relevant for acidic brines) and 25 °C, calculated using the Nernst equation. Dissolved Fe(II) concentrations were set to 10⁻⁴ M, and sorbed Fe(II) sites set to 10⁻⁶ M. For the quinone reaction, concentrations of Q and QH₂ were set equal to each other.

Reaction	E_H^0 (V)	$E_{H, pH\ 7}$ (V)	$E_{H, pH\ 4.5}$ (V)
Fe(III) + e ⁻ = Fe(II)	+0.77 ^b	+0.77	+0.77
$\frac{1}{2} Q + H^+ + e^- = \frac{1}{2} QH_2$	+0.70 ^c	+0.28	+0.43
Iron oxyhydroxide dissolution			
[Gth] α -FeOOH + 3H ⁺ + e ⁻ = Fe(II) + 2H ₂ O	+0.68 ^{calc}	-0.32	+0.12
[Ak] β -FeOOH + 3H ⁺ + e ⁻ = Fe(II) + 2H ₂ O	+0.75 ^{calc}	-0.25	+0.19
[Fh] amorph Fe(OH) ₃ + 3H ⁺ + e ⁻ = Fe(II) + 3H ₂ O	+0.97 ^{calc}	-0.04	+0.41
Iron oxyhydroxide growth			
[Gth] α -FeOOH + $\equiv Fe(III)OH$ + 2H ⁺ + e ⁻ = $\equiv Fe(III)OFe(II)^+$ + 2H ₂ O	+0.17 ^d	-0.60 ^a	-0.30 ^a
[Ak] β -FeOOH + $\equiv Fe(III)OH$ + 2H ⁺ + e ⁻ = $\equiv Fe(III)OFe(II)^+$ + 2H ₂ O	—	—	—
[Fh] Fe(OH) ₃ + $\equiv Fe(III)OH$ + 2H ⁺ + e ⁻ = $\equiv Fe(III)OFe(II)^+$ + 3H ₂ O	+0.24 ^d	-0.53 ^a	-0.23 ^a

^{calc} Calculated from Gibbs free energies, where ΔG_f^0 is -488.6 kJ/mol^b for Gth, -481.7 kJ/mol^e for Ak, and -699 kJ/mol^b for Fh

^a Assuming [$\equiv Fe(III)OFe(II)^+$] is 10⁻⁶ M (~ 1 % of initial [Fe(II)]) and [$\equiv Fe(III)OH$] is 10⁻⁵ M (calculated from the site density^d and the TEM surface area in Table 2)

^b Brezonik and Arnold (2011)

^c Schwarzenbach et al. (2003)

^d Silvester et al. (2005)

^e Navrotsky et al. (2008)

— Not found in the current literature

The kinetics of abiotic redox reactions were quantified to compare the redox reactivity of goethite, akaganeite, and ferrihydrite in acidic brine solutions. Benzoquinone reduction by adsorbed Fe(II) significantly decreased in 0.67 M CaCl₂ as compared to 0 M CaCl₂ (Fig. 4a). In contrast, the hydroquinone oxidation rate increased with higher CaCl₂ concentration (Fig. 4b) in the case of ferrihydrite, did not change with changing CaCl₂ concentration in the case of akaganeite, and was altogether undetectable in the case of goethite. Detailed reaction rate constants for each system and CaCl₂ concentration, along with surface area measurements from TEM and BET, are provided in Table 2. To determine the effect of ionic strength, rates of benzoquinone reduction as a function of CaCl₂ concentration were determined for Fe(II)/goethite

(Fig. 4c) and Fe(II)/ferrihydrite suspensions (Fig. 4d, rate constants in Table S3). With both iron oxyhydroxides, reaction rates decreased with increasing CaCl₂ concentration.

Table 2. Pseudo-first-order rate constants of benzoquinone (Q) reduction by adsorbed Fe(II) or initial rate of hydroquinone (QH₂) oxidation by goethite (Gth), akaganeite (Ak), ferrihydrite (Fh), or a combination of all three minerals. Reaction suspensions were in 40 mM acetate buffer at pH 4.5. R² values are in parentheses. ND = not detectable. NA = not applicable.

Particle(s)	SA _{TEM} (m ² /g)	SA _{BET} (m ² /g)	Total mass loading (g/L)	[CaCl ₂] (M)	Q → QH ₂ k _{obs} (h ⁻¹)	QH ₂ → Q d[Q]/dt (μM h ⁻¹)
Gth	170	140	0.325	0	1.02 ± 0.02 (1.0)	ND
				0.67	0.16 ± 0.01 (0.99)	ND
Ak	230	278	0.325	0	0.17 ± 0.01 (1.0)	0.72 ± 0.31 (0.84)
				0.67	0.061 ± 0.002 (1.0)	0.93 ± 0.15 (0.98)
Fh	510	130-280	0.325	0	0.64 ± 0.09 (0.98)	3.2 ± 0.3 (1.0)
				0.67	0.073 ± 0.004 (1.0)	8.4 ± 1.6 (0.99)
Gth+Ak+Fh			0.325	0	0.51 ± 0.01 (1.0)	NA
				0.67	0.091 ± 0.002 (1.0)	NA
Gth+Ak+Fh			0.975	0	0.85 ± 0.02 (0.99)	NA
				0.67	0.22 ± 0.01 (1.0)	NA

Rate constants for individual iron oxyhydroxides were also compared to the rate constants obtained using a mixture of three (Table 2, Fig. S7), which is more analogous to the natural modeled system. Similar to the individual results, the addition of 0.67 M CaCl₂ decreased benzoquinone reduction rate by adsorbed Fe(II). The observed rate for suspensions containing all three iron oxyhydroxides at a total mass loading of 0.325 g/L was approximately equal to the sum of one-third the rates observed for each mineral alone at 0.325 g/L. When normalized to mass loading, benzoquinone reduction rate is faster for the lower mass loading (0.325 g/L versus 0.975 g/L), despite the identical amount of Fe(II) added.

4. DISCUSSION

4.1. Accessible reactive surface areas of iron oxyhydroxides in acidic brines

4.1.1. Accessible surface area

315 Accessible reactive surface area of iron oxyhydroxides in acidic brines is one controlling
316 parameter for describing the relative reactivity of each mineral. In addition, other parameters
317 such as Fe(II)–Fe(III) reduction potentials during iron oxyhydroxide dissolution and growth
318 (Table 1) can control the reactivity of different iron oxide phases. Increasing CaCl_2 concentration
319 led to the formation of larger aggregates as evidenced by increasing hydrodynamic diameters and
320 decreasing zeta potentials (Fig. 2). It has been shown that larger aggregate size correlates to
321 decreases in accessible surface area of iron oxyhydroxide nanoparticles in typical aquatic
322 systems (Stemig et al., 2014). Given these results, accessible surface area of goethite, akaganeite,
323 and ferrihydrite nanoparticles is expected to decrease in natural acidic brine environments. While
324 the amount of adsorbed Fe(II) is limited at low pH (Fig. 3), the low amount of inner-sphere
325 complexation of Fe(II) may change the surface potential enough to affect aggregation at low
326 CaCl_2 concentrations, as seen nominally in Fig. 1. At high CaCl_2 concentrations, however, the
327 ionic strength primarily controls aggregation.

328 In this study, we provide hydrodynamic diameters collected by DLS (Fig. 2a), which is
329 an indirect but relatively efficient method for characterizing aggregate size in suspensions. At
330 large aggregate sizes, however, the limitations of the technique (Filella et al., 1997) along with
331 faster settling rates (Chekli et al., 2013) must be acknowledged, especially in the case of high
332 CaCl_2 concentrations seen here. Previous work indicated that when DLS results demonstrate
333 aggregates in the 100 nm size range, data from DLS and cryogenic transmission electron
334 microscopy (cryo-TEM), a direct method of characterizing aggregate sizes, match well. When
335 DLS results demonstrate larger sizes in the micron size range, cryo-TEM can provide more detail
336 regarding the size distribution, especially since DLS is so strongly dominated by the largest
337 suspended objects, yet the results are qualitatively consistent (Stemig et al., 2014).

4.1.2. Reactive surface area

Extent of Fe(II) adsorption was measured to assess the amount of reactive surface area available for each iron oxyhydroxide in 0 and 0.67 M CaCl₂. Our results (Fig. 3) suggest only a small fraction of total Fe(II) resides on the iron oxyhydroxide surface at any given time in an extremely acidic brine environment (pH < 4), with the largest fraction of adsorbed Fe(II) sites on goethite. In moderately acidic (pH 4 – 6) settings (e.g., Benison and Bowen, 2013; Korehi et al., 2014), a greater fraction of total Fe(II) residing on the surface may lead to faster kinetic rates of reactions involving adsorbed Fe(II) on iron oxyhydroxides.

The presence of 0.67 M CaCl₂ decreased overall Fe(II) adsorption for goethite and ferrihydrite (Fig. 4). Possible causes include less accessible surface area, decreased Fe(II) activity, and/or competitive Ca(II) adsorption. At high ionic strength ($I > 1$ M) in solutions of a single salt, the Stokes-Robinson semiempirical equation may be applied to estimate activity coefficients of divalent cations. This model describes an increase in activity coefficient as ionic strength rises beyond 0.5 M (Brezonik and Arnold, 2011). Assuming the ion size parameter for Fe(II) is similar to that of Ca(II), the activity coefficient of Fe(II) is estimated to be ~ 0.5 in 0.67 M CaCl₂, which may lead to decreased Fe(II) adsorption (see Fig. 4.4 in Brezonik and Arnold, 2011; other models may provide different activity coefficients, but it would be expected that the value would certainly be < 1). Previous studies have also shown that iron oxyhydroxide minerals weakly sorb Ca(II) (Stachowicz et al., 2008; Antelo et al., 2015) but sorb other metal ions more strongly (Ali and Dzombak, 1996; Weng et al., 2005), particularly when the pH is below the point of zero charge. This is the first study to our knowledge that has measured Fe(II) adsorption edges on akaganeite as a function of ionic strength and pH; although previous work has shown adsorption of other ions on akaganeite (Deliyanni et al., 2003; Kim et al., 2011). The fact that

high CaCl_2 concentration did not decrease Fe(II) adsorption indicates that there is a unique chemistry for akaganeite, such as competitive ligand exchange with chloride tunnel ions as described in the works of Song and Boily (2011; 2012) and Kozin and Boily (2013).

These adsorption edges were collected in the absence of a buffer to determine effect of pH. In the subsequent studies, 40 mM acetate buffer was used to maintain pH 4.5. While attempts were made to measure differences in Fe(II) adsorption on each mineral in this buffer, average dissolved Fe(II) concentrations were not statistically different and were within the quantification limit of 0.01 mM Fe(II) for the method. Acetate adsorption on an iron oxide has been described as solvent-surface hydration-separated ion pairs and surface hydration-shared pairs, which are favorable in mildly acidic conditions (Norén and Persson, 2007). Given what is known about acetate adsorption, we argue that even if Fe(II) adsorption decreases (due to competitive surface complexation) or increases (due to electrostatic interactions) in our buffered system, the pH and ionic strength trends are expected to remain the same.

4.2. Iron oxyhydroxide reactivity in acidic brines

4.2.1. Benzoquinone reduction

For reduction of benzoquinone (Fig. 4a), reaction rates were fastest with goethite, followed by ferrihydrite and then akaganeite, which can be attributed to the amount of adsorbed Fe(II) shown in Fig. 3 and, in the case of goethite and ferrihydrite, their reduction potentials. A reduction potential for Fe(II) -sorbed on akaganeite was not found in the literature; thus, it is difficult to compare akaganeite to goethite and ferrihydrite, although it is hypothesized that it would be less favorable given this data.

The presence of brine, in this case high CaCl_2 concentration, decreased the reaction rates for all three minerals (Fig. 4). Exploration of reaction rate as a function of ionic strength for

goethite and ferrihydrite (Fig. 4c and 4d) demonstrated that rates systematically decreased with increasing ionic strength, consistent with a loss of accessible reactive surface area due to either particle aggregation or decreased Fe(II) sorption. This trend is most evident in the comparison between reaction rates in 0.05 M and 0.67 M CaCl₂. For goethite, the two rates were statistically indistinguishable, consistent with a relatively small difference in measured aggregate size as seen in Fig. 2. With ferrihydrite, aggregate size largely increased between the two CaCl₂ concentrations, and the rate was much slower at the higher ionic strength.

4.2.2. *Hydroquinone oxidation*

The fastest rate of oxidation by ferrihydrite is agreeable with the low degree of crystallinity and favorable reduction potential, which drives reductive dissolution (Fig. 4b). Akaganeite was also faster than goethite (longer reaction times in 0.67 M CaCl₂ are shown in Fig. S5). In contrast to the benzoquinone reactions, hydroquinone oxidation by ferrihydrite was significantly faster in 0.67 M CaCl₂. Despite decreases in accessible surface area, the number of free reactive ≡Fe(III) sites increases in CaCl₂ with the inhibition of adsorbed Fe(II) (which drives the reverse benzoquinone reduction reaction), thus increasing oxidation rate.

In both redox systems, especially in the case of ferrihydrite (and after ~ 6 h for hydroquinone oxidation by akaganeite in Fig. S5), pseudo-first-order reaction kinetics do not always produce excellent fits, suggesting possible phase transformation, changes in aggregation, or changes in surface area. No evidence for new mineral phases was observed by XRD (Fig. S2, though a difference in preferred orientation was observed for the 0 M CaCl₂-benzoquinone-goethite and -akaganeite system, possible evidence of mineral growth). Numerous studies have detected phase transformations in similar suspensions at circumneutral pH (Hansel et al., 2005; Pedersen et al., 2005; Boland et al., 2014), yet Fe(II)-catalyzed transformations of iron-

containing minerals have been shown to slow with decreasing pH due to less Fe(II) complexation on the mineral surface (Liu et al., 2007; Burton et al., 2008) and in the presence of organic matter (Jones et al., 2009). In addition, no evidence for changing aggregate size of ferrihydrite during reaction with hydroquinone in 0 M CaCl₂ (Fig. S6) was detected. It is likely that the nonlinearity observed for the reaction kinetics for hydroquinone oxidation by ferrihydrite (Fig. 4b) is caused either by changes in the ferrihydrite surface or by the reverse reaction. For hydroquinone oxidation with ferrihydrite in 0.67 M CaCl₂, the maximum loss of ferrihydrite by reductive dissolution is ~ 1% (as calculated by mass balance), which would result in a small decrease in surface area but could result in a loss of the most reactive surface sites. In addition, the benzoquinone product could react with adsorbed Fe(II) produced from the reaction, especially in the absence of added CaCl₂.

4.2.3. Mixed mineral suspensions

Mixed mineral suspensions, which provide a better comparison to the natural acidic brine environment found in the Soudan iron mats, were also investigated (Fig. S7). Benzoquinone reduction rate was faster for 0.325 g/L total mass loading compared to 0.975 g/L. Both suspensions had the same amount of Fe(II) added and were well mixed based on the observation that the particles were completely suspended in the reactors. Also, DLS measurements aggregate size in 0 M CaCl₂ as measured by DLS was ~ 200 nm for both suspensions. For those reasons, it is more likely that differences in the amount and distribution of adsorbed Fe(II) among the three minerals is the cause, although attempts to quantify a statistical difference in Fe(II) adsorption were problematic due to the low degree of Fe(II) adsorption at pH 4.5, as observed for the single mineral studies. These results demonstrate that the consideration of the entire system, including

all reactive minerals present, is necessary when predicting the abiotic contributions to iron redox cycling in acidic brines.

4.3. Implications for iron geochemical cycling in acidic brines.

The unique chemistry between iron oxyhydroxides and organic species in acidic brines is significant for several systems with potential environmental impact. In acidic brines such as those found in the Soudan Mine, reaction with between adsorbed Fe(II) on an iron oxyhydroxide mineral and an oxidized quinone species is expected to be minor. Significant adsorption of Fe(II) is limited under such acidic conditions and only decreases further in waters with high ionic strength. In contrast, reductive dissolution is a possible contributor to iron cycling in acidic brines, with high ionic strength promoting oxidation of reduced quinone species by iron oxyhydroxides. Specifically, ferrihydrite was experimentally shown to be a strong abiotic oxidant under saline and acidic conditions which has significance for oxidative degradation of organic matter and dissimilatory iron reduction.

This work represents a controlled exploration of abiotic reactivity in conditions similar to the Soudan Mine groundwater seepages, and future work will explore the effect of using collected groundwater samples from the mine. While this location represents only one environment where these redox reactions are important, these findings have implications to other sulfur-deficient acidic brines or evaporative settings across a global setting, such as acidic brine lakes and acid mine drainage locations that contain precipitated iron oxyhydroxides. For example, abiotic oxidation of organic matter by iron oxyhydroxides could compete with acidophilic microbial iron cycling in the extremely acidic evaporative sites found in Western Australia. For moderately acidic brines, we have shown that estimates of iron oxyhydroxide abiotic reactivity are important for interpretations of iron cycling. In conclusion, although many

of the studies discussed previously have provided contributions to the understanding of biotic reactivity in these rare but distinctive environments, future study of the abiotic iron oxyhydroxide reactivity could greatly improve our understanding of these complex sites.

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SUPPLEMENTARY MATERIAL

Supplementary material associated with this article can be found, in the online version, at [DOI].

FIGURE CAPTIONS

Figure 1. a) Iron 1s EXAFS spectra for selected Fe standard materials and three Soudan Mine mats collected from the horizontal groundwater seeps of the 27th Level. b) Results of linear combination fitting of Fe EXAFS spectra for Soudan Mine Mats SM03, SM04, and SM05. The mol fraction of Fe corresponds to the fraction of total iron atoms residing in either a goethite-, akaganeite-, or ferrihydrite-like coordination environment.

Figure 2. a) Log number-based mean hydrodynamic diameter and b) zeta potential of goethite (Gth), akaganeite (Ak), and ferrihydrite (Fh) as a function of CaCl_2 concentration as measured using dynamic light scattering. Open symbols are data obtained from suspensions with no Fe(II) and closed symbols with 0.342 mM Fe(II). Samples were prepared in 40 mM acetate buffer at pH 4.5. Note x-axis break between 0.10 and 0.64 M CaCl_2 .

Figure 3. (a-c) Average percent of Fe(II) added that adsorbed on the mineral surface of a) goethite, b) akaganeite, or c) ferrihydrite as a function of pH, with either 0 M or 0.67 M CaCl_2 . Initial conditions of 0.325 g/L particle loading and 0.342 mM Fe(II) in water. (d-e) Percent of reactive sites occupied on the mineral surface as a function of pH for each iron oxyhydroxide in d) 0 M CaCl_2 or e) 0.67 M CaCl_2 .

Figure 4. a) Degradation of benzoquinone (Q) by adsorbed Fe(II) on goethite (Gth), akaganeite (Ak), or ferrihydrite (Fh) and b) production of benzoquinone from the oxidation of hydroquinone by each iron oxyhydroxide as a function of time. Suspensions were prepared with either 0 M (open symbols) or 0.67 M (closed symbols) CaCl_2 in 40 mM acetate buffer at pH 4.5. Solid lines are results of linear regression (data summarized in Table 2). Error bars are standard deviations from triplicate trials. Dashed lines represent the extrapolation of initial rates over longer reaction times. c-d) Benzoquinone (Q) degradation by Fe(II) adsorbed on either c) goethite or d) ferrihydrite in varied CaCl_2 concentration and 40 mM acetate buffer at pH 4.5. Solid lines are results of linear regression (data summarized in Table S2). Initial Fe(II) concentration was 1 mM for the benzoquinone reduction reactions.

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