

## A COMPARISON OF POINT OF ZERO CHARGE MEASUREMENT METHODOLOGY

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**Abstract**—Contaminant-transport modeling requires information about the charge of subsurface particle surfaces. Because values are commonly reused many times in a single simulation, small errors can be magnified greatly. Goethite ( $\alpha$ -FeOOH) and pyrolusite ( $\beta$ -MnO<sub>2</sub>) are ubiquitous mineral phases that are especially contaminant reactive. The objective of the present study was to measure and compare the point of zero charge (PZC) using different methods. The pyrolusite PZC was measured with three methods: mass titration (MT) (PZC = 5.9±0.1), powder addition (PA) (PZC = 5.98±0.08), and isoelectric point, IEP (PZC = 4.4±0.1). The IEP measurement was in agreement with literature values. However, MT and PA resulted in a statistically larger PZC than the IEP measurement. The surface area of pyrolusite, 2.2 m<sup>2</sup>g<sup>-1</sup>, was too small to permit PZC determination by the potentiometric titration (PT) method. Goethite PZC values were measured using MT (7.5±0.1), PT (7.46±0.09), and PA (7.20±0.08). The present work presents the first reported instance where MT and PA have been applied to measure the point of zero charge of either pyrolusite or goethite. The results illustrate the importance of using multiple, complementary techniques to measure PZC values accurately.

**Key Words**—Goethite, Pyrolusite, Point of Zero Charge, Potentiometric Titration, Mass Titration, Powder Addition, Isoelectric Point, Zeta Potential Charge, X-ray Diffraction, BET.

### INTRODUCTION

#### Background

Iron and Mn oxyhydroxides and oxides are an important class of minerals due to the abundance of these minerals in the environment. The low mineral solubility within environmental pH ranges results in the ubiquitous presence of these minerals in well aerated soils and sediments. Furthermore, these minerals have been shown to sorb disproportionately high concentrations of contaminants with respect to the total mass (Coston *et al.*, 1995; Hsi and Langmuir, 1985; Hu *et al.*, 2010; Kaplan *et al.*, 2004; Keeney-Kennicutt and Morse, 1985; Powell *et al.*, 2005; Shaughnessy *et al.*, 2003; Wilson, 2005).

Among Fe and Mn oxyhydroxides and oxides, goethite ( $\alpha$ -FeOOH) and pyrolusite ( $\beta$ -MnO<sub>2</sub>) are the most abundant in soils and are involved in the uptake of several toxic elements commonly found in the environment (Cornell and Schwertmann, 1996; Dixon and Weed, 1989). The ion affinity of this class of minerals is pH dependent. As the pH of the solution in contact with the mineral is reduced below the point of zero charge (PZC), the surface of the mineral becomes positively charged. Conversely, as the pH is increased above the PZC, the surface becomes negatively charged.

The PZC can be thought of as the point of zero net charge, *i.e.* where the total positive charges are equal to the total negative charges. The protonation and deprotonation of the surface hydroxyl groups can be represented as (Parks and Bruyn, 1962):



where MOH<sub>2</sub><sup>+</sup> and MO<sup>-</sup> represent the positive and negative surface sites, respectively. A small change in the pH can lead to a large increase or decrease of the electrostatic interaction between the ions and the ionizable surface sites depending on the titration curve. Knowledge of the PZC therefore plays a crucial role in understanding ion-sorption processes at the mineral/solution interface.

One approximation of the PZC is the measurement of the IEP (Sposito, 1989), which is determined by measuring the pH where the mineral particles do not move in an electric field (electrophoresis measurement) or coagulate in a suspension (flocculation measurement). If the PZC is determined by measuring the pH where the difference between H<sup>+</sup> and OH<sup>-</sup> adsorbed on the mineral surface is zero, it is called the point of zero net proton charge (PZNPC). This quantity is commonly obtained by acid/base titration (Stumm, 1992). Alternative methods to measure the PZNPC include MT (Noh and Schwarz, 1989) and PA (Jiratova, 1981; Mullet *et al.*, 1997; Mustafa *et al.*, 2002). The PZNPC and IEP coincide if no adsorption of ions other than H<sup>+</sup> and OH<sup>-</sup> occurs. If adsorption of non-determining ions (*i.e.* cations and anions that, once adsorbed to the mineral surface, do not

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alter the surface charge, *e.g.* perchlorate) occurs, the IEP and PZNPC will shift in opposite directions to each other (Stumm and Morgan, 1981). Adsorption of cations leads to a decrease in the PZNPC and to an increase in the IEP. Conversely, adsorption of anions leads to the opposite effect. For simplicity, the PZNPC will be denoted as PZC in the following discussion.

#### Measurement techniques

The PZC measurements of synthetic goethite and pyrolusite were conducted using MT, PT, PA, and IEP.

**Mass titration.** The MT technique was developed by Noh and Schwarz (1989) to estimate the PZC of simple oxides. The dry oxide must be a pure mineral phase and is assumed to be uncharged. When it is put into pure water, the pH of the suspension changes and the final pH value depends on the oxide concentration. The suspension reaches a constant value after the addition of an excess of solid. This limiting pH value can be interpreted as a function of the solid concentration according to:

$$N_t = \frac{(C_{OH} - C_H) \cdot ([MOH] + [MOH_2^+] + [MO^-])}{[MOH_2^+] - [MO^-]} \quad (2)$$

$N_t$  is the total number of ionizable sites on the mineral surface (it is representative of the mass of the solid);  $(C_{OH} - C_H)$  is the difference between the concentration of  $OH^-$  and  $H^+$  in the mineral suspension, and is therefore representative of the pH of the suspension;  $[MOH_2^+]$ ,  $[MOH]$ , and  $[MO^-]$  are the concentrations of positive, neutral, and negative sites, respectively.

From equation 2, as  $N_t$  approaches infinity and  $(C_{OH} - C_H) \neq 0$  (the case when the suspension pH is not equal to 7),  $[MOH_2^+] - [MO^-]$  approaches 0. Under these conditions, the net surface charge of the solid is zero and the PZC value is reached. If the PZC of the oxide is 7 (as is the initial pH of pure water) the suspension pH will not change with increasing mineral mass. In such a case  $(C_{OH} - C_H) = 0$  and the pH is independent of the mass ( $N_t$ ). Limitations to this technique include the need for the mineral solid to be insoluble in solution and restriction of the ratio of oxide to water by weight to <20% (above this value the solution becomes too dense for a proper pH measurement due to limitation of the liquid-junction potential). One of the great advantages of this method is that it can be performed in pure water, without the risk of specific sorption by background electrolytes. The importance of this fact will be discussed in further detail below with regard to the uncertainty it has introduced in previous pyrolusite PZC measurements using  $NaNO_3$ , presumed to be in an inert background electrolyte solution.

**Potentiometric titration.** Potentiometric titration is a widely used technique (Kosmulski, 2002) in which the mineral acts as a weak diprotic acid or base (Parks and

Bruyn, 1962) and can, therefore, be titrated by adding small amounts of a strong acid or base in the presence of a background electrolyte. The PZC can be estimated as the average between  $pK_1$  and  $pK_2$  (Figure 1). The PTs are performed on both the blank and the mineral suspension with a minimum of three different background electrolyte ionic strengths. The blank curve is then subtracted from the mineral curve and the common intersection point (CIP) among the three resulting curves, also known as the point of zero salt effect (PZSE), is considered the PZC. Sposito (1989) showed that the PZSE does not necessarily coincide with a zero surface charge. The PZSE is simply an invariant point for all the curves where the mineral surface is uninfluenced by the ionic strength of the solution. The PZC and PZSE therefore coincide only when: (1) the mineral is pure, (2) no inner-sphere adsorption occurs, and (3) zero net contribution exists for outer-sphere complexation by non-determining ions. In other words, these points match when the PZC is not influenced by the ionic strength and the mineral is pure. Other disadvantages of the PT technique are that curves must be collected in a minimum of three different concentrations of background electrolyte, the background electrolyte added can be adsorbed to a certain degree on the mineral surface, and the mineral must have a large surface area.

**Powder addition.** The PA technique is performed by adding identical amounts of mineral to a set of solutions of the same ionic strength at different pH values (Jiratova, 1981; Mullet *et al.*, 1997; Mustafa *et al.*, 2002). Powder addition changes the solution pH. For example, if the initial pH ( $pH_i$ ) is lower than the PZC of the solid, the mineral surface adsorbs protons and the final pH ( $pH_f$ ) will be higher. The reverse is true if the initial pH is higher than the PZC. The mineral surface desorbs protons and the final pH will be lower. The final pH values are usually measured 24 h after addition of the solid. The final pH minus the initial pH ( $\Delta pH$ ) is plotted vs.  $pH_i$ . The PZC occurs at the point where  $pH_f - pH_i = 0$ .

This technique can be compared to a PT performed at only one ionic strength value. The advantages of PA over PT are that it is faster and can be used with minerals that do not have a large surface area because the equilibration time is far longer than those commonly used in PT.

**Isoelectric point.** The zeta potential is defined as the charge a particle acquires in a specific medium. A suspension of particles possessing a surface charge will move in the presence of an electric field (*e.g.* electrophoresis). The direction in which particles move (*e.g.* towards a positive or negative electrode) is a clear indication of the charge carried, and the particle velocity is proportional to that charge. In an acidic pH, particles tend to acquire a positive charge, whereas in a basic pH particles tend to be negatively charged. If an acid or base

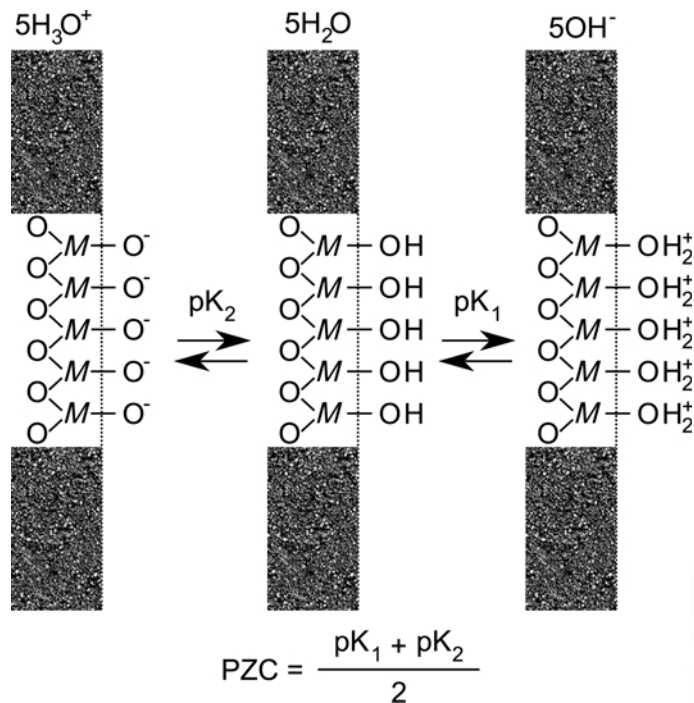


Figure 1. pH-dependent protonation and deprotonation of hydroxyl groups on the mineral surface (adapted from Tourinho *et al.*, 2002).

is added to a suspension of particles, a point may be reached where the charge is neutralized. When the zeta potential is plotted vs. pH, the point at which the zeta potential passes through zero is the isoelectric point from which the PZC can be inferred. It should be noted that zeta potential measurements not only measure the potential of the surface, but also species adsorbed on the surface, solvent molecules attached to surface ions, and counter ions in the double layer.

## EXPERIMENTAL

For each technique, existing procedures were used, as outlined below. A brief description is provided here.

### Materials

Commercial pyrolusite ( $\beta\text{-MnO}_2$ , obtained from Alfa Aesar, Ward Hill, Massachusetts, USA) 99.9% was sieved and the 63–212  $\mu\text{m}$  particle size fraction was characterized by X-ray diffraction (XRD), BET surface area measurements, scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX) before use. Goethite was synthesized by adapting the procedure of Schwertmann and Cornell (1991). Reagent-grade NaOH and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (both obtained from Sigma Aldrich, Germany) were used instead of KOH and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . To minimize silica contamination, all synthesis steps were conducted using plastic labware. The precipitate was washed with 18.2  $\text{M}\Omega\text{-cm}$  (Milli-Q) water and then suspended in dialysis tubing (SnakeSkin

Pleated Dialysis Tubing 3500 MWCO) in Milli-Q water exchange solution until the conductivity of the exchange solution was  $<2.0 \mu\text{S}$ . The sieved 63–212  $\mu\text{m}$  fraction of goethite was also characterized by XRD, BET, and SEM/EDX before use. The background electrolyte solutions used in the MT, PT, PA, and IEP techniques were prepared with reagent-grade  $\text{NaClO}_4$  (Sigma-Aldrich) dissolved in triply-distilled  $\text{CO}_2$ -free water.

### Characterization of mineral oxides

The goethite surface area was determined using a 5-point BET  $\text{N}_2$  adsorption on an ASAP 2010 Micromeritics Instrument (Norcross, Georgia, USA). Because of the smaller surface area, Ar gas was required to measure the surface area of pyrolusite. A NIST standard was included with these samples: NIST SRN 1900  $\text{Si}_3\text{N}_4$  with surface area =  $2.84 \pm 0.09 \text{ m}^2\text{g}^{-1}$ . The measured surface area of the standard was  $2.83 \text{ m}^2\text{g}^{-1}$ , which is within the error bar of the NIST standard. X-ray diffraction patterns of dried and finely ground goethite and pyrolusite samples were recorded on a Panalytical X'Pert Pro powder X-ray diffractometer using  $\text{CuK}\alpha$  radiation and a Ni filter. The mineral powder was placed on a zero background plate with a thin layer of immersion oil. The  $2\theta$  angle scan range was from 10.0 to 70.0°. Scanning electron microscopy was conducted on a LEO Model 440 (Peabody, Massachusetts, USA) and energy dispersive X-ray analysis was conducted on an INCAWave 7060 (Oxford Instruments, Concord, Massachusetts, USA).

### PZC measurements

**Mass titration method.** Mass titration on pyrolusite and goethite was performed under argon following the method proposed by Noh and Schwarz (1989). Mineral suspensions with a solid to water ratio of 1%, 5%, 10%, 15%, and 20% by weight were placed on a shaker in O-ring sealed tubes. These tubes were back-filled with argon and shaken until equilibrium was reached. The sample pH was checked after 24 h and then every week for several months using a glass pH electrode (Orion, 8103BNUWP, filling solution 3 M NaCl) at  $25 \pm 1^\circ\text{C}$ . The suspension pH at 20% was taken as the PZC.

**Potentiometric titration method.** All PTs were performed under  $\text{CO}_2$ -free argon atmosphere using an automatic titrator (751 GPD Titrino, Metrohm). The minerals were added to 15 mL of  $\text{NaClO}_4$  at concentrations of 0.001, 0.01, and 0.1 M. The solid/liquid ratio was fixed at  $6 \text{ g L}^{-1}$ . The suspension was equilibrated for 20 min under Ar flow and the pH was recorded. Before the analysis, a predetermined amount of NaOH was added to increase the pH to 11. The titrations were carried out

from high to low pH by adding 0.0773 M  $\text{HClO}_4$  at  $25 \pm 1^\circ\text{C}$ . The titration parameters were:  $1 \mu\text{L}$  as the minimum volume increment at the beginning and at the equivalence point; outside these ranges the increment was constrained between  $5 \mu\text{L}$  and  $50 \mu\text{L}$ . Each small volume of titrant was added as soon as a  $1 \text{ mV/min}$  signal drift criterion was met. Blank titrations were performed under the same conditions.

The surface charge density,  $\sigma_o$  ( $\text{C m}^{-2}$ ), was calculated using the equation:  $\sigma_o = B\Delta n_h$ , where  $\Delta n_h$  is the difference between the number of moles of titrant added to the suspension and the moles of titrant added to the blank, and  $B = F/mS$ , where  $F$  is the Faraday constant ( $96485 \text{ C mol}^{-1}$ ),  $m$  is the mass of the solid (g), and  $S$  is the surface area ( $\text{m}^2\text{g}^{-1}$ ).

**Powder addition method.** The PA method was performed using a procedure described by Mustafa *et al.* (2002). A set of 0.01 M  $\text{NaClO}_4$  solutions was adjusted to pH 4, 5, 6, 7, 8, 9, and 10 using  $\text{CO}_2$ -free NaOH and  $\text{HClO}_4$ . The initial pH ( $\text{pH}_i$ ) was recorded and a given amount of solid ( $5 \text{ g L}^{-1}$ ) was added to each solution. The tubes, back-

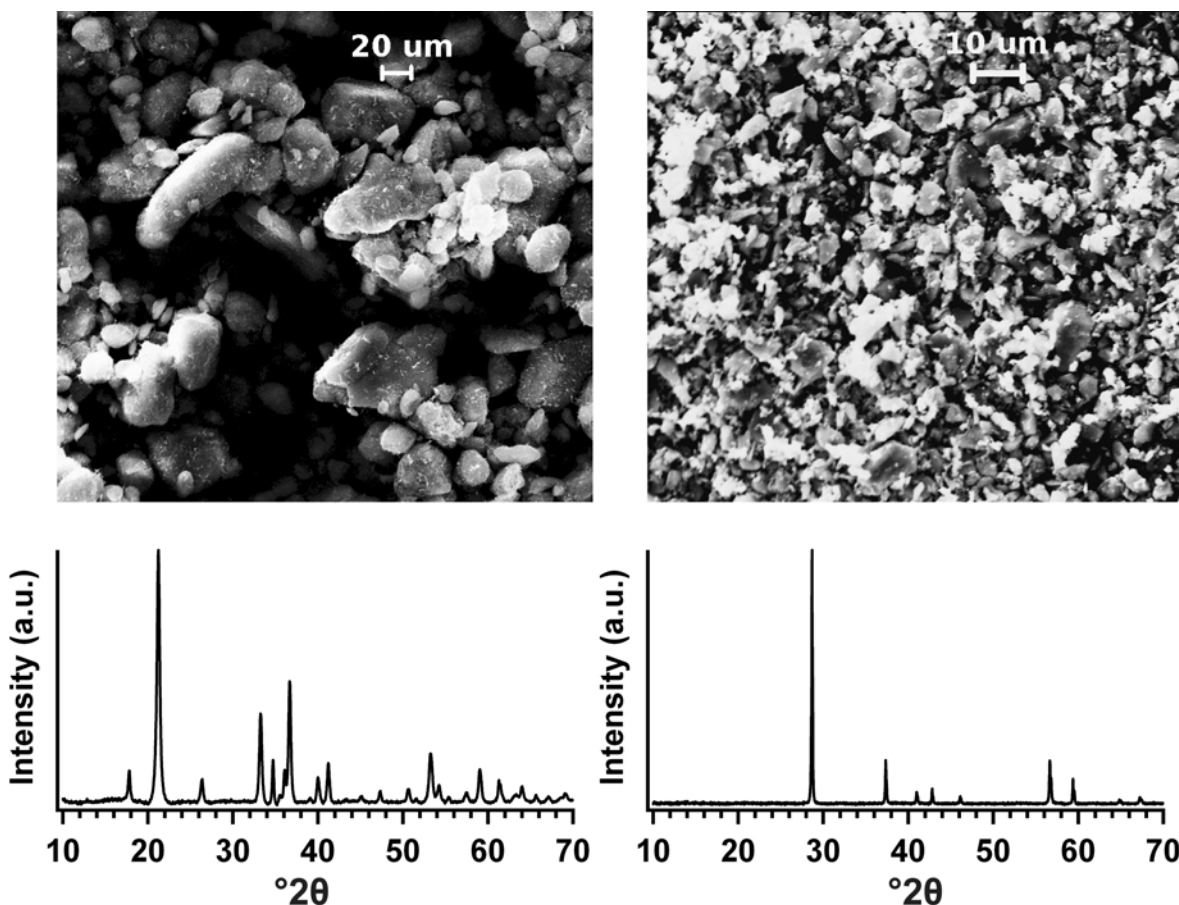


Figure 2. SEM images and XRD patterns for goethite (left:  $\alpha\text{-FeOOH}$ , surface area:  $32 \text{ m}^2\text{g}^{-1}$ ), and pyrolusite (right:  $\beta\text{-MnO}_2$ , surface area:  $2.2 \text{ m}^2\text{g}^{-1}$ ).

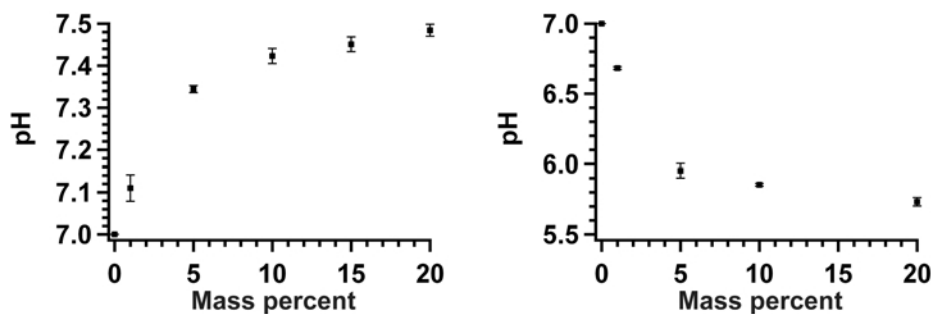


Figure 3. MT of goethite (left) and pyrolusite (right).

filled with Ar, were placed on a shaker and  $\text{pH}_f$  was measured after 24 h at  $25 \pm 1^\circ\text{C}$ . The PZC was determined using the method outlined in the introduction.

**Isoelectric point measurements.** The IEP was measured following a similar procedure to that outlined by O'Reilly and Hochella (2003) using a Brookhaven ZetaPlus zeta potential analyzer. A  $5 \text{ mg L}^{-1}$  suspension of the commercial pyrolusite ( $\beta\text{-MnO}_2$ , 63–212  $\mu\text{m}$  particle size fraction) in 0.001 M  $\text{NaClO}_4$  was pH adjusted using NaOH and  $\text{HClO}_4$  and purged with argon. The pH was recorded after allowing the solutions to equilibrate for 24 h. Zeta potential measurements were performed at  $25^\circ\text{C}$  and the data were reported as an average of 20 measurements. The zeta potential was plotted vs. pH and the value where the zeta potential equalled zero was taken to be the PZC.

## RESULTS

### Characterization of the mineral oxides

The goethite surface area was more than an order of magnitude greater than that of the pyrolusite,  $32.8$  and  $2.2 \text{ m}^2\text{g}^{-1}$ , respectively. The SEM images of goethite (Figure 2) show the expected morphology: round rod-like structures aggregated into larger particles (Schwertmann and Cornell, 1991). Scanning electron microscopy of pyrolusite shows highly crystalline particles on the order of  $<10 \mu\text{m}$  in size. Both goethite and pyrolusite were identified by their characteristic Bragg reflections (Figure 2). Both minerals were also crystalline and no evidence of significant impurities was found.

### PZC measurements

Using the MT method, the PZC of pyrolusite and goethite were  $5.9 \pm 0.1$  and  $7.5 \pm 0.1$  ( $\pm 1\sigma$ ), respectively (Figure 3). The attempt to measure the PZC of pyrolusite by the PT method was unsuccessful. This technique requires that the available surface area in aqueous media is large. For this reason, the PT method to measure the PZC on pyrolusite has previously been reported to be problematic (Healy *et al.*, 1966; Prelot *et al.*, 2003). This

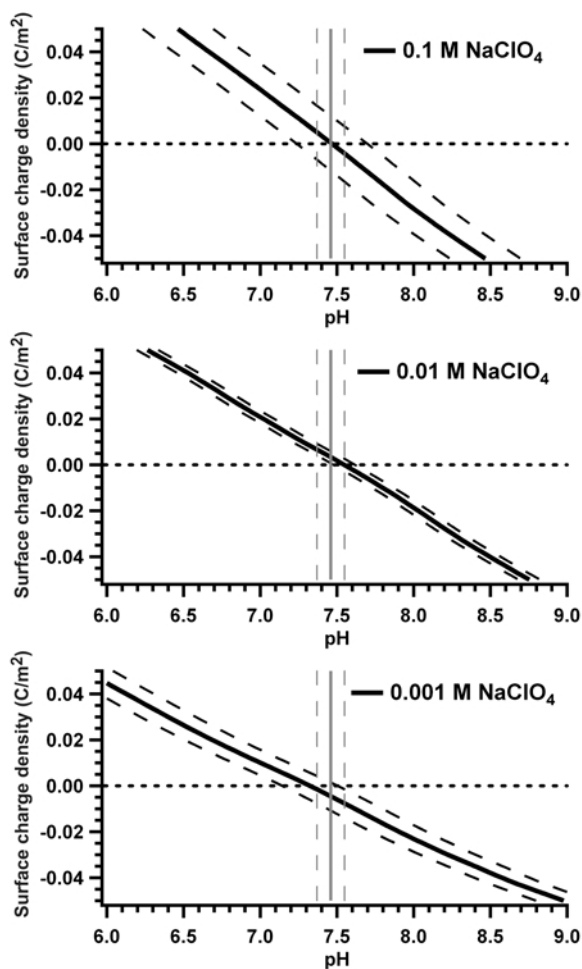


Figure 4. PT of goethite plotted as the surface charge density as a function of pH, in  $\text{NaClO}_4$  solutions. The point of zero net proton charge (PZNPC) at 0.1  $\text{NaClO}_4 = 7.47 \pm 0.23$ , at 0.01  $\text{NaClO}_4 = 7.55 \pm 0.07$ , and at 0.001  $\text{NaClO}_4 = 7.32 \pm 0.18$ . The tilted middle solid line shows the average titration curve while the tilted dashed lines to the left and the right show the upper and lower error bars in the titration at a  $1\sigma$  level. The gray vertical solid line shows the average PZC value measured from PT and the gray vertical dashed lines show the error bars of the measurement at the  $1\sigma$  level.

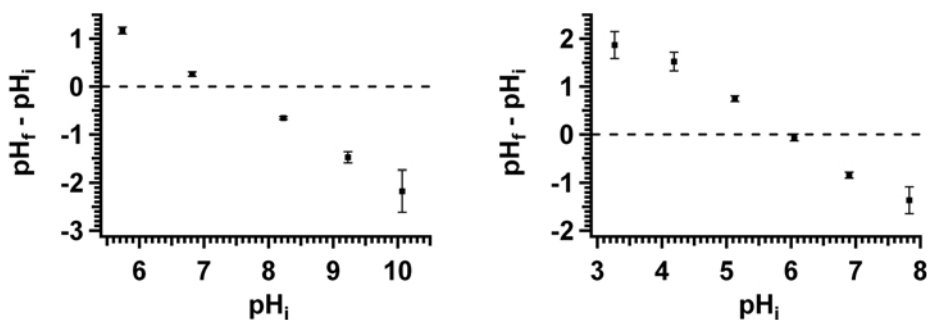


Figure 5. PA method results for goethite (left) and pyrolusite (right) in 0.01 M NaClO<sub>4</sub>.

issue did not exist with goethite as the goethite surface area is large ( $32 \text{ m}^2 \text{ g}^{-1}$ ). The point of zero salt effect (PZSE) of goethite is  $7.46 \pm 0.09$  (Figure 4), which is consistent with the PZC values of the MT and the PT methods, and coincides with zero surface charge density. From this result, one can assume that no specific adsorption of the background electrolyte (NaClO<sub>4</sub>) or surface complexation occurred and that the synthetic goethite is free of impurities. This is an important conclusion and will be discussed below in relation to IEP measurements of pyrolusite. Note that the BET-N<sub>2</sub> surface area includes the measurement of surface area and microporosity, and as such its usage to normalize the PT data in Figure 4 is not entirely correct. However, presentation of the data in this traditional format makes comparison of current with previous data easier (Kosmulski, 2002; Parks and Bruyn, 1962).

Using the powder addition method, the PZC values were determined to be  $5.98 \pm 0.08$  and  $7.20 \pm 0.08$  (Figure 5) for pyrolusite and goethite, respectively. As required by the procedure outlined by Jiratova (1981) and Mustafa *et al.* (2002), the final pH values were measured soon after the addition of the solid, within 24 h of initiating the measurement. pH values were checked after 24 h and regularly for 9 months and 2 months for pyrolusite and goethite, respectively. The PZC values were constant during this period.

The IEP values of the goethite PZC could not be measured, possibly because of polydispersivity (*i.e.* a measure of the variability of particles in a suspension that are assumed to exist in different spherical size classes based on dynamic light scattering measurements), which violates basic assumptions needed to solve the classical electrokinetic equations for such measurements. The pyrolusite measurements (Figure 6) followed the expected trend except for the data point at pH 6.85. The PZC was measured as  $4.4 \pm 0.1$ .

## DISCUSSION

Three pyrolusite PZC measurements were made: MT gave a value of  $5.9 \pm 0.1$ ; PA,  $5.98 \pm 0.08$ ; and IEP,  $4.4 \pm 0.1$ . PT could not be conducted on the pyrolusite

because the surface area of the mineral was too small. The IEP PZC was much more acidic than the other values but is consistent with the other IEP measurements (Table 1) (PZC = 4.4–7.3, 4.9, 6.5,  $\leq 4.3$ , 6.5, and 3.2). O'Reilly and Hochella (2003) reported a synthetic pyrolusite PZC value of  $\leq 4.3$  when Na<sup>+</sup> was the electrolyte (Table 1) and these Na<sup>+</sup> experimental conditions are most like those reported here. The cause for the statistically significant discrepancy between the rather similar MT and PA values ( $5.9 \pm 0.1$  and  $5.98 \pm 0.08$ , respectively), and the IEP values ( $4.4 \pm 0.1$ ) is currently unknown. The IEP measurements on pyrolusite in a 0.01 M KNO<sub>3</sub> matrix have been shown to cause the measured IEP value to increase to pH 6.5 (O'Reilly and Hochella, 2003) and is attributed to the K<sup>+</sup> interacting differently with the pyrolusite surface. The consistency of the present IEP measurements in NaClO<sub>4</sub> media with literature values measured in NaNO<sub>3</sub> media show that this effect is not manifested in a Na perchlorate matrix. The MT and PA measured PZC for pyrolusite is, however, significantly greater than the measured IEP value. Additional research is on-going to understand the cause of the differences in the PZC values measured between the IEP method and the MT and PA methods. O'Reilly and Hochella (2003) emphasized that the IEP is very sensitive to impurities. The consistency between

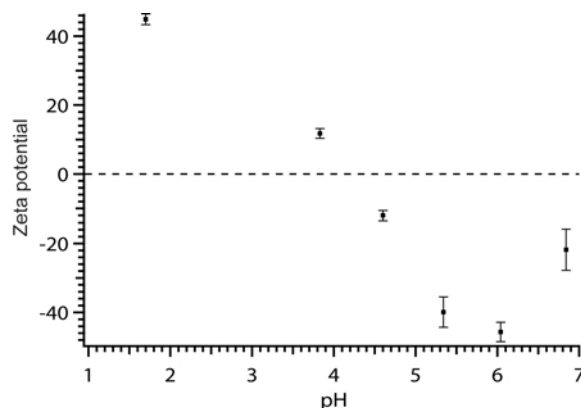


Figure 6. IEP measurements of the pyrolusite.

Table 1. Pyrolusite ( $\beta$ -MnO<sub>2</sub>) and goethite ( $\alpha$ -FeOOH) PZC values measured in the present study compared to literature values.

Material	Aqueous salt	Method <sup>†</sup>	PZC (pH)	Investigator
<b>Pyrolusite (<math>\beta</math>-MnO<sub>2</sub>)</b>				
Synthetic pyrolusite, Alfa Aesar	Water	MT	5.9±0.1	Present study (Figure 3)
Synthetic pyrolusite, Alfa Aesar	0.01–0.001 M NaClO <sub>4</sub>	PT	N/A	Present study (Figure 4)
Synthetic pyrolusite, Alfa Aesar	0.01–0.001 M NaClO <sub>4</sub>	PA	5.98±0.08	Present study (Figure 5)
Synthetic pyrolusite, Alfa Aesar	0.01 M NaClO <sub>4</sub>	IEP	4.4±0.1	Present study (Figure 6)
Pyrolusite	Varied	IEP	4.4–7.3	Kosmulski (2001)
Natural pyrolusite	0.01 M NaNO <sub>3</sub> 0.01 M KNO <sub>3</sub>	IEP	4.9 6.5	O'Reilly and Hochella (2003)
Synthetic pyrolusite	0.01 M NaNO <sub>3</sub> 0.01 M KNO <sub>3</sub>	IEP	≤4.3 6.5	O'Reilly and Hochella (2003)
<b>Goethite (<math>\alpha</math>-FeOOH)</b>				
Goethite	Water	MT	7.5±0.1	Present study (Figure 3)
Goethite	0.01–0.001 M NaClO <sub>4</sub>	PT	7.46±0.09	Present study (Figure 4)
Goethite	0.01–0.001 M NaClO <sub>4</sub>	PA	7.20±0.08	Present study (Figure 5)
Goethite		IEP	7.4–9.5	Cornell and Schwertmann (1996)
Goethite, from nitrate	0.01 M KCl	IEP	8.4	Chorover and Amistadi (2001)
Goethite, from nitrate	0.001–0.01 M NaNO <sub>3</sub>	CIP	7.9	Trivedi and Axe (2001)
Goethite, from nitrate	HNO <sub>3</sub> + NaOH	IEP	7.5	Juang and Wu (2002)
Goethite, from nitrate	0.1–0.7 M NaCl	Merge	8.5	Gao and Mucci (2001)
Goethite, from nitrate	0.001 M NaCO <sub>3</sub>	IEP	8.7	Kosmulski <i>et al.</i> (2003)
Goethite	0.01 M NaNO <sub>3</sub> 0.01 M KNO <sub>3</sub>	IEP	7 6.7	O'Reilly and Hochella (2003)
Synthetic goethite FeSO <sub>4</sub> + Na <sub>2</sub> CO <sub>3</sub>	0.01 M NaCl	IEP	9.1	Pozas <i>et al.</i> (2002)
Goethite		PT	7.55±0.15	Atkinson <i>et al.</i> (1967)
Goethite		PT	7.26	Sigg and Stumm (1981)
Goethite		PT	7–8	Sposito (1989)
Goethite, from nitrate	0.001–0.01 M NaCl	Acousto	8.1	Appel <i>et al.</i> (2003)
Goethite, from nitrate	0.01–0.5 M NaNO <sub>3</sub>	CIP	9 9.1	Gaboriaud and Ehrhardt (2003)
Goethite, from nitrate	0.015–0.24 M NaCO <sub>3</sub> or NaClO <sub>4</sub>	CIP	9.2 9 8.9	Villalobos <i>et al.</i> (2003)

<sup>†</sup> CIP = common intersection point of PT curves obtained at three or more ionic strengths;

IEP = isoelectric point; MT = mass titration; PA = powder addition; PT = potentiometric titration;

Acousto = IEP point obtained by the electroacoustic method.

the MT and PA measurements for pyrolusite suggest that these methods may tolerate the presence of impurities. Further study is certainly warranted. Also, further comparisons of measured pyrolusite PZC values are hindered by the absence of literature values measured using methods other than IEP determination. The need for PZC measurements to be conducted using orthogonal methods of determination is, thus, emphasized. Mass titration and PA yield a PZC for pyrolusite of 5.94±0.09, while the IEP measurements are consistent with literature values. Furthermore, the analytical error

associated with the mean values represents the variability surrounding the measurements of the synthetic pyrolusite and does not represent the variability that may exist between different pyrolusite minerals in nature, containing various compositions, impurities, and crystallinities. The variability associated with different pyrolusite minerals in nature is probably many times larger than the analytical error measured in this study and can result in PZC ranges of several pH units (Kosmulski, 2002; Kosmulski, 2009; Parks, 1965). The intent and scope of this work was to compare different methods of

measuring PZC and to measure the analytical error associated with these methods.

Three goethite PZC measurements were made for this study: MA ( $7.5\pm 0.1$ ), PT ( $7.46\pm 0.09$ ), and PA ( $7.20\pm 0.08$ ). These values agree well with each other and have high degrees of analytical accuracy. Kosmulski (2002) concluded that, of these three methods, the MT was the least reliable because it required the wetting of a mineral that may contain occluded acids and bases that can contribute to the natural pH of the dispersion. He observed in his large survey of PZC values that many of the outliers were those measured by this method. The method requires that the minerals be sufficiently washed of occluded salts, acids, and bases. Not to do so properly would clearly compromise results. Based on the measured data (Figure 5) and the calculated PZC, no evidence of the occluded salt problem was observed in the present study.

The PT PZC value of  $7.46\pm 0.09$  shows excellent agreement with the other three values available in the literature:  $7.55\pm 0.15$ , 7.26, and 7–8 (Table 1). The present study comprises the first report of measurements by MT and PA of the goethite PZC. The IEP measurements of PZC reported in the literature had a very wide range of 6.7 to 9.5 (Table 1). Based on the PZC measurements in the present study, the recommended goethite PZC value for modelers is  $7.39\pm 0.09$ .

## SUMMARY AND CONCLUSIONS

Two ubiquitous mineral oxides that commonly coat subsurface sands and clays, goethite and pyrolusite, were studied. These oxides have been shown to completely dominate sorption in several subsurface systems (Coston *et al.*, 1995). Knowledge of the distribution, protonation status, and oxidation state is essential for critically predicting actual or potential contaminant transport. Furthermore, high-quality, surface-charge data are also essential to model reactive transport properly.

Pyrolusite PZC measurements were made using three methods, two of which were not reported in the literature until now: MT (PZC =  $5.9\pm 0.1$ ) and PA (PZC =  $5.98\pm 0.08$ ). In both cases, the degree of accuracy was high and the agreement between the methods was good. The IEP measurement of PZC resulted in an appreciably more acidic PZC of  $4.4\pm 0.1$ , a value that is in agreement with previous reported values using the same measurement technique. However, the MT and PA data presented here bring into question the accuracy of the IEP method for determining the PZC of pyrolusite. The present study suggests that the true PZC of pyrolusite may be  $5.94\pm 0.09$ , significantly greater than previously measured values using the IEP method. Additional research is on-going to understand the cause of the differences in the PZC values measured.

Goethite PZC values were measured by three methods: MT ( $7.5\pm 0.1$ ), PT ( $7.46\pm 0.09$ ), and PA

( $7.20\pm 0.08$ ). Neither MT nor PA has been applied to the PZC measurement of goethite before. All three values showed reasonable agreement. The measured values fell within a rather wide range of literature values. The MT PZC value agreed very well with all four other reported values, suggesting that the proper use of this method may be simpler from an experimental view point, while retaining the accuracy of more time-intensive methods such as PT. Based on the average of these three measured values, the recommended goethite PZC value for modelers is  $7.39\pm 0.09$ .

Note that in nature several cationic and anionic impurities are present in goethite and pyrolusite phases and the extent of these impurities varies from site to site (Cornell and Schwertmann, 1996; McKenzie, 1989). Kosmulski (2002) after assembling a comprehensive table of PZC values of various mineral phases, concluded that the purity of the mineral is the most important factor responsible for discrepancies between values. Researchers and modelers should, therefore, conduct measurements using site-specific materials. Finally, the present work has shown the significance of using multiple, complementary techniques to obtain high-quality PZC values.

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