

## FILTRATION-RATE TECHNIQUE FOR DETERMINING ZERO POINT OF CHARGE OF IRON OXIDES

**Key Words**—Filtration rate, Goethite, Iron oxide, Potentiometric titration, Zero point of charge.

Interest in the preparation and use of goethite and other oxides as model sorbents in studies to explain the reaction of ions with soils, is increasing (Kuo, 1986; Martin and Smart, 1987; Zasoski and Burau, 1988). The zero point of charge (ZPC), which is the pH value of a solution in equilibrium with a particle whose net charge from all sources is zero (SSSA, 1987), is a characteristic frequently determined for such synthetic oxides. The ZPC of oxides serves as a convenient reference for predicting how the surface charge and potential on oxides depend on pH (Arnold, 1978).

The ZPC of oxides can be determined by electrokinetic and equilibrium electrochemical methods. Electrokinetic methods include microelectrophoretic and streaming potential techniques (Johansen and Buchanan, 1957). Potentiometric titration is the equilibrium electrochemical technique most often used to determine the ZPC of oxides and other materials (Bolt, 1957; Parks and de Bruyn, 1962). Potentiometric titration, however, requires special equipment. If the determination of surface charge density is not required, a simpler method may be preferred to potentiometric titration for determining the ZPC of oxides.

The present paper describes a simple filtration set-up and procedure for determining the ZPC of synthetic goethite and compares the results with those obtained by the potentiometric titration technique.

### MATERIALS AND METHODS

#### *Oxide preparation*

Goethite, was prepared in a polyethylene container from 10% NaOH and 0.2 M Fe(NO<sub>3</sub>)<sub>3</sub>; all chemicals were of analytical reagent grade. The gel was aged with continuous stirring for 10 days at room temperature at pH 11.7. The crystals were finally washed to pH 7 by repeated stirring in deionized distilled water, the excess water at the end of each washing cycle being removed with filter candles. The crystals had the following properties: surface area (ethylene glycol), 95.2 m<sup>2</sup>/g; principal X-ray powder diffraction peak, 4.17 Å; ratio of oxalate-soluble iron/total iron, 0.015; endothermic, differential thermal analysis peak, 285°C; color, yellow (10 YR 7/8); crystal shape, needlelike.

#### *Filtration-rate technique*

The set-up is presented in Figure 1. A suspension of the goethite was prepared with deionized distilled water (1.0 g/liter) and passed through a 300-mesh sieve. The

suspension was distributed in 100-ml portions into 125-ml Erlenmeyer flasks. The pH was adjusted differently in the flasks to cover the pH range 5 to 10, and the suspensions were allowed to equilibrate for about 48 hr. Immediately before filtering the suspension in each flask, the final pH was measured.

The suspension in the flask was mixed by a magnetic stirrer (SU). The flask was tightly sealed with a rubber stopper (RS 1) through which a narrow glass tube reached to about 1 cm from the bottom of the flask. The upper part of the glass tubing was connected by plexiglas tubing (PT) to the upper part of another glass tube that passed through a second rubber stopper (RS 2), tightly sealing the mouth of a Millipore tall-form glass filter holder (FH). A Millipore micropore (0.22- $\mu$ m pore size) filter paper (FP) was placed at the lower end of the filter holder. The stem portion of the filter holder passed through a third rubber stopper (RS 3) sealing the mouth of a graduated receiving cylinder (GC). Plexiglas tubing connected the upper part of a short glass tube passing through a second hole in the stopper (RS 3) of the receiving cylinder to another glass tube passing through one of two holes in a fourth rubber stopper (RS 4) sealing the mouth of a vacuum flask (VF). The vacuum flask was connected through a manostat (Ms) to a vacuum line (Vc).

The system was evacuated, and the suspension was drawn into the filter holder and filtered into the graduated cylinder. The time required to obtain a given volume of filtrate was recorded. The receiving cylinder was emptied, the filter holder cleaned, and the micropore filter paper replaced between filtrations. The filtration time (minutes/volume) was plotted as a function of suspension pH. At the ZPC, maximum flocculation resulted in the fastest filtration.

#### *Potentiometric titration*

The ZPC of the synthetic goethite was also determined by the potentiometric titration technique, as described by Parks and de Bruyn (1962). In the present study, the suspension concentration was 1 g of oxide in 300 ml of NaNO<sub>3</sub> solution having an ionic strength of  $1.0 \times 10^{-3}$  M or  $1.0 \times 10^{-2}$  M. The pH range studied was 5 to 11. Suspensions and blank solutions were titrated with 0.1 M NaOH.

### RESULTS AND DISCUSSION

A ZPC of 7.9 was obtained for the synthetic goethite ( $\alpha$ -FeOOH) by both the filtration-rate and potentiometric

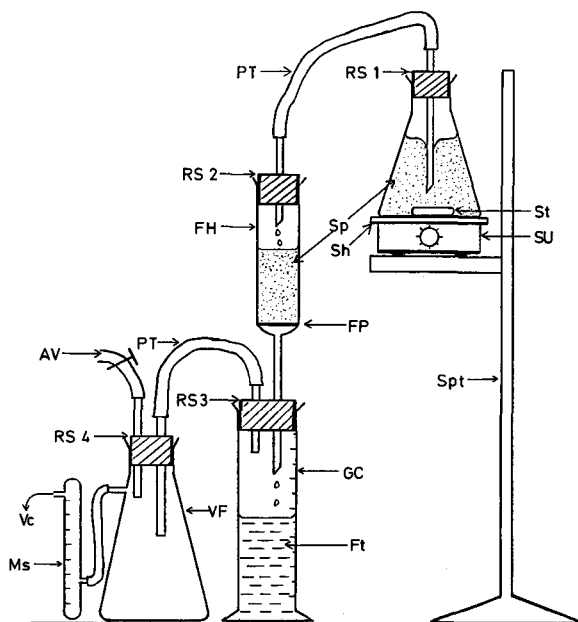


Figure 1. Experimental set-up for filtration-rate technique for measuring zero point of charge. RS 1 = rubber stopper number 1; RS 2 = rubber stopper number 2; RS 3 = rubber stopper number 3; RS 4 = rubber stopper number 4; PT = plexiglas tubing; Sp = oxide suspension; St = magnetic stirrer; FH = filter holder; Sh = heat shield; SU = magnetic stirring unit; FP = micropore (0.22  $\mu\text{m}$ ) filter paper; AV = air vent; VF = vacuum flask (trap for filtrate overflow); Spt = support; GC = graduated receiving cylinder; Vc = to vacuum; Ft = filtrate; Ms = manostat.

metric titration techniques (Figures 2 and 3, respectively).

Electrokinetic methods are based on the determination of the zero point of a property that depends on the presence of an electric double layer. The filtration-rate technique is based on the principle that at the ZPC, no net charge exists on the oxide particles to repel each other, resulting in maximum flocculation of particles; thus, the fine pores of the filter paper are not easily blocked, giving the fastest filtration. Lewandowski and Linford (1972) used a variation of the filtration set-up to establish optimal conditions for the bulk filtration of ferric hydroxide suspensions.

In addition to pH, other factors, such as the presence of electrolyte and the suspension concentration (oxide mass/volume), affect the rate of filtration. The surface charge density on oxides increases (becomes more negative or positive) with an increase in concentration of indifferent electrolyte at a given pH (see Figure 3), thereby affecting the degree of dispersion or flocculation and, thus, the rate of filtration. A very high suspension concentration would quickly produce a thicker oxide cake on the filter paper and retard or even stop filtration. In the filtration-rate technique, the suspension was prepared with deionized distilled water, not

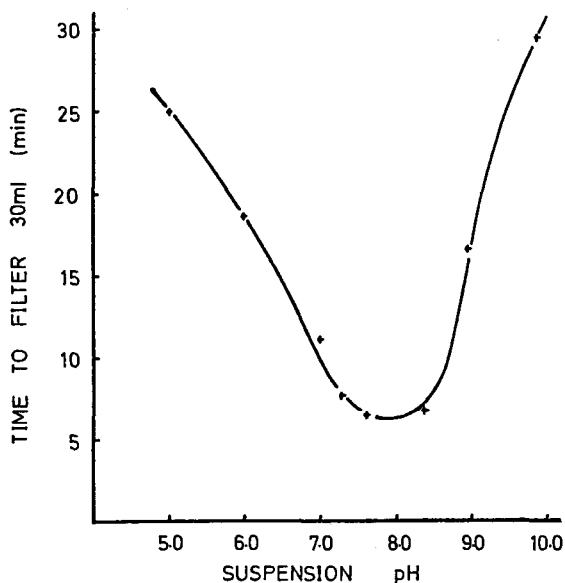


Figure 2. Determination of the zero point of charge of synthetic goethite by the filtration-rate technique. Filtration time is plotted as a function of suspension pH. Suspension concentration = 0.10%.

with electrolyte. The use of analytical reagent grade chemicals and repeated washing of the oxide in deionized water at the preparation stage ensured its purity from  $\text{Na}^+$  and other contaminant ions. Preliminary

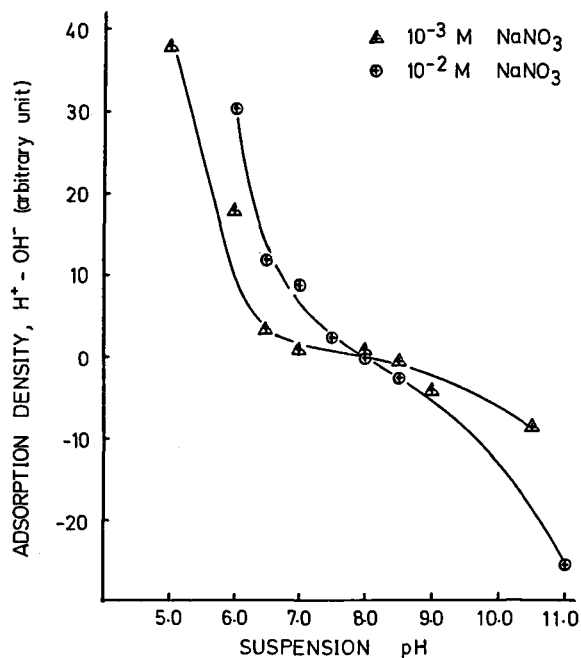


Figure 3. Determination of the zero point of charge of synthetic goethite by potentiometric titration. Adsorption density of potential-determining ions on the goethite is plotted as a function of pH and ionic strength, using  $\text{NaNO}_3$  as indifferent electrolyte.

trials showed that the filtration rate was reasonable at a suspension concentration of 1.0 g oxide/liter; the total time for eight filtration runs was 2 hr (Figure 2).

Potentiometric titration is the technique most often used to estimate the ZPC of oxides. This technique has the advantage that the titration data can be used also for quantitative estimates of the surface-charge density of oxides at various pHs. A plot of charge density vs. pH is not the same for different ionic strengths of the same indifferent electrolyte, except at the ZPC. Surface charge density may be expressed in such units as meq/g,  $\mu\text{eq}/\text{cm}^2$ , and  $\mu\text{Coulombs}/\text{cm}^2$ . In this work, labelling the Y-axis in Figure 3 in the usual charge density units was not necessary; it was sufficient only to locate the pH where the two curves intersect. The ordinate was simply labelled as the difference between the volume of base added to achieve any given pH increment in the blank and that required to achieve the same pH increment in the suspension for a given ionic strength.

The ZPC of oxides is influenced by the presence of potential-determining ions (PDI) in addition to  $\text{H}^+$  and  $\text{OH}^-$ . Parks (1967) distinguished between ZPC and the isoelectric point (IEP) of oxides; the ZPC is the pH at which the surface charge from all sources is zero, whereas the IEP arises from the interaction of  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ , and the solid alone. The values of ZPC and IEP are equal only in the absence of adsorbed species different from the PDI:  $\text{H}^+$  and  $\text{OH}^-$ . For iron oxides, Fe(III) hydroxo complex ions released from the solid phase by dissolution are also commonly regarded as PDI; however, Atkinson *et al.* (1967) pointed out that the surface charge contribution offered by the transfer of ferric hydroxo complex ions across the interface is negligible compared with that from  $\text{H}^+$  and  $\text{OH}^-$  ion transfer, because  $\text{H}^+$  or  $\text{OH}^-$  always greatly exceed the complex ion concentration in solution in the pH range 3.5–11.0. The goethite was not prepared in a glass reaction vessel, because in a slurry of such a high pH (11.7), silica could be solubilized out of the glass (Schwertmann, 1988); the presence of silicon in goethite would lower the ZPC (Brümmer *et al.*, 1988).

The ZPC of goethite is also influenced by temperature. Parks (1965) cited literature that indicated that the ZPC of natural goethite samples decreased from 6.7 at 25°C to 6.0 at 60°C, and to 3.2 at 100°C. The present study was made at room temperature, which did not vary over the 3-hr duration of the experiments.

Although goethite was used as the test material for the filtration rate technique, the technique should be suitable for the determination of ZPC of other oxides. The filtration-rate technique is straightforward and utilizes simple and common pieces of apparatus; it can therefore be easily adopted for routine determinations of ZPC of oxides, if a quantitative estimate of surface charge densities is not required.

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Department of Land, Air,  
and Water Resources  
University of California  
Davis, California 95616

AGYEMAN BOADI  
ANKOMAH<sup>1</sup>

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<sup>1</sup> Present address: Soil Science Section, Department of Crop Science, University of Science and Technology, Kumasi, Ghana.