

Determination of Point of Zero Charges of Manganese and Iron Oxides Using a Simple Coagulation Method

단순한 응결방법을 이용한 산화망간과 산화철의 Point of Zero Charge의 결정

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INTRODUCTION

The solids encountered in water suspension, soil, and geologic formation, whether natural or manmade colloid, sand, or silt, are electrically charged. Importance of surface electrical property of minerals has been recognized since coagulation (Breeuwsma and Lyklema, 1971), heat of emersion (Healy and Fuerstenau, 1965), surface tension (Parks and de Bruyn, 1962), electrophoretic mobility (Bryant and Williams, 1987; Carroll-Webbs and Walther, 1988), solubility (Parks and de Bruyn, 1962; White and Zelazny, 1986), and cation and anion exchange capacities (Gillman and Uehara, 1980; Schofield, 1949; van Raij and Peech, 1972) all depend on surface charge and the variation of surface charge with solution properties. The electrical charge is developed in two principal way: either from isomorphic substitution among ions of different

charges in crystal structure or from the reaction of surface functional groups with ions in solution (Sposito, 1989). Smectite and vermiculite have a high permanent negative charge and a cation exchange capacity due to the isomorphic substitution in the crystal structure. Oxides and hydroxides of aluminum (Al), iron (Fe), and manganese (Mn) have no or little permanent surface charge. However, they have anion and cation exchange capacities as a result of the adsorption of potential determining ions such as H^+ and OH^- .

In the case of Fe and Mn oxides, surface charge is determined by the equilibrium of H^+ and OH^- with Fe^{+3} or Mn^{+4} and O^{2-} in the crystal lattice (Parks, 1967). They are cation exchangers in a basic environment when the surface charge is negative. In an acid environment, the surface charge is positive and they are anion exchangers. When surface is uncharged, they have small exchange capacity

for both cation and anion.

The isoelectric point (IEP) and the PZC are convenient references for predicting the charge-dependent behavior of oxide minerals and their suspensions. The PZC is the pH at which the solid surface charge from all sources is zero. The IEP is a PZC arising from interaction of H^+ , OH^- , the solid, and water. Many techniques have been developed to measure surface charge, especially IEP and PZC, including potentiometric titration, electrophoretic mobility, ion retention, salt titration, mineral addition, and coagulation. Point of zero charge has commonly been determined using a potentiometric titration method and a electrophoretic mobility method. The coagulation method for PZC determination developed by Yopps and Fuerstenau (1964) has not frequently been employed because it needs special equipment for in situ determination of suspension stability. The objective of this study was developing a simplified coagulation method without the special apparatus for the determination of PZC.

MATERIALS AND METHOD

Materials

Reagent grade pyrolusite ($\beta\text{-MnO}_2$) (J.T. Baker Chemical Co., Phillipsburg, NJ, USA) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) (Fisher Scientific Co., Fair Lawn, NJ, USA) were used for PZC determination. Pyrolusite was ground to clay ($<2 \mu\text{m}$ in diameter) in distilled water using an agate mortar and pestle. The ground pyrolusite sample was freeze-dried. Hematite was used without grounding. The surface area of the samples was determined by the BET measurement of nitrogen gas (N_2) adsorption

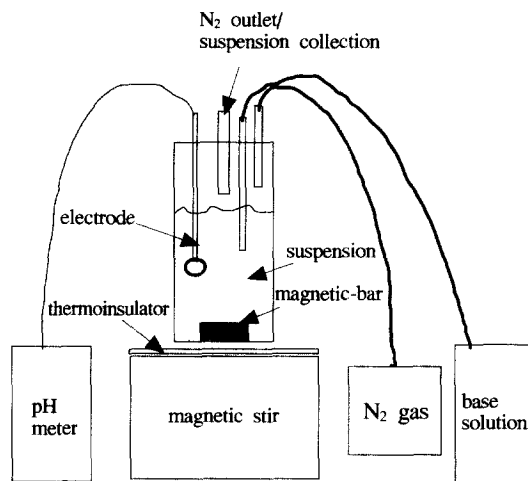


Fig. 1. Schematic diagram of simplified coagulation rate cell.

using an Autosorb-6 (Quantachrome Co., Boynton Beach, FL, USA).

Experimental Procedure

A mixture of 0.01 g of pyrolusite or hematite and 200 ml of 0.001M NaCl was stirred in a simplified coagulation rate cell (Fig. 1). After stirring for 1 hour, the pH of the suspension was adjusted to 3 with 0.1N HCl. Five milliliter of 0.1M NaOH was added and the suspension was stirred for 10 minutes. The pH of solution was measured and 5 ml of suspension was taken at 5 cm in depth. The light transmittance of the suspension was measured at 610 nm in wavelength for pyrolusite and at 650 nm for hematite at which each suspension had the highest absorption in preliminary UV-visible scanning, using a Spectronic 20 spectrophotometer (Miltonroy Co., Ivyland, PA, USA). The addition of base, and the measurements of pH and light transmittance were repeated to pH

13. The solution pH at maximum flocculation, the highest value of light transmittance, was assigned as PZC. All tests were done with triplicated samples.

RESULTS AND DISCUSSION

Surface areas of pyrolusite and hematite were 7.45 and 6.24 m² g⁻¹, respectively (Table 1). The maximum flocculation, the highest value of light transmittance, occurred at pH 7.2±0.1 for pyrolusite and at pH 8.5±0.2 for

Table 1. Surface area and PZC of pyrolusite and hematite.

	Surface area (m ² g ⁻¹)	PZC by coagulation	Published PZC
Pyrolusite	7.45	7.2±0.1	7.4*, 7.2‡, 9.3§
Hematite	6.24	8.5±0.2	8.4*, 8.1†

*: Stum, 1992; † : Kraepile *et al.*, 1998; ‡ : Eary and Rai, 1987; § : Park, 1967. All published data were determined with a titration method except the data from Park (1967), which was determined with calculation assuming the hematite was pure and no surface adsorption.

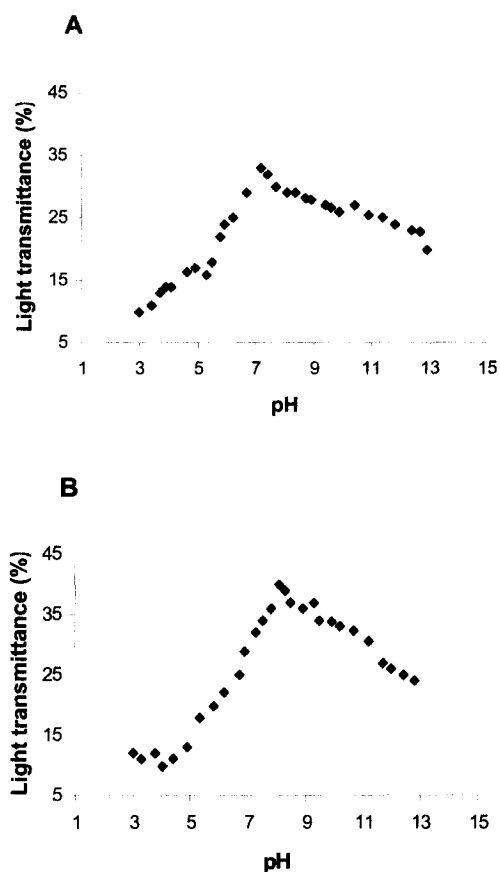


Fig. 2. Light transmittance of pyrolusite (A) and hematite (B) suspensions as function of pH.

hematite in the coagulation test (Table 1 and Fig. 2). The stability of colloidal suspensions results from the interaction of double layers. In the absence of specific adsorption, maximum coagulation occurs when double layers are absent or their thickness is minimum at the PZC. Light transmittance as function of solution pH showed asymmetry: steep increase below the pH for maximum flocculation and slow decrease above the pH. This means that the hysteresis of colloidal stability of pyrolusite and hematite occurs when the system changes from flocculation to dispersion. Higher salt content above the PZC may also be another contribution for the asymmetry due to the addition of the base (NaOH).

The PZC values determined by the coagulation method in this study showed only slight differences from the published values even though there is a big difference from the calculated PZC of hematite (Table 1). The differences may be due to experimental conditions such as matrix solution and sample treatment and the impurity of tested sample. Herrera Ramos and McBride (1996) demonstrated the changes of PZC by adsorption of anions and cations.

When goethite adsorbs multivalent anions, its PZC decreases comparing with adsorption of monovalent anions; when it adsorbed multivalent cations, its PZC increases. The PZC value of α -Al₂O₃ is pH 9.0 in KClO₄ solution and pH 9.1 in KNO₃ solution (Yopps and Fuerstenau, 1964). When α -Al₂O₃ is washed with acid, it has low PZC value too. The PZC of α -Fe₂O₃ decreases with increasing SiO₂ content (Park, 1967).

CONCLUSION

The PZC of the synthetic pyrolusite determined by the coagulation method is pH 7.2±0.1 and pH 8.5±0.2 for hematite. The simplified coagulation method can successfully be used in the determination of PZC of oxides.

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