氏　　　　　名	タ マ リ ン・シ ヒ テ Thamrin Sihite
授 与 学 位	工　学　博　士
学 位 授 与 年 月 日	平 成 2 年 3 月 28 日
学位授与の根拠法規	学位規則第 5 条第 1 項
研究科, 専攻の名称	東北大学大学院工学研究科 （博士課程）資源工学専攻
学 位 論 文 題 目	Surface Chemical Studies on the Stability of Iron (Ⅲ) Hydroxide Hydrosol （水酸化鉄（Ⅲ）ヒドロゾルの安定性に関する 界面化学的研究）
指 導 教 官	東北大学教授　臼井進之助
論 文 審 査 委 員	東北大学教授　臼井進之助　東北大学教授　中塚　勝人 東北大学教授　松岡　功　東北大学助教授　佐々木　弘

論 文 内 容 要 旨

The stability, i.e., dispersion and coagulation of Fe (Ⅲ) hydroxide hydrosol is related to many industrial processes. Usually, mine water contains a large amount of ferrous ions. Usually mine water is treated by a neutralization method after ferrous ions have been oxidized to yield ferric ions. In this process Fe (Ⅲ) hydroxide is precipitated. It is quite often experienced that heavy metallic ions, such as Cu^{2+}, Cd^{2+}, Hg^{2+} and hazardous ions are coprecipitated with the hydroxide precipitates. Therefore, the coaqulation of Fe (Ⅲ) hydroxide plays an important role in mine water treatment in view of not only removal of Fe ions but also removal of other hazardous ions included in the mine water. There have been many investigations regarding the stability of oxide hydrosols. However, very few experimental studies have been conducted on the colloid chemical or surface chemical properties of hydroxides.

The purpose of the present study was to investigate the stability, i.e., dispersion and coagulation, of Fe (Ⅲ) hydroxide hydrosols. The experiment involved the determination of the critical coagulation concentration (C.C.) of inorganic cations and anions (one of the most important parameters in discussing the stability of hydrosols), zeta potential measurements and potentio-

metric titration of Fe (Ⅲ) hydroxides in order to establish the relationship between surface charges of Fe (Ⅲ) hydroxides and pH of the solutions. The experiment also involved adsorption measurements of Cu^{2+} ions on Fe (Ⅲ) hydroxide surfaces in relation to the coprecipitation.

Experimental results of the stability have been analyzed in terms of the DLVO theory which considers the potential energy of interaction due to overlapping of electrical double layers and van der Waals interaction between particles.

The thesis consists of six chapters.

Chapter Ⅰ is an introduction to the thesis.

In chapter Ⅱ the coagulation studies which were conducted using well-defined monodispersed spherical hematite particles are discussed. Spherical hematite particles (diameter 0.13 μ m) were obtained by hydrolysis of a FeCl₃ aqueous solution at 100℃. Experiments involved the determination of the C.C. of K^+, Ba^{2+}, and La^{3+} in alkaline solutions (pH 1.03) where ferric oxides are negatively charged and in acidic solutions (pH 3.3) containing NO_3^- and SO_4^{2-} where ferric oxides are positively charged. Coagulation was assessed by measuring the size distribution of hematite particles as a function of the electrolyte concentration. The C.C. values increased with the increase in the valence of cations and anions in alkaline and acidic solutions in accordance with the Schulze-Hardy rule. The zeta potential mesurements were also carried out under condition identical to those of the coagulation experiments. The potential energy of interaction was calculated as a function of separation distance using the DLVO theory and the Hamaker constant of hematite in an aqueous medium was evaluated. The Hamaker constant did not show a constant value but depended on the valence of ions, i.e., the Hamaker constant tended to increase with an increase of the valence of counterions, suggesting that some other attractive forces other than the van der Waals force contributed to the coagulation of hematite particles in the case of polyvalent ions. The hematite system served as a reference to the coagulation study of Fe (Ⅲ) hydroxide hydrosols.

Chater Ⅲ describes the coagulation of Fe (Ⅲ) hydroxide hydrosols obtained by neutralizing Fe (NO₃)₃ aqueous solutions at room temperature. The coaqulation study was conducted in a similar manner to that of hematite hydrosols except that the coagulation behavior was assessed by measuring the absorbance of the sol as a function of electrolyte concentration. This system was also found to obey the Schulze-Hardy rule, i.e, the higher the valence of counterions the lower the C.C. for both cations and anions. However, it was found that the ratio of the C.C. showed some deviation from the inverse 6th power law with respect to the valence of the counterious in contrast to the prediction of the DLVO theory. Zeta potentials of Fe (Ⅲ) hydroxide

particles were measured as a function of the electrolyte concentration. From the zeta potential data combined with C.C.'s the double-layer interaction energy (V_R) between particles was calculated as a function of particle separation. The van der waals energy (V_A) between particles was calculated for various values of the Hamaker constant (A). The total energy of interaction V_T $(=V_R + V_A)$ was calculated. The best value of the Hamaker constant was selected in such a way that the potential energy barrier becomes zero. The analysis in terms of the DLVO theory showed that the Hamaker constants tended to increase with the increase in the valence of counterions as in the case of spherical hematite sols. The most reliable value of the Hamaker constant of Fe (III) hydroxide particles in water was assessed to be $5 \times 10^{-13} - 7 \times 10^{-13}$ erg, which was obtained for monovalent ions and is fairly close to the value, 4×10^{-13} erg, for hematite obtained by coagulation experiments with NO_3^- ions.

chapter IV describes the surface charge of Fe (III) hydroxides in contact with aqueous solutions, which governs the double—layer interaction between colloid particles and adsorption of ions from solutions. Surface charges were measured by potentiometric acid-base titration at various concentrations of KNO_3 as a supporting electrolyte. As a result, the point of zero charge (p.z.c.),i,e., the pH at which the net surface charge on Fe (III) hydroxide surfaces becomes zero, was determined to be 7.2. This value was close to the isoelectric point (i.e.p), pH 7.3, determined by electrophoretic mobility measurements.

The surface charge, σ_0, as a function of pH was analyzed on the basis of the surface site dissociation reaction,i.e.,

$$SOH_2^+ \rightleftarrows SOH + Hs^+ \qquad [4.1]$$
$$SOH \rightleftarrows SO^- + Hs^+ \qquad [4.2]$$

where, SOH_2^+, SOH, and SO^- represent positive, neutral, and negative surface sites, respectively, and Hs^+ refers to the surface concentration of H^+. By analyzing σ_0 vs. pH curves $\triangle pK (=pK_- - pK_+$, K_+ and K_- are equilibrium constants for Eqs. [4.1] and [4.2], respectively), an important parameter in determining σ_0, was assessed. It was found that $\triangle pK$ depended on the KNO_3 concentration (C); i.e., $\triangle pK = 1$ for $C = 1 \times 10^{-4}$ M and $C = 1 \times 10^{-3}$ M and $\triangle pK = 3$ for $C = 1 \times 10^{-2}$ M and $C = 1 \times 10^{-2}$ M. It was also shown that the surface potential of Fe (III) hydroxides obeyed the Nernst equation only for low electrolyte concentrations where $\triangle pK$ is small in magnitude.

In chapter V the adsorption of Cu^{2+} ions at the Fe (III) hydroxide-solution interface is described for studies conducted in acidic media (pH 4 to 7) by varying the concentration of KNO_3 as a supporting electrolyte, at $Cu(NO_3)_2$ initial concentrations of 1×10^{-6} and 1×10^{-5} M. It was found that Cu^{2+} ions were adsorbed on Fe (III) hydroxide surfaces even in acidic media where

the net surface charge of Fe (Ⅲ) hydroxide surface is positive. The adsorption amount of Cu^{2+} ions increased with increasing KNO_3 concentration and pH. The distribution of positive, neutral, and negative sites was calculated using $\triangle pK$ obtained in chapter Ⅳ. It was found that negative surface sites exist even in acidic media though their fraction is relatively small as compared to the neutral sites. The ratio of the amount of Cu^{2+} adsorbed to that of negative surface sites was found to be, at most, 0.6. Thus, it was concluded that the negative surface sites existing on Fe (Ⅲ) hydroxide surfaces were responsible for the adsorption of Cu^{2+}.

Chapter Ⅵ presents the study conclusions.

審 査 結 果 の 要 旨

　水酸化鉄（Ⅲ）ヒドロゾルの分散，凝集ならびにそれに関連する界面化学的性質は種々の工業分野に係わりを有するが，鉱業廃水処理の立場からは鉄イオンの中和処理，有害重金属イオンの共沈現象に関係する重要な問題である。従来から水中におけるコロイド粒子の安定性に関しては種々の研究が行われてきたが水酸化物に対する研究はきわめて少ない。

　本論文は水酸化鉄（Ⅲ）ヒドロゾルの安定制を支配する種々の要因に関し，界面化学的観点から検討を行ったもので全編6章よりなる。

　第1章は緒論である。

　第2章ではコロイド粒子の分散，凝集の理論的解析に適した標準試料として，加水分解法によって作製し単分散球形ヘマタイトヒドロゾルを用い，凝集特性の重要な指標となる種々の無機イオンの臨界凝集濃度（C.C.）を求め，並行して測定されたヘマタイトのゼータ電位の値から粒子間のvan der Waals力を決めるHamaker定数を検討した結果を述べている。

　第3章では中和法によって得られた水酸化鉄（Ⅲ）ヒドロゾルについて，陽イオンおよび陰イオンのC.C.を求め，C.C.と対イオン原子価との関係に関するSchulze-Hardy則が成立することを確めた。またC.C.とゼータ電位測定結果を用いて粒子間の相互作用エネルギーを解析し，水中における水酸化鉄（Ⅲ）のHamaker定数は1価イオンについて求められた値が妥当なものであることを示した。

　第4章はコロイド粒子の安定性にとって重要な表面電荷を検討したもので，電位差滴定法によって水酸化鉄（Ⅲ）の表面電荷密度におよぼすpHならびに指示電解質濃度の影響を明らかにした。この結果を解析して表面電荷決定反応の平衡定数を求め，さらに水中における水酸化鉄（Ⅲ）表面の電位とpHとの関係に考察を加えている。これらは貴重な知見である。

　第5章では重金属イオンの一例として銅イオンをとりあげ，その水酸化鉄（Ⅲ）に対する吸着を検討し，水酸化鉄（Ⅲ）表面が正の電荷を帯びる酸性水溶液中においても銅イオンが吸着することを見いだした。この理由について，第4章で得られた結果を用い水酸化鉄（Ⅲ）表面の電荷分布を検討して，銅イオンの吸着は酸性水溶液中においても存在する水酸化鉄（Ⅲ）表面の負電荷との結合によって合理的に説明されることを示した。これは興味ある結果である。

　第6章は結論である。

　以上要するに本論文は，鉱業廃水処理の上で重要な水酸化鉄（Ⅲ）ヒドロゾルの安定性と銅イオンの吸着に対する種々の要因を界面化学的観点から検討して有用な知見を得たもので，資源工学ならびに界面化学の発展に寄与するところが少なくない。

　よって，本論文は工学博士の学位論文として合格と認める。