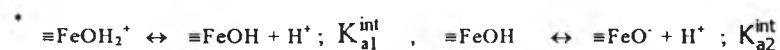# CHAPTER I

INTRODUCTION

The spread of heavy metal ions such as copper and zinc ions being discharged from various industrial activities (e.g. battery, paint, catalyst and polymer manufactures, etc) has become a serious problem. Such pollutant is usually not decomposed by biological or chemical means and can accumulate in soils for a long period of time and finally becomes toxic to plants, animals and human.

The concentration, transport and fate of metal ions in natural aquatic system are usually controlled by the adsorption processes on the mineral surface. A large fraction of minerals in soil consists of hydrous metal oxides such as iron, aluminium and manganese oxides. Hydrous ferric oxide, commonly known as goethite, has been studied extensively[1] due to its surface properties affecting the distribution of solution species in soils, rivers , lakes and groundwater. The adsorption of metal ions on goethite surface has been widely studied as a function of pH, temperature, ionic strength, metal ion concentrations and goethite concentrations [2-5]. It may also be influenced by the simultaneous adsorption of other anions. Among these, sulfate ions are found in numerous aqueous geochemical system. The acidic drainage water from mine waste deposits contains very high concentrations of sulfate that can be expected to influence the mobility of heavy metal ions in soils and in drownstream recipient. Surface complexation, kinetics, and mechanisms of adsorption have also been investigated by a number of reseachers[6-10].

From the study of the adsorption of Cd^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} on goethite surface as a function of pH, metal ion concentrations and adsorbent concentrations[11], it was found that each metal adsorbs in a narrow pH range where the amount of adsorption increases from 0 to near 100%. Considering the adsorption isotherm, it was suggested that the goethite surface was composed of many groups of binding sites, strong and weak. Similar results were found for the adsorption and release of Co^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+} and Mn^{2+} on goethite as a function of pH. Typical S-shaped adsorption edges for all metals were observed. These results indicate that metal adsorption on goethite is favored as the pH of solution increases and the surface charge decreases. The metal affinity for goethite surface follows the order of $Cu^{2+}> Pb^{2+}> Ni^{2+}> Co^{2+}>Mn^{2+}$. The degree of affinity is a function of site capacity, surface complexation constant, and the electronegativity of the ion. Furthermore, no changes in the amount of metal adsorbed were observed with increasing ionic strength of background electrolyte from 0.001 to 0.01 M, suggesting that metal ions are specifically adsorbed on goethite surface [12].

Anion adsorption on goethite surface is a mirror image of metal ion. The adsorption is strongest at low pH and generally decreases with increasing pH [13,14]. The effect of anion on adsorption of metal ions has been investigated by several researchers. For example, the presence and co-adsorption of sulfate ions were found to enhance the adsorption of Cd^{2+} on goethite [15]. Chloride ion had no influences on the Pb^{2+} surface complexation [16] but strongly influenced the adsorption behavior of Hg^{2+} [17]. The adsorption of Cu^{2+} was found to be enhanced at low pH in the presence of sulfate[18], etc.

A large number of Surface Complexation Models (SCMs) have been developed to describe metal ion adsorption processes on goethite surface [19-23]. These adsorption models assume that metal ions form complexes with surface functional groups in a manner similar to metal-ligand association in solution phase. These SCMs differ depending on the assumptions regarding the structures and compositions of the adsorbed species and on the physical description of the interfacial region. In a number of studies, for example, Lumsdon and Evans [24] investigated the parameters (the values for intrinsic acidity constants,[*] K_{a1}^{int} and K_{a2}^{int}, the inner(C_1) and outer(C_2) capacitances, and the electrolyte binding constants,[**] K_{Na}^{int} and K_{Cl}^{int}) of the Diffuse Double Layer Model(DDLM), the Constant Capacitance Model(CCM),and the Triple Layer Model (TLM) for goethite. For the three models, the parameters were evaluated from the potentiometric data by the FITEQL program. The best fit of the two intrinsic acidity constants obtained with DDLM was not as good as those found with CCM and TLM. For CCM the fit was sensitive to the change in C_1 values while for TLM it was sensitive to changes in C_1 and $\Delta pK_a \left(pK_{a2}^{int} - pK_{a1}^{int} \right)$ values. Muhammad and Dzombak [25] investigated the effects of phthalic and chelidamic acids on adsorption of Cu^{2+} in goethite suspensions by the Generalized Two Layer Model (GTLM). For adsorption of Cu^{2+}, only one surface species, $\equiv FeOCu^{+}$ was sufficient to fit the adsorption data over the defined ranges of copper concentration (0.0023-0.098 mM) and the pH (3-6.5) studied. In the presence of phthalic acid and chelidamic acids, adsorption of Cu^{2+} was significantly enhanced at low pH. Later in 1996[18], they investigated the adsorption of Cu^{2+},organic acids (phthalic acid and chelidamic acid) and sulfate in goethite suspensions. The adsorption of Cu^{2+} was

[*] $\equiv FeOH_2^{+} \leftrightarrow \equiv FeOH + H^{+}$; K_{a1}^{int} , $\equiv FeOH \leftrightarrow \equiv FeO^{-} + H^{+}$; K_{a2}^{int}

[**] $\equiv FeOH + Na^{+} \leftrightarrow \equiv FeO^{-}Na^{+} + H^{+}$; K_{Na}^{int}, $\equiv FeOH_2^{+}Cl^{-} \leftrightarrow \equiv FeOH + Cl^{-} + H^{+}$; K_{Cl}^{int}

also found to be enhanced at low pH in the presence of inorganic sulfate anion. Adsorption data for Cu^{2+} and SO_4^{2-} in Cu-SO$_4$ systems were described by GTLM proposing the ternary surface complexes, $\equiv FeOHCuSO_4$. Addition of sulfate to the Cu^{2+}- phthalic acid system had little effect on Cu^{2+} adsorption. However, addition of sulfate to Cu^{2+}-chelidamic acid system had a dramatic effect on the adsorption of Cu^{2+}. Sulfate significantly reduced Cu^{2+} adsorption, principally by competing with Cu^{2+}-chelidamic acid ternary surface complexes. Lovgren et al.[26] studied the adsorption of $Pb^{2+}, Cd^{2+}, Cu^{2+}$, and Zn^{2+} at low concentrations in goethite suspensions with varying solid concentrations as a function of pH using voltammetric techniques. The voltammetric measurement showed good agreement with CCM, except for Pb^{2+} and Cd^{2+}. The best fits of the data were found with the specific capacitance (C_1) 1.28 Fm^{-2}. In the case of Cu^{2+}, three surface species i.e., $\equiv FeOHCu^{2+}, \equiv FeOCu^{+}$, and $\equiv FeOCuOH$ were formed. Based on an extended version of CCM, the complexation of sulfate ions at the goethite-water interface has been studied using potentiometry and infrared spectroscopy by Persson and Lovgren [27]. An equilibrium model with the outer-sphere complexes: $\equiv FeOH_2^{+} SO_4^{2-}$ and $\equiv FeOH_2^{+} HSO_4^{-}$ formed was found to give the best description of the experimental data and was confirmed by the infrared and adsorption experiments at different ionic strengths. Moreover, other surface complexation models such as Basic Stern Model (BSM), Three Plane Model (TPM) and Charge Distribution MultiSite Complexation Model (CD-MUSIC) were studied by other reseachers [28]. However, CCM is one of the most frequently applied models.

Based on the former literatures, only a limited number of studies have dealt with the adsorption of copper and zinc ions in an extended range of the ionic strengths of background electrolyte in the presence of sulfate ion. The objectives of this research are therefore to investigate the adsorption behaviors of copper and zinc ions on goethite surface under the conditions close to natural aquatic systems. The acid-base and complexation reactions of Cu^{2-} and Zn^{2-} on goethite surface were studied by potentiometric method. The experiments were performed within the pH range $3.5 \leq pH \leq 9.5$ in 0.001-0.50 M $NaNO_3$ background electrolyte. The effect of sulfate ion was also investigated. The experimental data from potentiometric titrations were analysed by SUPERQUAD program and further calculations including surface charge term finally yield the surface complexation constants. The adsorption behaviors of Cu^{2+} and Zn^{2+} on goethite surface were simulated by MINEQL program [29], based on CCM.