

## CHAPTER VI

### CONCLUSIONS

In the present work, the acid/base and complexation reactions of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  on goethite surface were investigated by potentiometric method. From the analysis of data, three types of surface complex species were found, the nondeprotonated ( $\equiv\text{FeOHCu}^{2+}$ ,  $(\equiv\text{FeOH})_2\text{Zn}^{2+}$ ,  $\equiv\text{FeOHCuSO}_4$  and  $(\equiv\text{FeOH})_2\text{ZnSO}_4$ ), the deprotonated ( $\equiv\text{FeOCu}^+$ ,  $\equiv\text{FeOZn}^+$ ,  $\equiv\text{FeOCuSO}_4^-$  and  $\equiv\text{FeOZnSO}_4^-$ ) and the hydrolyzed species ( $\equiv\text{FeOCuOH}$ ,  $\equiv\text{FeOZn(OH)}_2^-$ ,  $\equiv\text{FeOCuOHSO}_4^{2-}$  and  $\equiv\text{FeOZn(OH)}_2\text{SO}_4^{3-}$ ).

However, for the nondeprotonated species,  $\text{Zn}^{2+}$  form a multidentate complex with two surface sites on goethite due to the lower electronegativity value and the larger ionic size of  $\text{Zn}^{2+}$  compared with  $\text{Cu}^{2+}$ . In the acidic range, the major surface species were nondeprotonated and deprotonated species while the hydrolyzed species became more important at high pH. The same trend were found for the stability of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}\text{-SO}_4^{2-}$  and  $\text{Zn}^{2+}\text{-SO}_4^{2-}$  complex systems i.e., the  $\log \beta$  values of nondeprotonated > deprotonated > hydrolyzed surface species. From the distribution diagrams of the surface complex species on goethite, the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  increased with increasing pH. The adsorption edge of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  was found to be in the pH range of 4-7 and 5-8, respectively. In the presence of sulfate ion, the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  was enhanced at low pH as a result of the  $\text{Cu}^{2+}\text{-SO}_4^{2-}$  and  $\text{Zn}^{2+}\text{-SO}_4^{2-}$  ternary surface complexes, ( $\equiv\text{FeOHCuSO}_4$  and  $\equiv\text{FeOZnSO}_4^-$ ). Little effect of ionic strengths on

the  $\log \beta$  values and the amount of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed on goethite surface were observed for 500-fold increase in ionic strengths.

In conclusion, we may represent the adsorption model based on CCM for the goethite- $\text{Cu}^{2+}$  and goethite- $\text{Zn}^{2+}$  systems as shown in figure 5.1. The adsorbed  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{H}^+$  are located at the surface or the 0-layer, and form the inner-sphere complexes with the surface sites. Sulfate ions are located in the diffuse outer layer and form the outer-sphere complexes. The goethite surface charge and potential are modified to the values  $\sigma_0$  and  $\psi_0$  by the adsorbed ions. Beyond this 0-layer, the charge ( $\sigma_{\text{ddl}}$ ) and potential ( $\psi_{\text{ddl}}$ ) in the diffuse outer layer assumed the bulk values.

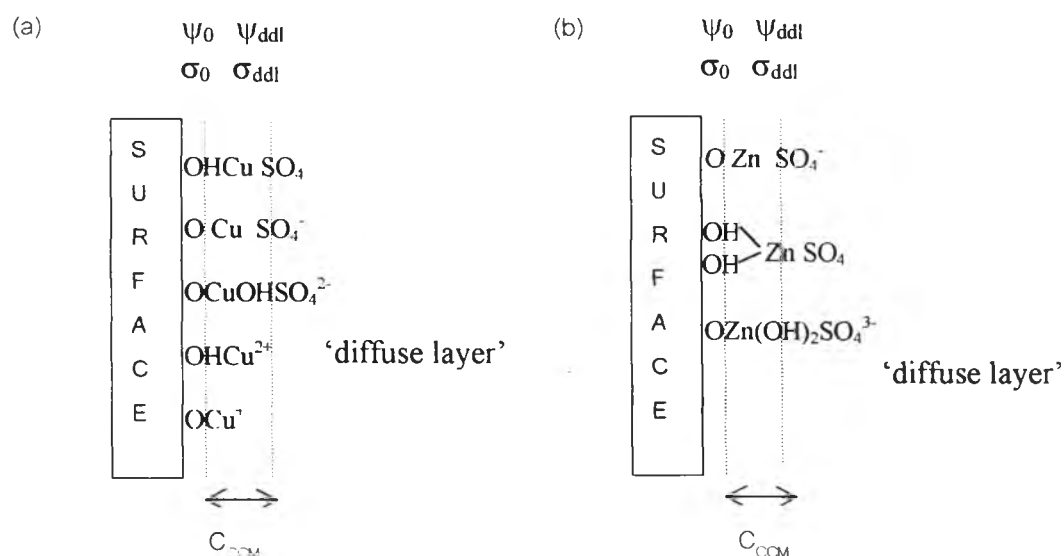


Figure 5.1 The schematic representation of the goethite/ solution interface (a)  $\text{Cu}^{2+}$ - $\text{SO}_4^{2-}$  and (b)  $\text{Zn}^{2+}$ - $\text{SO}_4^{2-}$  complex systems according to Constant Capacitance Model.

The results from this work give useful insights for the mineral-metal ions interactions. It should thus be worthwhile to further investigate the adsorption of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  or other metal ions on oxide surfaces focusing on;

1. The effect of the background electrolytes e.g.  $\text{NaCl}$ ,  $\text{KNO}_3$  and  $\text{NaClO}_4$ .
2. The effect of other anions or organic acids
3. The competition of these ions with varying conditions of the systems.
4. The adsorption with different surface complexation models
5. The adsorption on other metal hydroxides e.g. aluminium and manganese hydroxides.