

## **IV.8. CATION ADSORPTION BY HYDROUS IRON OXIDES (Rongguang Lin, Gerald Thomas and Burtron H. Davis).**

### **IV.8.1. ABSTRACT**

Equilibrium adsorption isotherms have been obtained of  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Ba^{2+}$  on iron oxyhydroxide and oxide samples. Cation adsorption appears to be similar for the various iron oxyhydroxide or oxide samples. The amount adsorbed depends upon the surface area and does not deviate strongly from the linear relation between the amount of cation adsorbed and the surface area. The data indicate that adsorption of the cations used in this study does not provide a very satisfactory method to incorporate basic cations into iron catalyst formulations.

### **IV.8.2. INTRODUCTION**

Studies of the adsorption of the hydrous metal oxides have appeared in a large number of scientific journals covering a wide range of disciplines. This interest may arise from practical considerations, such as the need to remove toxic metal from waste solutions or for the improvement of the flotation of a mineral. Recently, there has been considerable interest in the acid-base properties of the hydrous metal oxides, which has stimulated interest in models of the electrical double layer at the oxide-aqueous electrolyte interface. A number of details studied on cation adsorption have combined measurements of cation adsorption with measurements of other interfacial properties such as surface area, surface charge and electrokinetic potential.

Many factors affect the adsorbability of a dissolved species. Among these are chemical forms of adsorbent and adsorbate, solution pH, ionic strength, the presence

of competing adsorbates, identity and crystallinity of the metal oxide, time of contact, concentration of adsorbate, and temperature.

The principle governing reversible adsorption at low solution concentrations is Henry's law, which gives a linear adsorption isotherm passing through the origin (IV.8.1). At higher concentration, adsorption is less than expected from Henry's Law, a result arising by the filling a significant number of the total adsorption sites. The Langmuir isotherm takes this into account and has been widely used in both gas adsorption and solution adsorption studies (IV.8.2,IV.8.3).

Adsorption of cations by metal oxides is frequently found to be extremely rapid, most of the adsorption occurring within a matter of minutes (IV.8.4-IV.8.10).

Cation adsorption by iron oxides has been studied by several groups (IV.8.11-IV.8.16). However, adsorption studies on a complete set of iron oxyhydroxides and oxides does not appear to have been done. In this paper, adsorption data for potassium, magnesium, calcium and barium ions by  $\alpha$ -FeOOH,  $\gamma$ -FeOOH,  $\delta$ -FeOOH,  $\text{Fe}_3\text{O}_4$ ,  $\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\alpha$ - $\text{Fe}_2\text{O}_3$  are presented. These data were obtained to define the ease of removal of these ions when they are incorporated during catalyst precipitation as well as defining the feasibility of using selective chemisorption of these ions on the hydrous iron oxyhydroxide or oxide as an approach for adding promoters during catalyst preparation.

### **IV.8.3. EXPERIMENTAL**

#### **IV.8.3.a. Materials**

All chemicals are ACS reagent grade and were purchased from Aldrich. Doubly distilled water was used.

#### IV.8.3.b. Preparation of Iron Oxides and Oxyhydroxide

$\alpha$ -FeOOH. 315g of  $\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$  and 215g of NaOH were dissolved in 2000 mL of distilled  $\text{H}_2\text{O}$  to produce a suspension with a pH of 13.5. Oxygen was bubbled into the suspension at a flow rate of 20 mL/min. and the reaction took three hours. The solid was collected by filtration and washed four times with 600 mL of distilled water. The product was dried under a vacuum at 120°C for 12 hours. XRD data showed that the product was  $\alpha$ -FeOOH. The surface area was 38 m<sup>2</sup>/g.

$\gamma$ -FeOOH. 315g of  $\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$  and 78g of NaOH were dissolved in 2000 mL of distilled  $\text{H}_2\text{O}$  and the pH of the suspension was 8.1. Oxygen was flowed at 26 mL/min. through the suspension. During the oxidation reaction, the pH of the mixture was maintained at 7 by adding 1M NaOH as required. After 1 hour, oxygen flow was stopped and the orange solid was collected by filtration. The product was washed four times with 600 mL of distilled  $\text{H}_2\text{O}$  and dried in vacuum at 120°C for 12 hours. XRD showed that the product was  $\gamma$ -FeOOH. The surface area was 108 m<sup>2</sup>/g.

$\delta$ -FeOOH. 462g of  $\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$  and 166g of NaOH were added to 2400 mL of distilled  $\text{H}_2\text{O}$  to produce a suspension with a pH of 13.8. The suspension was cooled in an ice bath to 0°C, and the mixture was stirred for 30 minutes. Then 30%  $\text{H}_2\text{O}_2$  (130 mL) was pumped at a flowrate of 13 mL/min. into the suspension using a syringe pump. The color of the suspension rapidly changed from white to dark brown. The solid was collected by filtration and washed four times with 600 mL of distilled  $\text{H}_2\text{O}$ . The product was dried in vacuum at 120°C for 12 hours. The XRD data indicated that the product was  $\delta$ -FeOOH with a surface area of 171 m<sup>2</sup>/g.

$\text{Fe}_3\text{O}_4$ . 360g of  $\text{FeSO}_4 \bullet 7\text{H}_2\text{O}$  and 104g of NaOH were added to 2000 mL of distilled  $\text{H}_2\text{O}$ . After the mixture was stirred for 20 min., oxygen was bubbled into the

suspension at a flowrate of 20 mL/min. After two hours, a black product had formed and the oxygen flow was stopped. The solid was collected by filtration and washed four times with 600 mL of distilled H<sub>2</sub>O. The product was dried in vacuum at 120°C for 12 hours. The X-ray diffraction pattern of the product indicated that the product was Fe<sub>3</sub>O<sub>4</sub>. The surface area was 55 m<sup>2</sup>/g.

α-Fe<sub>2</sub>O<sub>3</sub>. The synthetic procedure used for α-Fe<sub>2</sub>O<sub>3</sub> is based on the method described by Cornell (IV.8.17). 300g of Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O in 2000 mL distilled water was heated to 90°C and ferrihydrite was precipitated by adding 1500 mL of NaOH (1M) that had been preheated to 90°C. Then 250 mL NaHCO<sub>3</sub> (1M), preheated to 90°C, was added to the brown voluminous precipitate and the suspension was heated at 90°C for 36 hours (pH = 8 to 9) in a closed polyethylene flask. The brownish-red product was shown to be α-Fe<sub>2</sub>O<sub>3</sub> by XRD data. The surface area of the product was 91 m<sup>2</sup>/g.

γ-Fe<sub>2</sub>O<sub>3</sub>. The preparation of γ-Fe<sub>2</sub>O<sub>3</sub> was based on modified procedure of Cornell (IV.8.17). A ferrous-ferric sulfate solution (108.4g of FeSO<sub>4</sub>•7H<sub>2</sub>O, 96g of NaOH and 95.5g of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•9H<sub>2</sub>O in 1300 mL of distilled H<sub>2</sub>O) was oxidized in a vessel at 0°C and at a constant pH of 14, using an oxygen flowrate of 26 mL/min. The oxidation took four hours and product was then collected by filtration and washed four times with 600 mL of distilled H<sub>2</sub>O. The dark brown solid was dried in vacuum at 120°C for 12 hours. The surface area of the product was 155 m<sup>2</sup>/g.

#### IV.8.3.c. Methods

To investigate the absorption of potassium ion on the iron oxides or oxyhydroxides, KNO<sub>3</sub> solutions of various concentrations were prepared and stored in

polyethylene bottles. In a typical experiment, 4g of iron oxide or oxyhydroxide was added to 50 mL of a  $\text{KNO}_3$  solution and the mixture was stirred in a closed flask at room temperature. After three hours, the solid was collected on a glass-fritted filter. The  $\text{K}^+$  concentration of the filtrate and the original  $\text{KNO}_3$  solutions were determined. The amount of  $\text{K}^+$  adsorbed was calculated as the difference in concentration between the original solution and the filtrate. Knowing the total volume of the solution used, the quantity of  $\text{K}^+$  adsorbed was calculated.

Adsorption experiments for  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  were carried out using the same procedure as described above for  $\text{K}^+$ , except that 2.5g of iron oxyhydroxide or oxide and 40 mL of salt solution were used in each experiment. To investigate the effect of pH on cation adsorption, the pH of the mixture of iron oxyhydroxide or oxide and alkaline earth solution was adjusted by adding 5N NaOH solution. In a typical experiment, a 40 mL of  $\text{Mg}^{2+}$  solution (0.033 M/L) was added to a flask which contained 2.5g of iron oxide or iron oxyhydroxide. A few drops of NaOH solution was added to the mixture, and stirred with a magnetic stirring bar. After three hours, the pH of suspension was measured using a pH meter.

#### IV.8.4. RESULTS AND DISCUSSION

$\text{K}^+$  Adsorption. Adsorption isotherms of potassium were obtained for the concentration range from  $10^{-3}$  to 1.25 M/L for  $\alpha$ -FeOOH,  $\gamma$ -FeOOH,  $\delta$ -FeOOH and  $\text{Fe}_3\text{O}_4$ . During adsorption, it was found that the pH of the suspension remained constant. The adsorption of  $\text{K}^+$  as a function of concentration is shown in Figure IV.8.1. The amount of  $\text{K}^+$  adsorbed (mmole K/g adsorbent) increases with an increase in the concentration of  $\text{K}^+$  when the quantity of adsorbent is held constant.

The amount of  $K^+$  adsorption per gram of adsorbent depends on the surface area of adsorbent, and increases with increasing surface area. The adsorption at low  $K^+$  concentrations is much lower than expected from the amounts adsorbed at higher concentrations.

$Ba^{2+}$ ,  $Ca^{2+}$  or  $Mg^{2+}$  Adsorption. Unlike  $K^+$  adsorption, the pH of the suspension decreased slightly during the first 10 min. following immersion of the solid in the salt solution, and remained essentially constant thereafter. The slight decrease in pH may result from ion exchange between the metal ions and protons on the surface of adsorbent. The initial concentration of  $Mg^{2+}$  was 0.033M for each experiment, and adsorption is reported as the percent of this amount that is adsorbed by the solid. Room temperature adsorption curves for  $Mg^{2+}$  on  $\alpha$ -FeOOH,  $\gamma$ -FeOOH,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> as a function of pH, are presented in Figure IV.8.2. The pH of the suspension following equilibration ranges from 6.5 to 10.2. If the pH of the suspension is higher than 10.5, there are complications due to precipitation of the metal hydroxide. The percentage of  $Mg^{2+}$  adsorbed by the iron compound exhibits a sigmoidal relationship with pH. The adsorption of  $Mg^{2+}$  for each of the iron compounds begins to increase rapidly at a pH of about 8; below these pH values, adsorption does not depend strongly on pH. Similar to  $K^+$  adsorption,  $Mg^{2+}$  adsorption depends on the surface area of solid phase; the higher the surface the higher the amount of  $Mg^{2+}$  adsorbed.

$Mg^{2+}$  adsorption isotherms for  $\gamma$ -FeOOH at two pH values of 6.5 and 9 are shown in Figure IV.8.3. For the experiments at a pH = 9, each  $Mg^{2+}$  solution was

adjusted to a pH of 9 before it was mixed with the  $\gamma$ -FeOOH solid.  $\text{Mg}^{2+}$  adsorption increases with the concentration of  $\text{Mg}^{2+}$  and with pH.

Adsorption isotherms for  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  on  $\gamma$ -FeOOH at pH of about 6.5 are shown in Figure IV.8.4. It appears that  $\gamma$ -FeOOH adsorbs  $\text{Ba}^{2+}$  to a greater extent than it does  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  for the same salt concentration. The data in Figure IV.8.4 show that the sorption capability of bivalent ions (mmole of metal ion adsorbed/ $\text{M}^2$ ) on  $\gamma$ -FeOOH is much greater than that of  $\text{K}^+$ . For an equilibrium concentration of 0.5M of the added ion, about 20 times as much  $\text{Ba}^{2+}$  is adsorbed as is  $\text{K}^+$ .

$\text{Ba}^{2+}$  adsorption isotherms for  $\gamma$ -FeOOH and  $\gamma$ - $\text{Fe}_2\text{O}_3$  at pH about 6.2 are shown in Figure IV.8.5. As in the case of  $\text{K}^+$  adsorption, the amount adsorbed depends slightly on the surface area of the solid.

#### IV.8.5. DISCUSSION

The adsorption of potassium and calcium ion appears to follow a similar adsorption dependency on surface area (Figure IV.8.6). If the surface is uniform and there are no interaction between adsorbed ions, the amount adsorbed should increase linearly with an increase in surface area. While the adsorption does increase as the surface area increases, the amount deviates from linearity for the higher surface area materials.

The adsorption of the bivalent cations increases in the order  $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Ba}^{2+}$ . This may be because  $\text{Ba}^{2+}$  is less strongly hydrated than  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . It is known that the adsorption affinity for cations increase in the order of decreasing hydrated-ion radius. This is explained qualitatively by assuming that the binding force

for adsorption is derived from coulombic interactions of the ion with the surface and that the adsorbed ions retain its primary hydration sheath (IV.8.18). The larger cations, such as  $\text{Ba}^{2+}$ , are more polarized and allows distortion to its hydration sphere to a greater extent than smaller, strongly hydrated cations such as  $\text{Mg}^{2+}$ . The ion with the smallest hydrated radius will therefore be able to approach the surface more closely and be held more strongly.

The shape of the isotherm for the adsorption of potassium ion deviates only slightly from that expected for one that obeys Henry's Law. The amount of  $\text{Mg}^{2+}$  adsorption, for a given concentration of  $\text{Mg}^{2+}$  per gram of adsorbent, depends upon the pH; with increasing pH the amount of  $\text{Mg}^{2+}$  adsorbed increases. It appears likely that the dependence of the adsorption on pH is a result of the replacement of at least one of the waters of hydration by  $\text{OH}^-$ . While the addition of an  $\text{OH}^-$  to the  $\text{Mg}^{2+}$  decreases the overall ionic charge, it provides the opportunity for adsorption to occur by formation of Mg-O-Fe bonding.

It does not appear that there is a significant variation of the adsorption of  $\text{K}^+$  by the various iron oxyhydroxide or oxide provided the difference in surface area is considered. For the incorporation of an ion onto a solid to be useful for catalyst preparation, it is desirable that the adsorption be nearly quantitatively at low concentrations. This is clearly not the case for  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{Ba}^{2+}$ . In the case of  $\text{Mg}^{2+}$ , adsorption increases with increasing pH but even in this case adsorption of the cation does not approach completion under reasonable adsorption conditions. Thus, it does not appear that adsorption is a useful approach to incorporate basic metal cation promotes into an iron catalyst formulation, as, for example, in the preparation of a promoted iron Fischer-Tropsch catalyst.



#### **IV.8.6. ACKNOWLEDGMENT**

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#### IV.8.7. REFERENCES

- IV.8.1. A. H. Yousef, M. A. Arata, M. A. Malati, *J. Appl. Chem. Biotechnol.*, **21**, 200 (1971).
- IV.8.2. B. Venkataramani, K. S. Venkatateswarlu and J. J. Shankar, *J. Colloid Inter. Sci.*, **67**, 187 (1978).
- IV.8.3. P. J. Anderson, *Proc. 2nd Int. Cong. Surf. Acitivity* 3, **67**, (1957).
- IV.8.4. S. D. Ahrland, I. Grenthe and B. Noren, *Acta. Chem. Scand.*, **14**, 1059 (1960).
- IV.8.5. Z. Kolarik, *Czech. Chem. Commun.*, **27**, 951 (1962).
- IV.8.6. S. M. Ahmed and D. Maksimov, *Can. J. Chem.*, **46**, 3841 (1968).
- IV.8.7. H. A. Posselt, F. J. Anderson, and W. J. Weber, *Environ. Sci. Technol.*, **2**, 1087 (1968).
- IV.8.8. F. Vgdra, *J. Electroanal. Chem.*, **25**, 13 (1970).
- IV.8.9. M. W. Rophael and M. A. Malati, *Chem. Ind.*, Vol.???, 768 (1972).
- IV.8.10. R. J. Zasoski and R. G. Burau, *Soil Sci. Soc. Am. J.*, **42**, 372 (1978).
- IV.8.11. A. Breeuwsma, PhD Thesis, Agricultural University, Wageningen, Netherlands, 1973.
- IV.8.12. M. H. Kurbatov, *J. Am. Chem. Soc.*, **71**, 858 (1949).
- IV.8.13. D. G. Kinniburgh, M. L. Jackson and J. K. Syers, *Soil Sci. Soc. Am. J.*, **40**, 796 (1976).
- IV.8.14. A. Breeuwsma and J. Lgklema, *J. Colloid Interface Sci.*, **43**, 437 (1973).
- IV.8.15. A. E. Albrethsen, PhD Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1963.

- IV.8.16. G. Y. Onoda and P. D. de Bruyn, *Surf. Sci.*, **4**, 48 (1966).
- IV.8.17. R. M. Cornell and V. Schwertman, "Iron Oxide in the Lab", 1992, pg 102.
- IV.8.18. V. A. Bessonov and N. N. Kyrlova, *Russian J. Colloid Sci.*, **36**, 772 (1974).

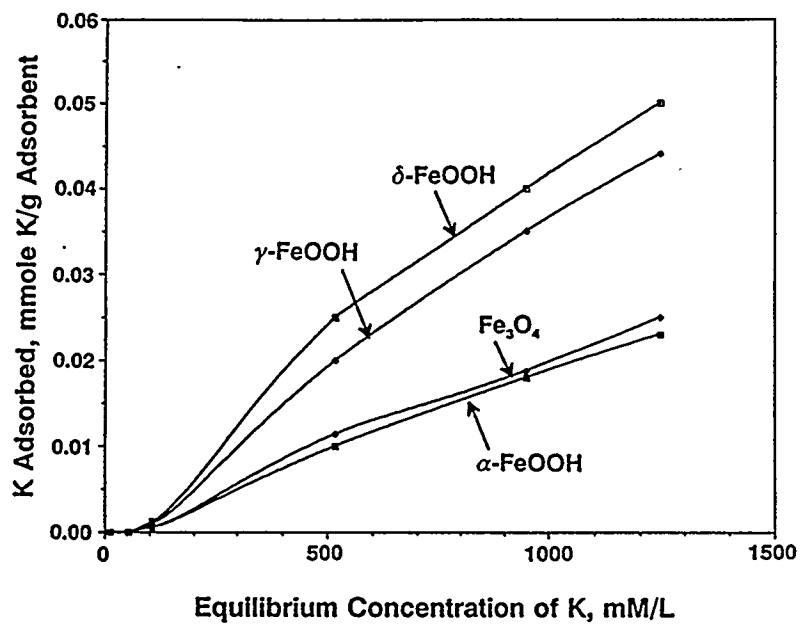


Figure IV.8.1. Isotherms for the adsorption of  $K^+$  on various iron oxyhydroxide and oxide samples at a pH of 7 and  $25^\circ\text{C}$ .

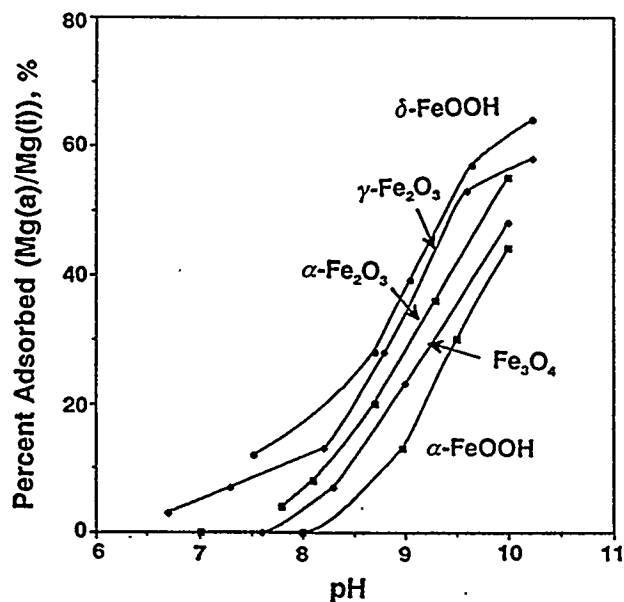


Figure IV.8.2. Adsorption of  $Mg^{2+}$  onto iron oxyhydroxide and oxide samples at various pH conditions [16 mL  $0.033\text{M } Mg(NO_3)_2$  per gram of iron compound].

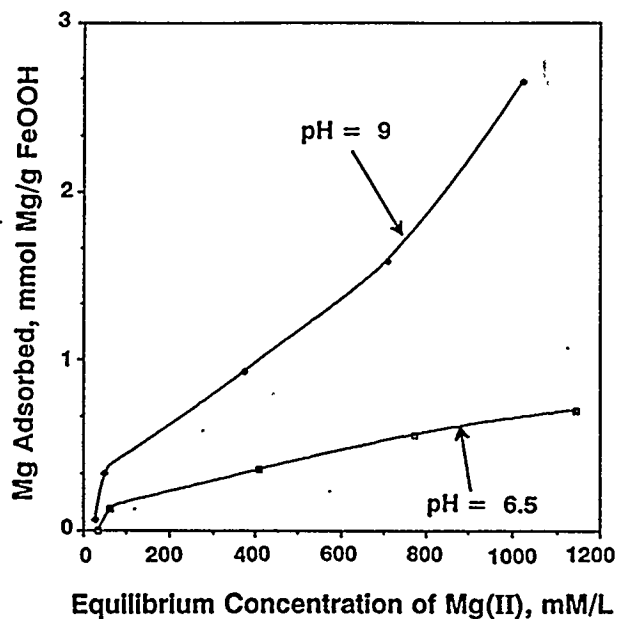


Figure IV.8.3. Adsorption isotherm for the adsorption of  $Mg^{2+}$  on  $\gamma$ -FeOOH at room temperature at pH = 6.5 (□ and 9.0 (●)).

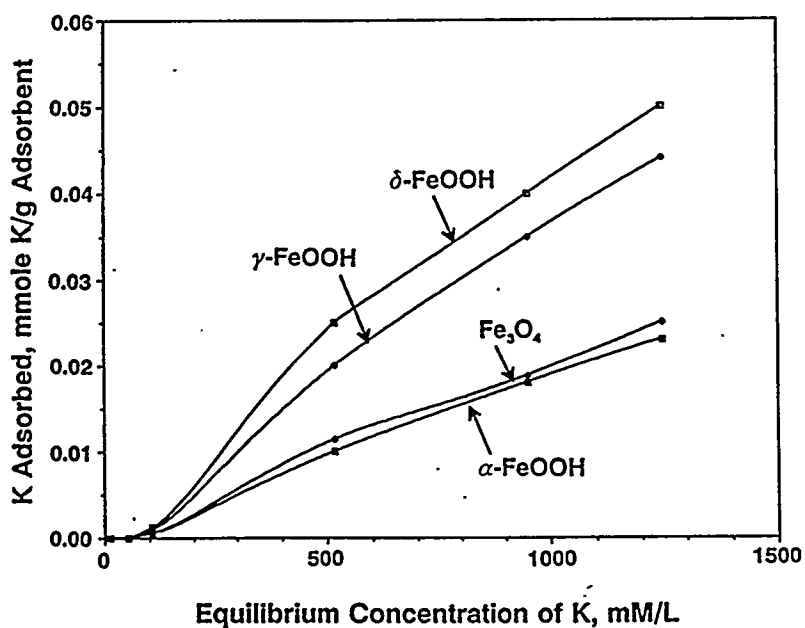


Figure IV.8.4. Adsorption isotherms for  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Ba^{2+}$  on  $\gamma$ -FeOOH (pH = 6.5; 25°C).

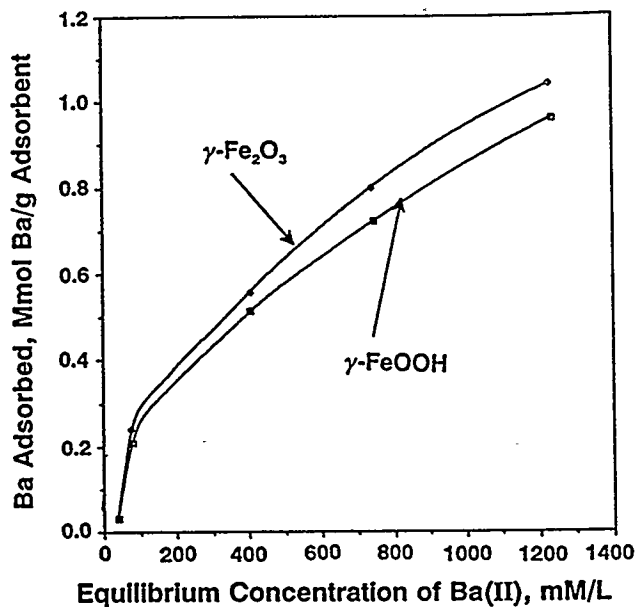


Figure IV.8.5. Adsorption isotherm for  $\text{Ba}^{2+}$  on  $\gamma\text{-FeOOH}$  ( $\square$ ) and  $\gamma\text{-Fe}_2\text{O}_3$  ( $\text{pH} = 6.5, 25^\circ\text{C}$ ).

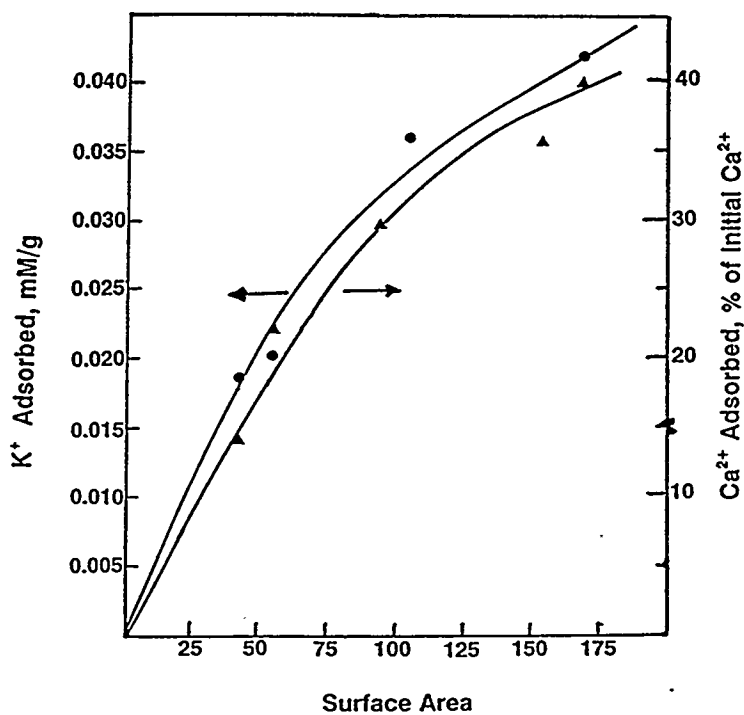


Figure IV.8.6. Adsorption of  $\text{K}^+$  ( $\bullet$ , mM/g at  $\text{pH} = 7.0$ ) and  $\text{Ca}^{2+}$  ( $\blacktriangle$ , mM/g at  $\text{pH} = 9.0$ ) for samples with increasing surface area.