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KINETICS OF SORPTION OF ZINC BY GOETHITE

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ABSTRACT

Zinc sorption by synthetic goethite (surface area 95.2m² g⁻¹; pH(PZC) 7.9) and production of acidity accompanying the sorption were studied as functions of reaction time and pH.

Kinetics of Zn sorption by goethite were conducted at 25°C at a single initial solution Zn concentration of 2.0 mg Zn L⁻¹ (3.06×10^{-5} M) at pH 5.4, 7.0, 7.8 and 8.5.

Zinc sorption increased with increase in pH. At pH 5.4 and 7.0, there was an initial rapid sorption that was followed by a slow one that lasted many hours. At pH 7.0 and 7.8, 50% of the added Zn was removed from solution in about ten minutes. At pH 8.5, however, sorption was so fast and complete as to be maximum (121.6 unmoles Zn g⁻¹) in less than ten minutes.

A lag in the release of H⁺ was observed at the initial sorption reaction times at pH levels below pH 8.5, and this lag suggested an initial Zn sorption reaction that was nonprotolytic, to be later followed or accomanied by a protogenic reaction.

At pH 7.8 and 8.5, the ratio of H⁺ released/ Zn sorbed at the final reaction times were 1.7 and 1.9, respectively. A relase of two moles of H⁺ accompanying a sorption of one mole of Zn was postulated to result lfrom a hydrolysis of Zn together with an exchange of the hydroxy Zn species with protons at the geothite surface:

$$Zn^{2+} + H_2O = ZnOH^+; \quad ZnOH^+ + SH$$
$$= SZnOH + H^+$$
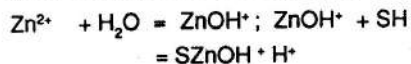
where SH represents adsorption sites on goethite surface.

Keywords: goethite, H release, kinetics, sorption, zinc

INTRODUCTION

Knowledge that Zn can be sorbed by soils is well established (Barrow, 1986; Pulford, 1986). Zn deficiency is frequent in many cropping situ- ations, for example, when acid soils are exces- sively limed. The element may also be present in toxic amounts, for example, following the spreading of sewage sludge (Pulford, 1986). Studies of the interaction of Zn with soil and soil components, therefore, are important from the point of view of both soil fertility and environ- mental science.

In soils, iron oxides are an important buffer system and exert a significant control on the concentration of Zn and other trace metals in the soil solution (Jenne, 1968). Goethite is often the most common iron oxide mineral in soils (Schwertmann and Taylor, 1977). Synthetic goethite is usually used in studies to understand the chemistry of interactions of ions with iron oxides in soils.

Kinetic procedures have been employed in the study of the mechanism of reaction of Zn with soil (Barrow, 1986) and with goethite (Brummer et al., 1988; Barrow et al., 1989). In a previous study of equilibrium sorption of Zn by goethite (Ankomah, unpublished), it was observed that Zn sorption was accompanied by a decrease in pH of the suspension and that pH had to be constantly adjusted to maintain a given desired pH level. The present paper reports on work conducted to study the time-course of the sorp- tion of Zn by goethite and the extent of produc- tion of accompanying acidity.

MATERIALS AND METHODS
Goethite Preparation

Synthetic goethite was prepared from 10% NaOH and 0.2 M Fe(NO₃)₃, the gel having been aged at pH 11.7 at room temperature with con- tinuous stirring for ten days, and the crystals washed finally to pH 7. It possessed the follow- ing characteristics: surface area (ethylene gly- col), 95.2 m² g⁻¹; X-ray peak, 4.17 ; pH(ZPC, 7.9: oxalate-soluble iron to total iron ratio (Feₒ.Feₜ), 0.015; DTA (endothermic) peak, 285°C; colour, yellow (10 YR 7/8); shape (crystal), needlelike about 0.4 um long; infrared peaks, 640, 793, 885, 1630, 3120, 3430cm⁻¹.

Sorption Procedure

Sorption kinetics were studied at a tempera- ture of 25.0 ± 0.5°C and at four pH levels of 5.4, 7.0, 7.8 and 8.5. The initial Zn concentration at all pH levels was 2.0 mg Zn L⁻¹ (3.06×10^{-5} M), and an indifferent electrolyte of NaNO₃ was maintained at 1.0×10^{-3} M. Suspension concen-

tration was 100 mg goethite in 400 mL of suspension.

100 mg of goethite (80-mesh) was suspended in 300 mL of water in a 500-mL Erlenmeyer flask and allowed to hydrate overnight. The suspension pH was adjusted to the desired level with 0.1 M HNO_3 or 0.1 M NaOH. In a separate container, premarked for 100mL., appropriate amounts of Zn nitrate and Na nitrate solutions were added, pH was brought to that of the suspension, and the volume made up to 100 mL with water.

The apparatus for the kinetic measurements is depicted in Figure 1. The 500-mL Erlenmeyer flask containing the goethite suspension was fitted with a stopper that had holes for a combination electrode, N_2 inlet tubing, addition port, NaOH delivery tube, and a polyethylene sampling tube. A gentle mixing was accomplished by flushing with N_2 gas and stirring with a bar-magnetic stirrer.

The time count was started as the 100 mL isoprotic Zn-Na nitrate solution was added to the 300 mL goethite suspension through the addition port. The pH was maintained contant at any given desired level during sorption by the release into the suspension of standard NaOH from a digital Metrohm Herisau Dosimat electricalburette activated by a Beckman auto-titrator. The concentration of the standard NaOH used was 4.75×10^{-4} M at pH 5.4, 7.0, and 7.8, and 0.092 M at pH 8.5.

The release of H^+ resulting from Zn sorption was measured as the amount of the standard NaOH (as indicated by the burette readings) released into the suspension at given times to keep suspension pH constant at the selected level. At selected times, 5-mL portions of the suspension were withdrawn through a 10-mL polyethylene syringe fitted to the sampling tube permanently inserted into the suspension. The
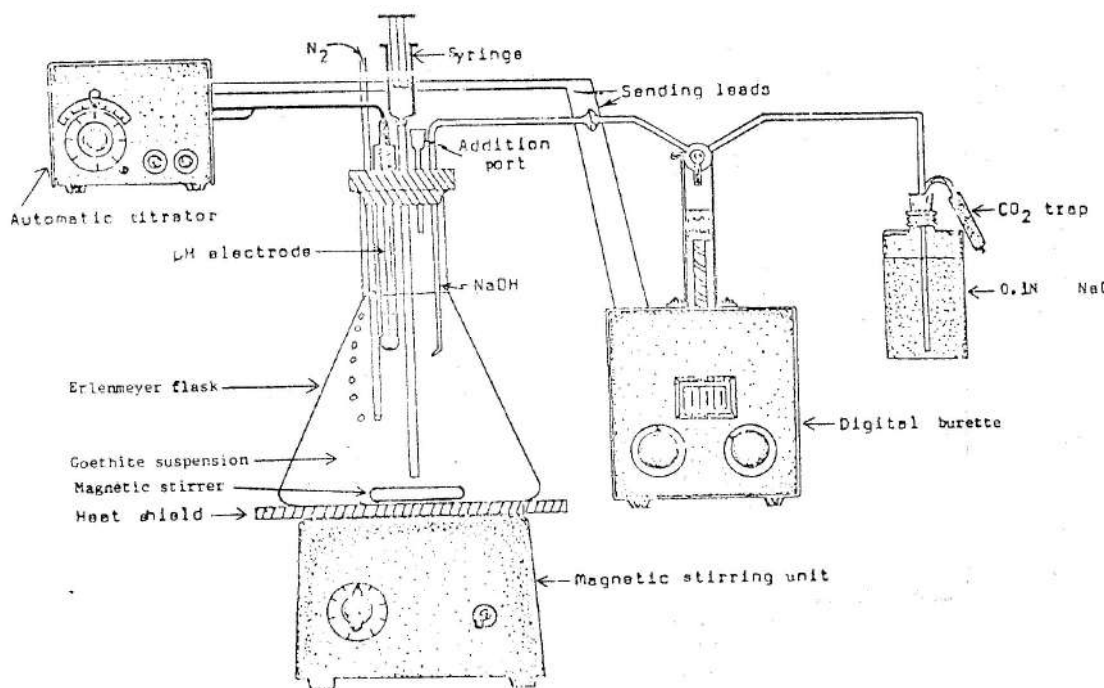

Fig. 1: Schematic diagram of the apparatus used in the measurement of the kinetics of Zn sorption by goethite

syringe contents were filtered through 0.22 umpore membrane filters. The filtration time, 10-15 seconds, was considered short enough not to affect interpretation of the results. Solution Zn concentration was determined by atomic absorption spectrophotometry. The amount or Zn sorbed was calculated from the difference between the initial an final Zn concentration in solution

RESULTS AND DISCUSSION

Figures 2 through 5 present the time-course of the sorption of Zn and the release of H^+ by goethite at the various pH levels. At pH 7.0 and 7.8, 50% of the added Zn was removed from solution in about 10 minutes. At pH 8.5, however, sorption was so fast as to be maximum (121.6 umole Zn g^{-1}) in less than ten minutes. A sorption of 122 umole Zn g^{-1} goethite constitutes a complete removal of Zn from solution in this study. Thus, at pH 7.8 and 8.5 there was virtually total Zn sorption at the times studied. At pH 5.4 and 7.0, the initial rapid sorption was followed by a slow one that lasted many hours. For example, at pH 7.0 a terminal sorption increment of 15 umole Zn g^{-1} (from 90 to 105 umole Zn g^{-1}) was accomplished in about 20 hours, compared with the initial sorption of 60 umole Zn g^{-1} in only about 20 minutes. In general, the very high rate of Zn sorption at higher pH levels indicate the pH-dependency of Zn sorption by goethite. The rapidity of the sorption especially at higher pH levels suggests that the sorption of Zn by goethite is basically a surface phenomenon or a reaction mediated by the surface.

Brummer et al (1988) and Barrow et al (1989) observed similar pattern of Zn sorption by goethite and explained the time-dependency of the interaction by assuming that the initial rapid sorption involved adsorption onto external goethite surfaces and the subsequent slow reaction involved a slow diffusion of the Zn ions into internal fixation sites.
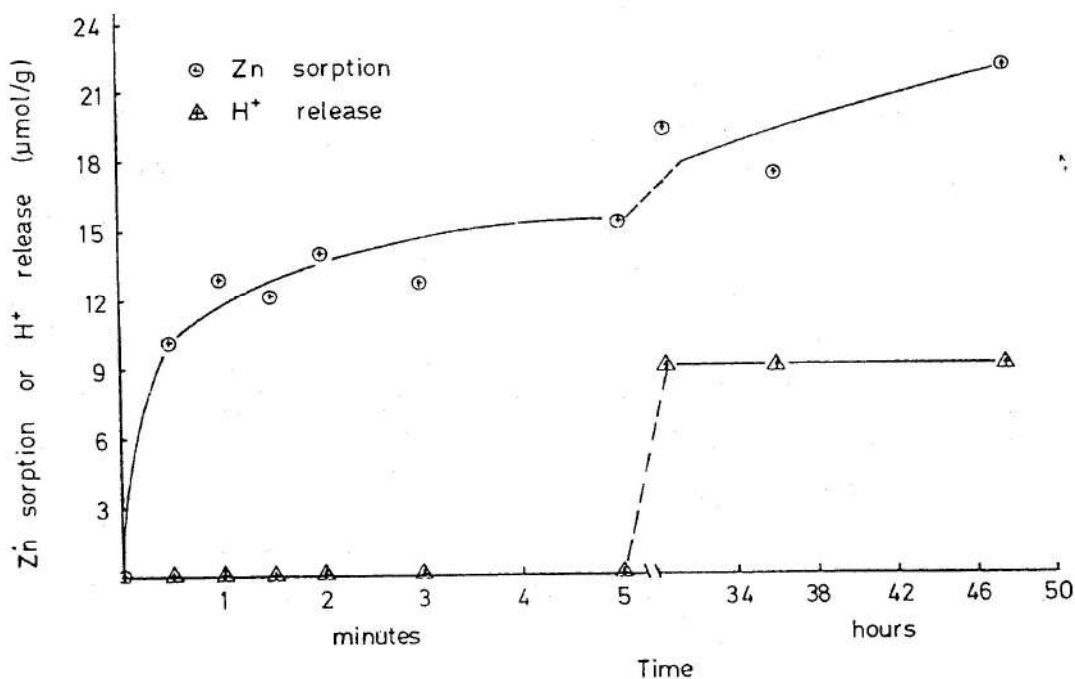

Fig.2: Kinetics of Zn sorption and H^+ release by goethite at pH 5.4. Weight of goethite = 100 mg; suspension volume = 400 mL
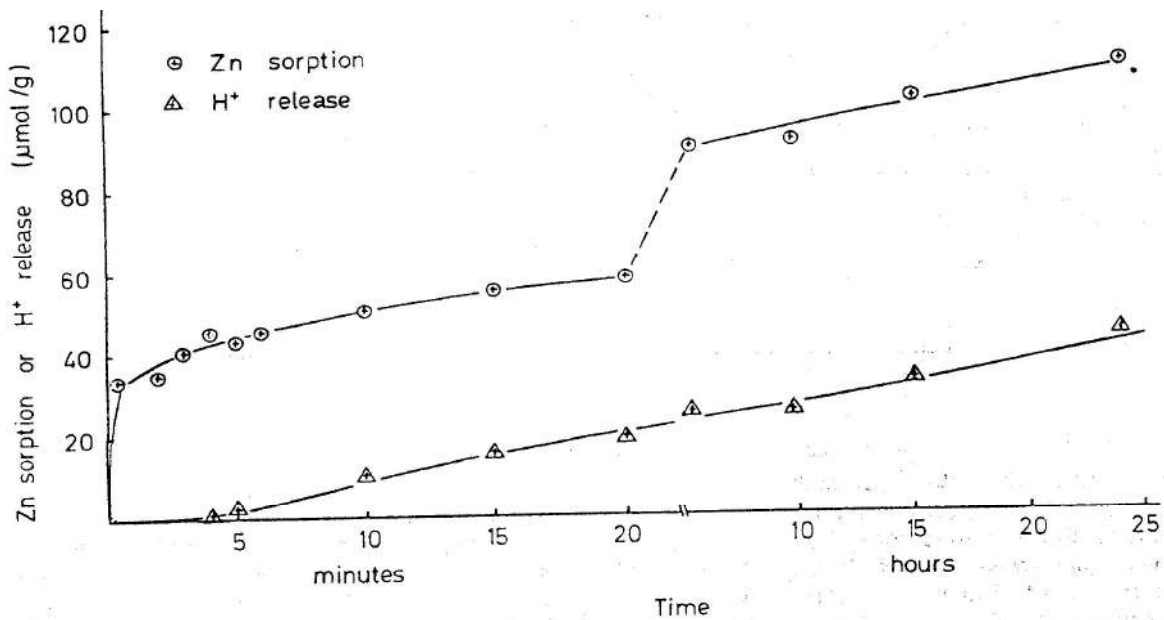
Fig.3: Kinetics of Zn sorption and H+ release by goethite at pH 7.0. Weight of goethite = 100 mg; suspension volume = 400 mL.

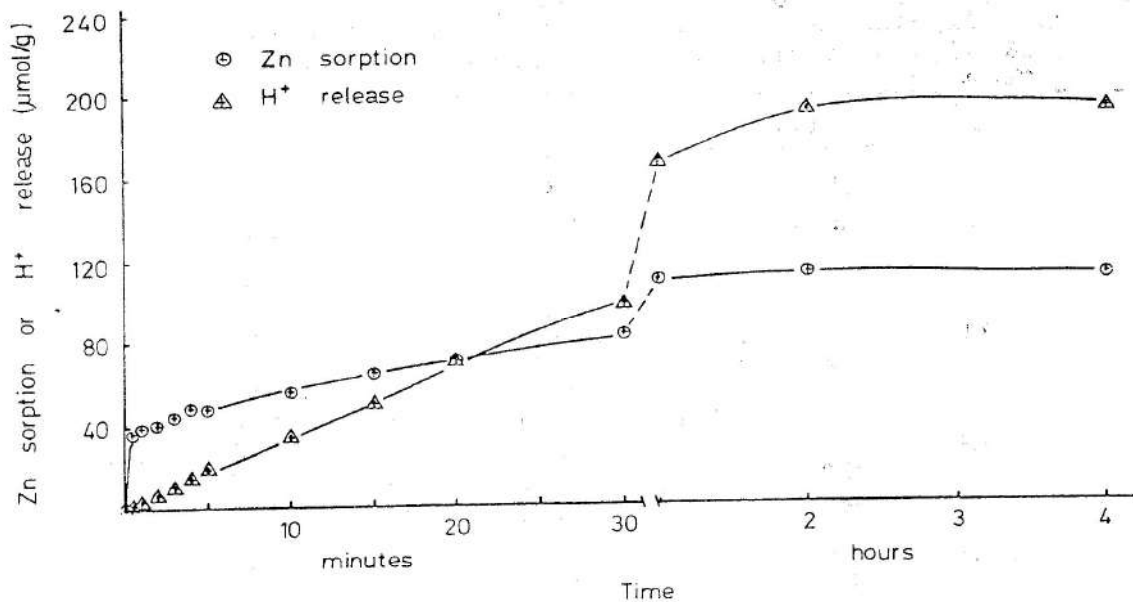
Fig. 4: Kinetics of Zn sorption and H+ release by goethite at pH 7.8. Weight of goethite = 100 mg; suspension volume = 400 mL.
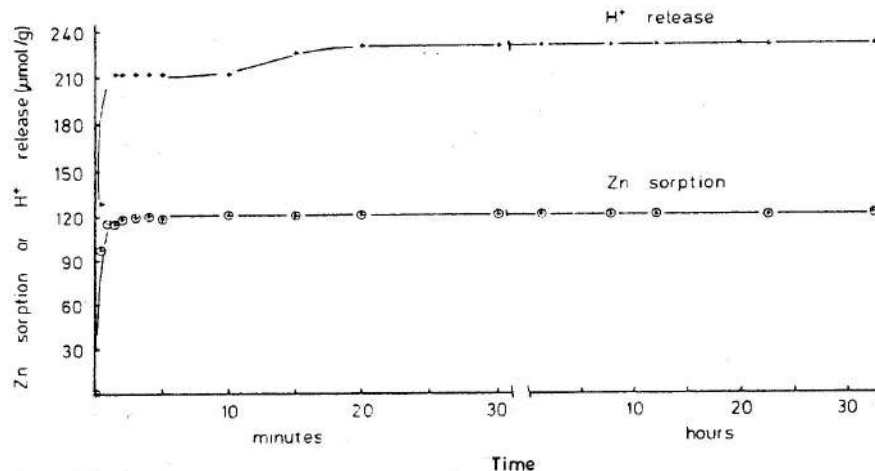
Fig.5: Kinetics of Zn sorption and H+ release by goethite at pH 8.5. Weight of goethite = 100 mg; suspension volume = 400 mL.

At pH 7.8 and 8.5 the H+ released/Zn sorbed ratio at the final times were 1.70 and 1.9 respectively (see Table 1). An H+/Zn ratio of 2 suggests a release of 2 moles of H+, or a consumption of 2 moles of OH- from solution for each mole of Zn^{2+} sorbed; the latter case would suggest a nucleation/precipitation of $Zn(OH)_2$ crystals. An H/Zn ratio of about 2 had also been reported for Zn sorption by MnO_2 (Loganathan, 1971) and by goethite (Forbes et al, 1976).

The affiinity of different heavy metals for goethite and other oxide surfaces has been found to be mainly determined by the ability of the metals to form hydroxy metal species

(Hodgson et al, 1964; Grimme, 1968; James and Healy, 1972; Forbes et al, 1976, Benjamin and Leckie, 1981). A hydrolyzed Zn species could then be retained at the goethite surface through exchange of protons from OH or OH_2 groups of the surface. The H+ released during sorption of Zn could therefore originate from the hydrolysis of Zn (reaction 1 below) and proposed exchange of hydroxy Zn species with surface protons (reaction 2 below)

$$Zn^{2+} + H_2O = ZnOH^+ + H^+ \qquad (1)$$

$$ZnOH^+ + SH = SZnOH + H^+ \qquad (2)$$

Table 1: Moles of Zn sorbed and moles of H released by goethite at different times of sorption, at four pH levels. Initial solution Zn level = 2 mg Zn L^{-1} (3.06 x 10^{-5} M); weight of goethite = 100 mg; suspension volume = 400 mL.

pH	Time		Zn sorption	H+ release	H/Zn
	min.	hrs.	—— umole g^{-1} ——		mole/mole
5.4	0.5	-	10.16	0.00	0.00
	5.0	-	15.34	0.00	0.00
	-	30.5	19.33	8.98	0.46
	-	47.5	22.03	9.03	0.41
7.0	0.5	-	33.65	0.00	0.00
	20.0	-	58.12	19.24	0.33
	-	5.3	86.75	23.85	0.28
	-	24.0	105.29	41.56	0.40
7.8	0.5	-	36.77	1.24	0.03
	20.0	-	70.60	69.54	0.99
	60	1.0	109.45	166.20	1.52
	-	4.0	112.21	190.62	1.70
8.5	0.5	-	97.65	128.80	1.30
	20.0	-	121.38	230.00	1.90
	-	7.7	121.20	230.00	1.90
	-	32.3	121.57	230.00	1.90

where SH represents adsorption sites on the goethite surface. The pK_1 value for equation (1) at zero ionic strength and 25°C is 8.96 (Base and Mesmer, 1976). Brümmer et al (1988) presented an equation to show that a relationship should exist between pH_{50} (the pH at which 50% of solution added metal becomes sorbed) and pK_1 values of heavy metals if sorption is related to the ability of the metals to form hydroxy complexes on oxide surfaces; they indeed observed that a lower pH_{50} of Zn relative to those of Ni and Cd correspond to the lower pK_1 of Zn relative to the pK_1 values of Ni and Cd (9.86 and 10.08 respectively; Baes and Mesmer, 1976). A lower PK_1 value of Zn therefore characterizes a high sorption affinity of Zn for goethite (Brummer et al, 1988) and sorption could be controlled to a considerable part by hydrolytic reaction of Zn on the goethite surface. Various attempts have been made at explaining the enhanced sorption of hydrolyzed metal ions (James and Healy, 1972; Stumm and Morgan, 1970).

At pH levels below 8.5 there was a lag in the release of H^+ at the initial reaction times; this lag is suggested to indicate an initial Zn sorption reaction that is not protolytic, to be later followed or accompanied by a protogenic reaction. The reaction during the initial nonprotolytic stages of the sorption process could involve displacement by Zn of water molecules from the surface; the sorbed $Zn(H_2O)_6^{2+}$ could then hydrolyze at the surface.

The results of this study indicate that the removal of added or native Zn from soil solution could be a very important phenomenon in iron oxide-rich tropical soils when their pH levels are adjusted upwards and therefore could have implications for soil fertility and environmental science.

ACKNOWLDGEMENT

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