

## REACTIONS OF ZINC WITH ACID AND BASE SATURATED DICKITES

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**Abstract**—The effect of pH, time and temperature on the interaction of zinc with acid and base saturated dickites has been investigated. Increase in pH resulted in an increase in adsorption of zinc in the higher concentration range. The adsorption increased rapidly and then slowly with increase in the time of interaction. The variation of rate constants and the half times of reaction suggested an exchange process controlled by film and possibly particle diffusion and thereafter fixation processes. The inferences found support from the nature of adsorption isotherms. Temperature affected adsorption with exothermic interactions. The activation energy of adsorption of zinc on Na-dickite was 14.0 kcal mole<sup>-1</sup>.

**Key Words**—Adsorption, Dickite, Exchange, Sodium, Zinc.

### INTRODUCTION

Among the micronutrients zinc salts have been recognized as valuable fertilizers and spray materials. Consequently the adsorption of zinc and its reactions with clays and soils have received increased attention during the last few decades. Elgabaly and Jenny (1943) showed that part of the zinc sorbed by montmorillonite could not be exchanged by ammonium acetate and it reduced the exchange capacity. Tiller and Hodgson (1962) showed that silicate clays adsorbed zinc by cation exchange and irreversibly by lattice penetration. Bingham et al. (1964) found that zinc could be an exchangeable cation and amounts in excess of CEC were retained as hydroxide which became unavailable due to fixation. Thus the activity of zinc in clays is due to several simultaneous interactions which are worth investigating.

The amount of zinc interacting with clays of different cation forms depends upon time of reaction, pH of the system, and concentration of zinc added. Kinetics or the concept of rate laws and order of reactions in soils and clays have been studied by Bunzl et al. (1976) as well as Selim et al. (1976) and others.

Dickite which is a polymorph of  $Al_4(Si_4O_{10})(OH)_8$  has a structure somewhat similar to kaolinite. According to Fordham (1973) it is believed to carry positive and negative sites at its edges and also some on its basal surfaces. Since adsorption and fixation of zinc is a significant process, the main purpose of this study was to investigate the interaction of zinc with dickite in its acid and base saturated forms in dilute-clay water suspensions.

### MATERIALS AND METHODS

Dickite used in these studies was obtained from Ward's Natural Science Establishment, Inc., Roches-

ter, New York, and was a monomineralic A.P.I. sample from Mexico. The less than 2- $\mu$ m suspension obtained after removal of organic matter, dispersion, and centrifugation was converted into Na-dickite by shaking several times with a 2 N solution of sodium chloride and washing with distilled water till free from chloride ions. Hydrogen-saturated dickite was prepared just prior to the required experiments by Aldrich and Buchanan's (1958) method. The concentration of the H-dickite suspension was 16.4 and that of Na-dickite 20.0 g per liter. The CEC of H- and Na-dickite as determined by Ganguli's (1951) method were 15.0 and 12.5 meq/100 g clay, respectively.

For a study of the effect of time on zinc adsorption by dickite, five sets of 10-ml suspensions of H- and Na-dickite were treated at 25°C with 0.5, 1, 2, and 7 ml of 0.04 N  $Zn(NO_3)_2$  solution. Further, one set with 7 ml of  $Zn(NO_3)_2$  and 10 ml of Na-dickite was also treated at 50°C. The mixtures were shaken for 15 min. Similar experiments were carried out at 30, 60, 180, and 360 min. The mixtures were then centrifuged and zinc estimated in the supernatants by EDTA titration. The extent of adsorption was estimated as the difference between the amount of zinc added and remaining in the supernatants. The results are presented in Figure 1.

For a determination of the effect of pH the supernatants were shaken with the requisite quantities of 0.1 N  $HNO_3$  or 0.1 N  $NaOH$  to give the required equilibrium pH. The adsorption of zinc was then carried out at 25°C and a time interval of 3 hr as described earlier. The results are recorded in Figure 3.

Experiments for a study of adsorption isotherms were conducted at the pH values of the unamended H- and Na-dickite suspensions by taking 10-ml suspensions of the clays in a large number of glass-stoppered tubes, adding various concentrations of 0.04 N Zn

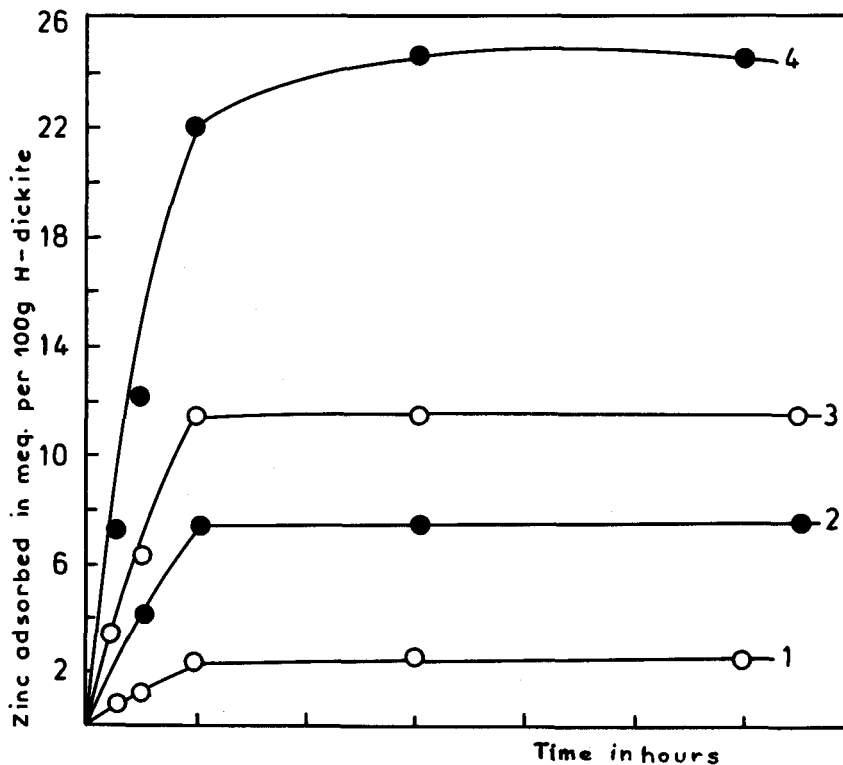


Fig. 1(a). Effect of time on the adsorption of zinc by H-dickite at 25°C. Concentration of zinc in meq per 100 g clay for curve 1 = 12.2, for curve 2 = 24.4, for curve 3 = 48.8, and for curve 4 = 170.8. CEC of H-dickite = 15.0 meq per 100 g clay.

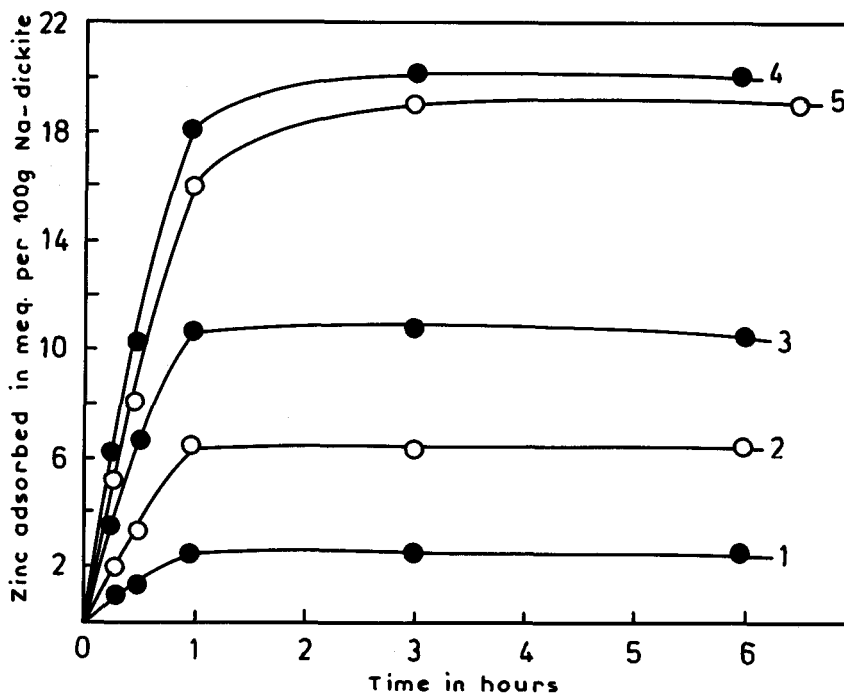


Fig. 1(b). Effect of time on the adsorption of zinc by Na-dickite at 25° and 50°C. Concentration of zinc in meq per 100 g clay for curve 1 = 10, for curve 2 = 20, for curve 3 = 40, and for curve 4 = 140 at 25°C, and curve 5 = 140 at 50°C. CEC of Na-dickite = 12.5 meq per 100 g clay.

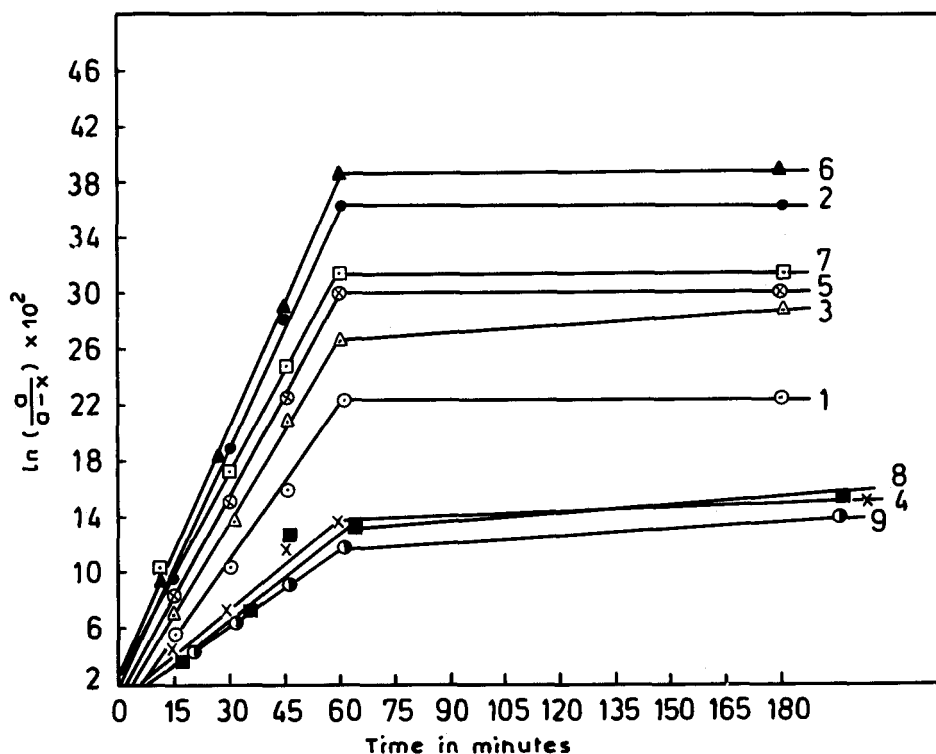


Fig. 2. Plot of  $\ln \frac{a}{a-x}$  against time for the reaction between zinc nitrate and H- and Na-dickite at 25° and 50°C. Concentration of zinc in meq per 100 g H-dickite at 25°C for curve 1 = 12.2, for curve 2 = 24.4, for curve 3 = 48.8, and for curve 4 = 170.8, and concentration of zinc in mol eq per 100 g Na-dickite at 25°C for curve 5 = 10, for curve 6 = 20, for curve 7 = 40, and for curve 8 = 140, and curve 9 = 140 at 50°C.

(NO<sub>3</sub>)<sub>2</sub>, adjusting the mixtures to a constant volume with distilled water and shaking the tubes at 25°C in the first set of experiments and at 50°C in the second set for 3 hr in each case. The suspensions were then centrifuged and the residual zinc estimated with standard EDTA solution. The difference gave the amount of zinc adsorbed. A plot of the adsorption isotherms is given in Figure 4.

## RESULTS AND DISCUSSION

The amount of zinc adsorbed as a function of time is plotted in Figure 1 for different concentrations of zinc nitrate added to the H- and Na-dickites, respectively. Although the systems approached equilibrium in 1 to 3 hr, adsorption rapidly and then slowly increased with time. The initial rapid adsorption appeared to be due to reversible exchange between zinc ions and the replaceable H or Na ions of the dickite surface. The slower increase in adsorption after nearly 60 min was due to either a slow penetration of Zn<sup>2+</sup> ions into the clay or fixation due to chemical forces. The reaction thus became more complex with lapse of time. Figure 1 also showed that the amount of adsorption increased as

more zinc ions were added to the aqueous suspension of clays.

Applying the simple kinetic rate laws, the order of reaction with respect to zinc was studied at different concentrations of zinc nitrate and at fixed concentration of the H- and Na-dickites. The initial reaction followed the first order kinetics (Figure 2, curves 1-9). Table I contains the representative results obtained in sets of experiments with different concentrations of zinc nitrate added to H- and Na-dickites. The results showed that the values of rate constants were largely invariant in the initial stages of the first order reaction. Further the values of the rate constant increased with concentration of metal ion added up to a concentration of 24.4 meq in H-dickite and 20 meq in Na-dickite, after which they decreased. On the other hand the half times of adsorption showed a decrease and thereafter an increase with increase in the concentration of metal ion added. The initial behavior up to a concentration of 24.4 meq in H-dickite and 20 meq in Na-dickite was characteristic of ion exchange processes controlled by film and possibly particle diffusion (Bunzl et al., 1976). The reverse behavior beyond the above concentration of zinc appeared to be due to a reaction mech-

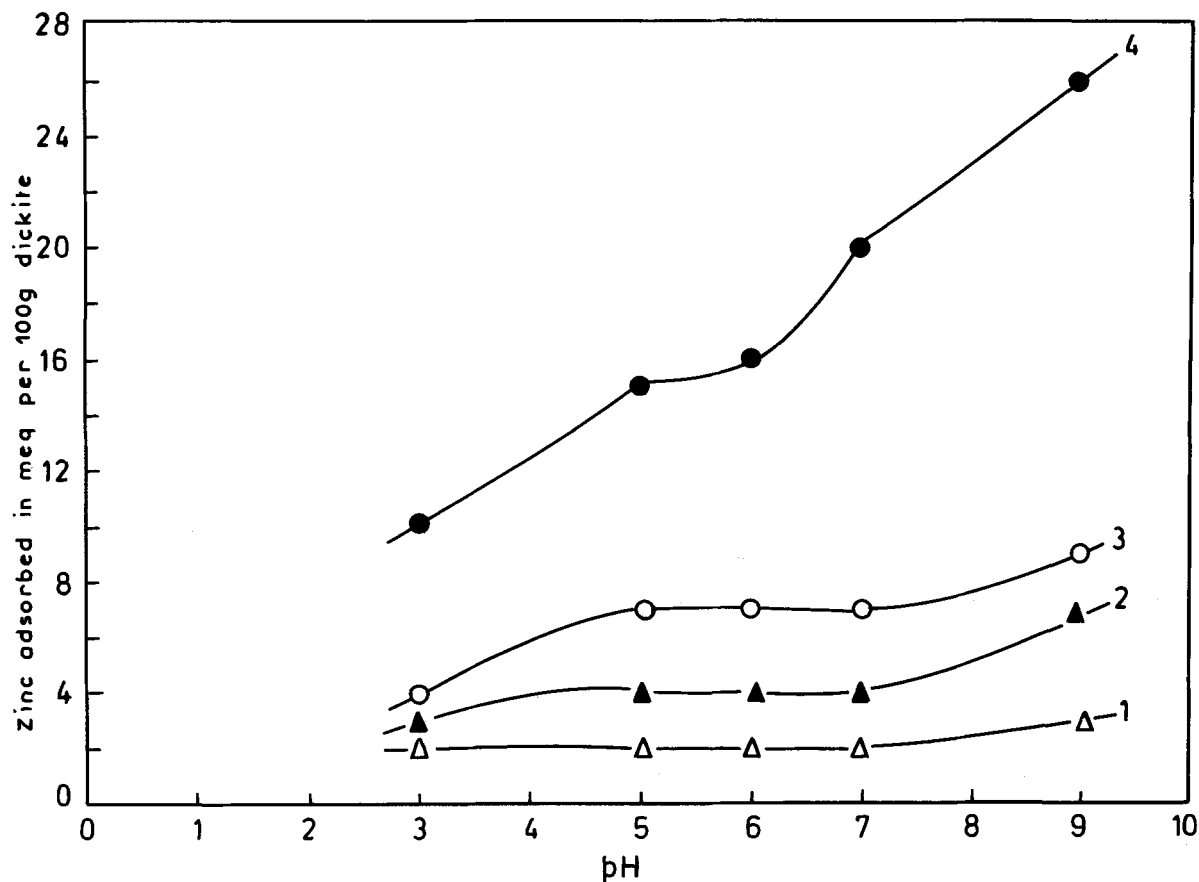


Fig. 3. Effect of pH on the adsorption of zinc by Na-dickite. Concentration of zinc in meq per 100 g clay for curve 1 = 10, for curve 2 = 20, for curve 3 = 40, and for curve 4 = 140. CEC of Na-dickite = 12.5 meq per 100 g clay.

anism other than exchange. It thus appeared that there was a difference in the mechanism of reaction of zinc with acid and base saturated dickites in the lower and higher ranges of zinc concentration.

Figure 3 illustrates the effect of pH on the adsorption of zinc by Na-dickite. In the high concentration range adsorption beyond the CEC appeared to be due to fixation and precipitation reactions as occurred with lapse of time and reported by earlier workers (Shuman, 1976).

An examination of the adsorption isotherms in dilute suspensions in the equilibrium concentration range of 0 to 2.8 mmoles of zinc per liter (Figure 4) at 25° and 50°C indicated that the lower temperature isotherms (curves 1 and 3) for adsorption of zinc on H- and Na-dickite were similar to class "H" or high affinity plus class "C" or linear; and marked by plateaus as defined by Giles et al. (1960). The initial part of the isotherm for H-dickite at 25°C was vertical and could be resolved into two portions separated by a slope, both indicating

rapid exchange adsorption, till a limiting value as indicated by a long flat plateau was reached at a value somewhat higher than the CEC.

An almost similar effect occurred during adsorption of zinc on Na-dickite with the long flat plateau being formed at the CEC. The two "H" portions indicated adsorption at two sites with different energy levels on H-dickite as advocated by Fordham (1973). When these sites were saturated, as indicated by the long plateau, new adsorption sites opened up due to the pressure of zinc ions producing a further rise with a change in the slope of the adsorption isotherms till it reached a constant value. These linear rising or "C" curves, both in the case of H-dickite and Na-dickite, were due to slow penetration and fixation of zinc ions in the lattice micropores of the dickites. The results were in agreement with the observations of earlier workers (Tiller and Hodgson, 1962) on the adsorption of zinc by clay minerals. The results also found support from the kinetic data discussed earlier in this communication which

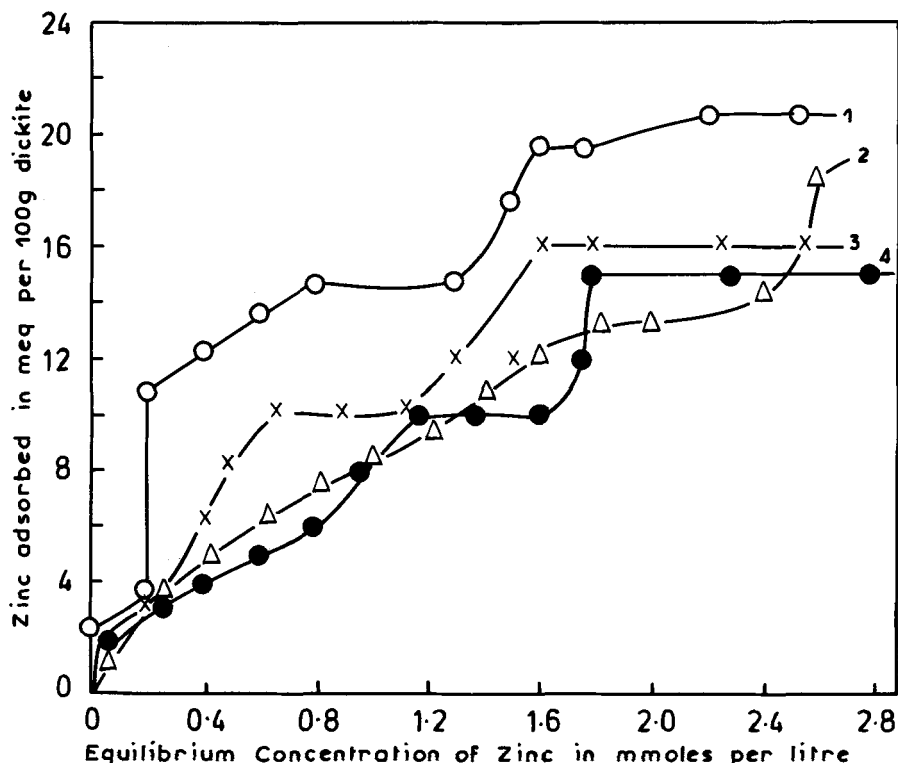


Fig. 4. Adsorption isotherms of H- and Na-dickite at 25° and 50°C. CEC of H-dickite = 15.0 meq per 100 g clay and of Na-dickite = 12.5 meq per 100 g clay. 1. ○ Hydrogen dickite at 25°C; 2. △ Hydrogen dickite at 50°C; 3. × Na-dickite at 25°C; 4. ● Na-dickite at 50°C.

were indicative of two kinds of interaction during adsorption of zinc on dickites.

The isotherms at 50°C (Figure 4, curves 2 and 4), both in the case of H-dickite and Na-dickite, exhibited almost the same kind of behavior except that at this temperature the initial "H" or high affinity portions were not so well formed. The initial adsorptive force at the higher temperature thus appeared to be lower. The curves also showed a decrease in adsorption with rise in temperature which was indicative of exothermic interactions. The average values of the rate constants for the Na-dickite system (Table 1) were  $2.25 \times 10^3 \text{ min}^{-1}$  at 25°C and  $1.90 \times 10^3 \text{ min}^{-1}$  at 50°C at a concentration of 140.0 meq of zinc. The activation energy ( $\Delta E$ ) of

adsorption of zinc over Na-clay was found to be 14.0 kcal/mole. Such a value could not be calculated in the case of adsorption of zinc on H-dickite due to uncertainty introduced by decomposition of H-clay with time at the higher temperature. A reference to Figure 4 (curves 1 and 3) further showed that in spite of a greater deflocculation effect and larger surface area exposed by Na-dickite, a greater amount of zinc was adsorbed by H-dickite than Na-dickite at the natural pH values (4.2 and 6.5, respectively) of the clays. The nature of the exchangeable cation thus determined the order of adsorption, the order being H-dickite > Na-dickite at a pH value below 7.

Table 1. Effect of time on the reaction of zinc with H- and Na-dickite at pH 4.2 and 6.5, respectively.

Time in minutes	H-dickite			Na-dickite		
	Conc. of zinc in meq/100 g clay	$k_1, \text{min}^{-1}$	$t_{1/2} = 0.693/k_1, \text{min}^{-1}$	Conc. of zinc in meq/100 g clay	$k_1, \text{min}^{-1}$	$t_{1/2} = 0.693/k_1, \text{min}^{-1}$
15	12.2	$3.94 \times 10^{-3}$	175.9	10.0	$5.57 \times 10^{-3}$	124.4
30		$3.44 \times 10^{-3}$	201.5		$5.03 \times 10^{-3}$	137.8
45		$3.55 \times 10^{-3}$	195.2		$5.01 \times 10^{-3}$	138.3
60		$3.72 \times 10^{-3}$	186.3		$5.01 \times 10^{-3}$	138.3
180		$1.24 \times 10^{-3}$	558.9		$1.67 \times 10^{-3}$	415.0
Average value		$3.18 \times 10^{-3}$	263.6		$4.46 \times 10^{-3}$	190.8
15	24.4	$6.58 \times 10^{-3}$	105.3	20.0	$6.65 \times 10^{-3}$	104.2
30		$6.29 \times 10^{-3}$	110.2		$6.19 \times 10^{-3}$	111.9
45		$6.27 \times 10^{-3}$	110.5		$6.40 \times 10^{-3}$	108.3
60		$6.02 \times 10^{-3}$	115.1		$6.43 \times 10^{-3}$	107.8
180		$2.00 \times 10^{-3}$	346.5		$2.14 \times 10^{-3}$	323.8
Average value		$5.43 \times 10^{-3}$	157.5		$5.56 \times 10^{-3}$	151.2
15	48.8	$4.81 \times 10^{-3}$	144.1	40.0	$6.13 \times 10^{-3}$	113.1
30		$4.60 \times 10^{-3}$	150.7		$5.91 \times 10^{-3}$	117.3
45		$4.64 \times 10^{-3}$	149.4		$5.55 \times 10^{-3}$	124.0
60		$4.43 \times 10^{-3}$	156.4		$5.61 \times 10^{-3}$	123.5
180		$1.60 \times 10^{-3}$	433.1		$1.87 \times 10^{-3}$	370.6
Average value		$4.02 \times 10^{-3}$	206.7		$5.01 \times 10^{-3}$	169.7
15	170.8	$2.92 \times 10^{-3}$	237.3	140.0	$2.93 \times 10^{-3}$	236.5
30		$2.47 \times 10^{-3}$	280.6		$2.48 \times 10^{-3}$	279.4
45		$2.62 \times 10^{-3}$	264.5		$2.69 \times 10^{-3}$	257.6
60		$2.29 \times 10^{-3}$	302.6		$2.30 \times 10^{-3}$	301.3
180		$0.86 \times 10^{-3}$	805.8		$0.86 \times 10^{-3}$	805.8
Average value		$2.23 \times 10^{-3}$	378.2		$2.25 \times 10^{-3}$	376.1
15	—	—	—	140.0	$2.41 \times 10^{-3}$	287.6
30		—	—		$2.07 \times 10^{-3}$	334.8
45		—	—		$2.00 \times 10^{-3}$	346.5
60		—	—		$2.20 \times 10^{-3}$	315.0
180		—	—		(at 50°C) $0.81 \times 10^{-3}$	855.6
Average value		—	—		$1.90 \times 10^{-3}$	427.9

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Резюме- Изучалось влияние pH, времени и температуры на взаимодействие цинка с диккитом, насыщенным кислотой и основанием. При увеличении pH увеличивалась адсорбция цинка при более высокой степени концентрации. Адсорбция сначала быстро увеличивалась и затем медленнее с увеличением времени взаимодействия. По изменению постоянных скорости и половины времени реакции можно предположить, что процесс обмена контролировался диффузией пленки и возможно частиц и затем процессами фиксации. Эти выводы были подкреплены характером изотерм адсорбции. Воздействие температуры на адсорбцию указывает на экзотермический характер взаимодействий. Активационная энергия адсорбции цинка на диккитом была  $14,0 \text{ Kcal mol}^{-1}$ .

Kurzreferat- Der Effekt von pH, Zeit und Temperatur auf die Einwirkung von Zink auf mit Säuren und Basen gesättigten Dickiten wurde investigated. Eine Erhöhung in pH resultierte in einer Erhöhung in Adsorption von Zink in der höheren Konzentrationsgruppe. Die Adsorption nimmt zuerst schnell zu und dann langsamer mit zunehmender Zeit der Einwirkung. Die Variation der Geschwindigkeitskonstanten und Halbwertszeiten der Reaktionen schlägt eine Austauschprozedur vor, die durch Film- und vielleicht Teilchendiffusion und danach durch eine Bindung kontrolliert wird. Die Folgerungen wurden durch die Natur der Adsorptionisothermen unterstützt. Die Temperatur übte einen Einfluß auf die Adsorption aus- mit exothermischer Wirkung. Die Aktivierungsenergie der Adsorption des Zinks auf Na-Dickit war  $14,0 \text{ kcal mole}^{-1}$ .

Résumé- L'effet de la température, du pH, et du temps sur l'interaction du zinc avec des dickites saturées d'acide et de base a été investiguée. L'augmentation du pH a résulté en une augmentation de l'adsorption de zinc dans le domaine de haute concentration. L'adsorption a augmenté rapidement et puis lentement avec l'augmentation du temps d'interaction. La variation du taux d'échange et des demi-vies de réaction a suggéré un processus d'échange contrôlé par la diffusion de film et possiblement de particule, et par la suite, de processus de fixation. Ces déductions ont été appuyées par la nature des isothermes d'adsorption. La température a affecté l'adsorption dans les interactions exothermiques. L'énergie d'activation d'adsorption du zinc sur la Na-dickite était  $14.0 \text{ Kcal mole}^{-1}$ .