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THE THERMODYNAMICS AND SOME PRACTICAL ASPECTS OF ZINC ADSORPTION ON CALCITE, DOLOMITE, AND CALCIAN-MAGNESITE MINERALS

by

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SECTION I. THE THERMODYNAMICS OF ZINC ADSORPTION ON CALCITE, DOLOMITE, AND CALCIAN-MAGNESITE.

INTRODUCTION

Zinc is one of the essential elements required for the normal growth of plants. The total amount of zinc commonly occurring in soils is usually many times greater than that necessary to supply the needs of actively growing plants. The ability of the soil to "fix" zinc in form unavailable for plant use, however, has made the zinc deficiency disease an important plant nutrition problem in the major fruit and nut growing regions of the West. Fixation mechanisms which have been postulated as contributing to zinc deficiency include organic complexes, precipitation of insoluble inorganic salts, and strong zinc-clay interactions. It may be possible that in certain soils naturally occurring soil minerals, other than the clay minerals, may also exert an influence on the capacity of the soil to retain zinc.

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The accumulation of lime minerals is a distinguishing profile characteristic of soils in arid and semi-arid regions. These minerals include: calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and magnesite ($MgCO_3$). Despite the widespread occurrence of these minerals in the soil system, relatively few data exist which specifically isolate the interaction between cations in solution and the solid phase of the above-named lime minerals.

It is generally believed that the adsorptive capacity of a mineral soil is manifested primarily in the clay fraction. However, it may be possible that some modification of this concept may have to be introduced when considering relatively unweathered soil systems.

All crystalline phases of matter in the soil capable of existing in a finely divided state, when dispersed in solution, inherently possess an adsorption potential because of the unsaturated forces which exist at all interfaces. Therefore, perhaps calcium carbonate and the other slightly soluble lime minerals can be regarded as potential adsorption sites for certain ions. The contribution that these minerals make to the adsorptive capacity of the soil for a given ion will depend not only on the magnitude of the attractive force that exists for the given ion at the interface of the crystalline phase, but also on the percentage of the total specific surface area of the soil that is contributed by the mineral phase in question.

Although many factors obviously affect the availability of zinc in calcareous soils, the prominence of lime minerals in many western soils is indicative of the importance of the zinc-lime mineral relationship in the clarification of soil factors which affect the availability of zinc.

The objectives of the study reported here are: (1) to obtain a quantitative measure of zinc adsorption on calcite, dolomite, and magnesite, and (2) to develop a theoretical approach to the surface phenomenon by which it may be possible to thermodynamically define the adsorption of zinc in a lime mineral system.

REVIEW OF LITERATURE

Adsorption of zinc on calcium carbonate

The relations between calcium carbonate and the zinc ion have been investigated by Canals, Marignan, and Cordier (1949, 1950). They studied the adsorption of zinc from solution on finely powdered calcium carbonate in the concentration range of 5×10^{-7} to 50×10^{-7} g.-ion of zinc per liter. Their data revealed that at 57° C. the adsorption of zinc was slightly less than at 20° C., but when the temperature was raised to 90° and 100° C. the adsorption of zinc increased over the amount adsorbed at 20° C. The presence of copper ions in the system greatly reduced the adsorption of zinc. This investigation, although not designed to yield any estimate of the surface energetics involved in the adsorption of zinc on calcium carbonate, does indicate that calcium carbonate must be regarded as an adsorptive phase for the zinc ion.

Calcium carbonate and zinc deficiency

The possibility that calcium carbonate may act as an adsorptive phase in the soil was postulated by Leeper (1952) who concluded that in calcareous soils, calcium carbonate may be a strong adsorbent for heavy metals. The presence of calcium carbonate in the soil system does not necessarily indicate that a zinc deficiency hazard exists. On the contrary, calcareous soils of Utah, for example, seldom suffer from zinc deficiency (Thorne and Wann, 1950). Thorne, Laws, and Wallace (1942) have shown calcareous soils to contain greater amounts of available as well as total zinc. They concluded that during the soil forming process the finer textured, more basic calcareous soils of limestone origin retained zinc more strongly than the zinc deficient soils derived from more siliceous parent material. It was found that the siliceous parent material, from which the zinc deficient soils were formed, contained the same amount of zinc as was found in samples of the limestone parent material. A possible factor in the ability of a calcareous soil to retain zinc could well be the adsorptive potential which the calcium carbonate displays for the zinc ion.

The presence of adequate quantities of zinc for normal plant growth in calcareous soils is not a universal condition, for Leeper (1948) has reported that "the unavailability of both manganese and zinc is particularly found in calcareous soils." Thus, the relationship between the occurrence of zinc deficiency and the calcium carbonate in the soil is not clearly defined.

Thermodynamics of adsorption at a solid-liquid interface

The initial task in the development of a theoretical approach by which it may be possible to determine the thermodynamics of zinc adsorption on a lime mineral surface is the establishment of an adsorption process or "reaction" from which an expression for the change in free energy can be derived.

The literature revealed that, compared with adsorption at the solid-gas interface, relatively few attempts have been made to thermodynamically describe the energetics occurring at the solid-liquid interface.

Alexander and Johnson (1950) regarded the surface, A, as one phase and the solution, B, as another phase and considered adsorption as the distribution of a component between the two phases. When equilibrium is established:

$$u_s^A = u_s^B \tag{1}$$

where $u_s = u_s^0 + RT\ln a_s$ is the chemical potential of the solute molecule in a given phase. If an ideal system is considered, at constant temperature and pressure, it can be shown that the decrease in free energy, ΔF, of a solute going from phase B to phase A is:

$$\Delta F = -RT\ln K + RT\ln \frac{c_s^A}{c_s^B} \tag{2}$$

where c_s is the concentration of the solute in its respective phase, K is the equilibrium constant, R is the universal gas constant, and T is the absolute temperature. If the reaction begins with c_s^B in some defined standard state and terminates with c_s^A in some defined standard adsorbed state, then equation (2) reduces to:

$$\Delta F^o = -RT\ln K \tag{3}$$

where

$$K = \frac{c_s^A}{c_s^B} \tag{4}$$

In equation (3), ΔF^o is the standard free energy change of transferring a mole of solute from its standard state in phase B to its standard state in phase A.

The equilibrium constant, K, can also be written as:

$$K = \frac{\Gamma}{\tau\, c_s^B} \tag{5}$$

where Γ is the amount of adsorbed solute per unit surface area and τ is the thickness of the adsorbed layer. Equation (5) still assumes the ideal behaviour of the adsorbed molecules.

A correction for non-ideal systems was presented by Fu, Hansen, and Bartell (1948). They derived the expression:

(6) $\log f^A = (u_o^B - u_o^A / 2.3RT) + \log a^B - \log m^A$

where f^A is the activity coefficient of the adsorbed molecule, u_o^B and u_o^A is the standard chemical potential of the molecule in its respective phases, a^B is the activity of the molecule in the solution phase, and m^A is the molality of the adsorbed molecule in phase A, the adsorbed phase.

If the adsorbed molecules remain ideal, a plot of log m^A vs. log a^B should yield a straight line. The observed deviations from a linear plot permit the calculation of the activity coefficient of the adsorbate.

Bartell, Thomas, and Fu (1951), using the above criteria for the measure of the ideality of the adsorbed molecules, applied equation (5) to the "ideal" portion of their adsorption isotherms and obtained an equilibrium constant for the adsorption of butyl alcohol on graphite and blood char. They assumed that the thickness of the adsorbed layer was equal to the cross-sectional diameter of the adsorbed molecules. After calculating the equilibrium constant, the standard free energy of adsorption was obtained from equation (3) and the standard enthalpy, ΔH^o, of adsorption was calculated from adsorption data collected at different temperatures and using the relation:

(7) $$\Delta H^o = R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{K_2}{K_1}$$

where K_2 and K_1 are the calculated equilibrium constants at temperatures T_2 and T_1, respectively. The authors failed, however, to present a definite physical picture of the standard adsorption reaction which was described by their calculated thermodynamic properties, ΔF^o and ΔH^o.

The approach to the thermodynamics of adsorption from solution which is presented in the preceeding paragraphs is not considered completely adequate to describe the thermodynamics of ion adsorption on a heteropolar surface. In the theory developed by Alexander and Johnson (1950), the adsorption process is based on a molecular distribution between two phases. Thus both the cation and anion of an electrolyte are regarded as contributing equally to the free energy of adsorption. However, it is quite conceivable that when considering a strong electrolyte the relative location of a given ion within the force field of the adsorbing surface will determine that ion's contribution to the free energy of the process. Hence a theory based on molecular distribution between the surface phase and the solution phase may not give a true estimate of the energetics of ionic adsorption. Another disadvantage of this theory is that, unless one assumes an ideal system, the activity coefficient of the adsorbed molecule must be determined to arrive at the value of the standard free energy change.

A comprehensive review of the thermodynamics used in describing the process of dye interaction at the fiber-liquid interface is presented by Vickerstaff (1950). Basically only two systems form the foundation of the thermodynamics of adsorption of dye on fiber. With modifications, these two systems are made to fit the specialized conditions of various dyeing processes.

System 1. Dye attracted to the fiber-solvent interfaces without being adsorbed on specific sites and with the possibility of forming a multimolecular layer.

The adsorbed phase, A, is considered to be anywhere within the restraint of the surface forces. The distribution of adsorbed dye molecules around the fiber being essentially described by a Guoy type diffuse double layer. When the reactants and products are in their defined standard states and equilibrium is established isothermally with the solution phase, B, the standard free energy is:

$$(8) \qquad -\ \Delta F^{o} = RT\ln \frac{[D]_{A}}{V} - RT\ln [D]_{B}$$

where $[D]_A$ is the concentration of unionized adsorbed dye molecules on the fiber in moles per kilogram dry fiber, $[D]_B$ is the concentration of dye in the solution phase in moles per liter, and V is the total volume of the surface phase in liters per kilogram dry fiber. The activity coefficient of the dye molecule in both phases is assumed one. This system is of the same nature as was previously described by Alexander and Johnson (1950).

If the dye is an ionizable salt, e.g., Na_zD, then the maintenance of electrical neutrality in the system requires that both the cation and anion must be transferred to the adsorbed phase A, thus:

$$(9) \qquad -\ \Delta F^{o} = RT\ln \frac{[D^-]_{A}}{V}\left[\frac{Na^+}{V}\right]^{z}_{A} - RT\ln [D^-]_{B}\ [Na^+]^{z}_{B}$$

where $[Na^+/V]_A$ is the concentration of sodium ion in the fiber in moles per kilogram of dry fiber and $[Na^+]_B$ is the concentration of sodium ion in moles per liter in the solution phase. D^- represents the dye anion and has the same dimensions as the dye molecule in equation (8). Equation (9) indicates that in the adsorbed state, A, both the cation and anion of the dye molecule are adsorbed equally and that the fiber exhibits no specificity for either ion.

System 2. Dye adsorbed on specific sites at the fiber-solvent interface in a monomolecular layer.

Here the fiber contains certain reactive sites which are capable of attracting dye molecules. When the site is occupied, it is no longer available for further adsorption. The sites are regarded as being so far apart as to eliminate interaction between adsorbed molecules. With these conditions, Fowler and Guggenheim (1939) calculated on the basis of statistical mechanics that the activity of the molecules in the adsorbed state may be represented by $\theta/(1 - \theta)$, where θ is the fraction of sites occupied by the dye. At constant temperature, the free energy change of the defined standard reaction involving unionized dye molecules is:

$$(10) \qquad - \Delta F^{\circ} = RT\ln \frac{\theta}{(1 - \theta)} - RT\ln [D]_B$$

R, T, and $[D]_B$ have the same significances as previously described. The standard adsorbed state is usually defined as $\theta = 0.5$. Vickerstaff (1950) derived a Langmuir-type adsorption isotherm starting with equation (10). When the dye is an ionizable salt, Na_zD, and if one can assume independent sites for the positive and negative ions with no interaction between sites, the free energy change of a defined standard reaction is written as:

$$(11) \qquad - \Delta F^{\circ} = RT\ln \left[\frac{\theta_{D^-}}{1 - \theta_{D^-}}\right] \left[\frac{\theta_{Na^+}}{1 - \theta_{Na^+}}\right]^z - RT\ln \left[Na^+\right]_B^z \left[D^-\right]_B$$

Here, since one assumes two distinct types of surface sites, the defined standard free energy change must take into account the surface sites occupied by both type ions of the ionized dye molecule. As written, equations (8) through (11) all assume ideal fiber-dye systems.

The standard heat of dyeing is calculated from the following relation between the absolute temperature and the standard free energy change:

$$(12) \qquad \Delta H^{\circ} = \frac{\partial (\Delta F^{\circ}/T)}{\partial (1/T)}$$

From the standard free energy and the standard heat of dyeing, the standard entropy of dyeing, ΔS°, can be calculated by the equation:

$$(13) \qquad \Delta F^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

The entropy of dyeing is regarded as a measure of the degree of orientation and restraint that the dye molecules suffer upon being adsorbed. However, no data for entropy change are presented.

In the systems presented by Vickerstaff (1950), adsorption is again considered as a transfer of a component between two phases. No attempt was made, in the case of the ionizable dye salt, to differentiate the ability of the different type ions to influence the free energy of the adsorption process. Throughout the discussion, the assumption of ideal dye systems also remains as an inherent source of error and difficulty when non-ideal systems are considered. Thus the disadvantages of using the theory of Alexander and Johnson (1950) are reproduced when using the methods as outlined by Vickerstaff (1950).

Although not used at a solid-liquid interface phenomenon, the approach developed by Kemball and Rideal (1946) for the determination of the thermodynamics of organic vapour adsorption on mercury might serve as a guide in the problem of the thermodynamics of ionic adsorption at a solid-liquid interface. By starting with a vapour at its standard pressure, P^o, and by varying the pressure to a value, $P_{eq.}$, which is in equilibrium with a chosen standard adsorbed state, the free energy change for a process conducted at constant temperature is given by:

$$\Delta F = RT\ln \frac{P^o}{P_{eq.}} \tag{14}$$

The adsorption or transfer of the vapour molecules at equilibrium pressure, $P_{eq.}$, to the standard adsorbed state is not accompanied by a change in free energy, since at equilibrium:

$$\Delta F_{gas} = \Delta F_{adsorbed} \tag{15}$$

Thus the total isothermal process of transferring a molecule from its standard vapour state to its standard adsorbed state is given by equation (14), which is equivalent to the standard free energy of adsorption.

The standard adsorbed state used by Kembal and Rideal (1946) was a constant 2-dimensional surface pressure expressed in dynes/cm. This pressure is related to a given amount of surface coverage by (deBoer, 1953) $FN = \sigma RT$, where F is the 2-dimensional pressure in dynes/cm., N is Avogadro's number, σ is the number of molecules adsorbed/cm.^{2} of surface, R is the molar gas constant in ergs/degree, and T is the absolute temperature. By finding the standard free energy change of adsorption at two temperatures, T_1 and T_2, the standard entropy of adsorption can be found:

$$(16) \qquad -\Delta S^o = \left[\frac{\partial(\Delta F^o)}{\partial T}\right]_p$$

The standard heat of adsorption can then be calculated from:

$$(17) \qquad \Delta F^o = \Delta H^o - T\Delta S^o$$

The two properties, ΔH^o and ΔS^o are derived for the mean temperature $(T_1 = T_2)/2$.

The use of an equation analogous to equation (14) for the standard free energy of a defined adsorption process at a solid-liquid interface would enable one to obtain the free energy change of the defined process without knowledge of the activity of the adsorbed ion or molecule, since it would be included in the definition of the standard adsorbed state. This approach, although eliminating the hazard of determining the activity coefficient of the adsorbate, still does not take into account any specific energy effects that may be caused by the relative distribution of ions near the surface, since the theory was developed for the adsorption of neutral gas molecules.

The work of Benton and Elton (1953) deals with the adsorption and distribution of ions in the double layer and their effect on the free energy of adsorption. They obtained adsorption data of electrolytes on silica and with the help of electrokinetic data calculated the number of ions in the fixed and diffuse portions of the double layer. This enabled them to determine the energies of adsorption of the individual ionic species involved.

The total number of ions adsorbed on the silica, A_t, is divided between the fixed and diffuse layers. The number of positive ions, n_+^D, and the number of negative ions, n_-^D, in the diffuse layer are given for a uni-univalent electrolyte by (Graham, 1947):

$$n_+^D = -2\lambda n_+^B \left[1 - \exp(-e\Psi_d/2kT) \right] \tag{18}$$

and

$$n_-^D = -2\lambda n_-^B \left[1 - \exp(e\Psi_d/2kT) \right] \tag{19}$$

where $\lambda = (EkT/ 8\pi\ n^B e^2)^{\frac{1}{2}}$, E = the dielectric constant, k = Boltzman's constant, T = the absolute temperature, n_+^B and n_-^B are the bulk concentrations of the positive and negative ions per $cm.^3$, respectively, e = the electronic charge, Ψ_d = the potential at the boundary between the fixed and diffuse layer, and $n^B = n_+^B + n_-^B$. The authors assume that the zeta potential, ζ, coincides with Ψ_d in equations (18) and (19). They did, however, recognize the possible error involved in making this substitution.

Equations (18) and (19) are based on the Boltzman distribution function which is valid only for ideal systems, the only work considered being the electrical work involved in transporting an ion from the bulk solution into the diffuse layer. Thus the estimation of the ion distribution in the diffuse layer will suffer accordingly as the system deviates from ideality.

The number of ions of species i per $cm.^2$, n_i^F, adsorbed in the fixed layer was calculated from:

$$n_i^F = A_{ti} - n_i^D \tag{20}$$

The values of n_i^D were obtained from equations (18) and (19) with $\psi_d = \zeta$.

By using the condition that at equilibrium the electrochemical potential of a given ionic species is equal in all phases in which it is soluble (Guggenheim, 1950), and by arbitrarily dividing the electrochemical potential of the ionic species involved in the adsorption phenomena into its chemical and electrical portions, the following equation was derived for the free energy of adsorption, E_i, per gram ion of species i.

$$E_i = RT\ln \frac{n_i^F}{n_i^B} - Z_i F \zeta \tag{21}$$

where Z_i is the valence of species i and F is a faraday of electricity.

In equation (21) Benton and Elton assume that the zeta potential also represents the average electrical potential in the fixed layer. This use of the zeta potential as the measure of the average potential within the fixed layer is regarded by the author as a hazardous assumption, since it implies that a direct and known relation exists between the potential that exists at the plane of shear and the surface potential of the solid under consideration. Because of the uncertainty attached to the significance of the zeta potential (Verwey and Overbeek, 1948), the validity of this assumption is not without question. Furthermore, the actual division of the electrochemical potential of an ionic specie into its components is regarded by some (Guggenheim, 1950) as having no physical meaning. It is noted, that the authors only regard ions that enter into the fixed portion of the double layer as contributing to the free energy of adsorption.

The review of literature revealed a surprising lack of data pertaining to the thermodynamics of ionic adsorption at the solid-liquid interface. The study of Benton and Elton (1953) was the only study which attempted to deal specifically with the free energy of adsorption of individual ions. The nature of their assumptions, however, tends to limit the usefulness of their approach.

The determination of the thermodynamics of zinc adsorption on lime minerals requires that a suitable theory be developed which not only correlates with the data collected, but one which is also thermodynamically rigorous in its derivation.

THEORY

In this study, Stern's modification on the Guoy-Chapman theory (Kruyt, 1952) of the electro-chemical double layer is used to describe the interaction of the zinc ion with lime minerals. For this purpose, specific and non-specific adsorption of ions from solution by ionic crystals are to be defined.

Non-specific adsorption occurs when no particular chemical or geometric relationship exists between the ions in solution and the adsorbing surface. The adsorption process is dominated by the charge that exists at or near the surface of the crystal. Adsorption in this sense is not truly a surface interaction, but it is regarded as essentially an ionic re-arrangement or orientation whose function is the maintenance of electrical neutrality in the system. Non-specific adsorption occurs predominately in the region of the double layer where the decline of the electric potential follows an exponential type curve, i. e., in the diffuse double layer.

Specific adsorption, on the other hand, is dominated by the affinity of the surface for a given ion and is considered an ion-lattice interaction. A relatively strong chemical or favorable geometric relationship can commonly be found between the adsorbed ion and the adsorbing surface. In specific adsorption, the surface charge plays a less important role in determining which ion is to be adsorbed than in the case of non-specific adsorption. The deciding criteria for adsorption is the free energy of attraction that exists between an ion and a given surface. It is helpful to think of the free energy change, ΔF, accompanying an isothermal adsorption process as determined by two factors: one is the enthalpy change, ΔH, related to the chemical forces; the other is the entropy change, ΔS, primarily related to the geometric freedom of the particles. Thus an ion whose charge has the same sign as the surface can be specifically adsorbed if the force of attraction is great enough to overcome the existing electrical barrier presented by the surface charge, and if its corresponding loss in entropy on being restrained by the surface forces is not so great as to outweigh the effect of the attractive forces. Specific adsorption occurs in a region which includes the surface layers of the crystal lattice as well as a monomolecular layer of ions or molecules in direct contact with the surface. The latter, outermost part of the specific adsorption region is known as the Stern layer. Here the electrical potential drop is actually unknown although it is usually considered as equivalent to that of a plane parallel condenser. This definition includes the possibilities that specifically adsorbed ions may be incorporated into the lattice or may be held in a partially hydrated state adjacent to the lattice.

In many cases the Fajans-Paneth rule (Fajans, 1931) may be used to get a first approximation of the specificity that may exist between the ion in solution and a given ionic lattice. This rule may be stated as follows: ions which form the least soluble or least dissociated compounds with oppositely charged ions on the surface will be most strongly adsorbed. Consider a system in which a zinc chloride solution is in contact with a positively charged carbonate mineral surface. Application of the Fajans-Paneth rule allows one to predict that the zinc ions may be specifically adsorbed on the carbonate mineral surface since the zinc and carbonate ions are known to form a relatively insoluble compound. The predicated adsorption process can be schematically written as:

$$(22) \qquad \underline{(XCO_3)^{n+}} + yZn_{aq}^{++} + 2yCl^{-}_{aq} \rightleftharpoons \underline{(XCO_3)^{n+}yZn^{++}} \Big| \; 2yCl^{-}$$

where $\underline{(XCO_3)^{n+}}$ represents the positively charged surface of an insoluble alkaline earth carbonate, X is a divalent alkaline earth, and y is any fractional number. It is postulated by the above formulation that the zinc ion is specifically adsorbed while the chloride ion is non-specifically oriented in the diffuse double layer since no particular chemical or geometric relationship is evident between the chloride ion and the crystal lattice in question.

To express the above adsorption process in a quantitative way, we evaluate the free energy change corresponding to the transfer of zinc and chloride ions from the bulk solution into the appropriate parts of the double layer or lattice. Our goal is to understand how the properties of the individual ions influence the driving force, ΔF^{o}, of the net adsorption process. Unfortunately, the necessity of preserving electrical neutrality makes it impossible to study a process in which only the cation or anion is adsorbed. Thus there is an inherent difficulty in deciding how much each kind of ion contributes to the net value of ΔF^{o}. It is suggested that this difficulty can be largely avoided if one assumes that the counter ion is non-specifically adsorbed, in the sense defined above.

The contribution that non-specific adsorption of a counter ion makes to the free energy of the system is now considered. Verwey and Overbeek (1948), regarding the diffuse layer as being part of the solution phase, concluded that the electrical energy liberated is just balanced by the decrease in entropy of the ion that occurs when it is transferred, at constant temperature and pressure, from the bulk solution to a region of higher concentration in the diffuse layer. Thus the net contribution of the oriented counter ions in the diffuse layer to the free energy of a system (neglecting PdV work) is zero. Strictly, this result can only apply to the limiting case in which the counter ion has the same close range environment in the diffuse layer as in the bulk solution. We shall define the ideal non-specific adsorption or orientation process as one which obeys the above condition. The distinction between ideal and non-ideal orientation has been neglected in this study because it is probably of minor importance when the specific adsorption of the other ion is strong.

The assumption that the chloride ion is ideally oriented in the diffuse layer of lime minerals and hence does not contribute to the free energy of the adsorption process seems justified because the chlorides of calcium, magnesium, and zinc are all soluble strong electrolytes and also because the dimensions and charge of the chloride ion are too far removed from those of the carbonate ion to fit into the lime mineral lattice. The radii of the chloride and carbonate ion are 1.81 Å and 1.25 Å, respectively (Evans, 1948).

With this assumption in mind, chloride can be eliminated from equation (22) and the free energy change, ΔF, may be determined from the following:

$$(23) \qquad \underline{(XCO_3)^{n+}} + Zn^{++}_{aq} \xrightleftharpoons{\mu\ \text{constant}} \underline{(XCO_3)^{n+}\,Zn^{++}{}_{\theta}}$$

Here μ represents the ionic strength of the solution and $\underline{(XCO_3)^{n+}Zn^{++}{}_{\theta}}$ is a surface complex or quasi-solid surface phase whose composition and activity, a_θ, is a function of fractional surface coverage θ. A sufficient measure of θ is the number of millimoles of zinc adsorbed per unit area of crystal surface. The activity, a_x, of the solid mineral phase, $(XCO_3)^{n+}$, also may depend on θ to the extent that changes in the electrical charge on the lattice affect its free energy.

For any process the free energy change is:

$$(24) \qquad \Delta F = \sum(n_i\,\bar{F}_i)_{\text{products}} - \sum(n_i\,\bar{F}_i)_{\text{reactants}}$$

where n_i equals the number of moles and $\bar{F}_i = \bar{F}_i^{\,o} + RT\ln a_i$ is the partial molal free energy of component i. Each of the two solid phases at $P = 1$ atmosphere has a fixed activity, as long as θ is fixed. It is customary to say that these solids are then in their standard states at unit activity, i. e., $\bar{F}_i = \bar{F}^o_{\ i}$ and $a_i = 1$.

Thus for the net process of equation (23) at $P = 1$ atmosphere we have:

$$(25) \qquad \Delta F_\theta = (\ \bar{F}^o_{\ \theta} - \bar{F}^o_{\ x} - \bar{F}^o_{\ Zn^{++}aq}) - RT\ln a_{Zn^{++}aq}$$

where ΔF_θ refers to the process conducted at a fixed θ. Here P, T, and R have their usual significances. At equilibrium, with P and T fixed, the two solid phases are in stable contact with each other and with a definite concentration of zinc ion in solution; the general condition for this state requires that $\Delta F_\theta = 0$. Hence:

$$(26) \qquad (\ \bar{F}^o_{\ \theta} - \bar{F}^o_{\ x} - \bar{F}^o_{\ Zn^{++}aq}\ ) = \Delta F^o_{\ \theta} = RT\ln a_{Zn^{++}aq,eq.}$$

where "eq." refers to equilibrium conditions. This is equivalent to:

$$(27) \qquad \Delta F^o_{\ \theta} = RT\ln(\ m_{Zn^{++},eq.}\ \gamma_{\ Zn^{++},eq.})$$

where the "m" and "γ" refer to the molality and activity coefficient, respectively, of the zinc ion in equilibrium with the standard surface complex and $\underline{(XCO_3)}^{n+}$.

If the temperature coefficient of ΔF^{o}_{θ} is determined, one can evaluate the standard entropy of adsorption, ΔS^{o}_{θ}, and the standard heat of adsorption, ΔH^{o}_{θ}, through the well-known relations:

$$-\Delta S^{o}_{\theta} = \left[\frac{\partial(\Delta F^{o}_{\theta})}{\partial T}\right]_{P} \tag{28}$$

ΔG

and

$$\Delta H^{o}_{\theta} = \Delta F^{o}_{\theta} + T\Delta S^{o}_{\theta} \tag{29}$$

Thus, by measuring at various temperatures the concentration of just the zinc ions in a solution equilibrated with the two solid phases, adsorbent and standard surface complex, it is possible to evaluate both the geometrical and energetic contributions of the driving force of the standard adsorption process. This standard process or "reaction" is defined through equation (23) as one in which zinc ion starts at its standard state of unit activity in the bulk solution, reacts with the surface of a given mineral in its standard state, and terminates with zinc in a standard adsorbed state. The standard adsorbed state is defined as a distinct phase existing as a surface complex of definite composition and unknown thickness, i. e., corresponding to some arbitrary fixed fractional surface coverage θ. For all three minerals in this study, θ is fixed at the convenient figure of 1.00×10^{-7} m.e. of zinc ion adsorbed per cm.^{2} of surface area, thus providing a rational basis of comparing surfaces. The importance of specifying a constant ionic strength, μ, in defining the standard process will be appreciated when it is realized that the value of μ establishes the activity coefficient, γ, of the zinc ion; it also determines the solubility of the mineral phase, thereby influencing the surface area; and for a given surface potential the structure of the double layer depends on μ. The individual activity coefficients of the zinc ion at various temperatures were calculated from the known ionic strength by a modified form of the Debye-Huckel theory as presented by Kortum and Bockris (1951). It is understood that the re-orientation of the counter ions in the diffuse layer always accompanies the standard adsorption reaction even though the anion does not appear in equation (23). The re-orientation does not contribute to the values of ΔF^{o}_{θ}, however, if our assumptions are valid.

MATERIALS AND METHODS

All minerals used in this study were obtained in their natural crystalline state[1] and prior to use were ground for approximately 40 hours in a ball mill charged with flint pebbles.

The surface area of the lime minerals

The surface area of the lime minerals used in this study was determined by the ethlylene glycol retention method as described by Bower and Gschwend (1952). Prior to the surface area measurements the minerals were equilibrated at 30° C. in a sodium chloride solution of 0.01 ionic strength and then filtered. The pre-treatment of the lime minerals in the sodium chloride solution permitted the surface area measurements to be taken under conditions similar to those that existed in the mineral systems when the adsorption isotherm data were collected. A sample of known surface area, obtained from the United States Salinity Laboratory, Riverside, California, was included in each batch of lime mineral samples whose surface area was to be determined. This was done to verify the point on the glycol retention curves where it was assumed that the monolayer of ethylene glycol was formed. The amount of glycol retained by duplicate samples was reproducible within 5 to 6 per cent. The amount of ethlylene glycol retained by the filtered minerals is shown in figure 1. The specific surface area, calculated from the data of figure 1, was 6.78 m^2/g. for calcite, 11.9

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[1] The calcite was obtained from Coleman and Bell Co., Norwood, Ohio, and was a standardizing frade Iceland Spar. The dolomite and calcian-magnesite were obtained from Ward's Natural Science Est., Inc., Rochester, New York.

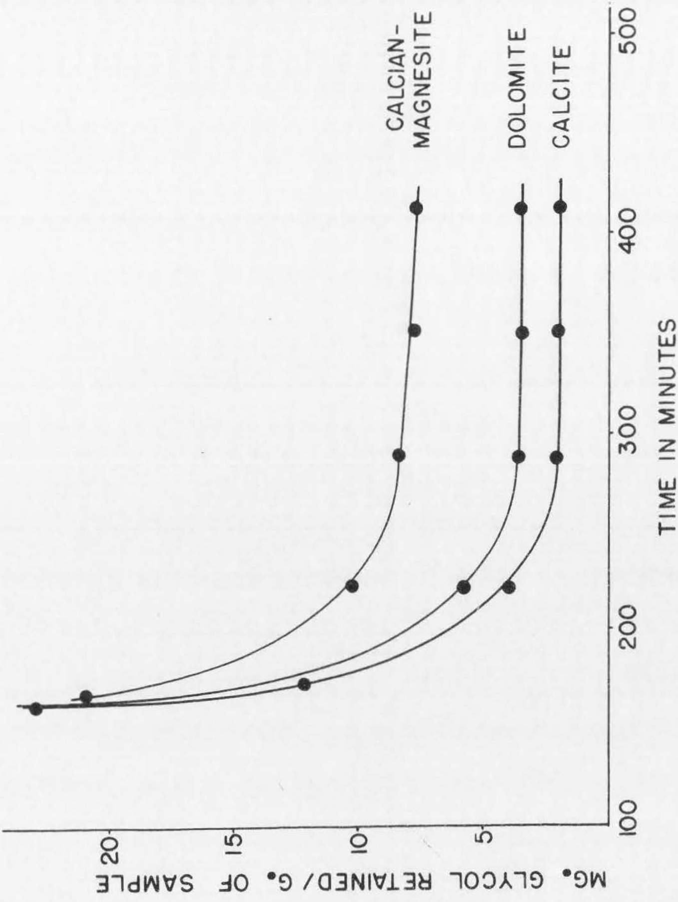

Figure 1. The retention of ethylene glycol by lime minerals

m^2/g. for dolomite, and 25.8 m^2/g. for calcian-magnesite.

Qualitative estimation of the surface charge of lime minerals

The zeta potential of the lime mineral used was qualitatively determined by using the principal of electro-osmosis (Kruyt, 1952). Two pieces of straight glass tubing, with an inside diameter of 4 mm., were connected for convenience by a piece of plastic tubing, 3 inches long, which permitted the system to be bent to resemble a U-tube. The mineral whose zeta potential was to be measured was packed to form an immovable mineral plug in the section of plastic tubing. A dispersing liquid was carefully introduced into both glass tubes until the mineral plug was thoroughly moistened. More liquid was then added until it reached the same level in both arms of the simulated U-tube. An electrode was inserted in the dispersing liquid in each tube and a 1 kilovolt potential was placed across the immovable mineral plug. The source of potential was a Nuclear Model 165 scaler (Nuclear Instrument and Chemical Corp., Chicago, Ill.) The dispersing liquid then assumed the charge opposite to the zeta potential of the mineral in the plug and rose in the glass tube which had the proper electrode. The apparatus was calibrated using negatively charged soil and clay as the porous plug, the dispersing liquid rising in the tube containing the negative electrode. The charge of the zeta potential using both re-distilled water and 0.01 N sodium chloride solution as the dispersing liquid was positive for all three lime minerals. It was assumed that the surface potential of the minerals had the same charge as the zeta potential, i. e., positive.

The chemical composition of the lime minerals

One-tenth gram of each mineral used in the study was treated with 0.1 N hydrochloric acid and heated until all acid-soluble material was dissolved. The solution was then diluted to 500 ml. with re-distilled water and analyzed for calcium and magnesium by titration with ethlyenediaminetetraacetate (United States Department of Agriculture, 1954). The ratio of magnesium to calcium found in solution was used as the ratio that existed in a given mineral.[2] No trace of magnesium was found in the dissolved calcite sample. Dolomite had a Mg/Ca ratio of 0.87, and calcian-magnesite (Dana, 1951) had a Mg/Ca ratio of 17.3. The calcian-magnesite will be referred to as ca-magnesite in the remainder of the study.

The water suspension pH of each mineral in equilibrium with the atmosphere was measured with a glass electrode and a Beckman Model H 2 pH meter (Beckman Instrument, Inc., South Pasadena, California). The pH measurements of the minerals were as follows: calcite, 8.42; dolomite, 8.65; ca-magnesite, 8.88. The pH of the minerals equilibrated with a sodium chloride solution which had an ionic strength of 0.01 was as follows: calcite, 8.28; dolomite, 8.48; ca-magnesite, 8.42. The lower pH values in the higher ionic strength systems is probably due to the reduced activity of the hydroxyl ions which are produced during the hydrolysis of the lime minerals.

Experimental procedure

A zinc chloride solution tagged with radioactive Zn^{65} was titrated with 0.010 N sodium hydroxide to the pH of a water suspension of the given mineral in equilibrium with the atmosphere. The solution was digested for 1 hour at 60° to 70° C., to help coagulate the precipitate, and cooled to room temperature (20°-24° C.) The pH was re-adjusted and the solution was filtered through Whatman No. 42 filter paper to

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[2] Analyses of the lime mineral solutions were done by the Soil Testing Laboratory, Campus.

remove the precipitated zinc hydroxide. The filtrate served as a source of tagged zinc ions. The concentration of zinc in the filtrate was determined by measuring the Zn^{65} activity in a given aliquot and comparing it with a standard of known zinc concentration.

Five milligrams of ground mineral were put in each of several 125 ml. Pyrex Erlenmeyer flasks and treated with varying amounts of zinc. The total volume of the system was maintained at 60 ml., and the ionic strength was kept constant at 0.01 by the addition of a sodium chloride solution. The suspensions were shaken at constant temperature until equilibrium was established. The temperature was maintained constant by partially submerging the Erlenmeyer flasks in a water bath. The temperature of the bath was controlled by an Aminco "Quikset" bi-metallic thermoregulator (American Instrument Co., Silver Spring, Md.) which had a sensitivity of 0.05° C. A mercury capillary tube thermometer was used to measure the temperature of the water bath. The thermometer was factory calibrated and had a range of 0° to 50° C. with 0.1° subdivisions. The mineral suspensions were quantitatively removed from the flasks and filtered under vacuum through three thicknesses of Whatman No. 42 filter paper in a Tracerlab Model E-8A stainless steel filtering apparatus (Tracerlab Inc., Boston, Mass.) The filtered suspensions were first washed with re-distilled water, then with 95 per cent alcohol to remove any trace of solution which may have been retained by the mineral suspension. The filter paper discs upon which the suspensions were collected were removed from the filtering apparatus and the mineral analyzed for Zn^{65}. The amount of zinc adsorbed on duplicate samples was reproducible within 5 per cent. Corrections were made on all data for zinc adsorption on the filter paper and on the Erlenmeyer flasks, as will be discussed later. After all corrections were made on the adsorption data, the equilibrium concentration of zinc ion was obtained by subtracting the amount of zinc adsorbed from the known amount of zinc initially added to the system. All water used throughout the study was re-distilled in Pyrex.

The rate of zinc adsorption on lime minerals

The procedure used to measure the rate of adsorption of zinc on a given mineral was identical to the method described above for obtaining adsorption isotherm data. The exception was that a given mineral was treated with only one concentration of zinc, i. e., 3.3×10^{-6} moles/liter, and that the adsorption of zinc was measured against time. The rate of adsorption was measured at 25.1° C., which was the lowest temperature used in obtaining adsorption data. At this temperature the rate of zinc adsorption on the mineral surface was assumed to be lower than the rate of adsorption at the higher temperatures used in the study (Glasstone, 1946). The results of zinc adsorption measured against time are shown in figure 2. The adsorption equilibrium, at 25.1° C., was reached in 6 hours in the calcite system, 60 hours in the dolomite system, and 48 hours in the ca-magnesite system.

Zinc adsorption on filter paper

To find the amount of zinc retained by the filter paper in the filtering apparatus, adsorption isotherms were run on Whatman No. 24 filter paper.

Three filter paper discs were placed in the stainless steel filtering apparatus and 60 ml. of tagged zinc solution, maintained at an ionic strength of 0.01 with sodium chloride, was filtered. The concentration of tagged zinc was varied to obtain an adsorption isotherm. The filter paper discs were washed with water, then with 95 per cent alcohol. The

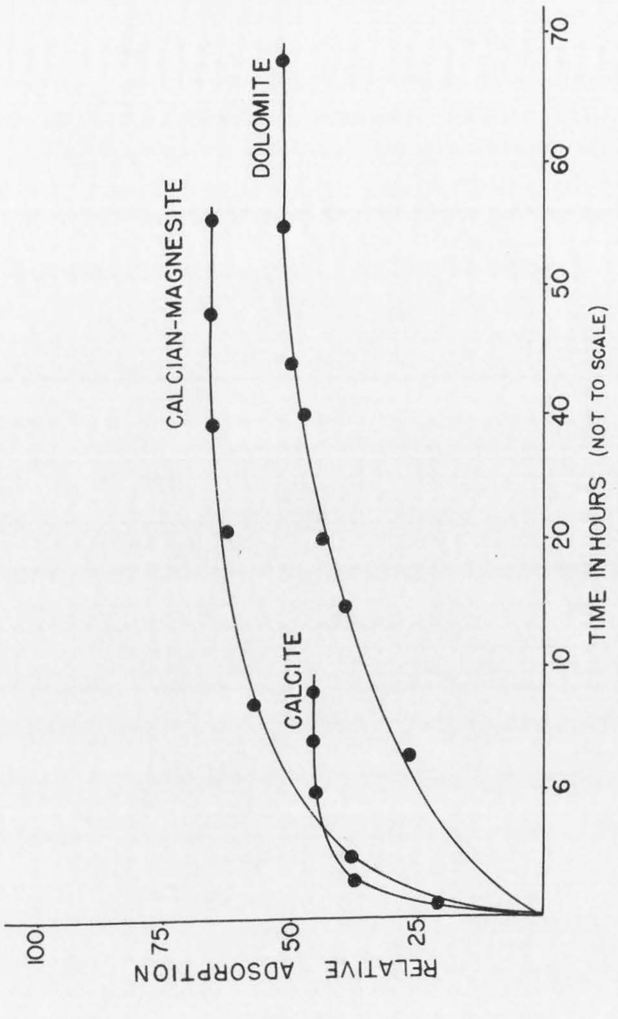


Figure 2. The rate of zinc adsorption on lime minerals at 25.1° C.

discs were removed from the filtering apparatus and their activity measured. Varying the pH of the zinc solution between 8.2 and 8.5 did not noticeably influence the adsorption of zinc by the filter paper. The data in figure 3 represent the adsorption at pH 8.38 which is the intermediate equilibrium pH of the lime minerals equilibrated in a system with an ionic strength of 0.01.

During the experimental procedure, used in obtaining adsorption isotherm data from the mineral systems, the activity measurement of the filtered mineral suspension included the total adsorption of zinc on the mineral plus the adsorption of zinc on the filter paper used in the filtering apparatus. By substracting the total measured amount of zinc adsorbed from the amount of zinc initially added to the system, an estimate could be made of the equilibrium concentration of zinc in a given mineral filtrate. The knowledge of the equilibrium concentration of zinc permitted an appropriate correction factor to be obtained from the adsorption isotherm shown in figure 3. This correction factor was subtracted from the total adsorption of zinc on the mineral and the filter paper discs. The amount of zinc adsorbed on the mineral was then obtained.

Zinc adsorption on Erlenmeyer flasks

The zinc adsorption on the flasks was determined because zinc ions are in contact with the inside surfaces of the Erlenmeyer flasks during periods of shaking.

Various amounts of tagged zinc solution were added to randomly selected Erlenmeyer flasks which were used during the study. The total volume of the zinc solution was kept at 60 ml. and the ionic strength maintained at 0.01 by the addition of a sodium chloride solution. The

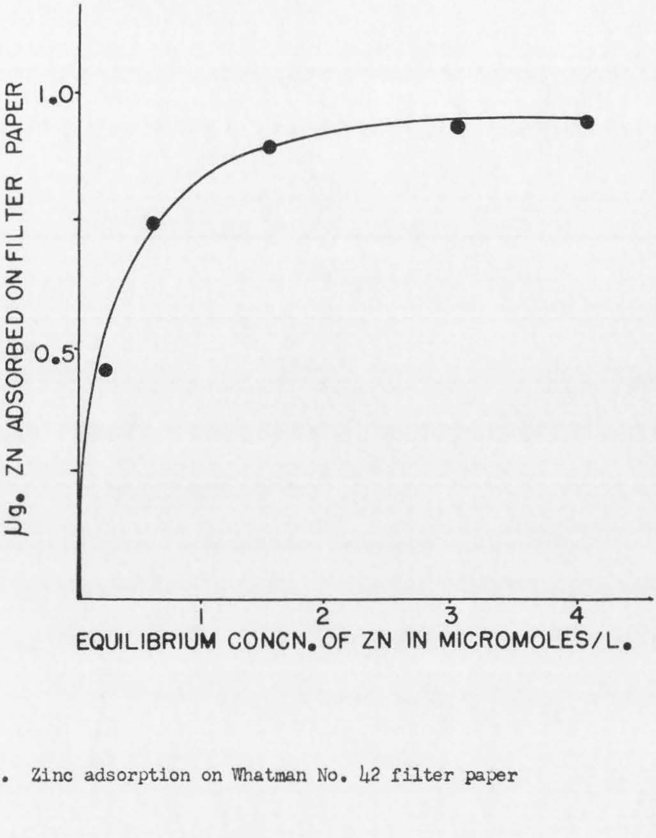


Figure 3. Zinc adsorption on Whatman No. 42 filter paper

pH of the solutions was kept at approximately 8.38 and the flasks were shaken for 6 hours at 30.0° C. Aliquots were taken from the flasks, evaporated under a heat lamp, and the activity measured. The difference between the concentration of zinc initially added to the flasks and the amount in solution after shaking was regarded as the amount of zinc adsorbed on the walls of the flasks. The average zinc adsorbed on the Erlenmeyer flasks in three determinations is shown in figure 4. Difficulty was encountered in maintaining a constant pH in the unbuffered systems during periods of shaking. The variation in pH between replications after shaking was from 0.2 to 0.3 units. The effect of temperature on the adsorption of zinc on the flask walls was not more thoroughly investigated since it was thought that the variation in the pH of the zinc solution precluded the possibility for greater accuracy in the effect of temperature on adsorption.

The correction for zinc adsorption on the Erlenmeyer flasks was applied after the amount of zinc adsorbed on a given lime mineral and the apparent equilibrium concentration of zinc were obtained. The apparent equilibrium concentration of zinc was calculated by subtracting the amount of zinc adsorbed on the mineral from the amount initially added to the system. From this apparent equilibrium concentration, the amount of zinc adsorbed on the flasks was obtained from figure 4. The amount of zinc adsorbed on the flasks was subtracted from the apparent equilibrium concentration to arrive at the "true" equilibrium concentration of zinc in a given lime mineral system.

Radioactivity measurements

All radiozinc was obtained from the Oak Ridge Laboratories of the Atomic Energy Commission. It was received in the form of zinc chloride and was assayed as 99 per cent pure. Working solutions of Zn^{65} were

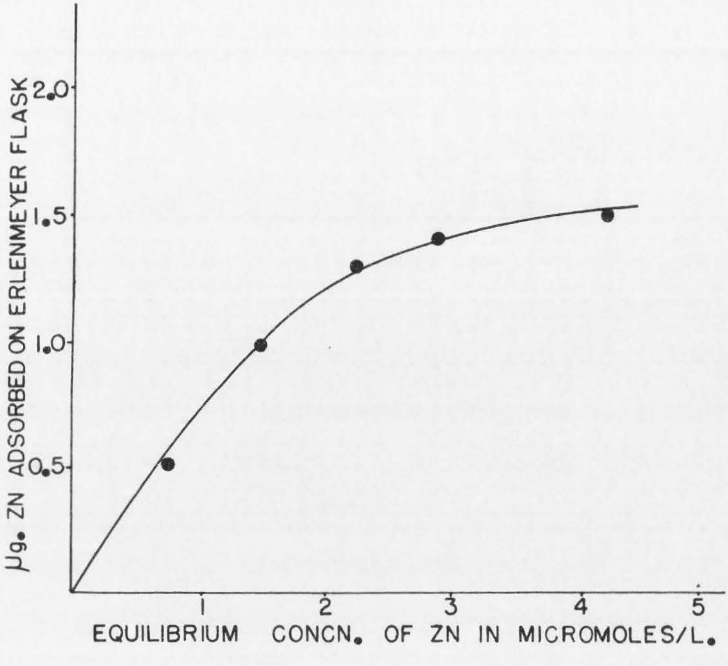


Figure 4. Zinc adsorption on Pyrex Erlenmeyer flasks

made by dilution of 1 part isotopic zinc chloride to 4 parts stable zinc chloride.

All radiation measurements were made with a Nuclear Model DS-1 scintillation detector supplied with a sodium iodide-thallium activated crystal. This detector is sensitive to gamma radiation. Because of the low resolving time of 20 x 10^{-6} seconds, the counts lost during a single radiation measurement were always less than 0.2 per cent of the counting rate. Thus no correction was made on the data for coincidence loss. By detecting only the gamma component of Zn^{65} radiation, the need for self adsorption corrections was also eliminated. All activities measured were compared with a standard of known zinc concentration. The standard used had the same pile date as the zinc used in the working solution; hence no correction was made on the data for activity decay. The statistical counting "error" calculated as the standard deviation varied between 1.8 to 1.25 per cent for all samples measured.

RESULTS AND DISCUSSION

Figure 5 (see Appendix A for tables of numerical data) shows the adsorption of zinc on calcite and the effect of temperature on this reaction. The adsorption decreases with increasing temperature, indicating an exothermic process. The adsorption isotherms indicate a region of surface saturation followed by increased adsorption at an equilibrium concentration of approximately 4.3×10^{-6} M. Since multilayer adsorption at a solid-liquid interface is quite rare (deBoer, 1953), the final increase in adsorption may be attributed to a second type of adsorption site in the Stern layer which becomes important as the concentration of zinc ion exceeds the saturation of type 1 sites. Only the surface phase corresponding to type 1 sites will be considered in this study. The formation of zinc carbonate is not possible because the activity of the zinc ion is below that required to precipitate zinc carbonate in a calcite system, according to the known solubility products and activity coefficients.

Figure 6 (see Appendix A) represents the adsorption of zinc on dolomite. The surface reaction differs noticeably from the reaction that occurred in the calcite system. No surface saturation is evident in the concentration range of the zinc used and an increase in temperature causes an increase rather than a decrease in the adsorption of zinc, thus indicating a distinct difference in the relation of the zinc ion to the dolomite surface as compared with the calcite surface.

Data collected in the ca-magnesite system are shown in figure 7

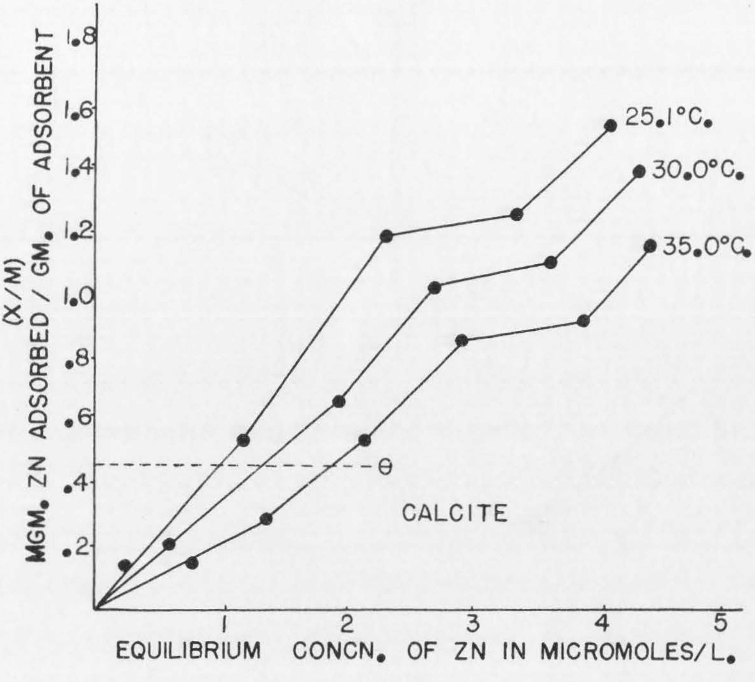


Figure 5. The effect of temperature on the adsorption of zinc by calcite. θ corresponds to 1 x 10^{-7} me. zinc/cm^2 of calcite surface.

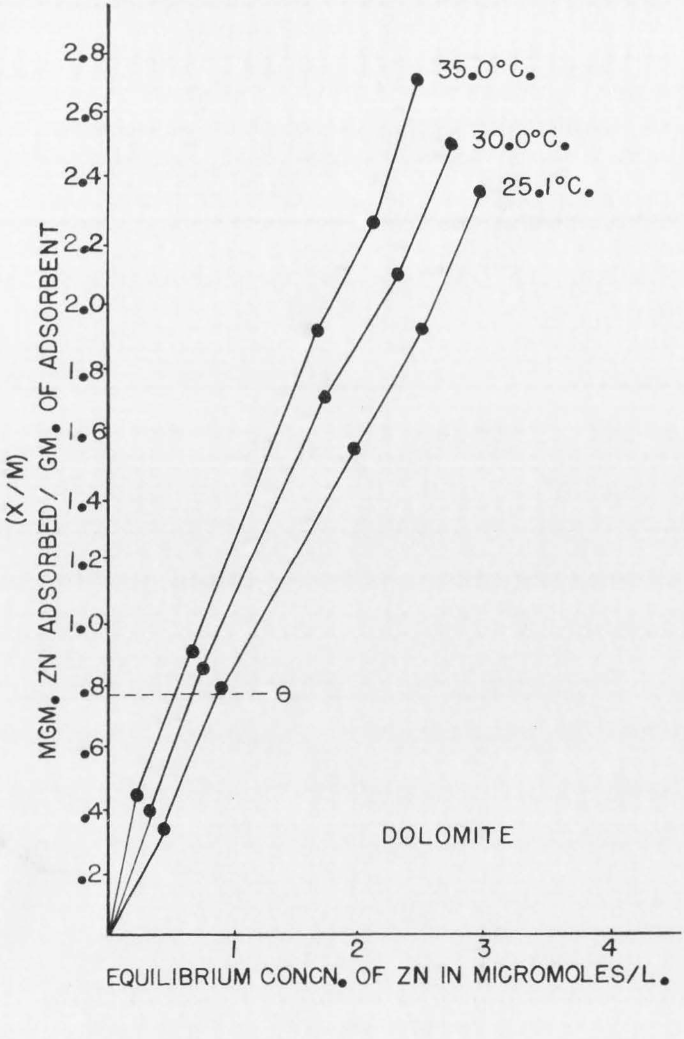


Figure 6. The effect of temperature on the adsorption of zinc by dolomite. θ corresponds to 1 x 10^{-7} me. zinc/cm^2 of dolomite surface.

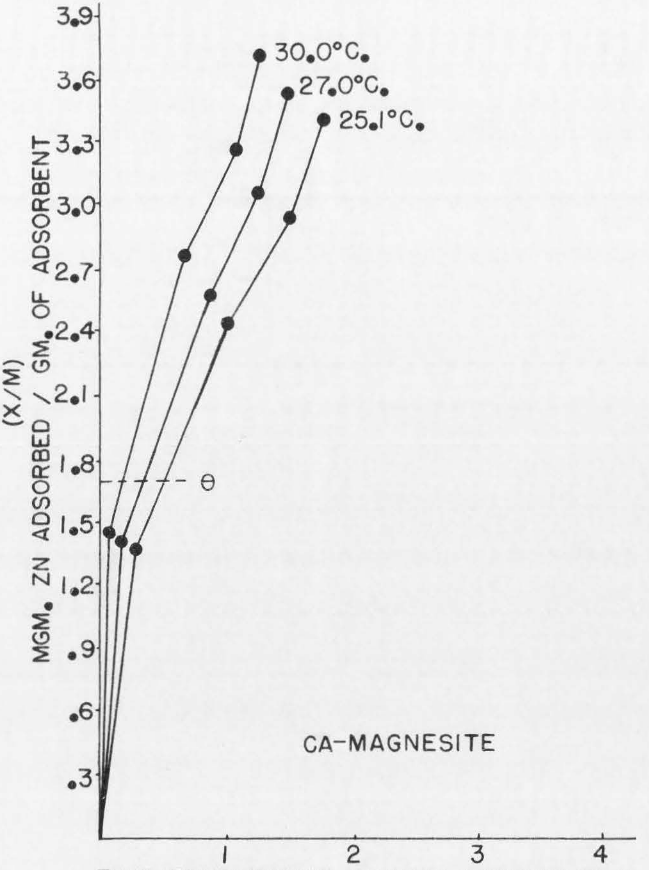


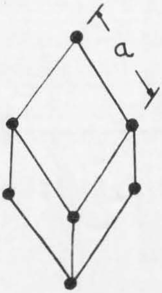
Figure 7. The effect of temperature on the adsorption of zinc by calcian-magnesite. θ corresponds to 1 x 10^{-7} me. zinc/cm.^{2} of calcian-magnesite surface.

(see Appendix A). By increasing the percentage of magnesium carbonate in the mineral, the total adsorption of zinc per unit area is increased and, as in the dolomite system, the reaction is endothermic. The isotherm data were taken over a smaller temperature range in the ca-magnesite system because the strong interaction of the zinc ion with the surface prevented the full effect of temperature to be observed over a greater range for the same fractional surface coverage, θ.

A clearer picture of zinc adsorption on lime minerals can be realized if the results are regarded on a unit surface area basis instead of a unit mass basis. A calculation based on zinc adsorption at 25.1° C. and at an equilibrium concentration of 1×10^{-6} M. gives the ratio of zinc adsorbed per square meter of mineral surface as 1 : 1.12 : 1.44 for calcite, dolomite, and ca-magnesite, respectively. This ratio is a function of temperature and the equilibrium concentration and will vary as the conditions are altered. The results, however, show considerably less adsorptive difference between minerals than is shown by the adsorption isotherms.

A calculation based on the known structure and area of a unit cell face, as shown in figure 8, indicates that an appreciable fraction of the possible adsorption sites on all three minerals are covered by the zinc ion even at solution concentrations as low as a few micromoles per liter. Thus the standard surface complex adopted here corresponds to a coverage of about 10 per cent of the available sites assuming that each X^{++} position in a cleavage plane could be occupied by a zinc ion. This relatively high affinity of the XCO_3 surfaces for the zinc ion is in harmony with the Fajans-Paneth rule cited earlier.

It should be noted that the reproducible curves of figures 5, 6, and 7 are characteristic of adsorption processes and cannot be explained



SCHEMATIC UNIT LATTICE

	a	IONIC RADII	K_{SP}	SPACE GROUP
$CACO_3$	6.36A°	1.06A°	4.8×10^{-9}	$R\bar{3}C$
$MGCO_3$	5.63A°	0.78A°	1.0×10^{-5}	$R\bar{3}C$
$ZNCO_3$	5.67A°	0.83A°	9.9×10^{-11}	$R\bar{3}C$

Figure 8. Schematic unit lattice of the calcite group minerals (only metallic ions represented)

by postulating an ordinary chemical reaction between the zinc ion and the carbonate radical. In the case of ca-magnesite, one might have expected a precipitation of zinc carbonate, knowing the relatively high carbonate ion concentration furnished by a saturated solution of pure magnesium carbonate (see figure 8). Adsorption equilibrium, however, was obtained when only a small percentage of the ca-magnesite surface was covered by zinc. Even at the highest concentration of zinc ion the amount of zinc adsorbed was considerably less than that required for a monolayer of zinc carbonate. A zinc carbonate precipitation, once started, would have led to a complete coverage of the surface. Furthermore, under the condition of constant ionic strength, the carbonate concentration in the equilibrium solution would be constant over the entire range of each isotherm. Thus it would require that the zinc ion concentration assume a constant value if zinc carbonate were present, which is contrary to data. The behavior of ca-magnesite can probably be explained by the modification of properties caused by the substitution of calcium ion in the magnesium carbonate lattice.

Explanation of isotherms in terms of crystal structure

The modification of interionic distances in the crystal lattice by the introduction of the magnesium ion in the calcite lattice is considered to be the source of the differences in adsorptive properties among the minerals studied.

Figure 8 shows the similarity of the usually quoted ionic radii (Evans, 1948) of the magnesium and zinc ions, 0.78 Å and 0.83 Å, respectively. This suggests that the zinc ion could fit very well into the magnesium carbonate lattice, while it is too small to fit well into the lattice of calcium carbonate. Figure 8 adds further support to this supposition by showing that the unit cell lengths of zinc carbonate and magnesium carbonate are nearly equal and considerably different from that of calcium carbonate (Dana, 1951). All three structures are shown to have identical unit lattice space groups, belonging to the rhombohedral division of the hexagonal class with a threefold inversion axis with a plane of symmetry parallel to that axis (Lonsdale, 1949; Dana, 1951). Dolomite has a similar calcite-type lattice structure with intermediate lattice constants and only a slightly different space grouping (Dana, 1951).

The greater polarizability (Weyl, 1951) and polarizing power of the zinc ion, resulting from its 18-electron outer shell and relatively large charge density, compared to the magnesium ion would allow one to expect that the zinc ion would compete favorably with the magnesium ion for lattice sites. The adsorption data from the dolomite and ca-magnesite systems add support to the idea that a favorable relation exists between the zinc ion and the magnesium carbonate lattice.

Thermodynamics of zinc adsorption in relation to ion hydration

The thermodynamic values calculated from the adsorption data for the defined standard adsorption process are given in table 1.

The assignment of the probable errors presented in table 1 are based on the 5 per cent reproducibility of zinc adsorption on duplicate mineral samples along with the variability of 0.05° C. in the temperature control of the water bath. The probable ΔF^{o}_{θ} error was calculated from adsorption data, while the ΔS^{o}_{θ} and ΔH^{o}_{θ} error terms were the result of carrying the experimental uncertainty through the mathematical procedure involved in their determination.

The standard free energy of adsorption, ΔF^{o}_{θ}, is a measure of

Table 1. Thermodynamic data for zinc adsorption on calcite, dolomite, and calcian-magnesite. The standard reaction defined by equation 23.

	$\Delta F^{\circ}_{\theta}$	$\Delta H^{\circ}_{\theta}$	$\Delta S^{\circ}_{\theta}$
CALCITE			
27.5°C.	- 8.44 Kcal.	- 11.4 Kcal.	- 10 E.U.
32.5°	- 8.39	- 12.1	- 12
Prob. Error	± .03	± 2.4	± 8
DOLOMITE			
27.5°C.	- 8.92 Kcal.	+ 8.21 Kcal.	+ 56 E.U.
32.5°	- 8.89	+ 7.91	+ 55
Prob. Error	± .03	± 2.4	± 8
CA-MAGNESITE			
26.1°C.	- 9.01 Kcal.	+ 22.7 Kcal.	+ 106 E.U.
28.5°	- 9.22	+ 21.2	+ 101
Prob. Error	± .03	± 5.9	± 20

how much the concentration of zinc ion in solution must diminish, starting with $a_{Zn^{++}} = 1$, before equilibrium is established. The greater the adsorption of zinc in a given system for a given equilibrium zinc ion concentration, the more negative is the value of the standard free energy.

At constant pressure, and with no non-mechanical work being done by the system, ΔH^{o}_{θ} is the heat of adsorption of the standard adsorption process. The ΔH^{o}_{θ} values of the systems studied mean that the adsorption of zinc on calcite is exothermic but becomes endothermic as magnesium carbonate is introduced into the lattice. Because of the hydrated nature of the zinc ion it is thought that the removal or partial removal of the hydrated shell during adsorption functions as the major consumer of the energy that is adsorbed in the dolomite and ca-magnesite systems. In the endothermic systems, the ΔH^{o}_{θ} values can also serve as a measure of the minimum activation energy governing the rate of adsorption as a function of temperature (Glasstone, 1946).

It is noted that even though the standard adsorption process for dolomite and ca-magnesite are endothermic, the reactions proceed spontaneously. The reason for this is the presence of a favorable entropy term which is of sufficient magnitude to produce the necessary negative free energy change.

The change in entropy of a system, ΔS, is sensitive to structural changes that may occur in a system and can be regarded as a measure of the order or disorder produced in a system during reaction.

Intuitively, one would expect that the adsorption of ions from solution would produce more order in a given system since the random motion of the ionic species in solution has become subjected to the restraining adsorption force of the surface, i. e., the entropy change ΔS_{adsorb} would be exptected to have a negative value. However, the hydrated nature of the adsorbed ion must also be considered in order to obtain a complete picture of the entropy change occurring during adsorption. A hydrated ion that is strongly adsorbed is likely to be at least partially dehydrated upon entering the adsorbed ionic layer. During the process of dehydration, the water molecules which were originally oriented about the hydrated ion are liberated and their return to the solution phase tends to increase the disorder of the system, i. e., this part of ΔS_{adsorb} is positive. For example, the complete dehydration of hypothetical one molal calcium ion, magnesium ion, or zinc ion, forming liquid water and the gaseous ion at the same concentration, involves the large positive ΔS values of 35.7, 57.3, and 50.1 calories/mole degree (Rice, 1940; Quill, 1950). Thus the large positive ΔS^{o}_{θ} values in table 1 can be understood only by considering the contribution of the dehydration process.

The negative standard entropy value in the calcite system suggests that the hydration shell that exists around the zinc ion is still relatively intact after adsorption on calcium carbonate. Even in this case, however, a mechanism involving drastic zinc ion dehydration is conceivable though unlikely because of the possibility that calcium ions are liberated during adsorption and in turn tie down most of the water molecules liberated from the zinc ions.

The large positive standard entropy values in the dolomite system can be explained qualitively by the dehydration of the adsorbed zinc ions when they react with the magnesium carbonate-type lattice. As is expected, the standard entropy of adsorption in the ca-magnesite system indicates still greater dehydration per mole of adsorbed zinc ion. The large entropy change in the dolomite and ca-magnesite systems strongly suggests that the zinc ion is actually incorporated in or built on to the crystal lattice of these two lime minerals. The direct replacement of magnesium ions in the crystal lattice by zinc is not likely since the process of magnesium ions going into solution would introduce a negative entropy term which would tend to balance the net positive contribution of zinc ion adsorption. Thus, if ion exchange in the crystal lattice were the predominant reaction, ΔS^{o}_{θ} would be of much smaller magnitude. Kruyt (1952) further states that ion exchange is not a common phenomenon in a system containing a well-aged crystal lattice.

It is possible to account for the unusually large ΔS^{o}_{θ} value of about 100 E. U. for ca-magnesite if one assumes that zinc ions fit into surface defects or holes in the magnesium carbonate-type surface which initially contain bound water. If the entropy change on dehydrating the holes were about equal to that of dehydration of the magnesium ion, the entropy of zinc ion adsorption would be about + 50 (dehydration of Zn^{++}_{aq}) + 60 (dehydration of hole) - 20 (condensation of zinc ion in the lattice) = 90 calories/mole degree. This is the right order of magnitude when compared with the calculated value obtained from experimental data. The value -20 E. U. for the condensation of zinc ions on the surface of lime minerals is obtained from Rice (1940), who shows data that indicate that the entropy change per ion in the formation of a salt from a molal concentration of gaseous ions is about - 20 E. U. regardless of the type of ion involved. The role of zinc ion, then, would be to displace water from the holes and "heal" the surface defects. The existence of such defects in magnesium carbonate is much more likely because the former substance loses carbon dioxide much more readily.

Although the study was not designed to measure the kinetics of the adsorption process, it is noted that the rate of attaining adsorption equilibrium in the dolomite and ca-magnesite systems was 8 to 10 times slower than in the calcite system. If we can consider the adsorption process as a simple, non-chain reaction and assume that the frequency factor does not vary greatly between systems, then as a first approximation the data support the concept that the activation energy of adsorption in the dolomite and ca-magnesite systems is a greater magnitude than in the calcite system (Glasstone, 1946). This observation also lends support to the hypothesis of zinc ion dehydration upon adsorption.

Hence by defining a standard adsorption process and then finding how the standard free energy of adsorption varies with temperature, thermodynamic data were obtained from the lime mineral systems which not only allow an exact and meaningful comparison of adsorption energetics but also permit some insight into the mechanism of zinc adsorption.

SECTION II. THE UPTAKE OF ZINC FROM SOLUTION BY CORN PLANTS AS AFFECTED BY THE PRESENCE OF CALCITE AND DOLOMITE.

INTRODUCTION

The study just reported has indicated that the adsorption of zinc on lime minerals is a function of the type of mineral surface present in the system and the temperature at which the adsorption process takes place.

A defined standard adsorption process has been thermodynamically described in a chemically defined lime mineral system. However, the criteria for evaluating the practical implications of this adsorption phenomenon is considered to be the effect of these various lime minerals on the uptake of zinc by plants. If the nature of the lime mineral present in a soil system has an influence on the amount of zinc available for plant nutrition, it may be possible that this factor may have to be considered when making future field recommendations.

To investigate a more practical aspect of the adsorption of zinc on naturally occurring lime minerals and also to serve as a means of further clarifying the factors which influence the availability of zinc in alkaline soils, an experiment was conducted to observe the effects of various lime minerals on the uptake of zinc from solution by corn plants.

EXPERIMENTAL PROCEDURE

Hybrid field corn was germinated and grown in a pure silica sand culture. The plants were thoroughly watered every other day with Hoagland's nutrient solution (Hoagland and Arnon, 1950) which was complete except for zinc, which was omitted to establish stress for the ion in the corn plants. After 21 days' growth the corn plants were used in the uptake study.

Five mg. of either calcite or dolomite was added to each of several 25 x 200 mm. Pyrex test tubes. These minerals have been thoroughly described in the previous study. A sodium chloride solution was added to the test tubes which maintained the volume constant at 60 ml. and a constant ionic strength of 0.01. Zinc treatments were added as tagged zinc chloride. Because of the acidic nature of the zinc chloride solution, a calculated excess of the 5 mg. of lime mineral was initially added to the test tubes to account for the loss of mineral due to interaction with the acidic treatments. The resulting mineral systems were identical to the systems which were thermodynamically defined in the previous study. The tubes were held in an appropriate rack and suspended in a water bath maintained at either 25.1° or $30^{\circ} \pm 0.1^{\circ}$ C. A length of fine bore capillary tubing served as an aerating tube in each test tube. The air flow was first saturated by bubbling it through water prior to use in aeration. The flow of air swept the bottom of the test tubes so that the majority of the ground mineral was in suspension. Re-distilled water was added periodically to the test tubes to maintain a constant volume. The suspensions were bubbled until equilibrium was established between the zinc ion in solution and the given mineral surface. The equilibrium time was determined in the preceding study. After equilibrium was established, the corn plants were taken out of the silica sand, their roots were thoroughly washed free of sand, and the plants were transferred to No. 9 corks having a central hole 10 mm. in diameter and a longitudinal notch along the side about 3 mm. deep and 5 mm. wide. The corks were coated with paraffin wax. Two seedlings were placed in each cork and the cork was inserted in the test tube so that the plant roots were in the suspension. The experimental set up is essentially the same as used by Epstein and Stout (1951) in their micronutrient studies. After 23 hours of growth under artificial lighting, the corn plants were removed from the test tubes; the tops of the plants were removed, washed in dilute hydrochloric acid and distilled water, and dried in an oven (56°-79° C.) for 24 hours. The dried corn tops were pressed into pellets, weighed, and then the pellets were measured for activity. The amount of zinc measured in the corn tops was used as the index of zinc uptake by the plant from solution.

The experiment consisted of 3 replications of 2 corn plants each, 3 levels of zinc treatment, 2 temperatures, and 2 lime minerals.

RESULTS AND DISCUSSION

Figures 9 and 10 show the plot of the uptake of zinc by corn plants vs. the equilibrium concentration of zinc ion in solution at the beginning of the uptake period. The equilibrium concentrations were calculated from the adsorption isotherm data presented in figures 5 and 6 and Appendix A of the previous study.

Figure 9 shows that at 25.1° C. a strong linear relationship exists between plant uptake of zinc and the amount initially in solution. The regression coefficient and equation of the line was calculated to be 0.975 and $\bar{Y}_x = .408X - .195$, respectively. The rather high regression coefficient is not entirely unexpected since the solutions were of a very dilute nature and the corn plants probably had developed some deficiency for zinc ion.

The pH of the mineral systems were measured immediately after harvesting and the results are as follows: calcite, 8.07 with $\sigma = 0.1$; dolomite, 8.03 with $\sigma = 0.06$. The pH of the calcite and dolomite suspensions were considered to be equal.

Figure 10 shows a very similar relationship at 30° C. Here the regression coefficient and equation of the line was calculated to be 0.941 and $\bar{Y}_x = .378X + .035$, respectively.

The pH measured immediately after harvesting was as follows: calcite, 6.96 with $\sigma = 0.07$; dolomite, 6.93 with $\sigma = 0.08$. Here again both mineral systems were essentially at the same terminal pH value. The reason for the lower pH values at the higher temperatures is considered to be the inability of the aeration system to cope with

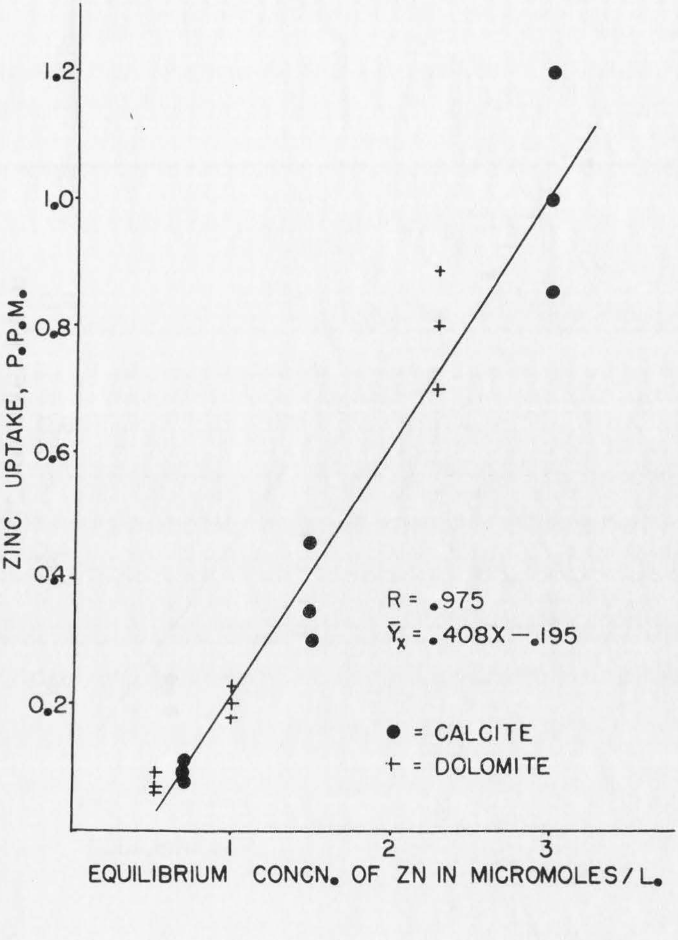


Figure 9. The uptake of zinc by corn plants as affected by the presence of calcite and dolomite at 25.1° C.

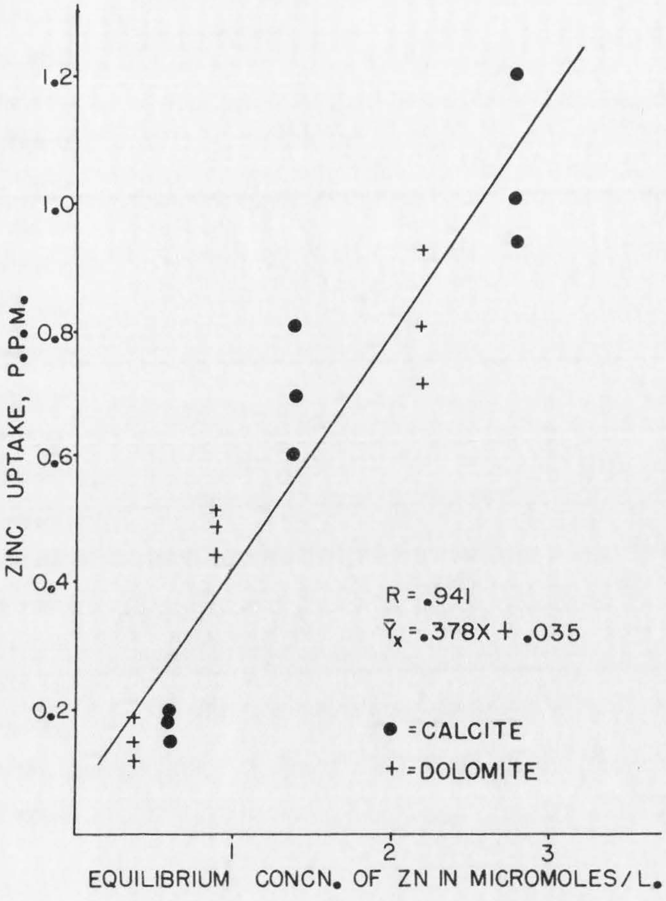


Figure 10. The uptake of zinc by corn plants as affected by the presence of calcite and dolomite at 30.0° C.

the increased respiratory activity of the corn roots. It is noted that a slight increase in zinc uptake occurred at the higher temperature in both mineral systems. This probably results from the combined effects of greater metabolic activity of the corn plant and to the fact that some mineral adsorbing surface may have been destroyed by the lowering of pH. However, the lower pH of the system and the higher temperature still did not alter appreciably the linear relationship between zinc uptake and the equilibrium concentration of zinc in solution.

The data indicate that zinc uptake is dependent on the mineral in suspension only to the extent that the given mineral controls the equilibrium concentration of zinc in solution. Thus with the same initial treatment of zinc, a dolomite system provides less zinc for plant utilization than a calcite system because dolomite reduces the equilibrium concentration of zinc to a lower level. The straight line relations as shown in figures 9 and 10 indicate that at the various fractional surface coverages of the mineral in question the kinetics of desorption is not a limiting factor during the uptake period.

This study has shown that, in the concentration range of the zinc used, the dominating factor in the uptake of zinc from solution by field corn is the equilibrium concentration of zinc that exists in a given mineral system.

SUMMARY AND CONCLUSIONS

The studies reported here represent an attempt to clarify the relation between the zinc ion and the naturally occurring lime minerals which are prevalent in western soils. Because of the low concentrations of zinc utilized in these investigations, radio tracer techniques using Zn^{65} were employed throughout the studies to facilitate analysis.

In Section I a theoretical approach is developed for the adsorption of zinc on calcite, dolomite, and calcian-magnesite. A theory is presented in which zinc ion is specifically adsorbed by the lime minerals and the chloride counter ion is non-specifically adsorbed by the surface in question.

For purposes of determining the standard free energy of adsorption, ΔF°, a standard adsorption process is defined with the assumption that the orientation of counter ions does not contribute significantly to the free energy of the process. The standard adsorbed state in this study is defined as an arbitrarily selected fraction of surface coverage, θ.

Adsorption isotherm data collected at various temperatures permitted the determination of the temperature coefficient of ΔF°. From this determination, the standard entropy, ΔS°, and the standard heat of adsorption, ΔH°, was calculated.

The adsorption isotherm data showed that the adsorption of zinc on ca-magnesite was greater than on calcite, while the adsorption on dolomite was intermediate.

The calculated thermodynamic data showed that the interaction of zinc with calcite was distinctly different from the interaction of zinc with dolomite and ca-magnesite. The former reaction was exothermic while the latter reaction was endothermic. The thermodynamic data were interpreted as meaning that strong dehydration of zinc ion occurred when it is interacted with the minerals that contained magnesium carbonate. Zinc dehydration was not evident in the calcite system. These data infer that the zinc ion is incorporated in or built on to the dolomite and ca-magnesite lattice where one of its functions may be the "healing" of surface defects.

Consideration of the ionic radii, crystal structure, and lattice constants of the involved ions and carbonate lattices also support the theory of strong zinc interaction with the magnesium carbonate surface.

Because of the difference in the effect of temperature on the adsorption of zinc by the various minerals, direct application of this study to the soil system must be made with caution. However, in the temperature range of this theoretical study one may infer that zinc availability would be more limited on a soil containing appreciable magnesium carbonate than on a soil containing calcium carbonate.

To supplement the thermodynamic study and to test the inference stated above, a study was conducted to measure the effect of calcite and dolomite on the uptake of zinc by corn plants from mineral systems which had been thermodynamically defined in Section I.

The results of this investigation, as presented in Section II, indicated that the determining factor in the uptake of zinc by corn plants was the concentration of zinc in solution. The dominating influence of the solution concentration of zinc was independent of the temperature range used in the study and the final pH of the mineral systems. Thus the lime mineral that reduced the equilibrium concentration of zinc to the lower level had the greater effect on zinc availability.

The zinc uptake data thus concur with the inference obtained from adsorption studies. Hence the statement is strengthened that, under a given set of conditions, a soil containing lime minerals of predominately magnesium carbonate would tend to retain zinc to a greater degree than a soil containing mainly calcium carbonate. The possibility thus exists, that in a given temperature range, a dolomitic soil would foster zinc deficiency more than a calcareous soil if the total zinc concentration in the soil is approaching the critical level.

Thus by the application of basic laws of chemical thermodynamics it is not only possible to obtain a quantitative measure of the energy relations between zinc ion and the lime mineral surface, but it also permits some insight into the mechanism of adsorption. The results give logical explanation of the observed experimental data and enable some prediction of the behavior of zinc in the lime mineral systems studied.

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APPENDIX A

ISOTHERM DATA OF ZINC ADSORPTION ON CALCITE AT VARIOUS TEMPERATURES*

Temperature	C_0	X/M	C
25.1° C.	0.54	0.75	0.32
	2.16	2.70	1.19
	4.32	6.02	2.32
	5.40	6.32	3.36
	6.45	7.91	4.00
30.0° C.	1.08	1.12	0.55
	3.24	3.40	1.95
	4.32	5.21	2.65
	5.40	5.59	3.62
	6.45	7.21	4.30
35.0° C.	1.08	0.81	0.74
	2.16	1.55	1.35
	3.24	2.71	2.20
	4.32	4.40	2.88
	5.40	4.62	3.87
	6.45	6.02	4.38

* C_0 = initial amount of zinc added in micromoles/liter, X/M = micrograms of zinc adsorbed/5 mg. of adsorbent, and C = equilibrium concentration of zinc in micromoles/liter.

ISOTHERM DATA OF ZINC ADSORPTION ON DOLOMITE AT VARIOUS TEMPERATURES*

Temperature	C_0	X/M	C
25.1° C.	1.08	1.70	0.42
	2.16	3.81	0.87
	4.28	7.65	1.98
	5.40	9.52	2.48
	6.45	11.7	2.92
30.0° C.	1.08	1.95	0.37
	2.16	4.21	0.81
	4.28	8.45	1.72
	5.40	10.3	2.30
	6.45	12.5	2.71
35.0° C.	1.08	2.25	0.31
	2.16	4.44	0.74
	4.28	9.51	1.67
	5.40	11.2	2.15
	6.45	13.5	2.42

* C_0 = initial amount of zinc added in micromoles/liter, X/M = micrograms of zinc adsorbed/5 mg. of adsorbent, and C = equilibrium concentration of zinc in micromoles/liter.

ISOTHERM DATA OF ZINC ADSORPTION ON CA-MAGNESITE AT VARIOUS TEMPERATURES*

Temperature	C_0	X/M	C
25.1° C.	1.08	3.62	0.15
	2.16	7.16	0.25
	3.24	12.5	1.09
	5.40	15.0	1.53
	6.45	17.3	1.90
27.0° C.	2.16	7.21	0.20
	3.24	13.2	0.88
	5.40	15.6	1.25
	6.45	18.3	1.50
30.0° C.	2.16	7.35	0.15
	3.24	14.1	0.75
	5.40	16.5	1.01
	6.45	19.1	1.15

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* C_0 = initial amount of zinc added in micromoles/liter, X/M = micrograms of zinc adsorbed/5 mg. of adsorbent, and C = equilibrium concentration of zinc in micromoles/liter.