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**Final Examination
PLSC/CHEM 608
May 24, 2004**

- (48) I. Ion exchange absolutely has been one of the foundations in soil chemistry. The ability for one ion to exchange for another on clay minerals, organic matter, and amorphous materials is important since it determines the ability of a soil to retain ions necessary for plant growth and retardation of leaching into the soil profile. Ion exchange was first examined by J. Thomas Way in the mid-1800s. His experiments, while simplistic in design, were incredibly ingenious in determining that cations exchanged for cations and anions replaced anions. Many researchers have built upon the hallmark work of Way and in 1932, Albert Vanselow applied chemical thermodynamics to explain ion exchange dismissing the argument of whether or not ion exchange was an “exchange” or an “adsorption” phenomenon. Considering the above information, examine the following cation exchange reaction and answer the questions that follow.



- A. According to classical thermodynamics, how would one express the “true” equilibrium exchange constant (K_{eq}) for Eq. [1]? Be specific in defining terms!
- B. How would K_v (Vanselow selectivity coefficient) be determined for this reaction? Only set up the equation, but clearly define terms.
- C. For the above reaction, would K_v equal K_{eq} ? Why?

- D. How would one calculate the Kerr selectivity coefficient (K_K) for the above exchange reaction?
- E. Would the exchange process in Eq. [1] behave ideally? Why or why not?
- F. If Ca^{2+} were preferred over Mg^{2+} on the soil, what would the selectivity isotherm look like? Label the axes carefully.
- G. If the ΔG^0 and ΔH^0 for Ca-Mg exchange in Eq. [1] were both negative in magnitude, what conclusions could one make about the exchange process?
- H. How would one calculate the K_{ex} for the above reaction? Show by equation and through a graph. Briefly describe the experimental protocol to follow.

- I. Sketch a probable K_v vs. \bar{X}_{Ca} (equivalent fraction of Ca on soil) plot for this exchange system. What kind of ion selectivity information could you collect from this plot?
- J. How could one calculate the ΔG^0 for the reaction in Eq. [1] from kinetic measurements? Be specific with the equations. For a kinetic approach to be valid, what two assumptions must be true?
- K. How would one collect data and plot them to determine the energy of activation (E_a) for the reaction in Eq. [1]? Be specific! Would you expect the E_a value to be high or low? Why?
- L. Set up the equation to determine CEC if 120 mg of Mg^{2+} are displaced from the soil.

- (16) II. You are a consultant for a large environmental firm in Delaware. You are asked to evaluate the sorption/desorption of trace metals such as Ni, Co and Cr on/from soils that are contaminated and uncontaminated. You take numerous soil samples and analyze for basic physico-chemical and mineralogical properties. Some of these properties are given below.

Basic Soil Physiochemical and Mineralogical Properties

<u>pH</u>	<u>CEC</u> (cmol kg^{-1})	<u>SOM</u> (%)	<u>Clay Content</u> (%)	Mineralogy of <2 μm Fraction
5.0	6.5	3	15	Kaolinite ₁ , Chloritized Vermiculite ₂ , Mica ₃ , Goethite ₄

Metal Oxides

Fe-oxides

Medium

Mn-oxides

Medium

Al-oxides

Low

Answer the following questions:

A. The EPA wants time-dependent data on Ni sorption/desorption since the total Ni content in contaminated soils greatly exceeds safe levels. You decide to compare the Ni release kinetics from the contaminated soil to the same uncontaminated soil in which you added Ni to attain the same Ni level as in the field-contaminated soil. The added Ni was reacted with the soil for up to 24 days.

1. What sorption kinetic method would you use and why?
2. How would the Ni desorption release compare for the lab vs. field contaminated soils? Why?
3. You are also asked to model the sorption/desorption kinetic data. What model(s) would you use and why?

4. Sketch a typical sorption kinetic plot for Ni sorption on the uncontaminated soil for a period up to 48 hours. You then conduct desorption studies and find that only 30% of the sorbed Ni is released. What could explain the lack of sorption reversibility?

(36) III. Quickies

1. Who was J. Thomas Way?
2. What does a mechanistic rate law assume?
3. Give an example of a chemical relaxation kinetic method?
4. Why could NH_4OAc remove more exchangeable K^+ than $\text{Mg}(\text{OAc})_2$?
5. Why is organic chemical sorption often irreversible on humic substances?

6. How does surface chemical dissolution differ from transport-controlled dissolution?

7. Name two rate-limiting processes that are important in soil chemical reactions?

8. How could sulfate be sorbed (mechanisms) on kaolinite?

9. How is synchrotron light generated?

10. How would you identify kaolinite by x-ray diffraction (XRD)?

11. Name two surface complexation models?

12. Name two acid organic matter functional groups?