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# **The Transport of Contaminants from Energy Process Waste Leachates Through Subsurface Soils and Soil Components Laboratory Experiments**

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**THE TRANSPORT OF CONTAMINANTS  
FROM ENERGY PROCESS WASTE LEACHATES THROUGH  
SUBSURFACE SOILS AND SOIL COMPONENTS  
LABORATORY EXPERIMENTS**

by

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**ABSTRACT**

The subsurface transport and attenuation of inorganic contaminants common to a variety of energy process waste leachates are being studied using laboratory column methods. Anionic species currently being emphasized are As, B, Mo, and Se. Transport of the cations Cd and Ni is also being studied. The solid adsorbents consist of three soil mineral components (silica sand, kaolinite, and goethite), and four subsurface soils (a dunal sand, an oxidic sandy clay loam, an acidic clay loam, and an alkaline clay loam). Breakthrough patterns of these species from packed soil columns are followed by monitoring eluent concentrations vs time under carefully controlled laboratory conditions. This report describes the experimental methods being used, the results of preliminary batch adsorption studies, and the results of column experiments completed through calendar year 1981.

Using column influent concentrations of about 10 mg/l, adsorption (mmoles/100 g) has been determined from the eluent volume corresponding to 50% breakthrough. On silica sand, kaolinite, dunal sand, and goethite, respectively, these are  $2.0 \times 10^{-4}$ , 0.020, 0.013, and 0.31 for cadmium,  $4.4 \times 10^{-4}$ , 0.039, 0.020, and 0.98 for nickel. On kaolinite, dunal sand, and goethite, respectively, adsorption values (mmoles/100 g) are As (0.24, 0.019, and 20.5), B (0.041, 0.0019, and 1.77), Mo (0.048, 0.0010, and 5.93), and Se (0.029, 0.00048, and 1.30). Arsenic is the most highly adsorbed contaminant species and goethite has the largest adsorption capacity of the adsorbents.

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## I. INTRODUCTION AND BACKGROUND

In January 1980 the Los Alamos National Laboratory began generic studies on the movement of inorganic species determined to be important in leachates from energy process wastes through subsurface soils. The emphasis is on contaminants from conventional coal combustion processes and other energy processes such as coal conversion, oil shale, and uranium milling.

The research is based on a scenario of surface or near-surface disposal of solid wastes such as shown in Fig. 1. In this scenario, the surface or A soil horizons (and perhaps the B horizons as well) are scraped away to prepare a large area upon which waste can be deposited and compacted in layers. Such sites are often located in a valley or depression. After the disposal site has been filled with waste, it is contoured, topsoil may be added, and it is revegetated or otherwise reclaimed. Some efforts

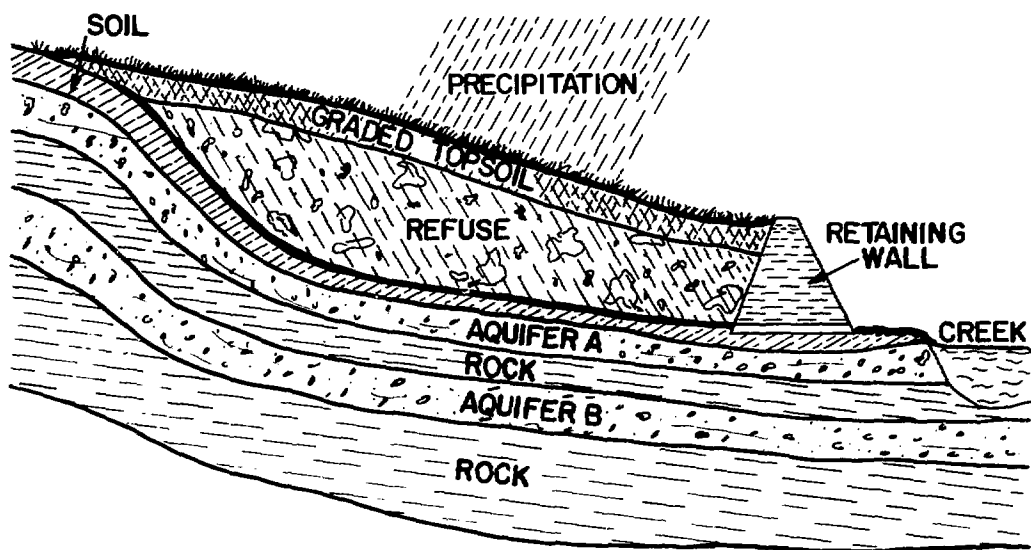


Fig. 1. Near-surface burial of coal refuse.

may be made to divert surface water away from the site. The waste material may be heterogeneous, but even if it is fairly homogeneous it is likely to be quite permeable compared to surrounding compact soils and consolidated geologic materials. Such permeable materials can be leached by percolating waters and thus transport soluble contaminants from the waste into underlying soils and groundwater.

The most important *physical* variable in subsurface solute transport is water velocity. If the water does not move, the contaminants cannot be transported to any great extent. Preventing water movement is the philosophy behind the use of impermeable liners. Such liners may be useful for disposal or temporary storage of highly toxic wastes, but their utility for permanent disposal of high-volume, relatively nontoxic wastes, such as those from most energy producing technologies, is not recommended. The philosophy of the "leaky bathtub" is felt to be more practical for disposal of these wastes. This idea refers to the slow, controlled release of materials from a waste so that any potentially noxious species are safely assimilated back into natural systems. In practice this might be realized by ensuring that contaminant fluxes are low enough that the natural concentrations in waters near the disposal site are not altered by more than one standard deviation. Such a philosophy implies that acceptable contaminant fluxes will be defined by the natural condition of the disposal site region.

The concept of a leaky bathtub espouses the use of natural mitigation processes to minimize the transport of contaminants into subsurface water systems. In terms of our near-surface disposal scenario, retardation of solute transport by subsurface soils or other geologic materials has been shown by several investigators to be one such important mitigating factor.<sup>1-4</sup> Thus, referring back to water velocity as the most important physical parameter in solute transport, given a natural subsurface system with a certain water velocity, the most important parameter affecting solute transport is how the solute interacts chemically with the substrate through which the water is moving. The following examples will illustrate this idea. Acidic leachates (from coal mineral wastes, low temperature, reductive coal conversion processes, and uranium milling wastes from acidic extraction processes) often contain elevated concentrations of metals such as Al, Fe, Co, and Zn. These leachates, upon entering a somewhat permeable calcareous subsoil or geologic strata, will be neutralized and most metals will be removed from solution by precipitation as carbonates and/or hydroxides. This constitutes a case of considerable chemical interaction between solute and adsorbent. Thus, regardless of water velocity, these potentially noxious contaminants will not be transported to any significant extent. Examples of this phenomenon have been demonstrated in the laboratory and in the field.<sup>5-7</sup> The transport of chloride ion through soils illustrates a

case of little or no chemical interaction. In transport through many soils,  $\text{Cl}^-$  is so unreactive that it is used as a tracer to determine solute dilution by physical dispersion processes alone. (We note that  $\text{Cl}^-$  is not always a good tracer. Anion exclusion and  $\text{Cl}^-$  interaction with oxides of aluminum and iron are known to occur and can cause  $\text{Cl}^-$  transport to deviate from that of an inert tracer.)<sup>8,9</sup>

The research presented here is predicated on the need to develop capabilities for predicting the movement of leachate contaminants through subsurface soils and groundwaters. Los Alamos National Laboratory (Los Alamos) is collaborating with three other research groups in studies aimed at developing capabilities for predicting the transport rates of organic and inorganic contaminants from energy processing waste leachates through soils and groundwaters. Studies at Los Alamos center on the adsorption of inorganics by soils and soil components as herein described. Research at the University of Notre Dame is concerned primarily with the development of computer models to simulate the flow, transport, and chemistry of contaminants through saturated soil and groundwater systems and the development of equilibrium adsorption data for use in the chemical submodels. Lawrence Livermore National Laboratory (LLNL) is focusing on the transport and interaction of organic contaminants in soils, and studies at the University of Wisconsin are concentrating on the development of basic kinetic and equilibrium data for the chemical species of interest in the other programs. These groups will use the same soils and soil component materials provided from specially prepared batches at Los Alamos. Soil column studies at Los Alamos and LLNL will be used at Notre Dame for model testing purposes. Tentative longer range plans include testing of the model at a field location.

## II. SUMMARY

These investigations are primarily concerned with the development of capabilities for predicting the subsurface transport and attenuation of contaminants in energy process waste leachates through soils using laboratory column methods. We are collaborating with three other research groups in these overall efforts. Work at the University of Notre Dame is developing computer models to simulate the transport and chemistry of contaminants. Studies at the University of Wisconsin are investigating basic kinetic and equilibrium aspects of critical importance for defining the chemistry of

soil/solute interaction in the models, and research at LLNL is focusing on the soil interactions of potential organic contaminants. The column experiments are performed under carefully controlled conditions so that the resulting breakthrough patterns may be used to test the solute transport models.

Studies at Los Alamos consist of the following tasks:

- (1) Identification of inorganic contaminants of importance in energy process waste leachates,
- (2) preparation and characterization of subsurface soils and selected soil mineral components for use by all participants in the integrated studies, and
- (3) development and execution of laboratory based column transport experiments for selected inorganic species.

Regarding the first task, we have performed a number of laboratory experiments and researched the literature to identify contaminants that commonly appear as potential problems in energy process waste leachates. Major chemical components vary, primarily as a function of the mineralogy of the solid waste. For potentially acid-generating wastes, such as those with significant amounts of reduced sulfur minerals, Al, Fe, Mn, and  $\text{SO}_4^{2-}$  tend to dominate the chemistry, although Ca and Mg are also present in substantial concentrations. In near neutral to slightly alkaline wastes, Ca, Mg, and  $\text{SO}_4^{2-}$  are the dominant soluble species. Chemically significant quantities of carbonate are also often present.

The trace elements are of special interest in these studies. The elements As, B, Cd, Co, F, Mo, Ni, Se, V, and Zn are most frequently identified as problematic in a variety of waste leachates. Other species, for example, Ra and U in mill tailings, are potential problems for selected wastes only. For initial emphasis, we have chosen the anionic species As, B, Mo, and Se and the divalent cations Cd and Ni. Subsequent plans are to determine the effect of sulfate on transport of the cations as well as the transport of the selected contaminants in leachates from real wastes.

For study of adsorption properties, we have selected the three common soil mineral components silica sand, kaolinite clay, and an iron oxide, and four real subsurface soils - a dunal sand, an oxidic sandy clay loam, an acidic clay loam, and a calcareous clay loam. These materials have been prepared in batches, homogenized, and distributed to the other participants so that all are working with the same adsorbing solids.

The solid adsorbents have been characterized by physical, chemical, and mineralogical properties believed potentially important in determining their capacities for interacting with contaminants (Tables I and II). Characterization results show a range of organic content, cation exchange capacities, free iron, aluminum and manganese concentrations, clay content, carbonate content, and specific surface area. Thus these adsorbents represent a variety of soil types likely to be important to the disposal of energy process wastes and should be useful for explaining results of contaminant attenuation experiments.

Experimental methods for performing the soil column transport studies are patterned after procedures perfected by the US Geological Survey-Water Resources Laboratories in Menlo Park, California, over a period of several years. These procedures have been shown to be effective at providing results that most closely simulate the assumptions implicit in the solution of the one-dimensional, steady state transport of an inert solute through porous media.

Batch adsorption experiments show that, at low initial concentrations, all the adsorbent materials, except silica sand and the dunal sand, remove a large percentage of each contaminant from solution. None of the contaminants are adsorbed by silica sand, and only Cd and Ni at low initial concentrations are appreciably removed by the dunal sand. Goethite is very effective at removing As, Cd, and Ni from solution, somewhat effective for Se and Mo, and fairly ineffective for B. In these experiments, of the anions only Mo adsorption seems to be affected by pH to any large extent.

A number of column adsorption experiments have been completed.\* Tracer runs were performed in duplicate for each soil column. In these experiments Ni and Cd were studied together, that is, the same influent solution contained  $\sim 10$  mg/l of both elements. Transport of the anion forming elements As, B, Mo, and Se was also studied by combining them in one solution. The experiments completed are

- transport of solutions containing  $\sim 10$  mg/l Cd and Ni in 0.033M  $\text{Ca}(\text{NO}_3)_2$  through silica sand and kaolinite on sand,
- transport of solutions containing  $\sim 10$  mg/l Cd and Ni in 0.1M  $\text{KNO}_3$  through dunal sand and goethite on sand, and

- transport of solutions containing  $\sim 10$  mg/l As, B, Mo, and Se through kaolinite on sand, dunal sand, and goethite on sand.

The order of decreasing adsorption capacity is goethite  $\gg$  kaolinite  $>$  dunal sand soil  $>$  silica sand. In terms of moles of element adsorbed per unit mass of adsorbent, the order of affinity for goethite is  $\text{As} \gg \text{Mo} > \text{B} \approx \text{Se} > \text{Ni} > \text{Cd}$ . For adsorption on kaolinite the corresponding order is  $\text{As} \gg \text{Mo} \approx \text{B} \approx \text{Ni} > \text{Se} > \text{Cd}$ , and for the dunal sand we have  $\text{Ni} \approx \text{As} > \text{Cd} > \text{B} > \text{Mo} > \text{Se}$ . Thus goethite has the highest adsorption capacity for these elements and arsenic is usually the most highly adsorbed. Silica sand and the dunal sand soil have very little sorbing capacity, whereas kaolinite has some, but much less than that of goethite.

### III. RESULTS

#### A. Task I - Contaminant Identification

Regarding the first task, a report published earlier discusses results of our experimental research aimed at determining chemical element concentrations in solids and liquids associated with flue gas desulfurization at coal fired power plants.<sup>10</sup> In addition, we have reviewed the literature and other sources to obtain current information on contaminants identified as important in leachates from other energy process wastes. These studies have demonstrated the presence of potentially noxious contaminants in leachates from a variety of energy process wastes. These include B, Cd, K, and  $\text{SO}_4^{2-}$  in coal conversion wastes,<sup>11</sup> As, Cd, Ni, and Se in acidic coal cleaning wastes,<sup>12,13</sup> Ni, Se, Cd, B, As, Zn, Mo, and V in coal ash and FGD scrubber wastes,<sup>10</sup> U, Se, Mo, As, and V in uranium tailings<sup>14</sup>, and As, B, F, K, Li, Mo, Ni, and V in spent oil shales.<sup>15</sup> Additionally, terrestrial plants have been observed to accumulate elevated levels of B, Be, Ni, Cd, Zn, and Co when grown on mixtures of coal gasification ash and soil.<sup>16</sup> Some of these species, for example, Cd, Ni, and Zn, are generally mobile in acid systems and thus might be most problematic in the eastern US. Others such as B, F, Se, and Mo are often more mobile under alkaline conditions and thus may be of more concern in the arid to semiarid soil environments more important in the western US. Leaching of contaminants from these wastes presents a potential for contamination of subsurface water supplies.

Initial elements selected for study are As, B, Mo, and Se as minor or trace anionic species and Cd and Ni as

\*These are summarized in Table VII.

TABLE I

PHYSICAL AND CHEMICAL PROPERTIES OF  
MATERIALS USED IN TRANSPORT EXPERIMENTS

	pH <sup>a</sup>	Carbonate <sup>b</sup> (%)	Cation <sup>c</sup> Exchange Capacity (meq/100 g)	Organic <sup>d</sup> Carbon (%)	Extractable (%) <sup>e</sup>			Surface <sup>f</sup> Area (m <sup>2</sup> /g)	Per Cent <sup>g</sup>		
					Al	Fe	Mn		Clay	Silt	Sand
Dunal Sand	6.6	0.1	0.24	0.04	0.018	0.1	0.002	0.4/3	0	0	100
Sandy clay loam	5.3	<0.1	6.1	0.09	0.20	2.8	0.017	25/59	36	3	61
Acidic clay loam	5.4	<0.1	24.7	0.90	0.10	0.64	0.09	26/172	43 <sup>h</sup>	38	19
Calcareous clay loam	8.1	8.8	20.9	0.12	0.15	2.1	0.15	>30/150	55 <sup>h</sup>	37	8
Kaolinite	5.2	<0.1	4.2	0.15	0.014	0.01	0.0004	17/50	89	11	0
Goethite	6.4	—	—	NA	0.045	3.5	0.005	7/7	—	—	—
Silica sand	5.2	0.1	—	0.03	0.006	0.014	0.002	<0.1/4	0	0	100

<sup>a</sup>1:1 soil suspension.

<sup>b</sup>Titrateable carbonate.

<sup>c</sup>Ammonium retention at pH 7.

<sup>d</sup>Walkley-Black procedure.

<sup>e</sup>Dithionite-citrate extractable.

<sup>f</sup>Surface area by BET (nitrogen absorption) above slash, by EGME procedure below slash.

<sup>g</sup>After grinding to -100 mesh.

TABLE II  
MINERALOGY OF SUBSURFACE SOILS  
USED IN TRANSPORT EXPERIMENTS

	<u>Quartz</u>	<u>Calcite</u>	<u>Kaolinite</u>	<u>Illite</u>	<u>Montmorillonite</u>	<u>Mixed-Layer Clays</u>
Dunal <sup>a</sup> sand	Virtually 100% Quartz					
Sandy clay loam	62	0	10	0	0	28
Acidic clay loam	48	0.4	0.7	5.1	0	12
Calcareous clay loam	40	6.5	1.2	7.3	0	17

<sup>a</sup>Mineralogy not performed on this soil.

trace metals. KNO<sub>3</sub> is used to adjust ionic strengths to values comparable to those of real leachates. The effect of sulfate on cation transport is planned, as are experiments using real leachates.\*

## B. Task 2 - Materials Preparation and Characterization

### 1. Selection of Subsurface Soils and Mineral Components

Transport experiments are being performed using four real subsurface soils and three soil mineral components. Subsoils (below the surface or A horizon) were selected to be consistent with near-surface disposal where topsoils have been scraped away or otherwise removed during site preparation or surface mining operations. Subsurface soils usually have less organic content, higher clay content, and, often, higher oxide content than surface soils.<sup>17,18</sup> Also, they are generally less weathered and leached. Because it was thought desirable to study simpler systems before advancing to more complicated real soils, we chose to investigate the transport of selected species through some common mineral compo-

nents of soils. Goethite ( $\alpha$ -FeOOH), silica sand (SiO<sub>2</sub>), and kaolinite were chosen for this purpose because they are among the most common minerals found in soils.<sup>19</sup> In addition, they represent extremes in terms of sorption capacity for cations and anions. Silica and kaolinite have low exchange capacities, whereas, depending on pH, goethite has a high sorption capacity for most species. We have chosen real subsurface materials that have chemical and mineralogical properties of importance and that reflect the mineral components being studied. These consist of high clay acidic and calcareous soils, a high iron oxide soil, and a dunal sand. The dunal sand is nearly all silica quartz. The oxide soil also has a considerable clay content (36%), much of which is kaolinite. The calcareous and acidic soils consist of 55% and 43% clay size particles, respectively. Mineralogically, most of this clay is either illite or mixed layer clay with very little kaolinite. Free iron content of the calcareous soil is 2.1% and that of the acidic soil is 0.6%. Our intent is to progress from the relatively simple to the more complex and in so doing to acquire a degree of understanding concerning the chemical mechanisms of importance to the transport of selected contaminant species.\* We have deliberately altered the grain size

\*See Appendix A for some additional discussion regarding the contaminant species selected for study.

\*See Appendix B for some additional discussion on the adsorbents being studied.

distribution of the low permeability materials to make them sufficiently permeable to allow flow-rate control at values that will enable completion of column attenuation experiments in reasonable time periods (months rather than years). An additional criterion in flow velocity selection is an attempt to maintain equilibrium conditions within the soil bed. It is recognized that there will likely be some *nonequilibrium* processes occurring under selected flow conditions. Experiments here and in coordinated studies at the University of Wisconsin are investigating possible kinetic effects. The flow velocity of 1 cm/h that we have selected constitutes a compromise between the above mentioned factors.

## 2. Preparation of Subsurface Soil Materials and Mineral Components

The four subsurface soils were obtained from the B and C horizons. The dunal sand is from Indiana, the oxidic sandy clay loam from Georgia, the acidic clay loam and calcareous clay loam are from Illinois. These soil materials were dried, crushed (clumps broken up), and sieved to remove the >2 mm fraction, as necessary. The large, as-received, batches were split into smaller batches, each representative of the as-received material, and stored. Quantities used were taken from these batches. The oxidic sandy clay loam and the dunal sand were used in this form. The two clay loam soils were processed further. They were ground to less than 200 mesh (0.074 mm) and coated on sand as described below.

Sand coated soils were prepared by adding mixtures of 90% acid-washed silica sand and 10% soil to a 1M  $\text{CaCl}_2$  solution at a solid-to-liquid ratio of 4:1. These mixtures were evaporated on a rotary evaporator until the water was removed and then pan dried in an oven at 60°C over night. A kaolinite-sand mixture was also prepared in this way. These materials were then broken up and crushed by hand and material smaller than 100 mesh was stored. This -100 mesh material was used in subsequent transport and adsorption experiments.

The goethite-coated sand was prepared as follows. Sufficient 2M KOH was added to 1M  $\text{Fe}(\text{NO}_3)_3$  to obtain a pH of 1.9. This mixture was allowed to react for 48 h at room temperature, then adjusted to a pH of 11.7 with 2M KOH, and placed in a 60°C oven for 3 days. After heating, a gelatinous precipitate of ferric oxide was present. This material was washed three times with distilled water after siphoning off the liquid phase as much as possible. Subsequent to the third addition of

distilled water, the precipitate dispersed to form a colloidal suspension, which was adjusted to pH 7 with 0.1M  $\text{HNO}_3$ . This solution resulted in a precipitate that again separated into liquid and gelatinous solid phases. After removal of the liquid phase, the gelatinous ferric oxide slurry was combined with 500 g of acid-washed silica sand and evaporated using a rotary evaporator and heat gun until nearly dry and then dried in a 100°C oven for 24 h. Analysis of this material by x-ray diffraction confirmed its identity as goethite; no other crystalline forms of ferric oxide were present. A total of 7 kg of goethite and sand were prepared by such procedures. The final mixture contained about 94% sand and 6% goethite as estimated from the citrate-dithionite extractable iron content. All transport and batch adsorption experiments are performed using aliquots taken from these batches, which were homogenized and stored in polyethylene bags.

## 3. Characterization of Materials

A number of physical and chemical measurements have been performed on these materials. These are organic carbon content, total carbonate content, cation exchange capacity, dithionite extractable Al, Fe and Mn, pH, grain size, specific surface area, and mineralogy. Several of these measurements have been compared among three different laboratories to validate them. Results are given in Tables I and II. Parameters measured include those believed to be involved in determining the chemical interactions between soil and solute species and should be useful in explaining results of the solute attenuation experiments. Additionally, such information is necessary for the development of methods for predicting the movement of solutes in soils as a function of soil properties.

### C. Task 3 - Soil Columns, Methods Development, and Experimental Procedures

A primary objective of this research is to develop data on the one-dimensional transport of solutes through soil columns. These data are to be used to test and validate a groundwater transport model. Consequently, it is important to maintain control of experimental variables that can affect solute transport in porous media. The equation<sup>20</sup> describing the one-dimensional, steady state transport of an inert solute through porous media is



$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} - \bar{U} \frac{dC}{dx} \quad (1)$$

where  $C$  = tracer concentration, function of  $x$ ,  $t$  ( $\text{g}/\text{cm}^3$ ),  
 $t$  = time (h),  
 $x$  = distance into soil bed (cm),  
 $D$  = dispersion coefficient ( $\text{cm}^2/\text{h}$ ), and  
 $\bar{U}$  = average interstitial water velocity (cm/h).

The solution of this equation for the following initial and boundary conditions is given by Eq. (2).<sup>20</sup>

$$C(\infty, t) = 0$$

$$C(x > 0, t = 0) = 0$$

$$C(x = 0, t > 0) = C^0$$

$$C/C^0 = \frac{1}{2} \operatorname{erfc} \frac{L - \bar{U}t}{2\sqrt{Dt}} + \exp \frac{\bar{U}L}{D} \cdot \operatorname{erfc} \frac{L + \bar{U}t}{2\sqrt{Dt}} \quad (2)$$

Assumptions or conditions implicit in this solution are

- (1) the soil bed is homogeneous and isotropic,
- (2) the soil bed has a constant water content,
- (3) the water flux is constant,
- (4) the density and viscosity of the displacing solution is the same as that of the displaced solution,
- (5) there are minimal effects of the experimental apparatus on dispersion, and
- (6) the boundary and initial conditions are satisfied during execution of experiments.

Considerable effort has been expended to ensure that these conditions are satisfied by our experimental procedures and apparatus. Design, loading, and packing of columns are based on procedures developed by the US Geological Survey over a period of several years of working on similar experiments.<sup>21,22</sup> The column design minimizes apparatus effects, that is, the apparatus void volume is small relative to that of the soil. The sealed design of this column apparatus allows careful control of flow rates by the rate of introduction of water. Figure 2 is a detailed drawing of the column apparatus from which it could be built. The lucite column itself can be cut to any desired length. We use a 10-cm column. Loading of columns is accomplished by adding soil to several 10-cm lucite columns taped together. The soil is added through a funnel with a 1-m long by 1-cm diam exit tube in a circular pattern while the bottom of the

taped columns is being gently tapped against the floor at a frequency of about once per second. After the entire length has been filled, they are separated, the end sections are discarded, and the interior columns are capped for use in transport experiments. This method of packing ensures, as much as practical, a homogeneous soil bed both radially and vertically and is an attempt to duplicate manually the procedure discussed in Ref. 22.

During water saturation of the soil bed the primary concern is the exclusion or removal of air bubbles from the soil pore spaces. This is accomplished by first saturating the bed with carbon dioxide and then allowing water to slowly percolate into the bed from the bottom until it is completely saturated. Flow direction is then reversed and several pore volumes of 0.1M  $\text{KNO}_3$  are passed through the column to wash it and remove the  $\text{CO}_2$ . Physical mixing of solute by dispersion in the entire column system is next measured using a tracer, either chloride ( $\text{Cl}^-$ ) or tritiated water in a 0.1M  $\text{KNO}_3$  solution. The introduction of solute is accomplished by first draining the column to the top of the soil bed and then carefully introducing about 20 ml of solute solution to the top of the bed with a pipette. The column is again sealed by capping and attaching the tubing from the pump and contaminant reservoir that had previously been filled with the solute solution. There are no significant differences in viscosity between the solution in the column and the solute solution being introduced. Densities of the two solutions are matched as nearly as possible with the displacing solution having a slightly lower density to minimize any mixing or dispersion induced by density differences. A constant rate of water flow through the column is maintained using a peristaltic pump. Experiments are performed at a flow rate of about 5 ml/h, which corresponds to interstitial water velocities of 0.5-1.0 cm/h.

Flow velocities have been shown to have an effect on the attenuation of metals by different soils.<sup>23</sup> Such effects should be expected given the rates of different chemical reactions and the physical and chemical complexity of soil materials. Although an investigation of kinetic effects is not a direct goal of this research, it seems prudent to perform the transport experiments at flow velocities where chemical equilibrium should be a reasonable approximation for most soil/solute combinations. At a minimum we feel that flow rates should be appropriate to avoid nonequilibrium from diffusion-controlled processes in aggregated soils. Also of importance is a necessity for completing experiments within reasonable time periods, which we define as weeks to months, rather than years.

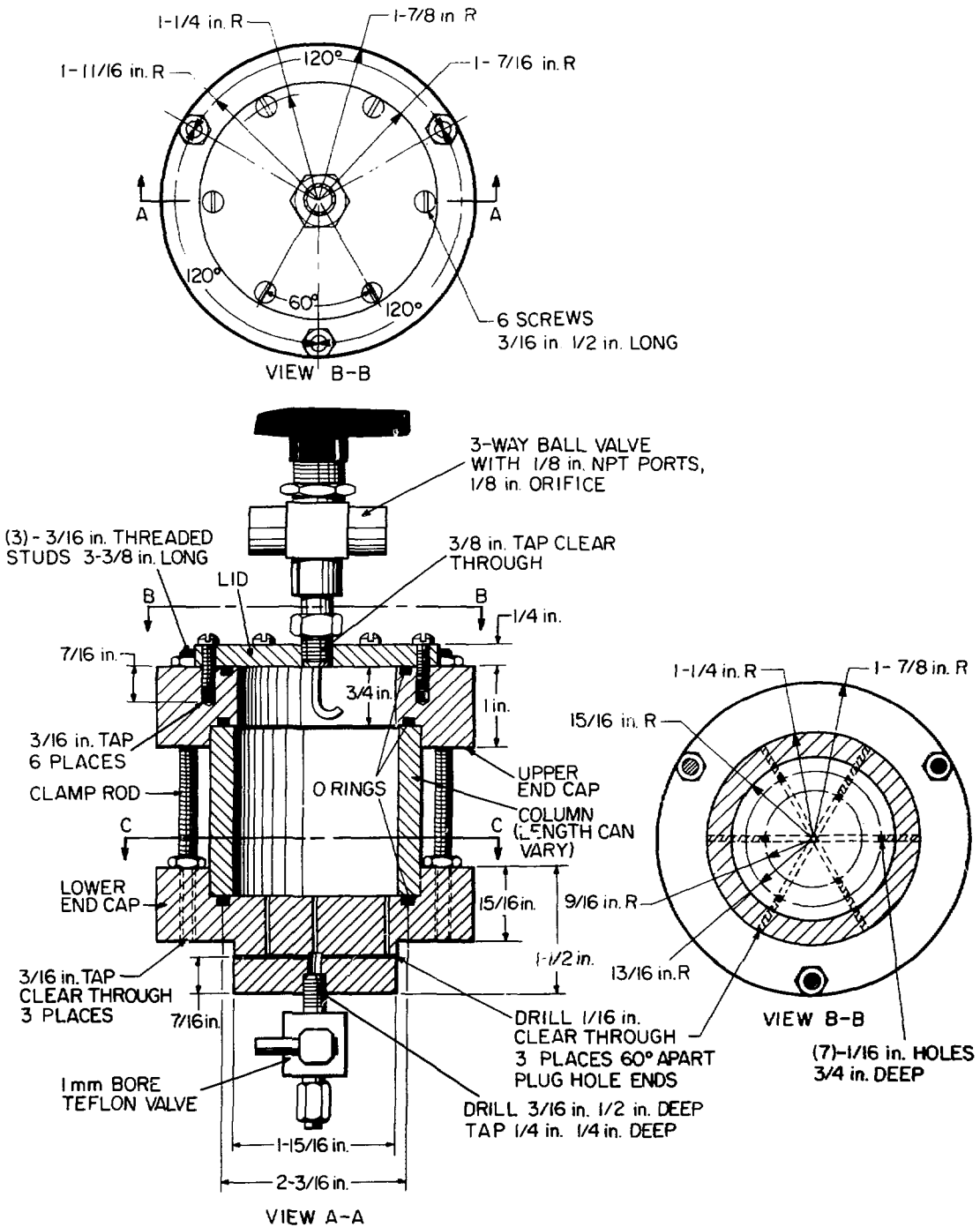


Fig. 2. Column apparatus for simulating one-dimensional solute transport.

The flow rate of 5 ml/h we have chosen corresponds to fluxes in our materials of 0.5 to 1.0 cm/h and is based on the work of Alesh et al.,<sup>24</sup> Rao et al.,<sup>25</sup> and a set of experiments we performed on the transport of 50 ppm B and Cd through kaolinite coated on silica sand.

Our experiments indicate that the chemical attenuation of B and Cd in kaolinite does not significantly differ at flows of 1, 5, and 10 ml/h. The only significant difference caused by variations in flow rate in the breakthrough curves was an increase in tailing at the high concentration end of the breakthrough curve. This

undoubtedly caused by an increase in dispersion or physical mixing at higher flow rates. Chemistry of interaction, as measured by the eluent volume at 50% breakthrough, is not appreciably changed by the different flow rates. Tailing similar to our observations has been observed at flow velocities higher than those used here. The tailing was interpreted as a result of non-equilibrium between interpore water and intrapore water.<sup>25</sup> However, according to this same study, such effects do not occur under the conditions of our experiments. Based on our work and that of others<sup>23-25</sup> we have selected a flow rate of 5 ml/h (interstitial velocities of 0.5-1.0 cm/h). This rate is a compromise between experimental practicality and a desire to maintain chemical equilibrium between soil bed and solute. We recognize there will probably be some nonequilibrium processes occurring at the flow velocity selected. Experiments here and in coordinated studies at the University of Wisconsin are investigating possible kinetic effects.

## D. Task 3 - Adsorption Experiments. Batch and Column

### 1. Batch Adsorption Studies

Preliminary batch studies were performed on all of the materials used in this research to assess the potential magnitude of adsorption. Five-gram samples of each soil material together with 50 ml of a solution containing a known quantity of adsorbate were placed in a polyethylene centrifuge jar. The anionic elements As, B, Mo, and Se were combined in one solution, the cations Cd and Ni in another. The pH of each solution was taken before, during, and after the experiments, which involved agitating for 2 days on a mechanical shaker. The slurries were then centrifuged at 13 000 rpm for 10 min and decanted into prewashed vials. A control with no solid was also carried through the procedure. Initial concentrations were usually 100, 10, and 1 mg/l. Because no

attempt was made to control pH, the final pH was determined by the solution and soil material. The mass of each element adsorbed per gram of adsorbent varied considerably from material to material because of variations in pH as well as differences in adsorption properties of each material. The results are summarized in Table III. A complete tabulation of results is provided in Appendix C (Tables C-I—C-VI).

As expected, silica sand does not appreciably remove any of the contaminant species from solution. The dunal sand removed about 90% of the Cd and Ni at 1 mg/l initial concentration ( $C^0$ ), but much lower percentages at  $C^0$  values of 10 and 100 mg/l. Equilibrium pH of the dunal sand solutions was 5.1-5.6. Except for arsenic, none of the anionic species are adsorbed by the dunal sand. As much as 30% of the arsenic may be removed. As shown in Table I, cation exchange capacity of dunal sand is very low (0.24 meq/100 g) as are extractable Fe (0.1%), Al (0.02%), and Mn (0.002%). Thus we do not expect much trace element removal by this material.

In spite of a low surface area and cation exchange capacity (Table I), kaolinite coated onto silica sand has a high capacity for the cations Cd and Ni, as well as As. Adsorption of Mo and Se is also significant, whereas that of B is not. Equilibrium pH of these solutions is in the range of 4.1-4.9. At such pH, adsorption of negatively charged anions should occur if it is going to occur at any pH. At pH greater than the isoelectric point, a material is negatively charged. The isoelectric pH of kaolinite minerals is reported to be about 4. It is unlikely that we would encounter natural situations with aqueous pH any lower than 4, thus the experimental pH constitutes a lower limit for most anticipated real situations. Cases where leachates are quite acidic, such as acid mine drainages, would not usually be expected to remain so upon entering the soil environment.

The bottom four materials in Table III remove a large amount of all species except boron from our experimental solutions. Boron is not appreciably removed or sorbed by any of the materials. At the pH of these experiments boron is present as the uncharged  $B(OH)_3$  species. Apparently this species does not interact with these materials by either a chemical or a physical mechanism. At  $C^0$  of 1 mg/l, Cd, Ni, and As are nearly completely removed by these four soil materials even though equilibrium solution pH spans a range of 4.7-9.8. In real leachates, concentrations of these elements would not exceed 1 mg/l except for unusual circumstances. The remaining three species, B, Mo, and Se, exhibit much variability in extent of adsorption by these soil materials.

TABLE III

PERCENTAGES OF TOTAL CONTAMINANT REMOVED  
BY SOIL MATERIAL FROM SOLUTIONS WITH  
INITIAL CONCENTRATIONS OF 1, 10, AND 100 mg/l<sup>a</sup>

Material	Cd	Ni	As	B	Mo	Se
Silica sand	0 - 15	0 - 8	<5	<5	0	0
Dunal sand	0 - 90	0 - 90	4 - 30	<5	0	0
Kaolinite <sup>b</sup>	35 - 95	35 - 95	25 - 100	2 - 10	40 - 50	20 - 40
Sandy clay loam	5 - 90	1 - 90	70 - 100	2 - 30	90 - 100	25 - 50
Acidic <sup>b</sup> clay loam	85 - 99	80 - 97	80 - 100	2 - 10	80 - 97	10 - 40
Calcareous <sup>b</sup> clay loam	95 - 100	80 - 100	70 - 100	2 - 30	4 - 30	40 - 70
Goethite <sup>b</sup>	100	100	100	<5 - 25	<30	30 - 60

<sup>a</sup>Initial Se concentrations were 2.5 and 25 mg/l.

<sup>b</sup>These materials are coated onto sand.

Molybdenum present at low concentrations ( $C^0 = 1$  mg/l) in initial solutions is highly adsorbed by the sandy clay loam (pH = 4.9) and the acidic clay loam soil (pH = 4.7) but is much less adsorbed by the calcareous clay loam (pH = 7.6) and goethite-sand (pH = 9.8). Thus molybdenum adsorption seems to be sensitive to pH. Our measured selenium concentrations were quite variable and the lowest initial concentrations (0.25 mg/l) were not measured by the analytical technique used. There is some removal of selenium by these four soil materials, but much less than corresponding adsorption of arsenic and molybdenum. Selenium adsorption does not appear to be as pH sensitive as is molybdenum adsorption.

These results do not show a strong pH effect on contaminant adsorption at low initial concentrations (1 mg/l) except for molybdenum. For example, when 50 µg

of Cd and Ni in 50 ml are equilibrated with 5 g of each soil material, they are 90 to 100% removed from solution in every case except silica sand. Equilibrium pH values of these solutions were 4.4, 4.4, 4.7, 4.9, 7.6, and 9.8. The same is usually true for As. Molybdenum adsorption is pH sensitive as evidenced by its adsorption on calcareous clay loam and goethite-sand relative to that in the acidic clay loam and the sandy clay loam.

## 2. Batch Adsorption on Goethite

A more extensive and controlled batch adsorption experiment using the anions only was performed with goethite-coated sand at two different pH values (6.6 and 8.4). The following solutions were prepared in 0.1M KNO<sub>3</sub>.

Solution	Approximate Initial Concentration (mg/l)			
	As	B	Mo	Se
I	500	50	100	50
II	250	30	75	30
III	100	10	50	10
IV	50	1	10	1

KOH or HNO<sub>3</sub> were used to adjust pH to either 6.6 or 8.4 as required. To 2.5 g of goethite-sand in a polyethylene centrifuge tube was added 25 ml of the appropriate solution in triplicate. These vials were placed in a temperature controlled water bath shaker at 23°C and agitated. Each day they were checked for pH and adjusted until successive pH measurements were the same. They were then centrifuged for 10 min at 17 000 rpm, decanted, and the solutions analyzed for As, B, Mo, Se, and Fe by a DC arc plasma procedure.

Results of this experiment are shown in Table IV. Specific adsorption or per cent adsorption do not vary much between the two pH values. The greatest difference is illustrated by the final concentrations of molybdenum after equilibration with an initial solution containing 11 mg/l of molybdenum. Here the equilibrium concentration of 0.07 mg/l at pH 6.6 is much lower than the corresponding pH 8.4 concentration of 3.6 mg/l. This constitutes a difference of 100% removal vs 77% removal, or, viewed in terms of per cent remaining in the solution, 0% vs 23%. At both pH values, As and Mo are highly adsorbed from the solution with the lowest initial concentrations, whereas B and Se are only moderately adsorbed - about 15% and 33%, respectively. These adsorption data are in general agreement with those for goethite presented above at pH values of 9.7 and 9.8. Again molybdenum is the exception as its adsorption decreases to 30% at pH 9.8 (equilibrium concentration 0.8 mg/l) compared to 77% at pH 8.4 and 100% at pH 6.6.

These batch experiments indicate that adsorption of As, B, and Se from solutions containing them in low concentrations on goethite is not very sensitive to pH. In contrast, Mo adsorption does show a pH dependence. The goethite affinity for these elements in order of decreasing adsorption is As >> Mo >> Se > B. The results are of importance to our soil column experiments as an indication of pH sensitivity of adsorption, that is, how important is measurement and control of pH to the success of model predictions of column breakthrough and as an indication of the time to breakthrough of the various species.

### 3. Soil Column Transport Studies

Concomitant with the above development endeavors we have been proceeding with soil column transport studies. Initial experiments on Cd and Ni transport through silica sand and kaolinite-coated sand were performed using a glass column welded to a 60-ml buchner funnel with flow rate under pump control. Saturation of the soil bed was maintained by elevating the exit tubing to a height above that of the top of the soil bed. This apparatus caused much apparatus-induced physical mixing but was quite satisfactory for determining adsorption. The apparatus-induced dispersion could be accounted for by the tracer studies.

Since completion of the new column design, as discussed in Sec. III.C, additional experimental soil column breakthrough curves have been finished using this design. These are As, B, Mo, and Se in kaolinite sand, dunal sand, and goethite sand, and Cd and Ni in dunal sand and goethite sand. In several cases desorption in the column has also been performed to determine the reversibility of the adsorption reaction. The desorbing solution is the same as the adsorbing solution less the solute species being studied, for example, 0.1M KNO<sub>3</sub>.

*a. Cd and Ni Transport Through Silica Sand.* Column data are in Table V. After washing with 30 pore volumes, the Cl<sup>-</sup> tracer (2560 mg/l) was passed through the columns until complete breakthrough. The Cl<sup>-</sup> was then washed from the bed with several pore volumes of 0.033M Ca(NO<sub>3</sub>)<sub>2</sub> before introducing the solution of Cd and Ni in 0.033M Ca(NO<sub>3</sub>)<sub>2</sub>. The experiment was continued until Cd and Ni eluent concentrations were either the same as the influent values or leveled off to a slowly changing value. Eluent pH was monitored at intervals throughout the experiment and was very close for the two duplicate columns; 5.52 for column C eluent and 5.47 for column D.

Breakthrough curves are shown in Fig. 3 for the two duplicate columns. Replication was excellent. Chloride breakthrough occurred at one pore volume as expected for a noninteracting tracer. Cd and Ni breakthrough, as defined by the pore volume where eluent concentration divided by influent concentration (C/C<sup>0</sup>) is equal to 0.5, occurred at about 1.1 pore volume. Cadmium breakthrough was slightly later than nickel in both columns. Nickel eluent concentrations began to level off at a value

TABLE IV

ADSORPTION OF As, B, Mo, AND Se ON  
A GOETHITE-COATED SAND AT 2 pH<sup>a</sup>

	pH = 6.6					pH = 8.4			
	Initial Conc. (mg/l)	Equil. Conc. (mg/l)	Per Cent Adsorbed	Specific Adsorption		Equil. Conc. (mg/l)	Per Cent Adsorbed	Specific Adsorption	
				( $\mu\text{g/g}$ ) <sup>a</sup>	(mmoles/100 g) <sup>b</sup>			( $\mu\text{g/g}$ ) <sup>a</sup>	(mmoles/100 g) <sup>b</sup>
As	503 $\pm$ 7	401 $\pm$ 15	19	950 $\pm$ 130	22.2	390 $\pm$ 12	26	1300 $\pm$ 100	30.4
	270 $\pm$ 7	141 $\pm$ 10	47	1260 $\pm$ 40	29.5	150 $\pm$ 10	45	1220 $\pm$ 60	28.6
	106 $\pm$ 4	2.9 $\pm$ 1.3	97	1030 $\pm$ 50	24.1	10.8 $\pm$ 0.8	90	950 $\pm$ 50	22.2
	56 $\pm$ 4	0.2 $\pm$ 0.1	100	560 $\pm$ 30	13.1	0.25 $\pm$ 0.13	100	560 $\pm$ 30	13.1
B	46 $\pm$ 1	45 $\pm$ 2	2	9 $\pm$ 6	1.5	41 $\pm$ 2	5	65 $\pm$ 20	10.5
	29 $\pm$ 1	26 $\pm$ 1	9	25 $\pm$ 10	4.1	26 $\pm$ 1	14	40 $\pm$ 5	6.5
	7.8 $\pm$ 0.5	7.1 $\pm$ 0.5	13	10 $\pm$ 2	1.6	6.8 $\pm$ 0.4	15	22 $\pm$ 5	1.9
	2.4 $\pm$ 0.1	2.1 $\pm$ 0.2	13	3 $\pm$ 1.4	0.5	2.1 $\pm$ 0.1	17	4.1 $\pm$ 1.2	0.67
Mo	92 $\pm$ 4	75 $\pm$ 3	17	160 $\pm$ 25	2.9	78 $\pm$ 5	20	180 $\pm$ 40	3.3
	74 $\pm$ 3	50 $\pm$ 2	31	230 $\pm$ 20	4.2	60 $\pm$ 2	20	150 $\pm$ 10	2.7
	41 $\pm$ 2	13 $\pm$ 3	68	280 $\pm$ 20	5.1	31 $\pm$ 2	66	270 $\pm$ 40	4.9
	11 $\pm$ 1	0.07 $\pm$ 0.06	100	115 $\pm$ 10	2.1	3.6 $\pm$ 1.2	77	85 $\pm$ 9	1.6
Se	46 $\pm$ 2	42 $\pm$ 2	10	44 $\pm$ 5	0.98	40 $\pm$ 2	16	75 $\pm$ 13	1.7
	29 $\pm$ 1	24 $\pm$ 1	17	47 $\pm$ 6	1.04	25 $\pm$ 1	15	43 $\pm$ 3	0.96
	8.4 $\pm$ 0.5	6.2 $\pm$ 0.5	29	24 $\pm$ 3	0.53	6.8 $\pm$ 0.3	21	18 $\pm$ 2	0.40
	1.1 $\pm$ 0.2	0.7 $\pm$ 0.1	33	3.6 $\pm$ 1.2	0.080	0.8 $\pm$ 0.1	34	3.7 $\pm$ 1.7	0.082

<sup>a</sup>Specific adsorption in micrograms of solute removed from solution per gram of goethite-coated sand.

<sup>b</sup>Corrected for dilution by sand, 5.57%  $\alpha$ -FeOOH.

TABLE V

## DATA FOR Cd AND Ni TRANSPORT EXPERIMENTS

Bed Material	Experiment	Total Adsorbent Mass (g)	Bed Pore Volume (cm <sup>3</sup> )	Bed Length (cm)	Bed Diameter (cm)	Flow Rate (cm <sup>3</sup> /h)	Interstitial Velocity (cm/h)	Porosity	pH	Final or Equilibrium Concentration (mg/L)		Adsorption (meq/100 g)	
										Cd	Ni	Cd	Ni
Silica Sand (SC)	Cl <sup>-</sup> on <sup>a</sup>	350	72	11.5	4.68	5.5	0.89	0.36	-	-	-	-	-
	Adsorption <sup>b</sup>	350	72	11.5	4.68	4.7	0.75	0.36	5.5 ± 0.2	9.63	12.9	3.9 × 10 <sup>-4</sup>	9.0 × 10 <sup>-4</sup>
Silica Sand (SD)	Cl <sup>-</sup> on <sup>a</sup>	350	78	11.6	4.72	5.1	0.77	0.38	-	-	-	-	-
	Adsorption <sup>b</sup>	350	78	11.6	4.72	4.8	0.71	0.38	5.5 ± 0.2	9.63	12.9	4.2 × 10 <sup>-4</sup>	8.8 × 10 <sup>-4</sup>
Kaolinite Sand (KE)	Cl <sup>-</sup> on <sup>a</sup>	265	51.5	9.45	4.65	5.01	0.92	0.33	-	-	-	-	-
	Absorption <sup>b</sup>	265	51.5	9.45	4.65	5.10	0.92	0.33	6.3 ± 0.1	9.6 ± 0.1	12.9 ± 0.2	0.042	0.081
	Desorption <sup>c</sup>	265	51.5	9.45	4.65	5.50	0.98	0.33	6.3 ± 0.1	<0.01	<0.01	-	-
Kaolinite Sand (KF)	Cl <sup>-</sup> on <sup>a</sup>	265	51.2	9.46	4.70	4.59	0.85	0.31	-	-	-	-	-
	Absorption <sup>b</sup>	265	51.2	9.46	4.70	4.55	0.85	0.31	6.3 ± 0.1	9.6 ± 0.1	12.9 ± 0.2	0.039	0.076
	Desorption <sup>c</sup>	265	51.2	9.46	4.70	5.00	0.93	0.31	6.3 ± 0.1	<0.01	<0.01	-	-
Dunal Sand (MSA)	Cl <sup>-</sup> on <sup>a</sup>	345	82	10.17	5.08	5.05 ± 0.03	0.62	0.40	-	-	-	-	-
	Absorption <sup>b</sup>	345	82	10.17	5.08	5.17 ± 0.04	0.64	0.40	7.1 ± 0.1	9.6 ± 0.2	12.9 ± 0.3	0.026	0.039
	Desorption <sup>c</sup>	345	82	10.17	5.08	4.95 ± 0.07	0.61	0.40	6.7 - 7.1	<0.01	<0.01	-	-
Dunal Sand (MSB)	Cl <sup>-</sup> on <sup>a</sup>	342	80	10.18	5.05	5.06 ± 0.05	0.65	0.39	-	-	-	-	-
	Absorption <sup>b</sup>	342	80	10.18	5.05	4.83 ± 0.04	0.62	0.39	7.1 ± 0.1	9.6 ± 0.2	12.9 ± 0.3	0.026	0.038
	Desorption <sup>c</sup>	342	80	10.18	5.05	4.74 ± 0.05	0.61	0.39	6.7 - 7.1	<0.01	<0.01	-	-
Goethite Sand (GC)	<sup>3</sup> H on <sup>a</sup>	322	85	10.18	5.07	5.69	0.72	0.39	-	-	-	-	-
	Absorption <sup>b</sup>	322	85	10.18	5.07	4.78	0.61	0.39	5.61 ± 0.05	17.20	13.00	0.62	1.96
	Desorption <sup>c</sup>	322	85	10.18	5.07	4.70	0.60	0.39	5.48 ± 0.05	0.02	0.01	-	-

<sup>a</sup>Numbers in this row pertain to chloride tracer experiment.

<sup>b</sup>Numbers in this row pertain to Ni and Cd adsorption experiment.

<sup>c</sup>Numbers in this row pertain to Ni and Cd desorption experiment.

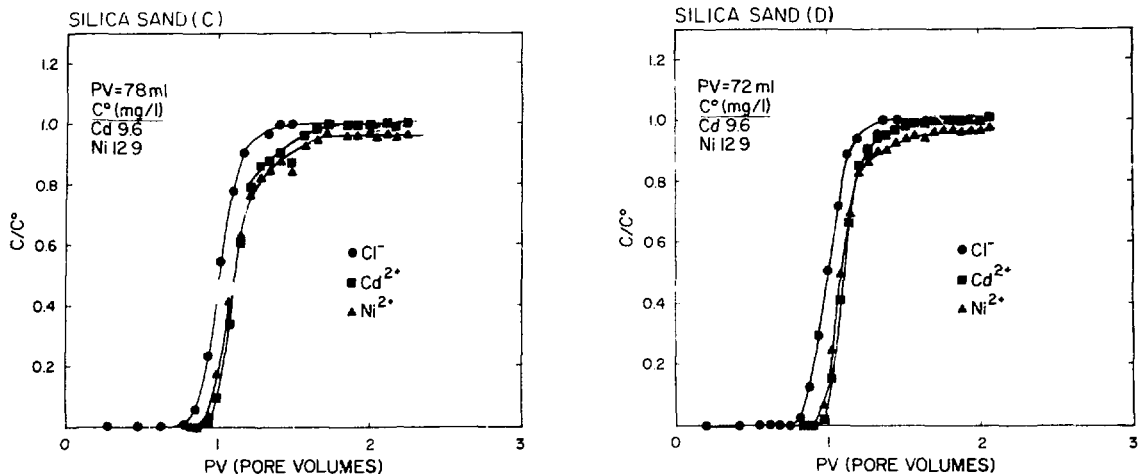


Fig. 3. Duplicate experimental breakthrough curves for  $\text{Cl}^-$ , Cd, and Ni in silica sand.

lower than influent and slowly increase, whereas Cd showed no such tailing. (We have subsequently observed similar Ni behavior in other soil materials.) Quantities of Cd and Ni adsorbed or exchanged in the sand were 4.0 and  $8.9 \times 10^{-4}$  meq/100 g, respectively. Thus, as expected for a silica sand, very little solute was retained. This is also made quite evident by the similarity between the tracer breakthrough and that of Cd and Ni in Fig. 3. These results confirm that silica sand is relatively inert and thus will not contribute significantly to adsorption when used as a substrate for coating (or diluting) other soils or mineral components of soils.

**b. Cd and Ni Adsorption and Desorption on Kaolinite Sand.** This experiment was performed using the same procedures and column design as for Cd and Ni adsorption by silica sand. After saturation of the kaolinite with Cd and Ni, they were desorbed with a solution virtually the same as the adsorbing solution, but without Cd and Ni, to investigate the reversibility of the adsorption reaction.

The data for this experiment are presented in Table V. Breakthrough curves in Fig. 4 for column KF show little adsorption of either Ni or Cd by kaolinite compared to  $\text{Cl}^-$ . Results for the duplicate column KE were the same within the uncertainty of experimental measurements. Desorption of Ni and Cd is quite similar to adsorption except for some tailing in the Cd desorption curve.

At this time we have no explanation for the Cd tailing upon desorption nor for the observation that relative Ni

concentrations tend to approach 1.0 very slowly. Recall a similar Ni pattern with silica sand (Fig. 3). Relative nickel concentrations do approach 1.0 after several pore volumes, suggesting a slow kinetic process as one possible explanation. Using the pore volume breakthrough, Cd and Ni adsorption are calculated at 0.040 and 0.078 meq/100 g, respectively, compared to a cation exchange capacity (Table I) of 4.2 meq/100 g. Thus the majority of kaolinite exchange sites must be occupied by calcium because of its presence in large excess ( $0.0333\text{M}$  concentration) compared to Cd and Ni ( $8.5 \times 10^{-4}\text{M}$  and  $2.2 \times 10^{-4}\text{M}$ , respectively) in the influent solution.

**c. Adsorption and Desorption of Cd and Ni on Dual Sand.** These and all subsequent experiments were conducted with the experimental apparatus and procedures discussed in Sec. III.C. After column loading,  $\text{CO}_2$  saturation, and saturation and washing with 0.1M  $\text{KNO}_3$ , chloride tracer adsorption and desorption runs with KCl were performed. The chloride was then removed from the column with 0.1M  $\text{KNO}_3$ .

A solution containing 9.6 and 12.9 mg/l of Cd and Ni in 0.1M  $\text{KNO}_3$  (the exact molarity of  $\text{KNO}_3$  was determined by the quantity required to make it 1% less dense than the solution being desorbed to minimize density efforts) was then used to develop breakthrough curves as shown in Fig. 5. Column parameters and other data are in Table V. The  $\text{Cl}^-$ , Cd, and Ni 50% breakthrough occurred at 1.0, 7.5, and 4.7 pore volumes, respectively. The amounts of Cd and Ni adsorbed are



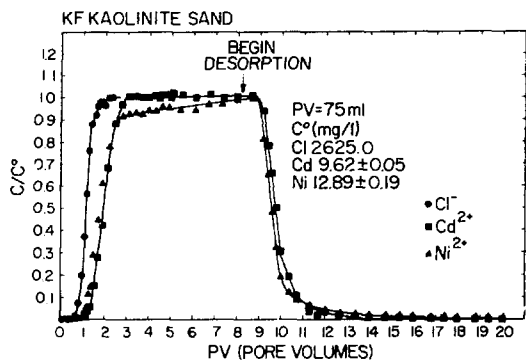


Fig. 4. Kaolinite coated onto sand:  $\text{Cl}^-$ , Cd, and Ni breakthrough curves.

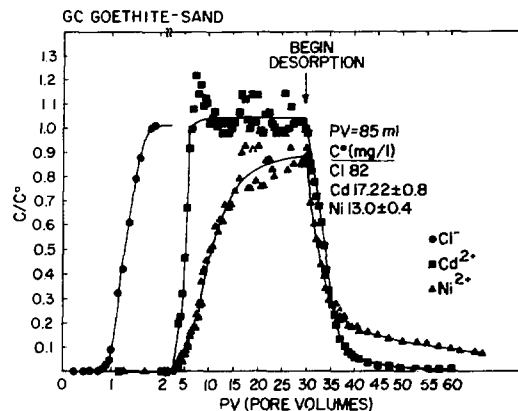


Fig. 6. Goethite coated onto sand:  $\text{Cl}^-$ , Cd, and Ni breakthrough curves.

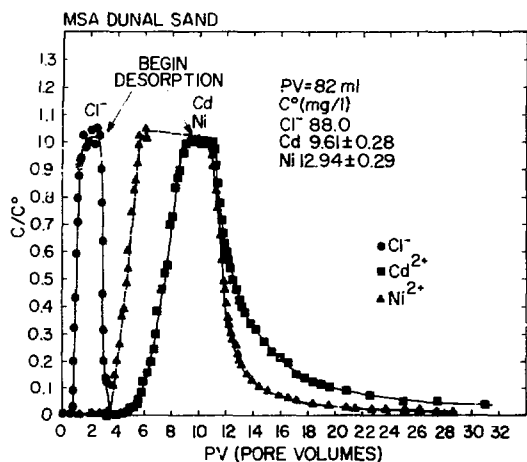


Fig. 5. Dunal sand: breakthrough curves for  $\text{Cl}^-$ , Cd, and Ni.

0.026 and 0.038 meq/100 g, respectively. The cation exchange capacity of the dunal sand (Table I) is 0.24 meq/100 g. Desorption is also shown in Fig. 15.

**d. Adsorption and Desorption of Cd and Ni on Goethite-Sand.** The column parameters, influent concentrations, and eluent pH are shown in Table V. Breakthrough curves are shown in Fig. 6. This was the first set of experiments using tritiated water as the inert tracer. This was necessary because 50% breakthrough for  $\text{Cl}^-$  occurred significantly beyond one pore volume. In contrast, the same point for tritiated water occurred at one pore volume. Fifty per cent breakthrough occurred at 1.30, 5.30, and 10.30 pore volumes for  $\text{Cl}^-$ , Cd, and Ni, corresponding to adsorption of 0.33, 0.62, and 1.96 meq/100 g, respectively. As for previous materials, Ni

never reached complete breakthrough but appeared to be slowly approaching it. This pattern was observed in desorption, as well as adsorption.

#### 4. Anion Transport in Kaolinite-Sand, Dunal Sand, and Goethite-Sand

Transport of the anionic elements As, B, Mo, and Se is also being studied. Presently, results for these are available in kaolinite on sand, the dunal sand soil, and goethite on sand. The column parameters and adsorption to 50% breakthrough are shown in Table VI. Breakthrough curves, including adsorption and desorption, are shown in Figs. 7-9.

In kaolinite, the curves (Fig. 7) have good shapes except for some apparent excess immediately following breakthrough for B, Se, and Mo. Arsenic tails a little in adsorption and desorption, and never reaches a  $C/C^0$  value of 1.0. Chloride is intended as an inert tracer in this work and has a 50% breakthrough very near 1 pore volume, that is, about 1.15 pore volumes. Breakthrough to 50% for B, Se, Mo, and As occurs at 1.40, 2.35, 3.45, and 10.15 pore volumes, respectively (Fig. 7). Thus, As is highly adsorbed compared to B, Se, and Mo. Adsorption in mmoles per 100 g of kaolinite (corrected for the sand) for each of these is given in Table VI.

Adsorption values for these elements on the dunal sand (duplicate) are also shown in Table VI. The breakthrough curves in Fig. 8 show how they sorb and desorb vs eluent pore volumes. At 1 pore volume,  $\text{Cl}^-$  reaches 50% breakthrough as expected for an inert tracer. B, Se, Mo, and As attain 50% breakthrough at 1.10, 1.15, 1.45, and 7.55 pore volumes, respectively. Thus, similar to kaolinite, As is the most highly retained

TABLE VI

## EXPERIMENTAL PARAMETERS AND RESULTS FOR TRANSPORT OF As, B, Mo, AND Se THROUGH LABORATORY SOIL COLUMNS

Bed Material	Experiment	Total Adsorbent Mass (g)	Bed Pore Volume (cm <sup>3</sup> )	Bed Length (cm)	Bed Diameter (cm)	Flow Rate (cm <sup>3</sup> /h)	Interstitial Velocity (cm/h)	Porosity	Eluent pH B, Mo, Se	Eluent pH Arsenic	Adsorption (mmoles/100 g)			
											As	B	Mo	Se
Kaolinite Sand (KG)	Cl <sup>-</sup> on	312	67.5	10.20	5.05	5.08	0.71	0.33	-	-	-	-	-	-
	Adsorption	312	67.5	10.20	5.05	5.08	0.77	0.33	7.20 ± 0.15	7.06 ± 0.21 <sup>a</sup>	0.26	0.045	0.050	0.030
	Desorption	312	67.5	10.20	5.05	4.93	0.75	0.33	6.32 ± 0.11	6.30 ± 0.11	-	-	-	-
	Cl <sup>-</sup> off	312	67.5	10.20	5.05	4.93	0.75	0.33	-	-	-	-	-	-
Kaolinite Sand (KH)	Cl <sup>-</sup> on	311	67.5	10.20	5.04	5.01	0.76	0.33	-	-	-	-	-	-
	Adsorption	311	67.5	10.20	5.04	5.01	0.76	0.33	7.14 ± 0.10	6.90 ± 0.27 <sup>b</sup>	0.21	0.037	0.046	0.028
	Desorption	311	67.5	10.20	5.04	4.95	0.75	0.33	6.30 ± 0.12	6.23 ± 0.14	-	-	-	-
	Cl <sup>-</sup> off	311	67.5	10.20	5.04	4.95	0.75	0.33	-	-	-	-	-	-
Dunal Sand (MSA)	Cl <sup>-</sup> on	345	83.5	10.17	5.08	4.96	0.60	0.41	-	-	-	-	-	-
	Adsorption	345	83.5	10.17	5.08	4.92	0.59	0.41	7.34 ± 0.25	7.18 ± 0.27	0.019	0.0019	0.00107	0.00055
	Desorption	345	83.5	10.17	5.08	4.88	0.60	0.40	6.78 ± 0.15	6.78 ± 0.15	-	-	-	-
	Cl <sup>-</sup> off	345	83.5	10.17	5.08	4.89	0.60	0.40	-	-	-	-	-	-
Dunal Sand (MSB)	Cl <sup>-</sup> on	342	80.5	10.18	5.05	4.42	0.55	0.40	-	-	-	-	-	-
	Adsorption	342	80.5	10.18	5.05	4.38	0.55	0.40	7.32 ± 0.13	7.20 ± 0.18	0.019	0.0019	0.00093	0.00040
	Desorption	342	80.5	10.18	5.05	4.44	0.57	0.39	6.95 ± 0.15	6.95 ± 0.15	-	-	-	-
	Cl <sup>-</sup> off	342	80.5	10.18	5.05	4.44	0.57	0.39	-	-	-	-	-	-
Goethite Sand (GA)	Cl <sup>-</sup> on	327	80	10.21	5.07	5.35	0.70	0.38	-	-	-	-	-	-
	Adsorption	327	80	10.21	5.07	5.14	0.67	0.38	c	-	20.5	1.75	6.11	1.36
	Desorption	327	80	10.21	5.07			0.38	d	-	-	-	-	-
		327	80	10.21	5.07			0.38	-	-	-	-	-	-
Goethite Sand (GB)	Cl <sup>-</sup> on	334	80	10.21	5.07	4.50	0.59	0.38	e	-	-	-	-	-
	Adsorption	334	80	10.21	5.07	5.34	0.70	0.38	e	-	-	1.79	5.75	1.23

<sup>a</sup>From C/C<sup>0</sup> = 0.8 to C/C<sup>0</sup> = 0.9, eluent pH decreased from 6.8 to 6.4.

<sup>b</sup>From C/C<sup>0</sup> = 0.1 to C/C<sup>0</sup> = 0.9, eluent pH decreased from 7.1 to 6.5.

<sup>c</sup>Pore volumes 0-29, pH = 6.38 ± 0.01.

Pore volumes 30-80, pH = 6.77 ± 0.10.

Pore volumes 81-151, pH = 8.35 ± 0.29.

Pore volumes 152-286, pH = 7.66 ± 0.29.

Pore volumes 286-365, pH = 7.06 ± 0.16.

<sup>d</sup>Pore volumes 0-17, pH = 6.57 ± 0.05.

Pore volumes 19-48, pH = 5.77 ± 0.28.

<sup>e</sup>Similar to results for experiment GA above.

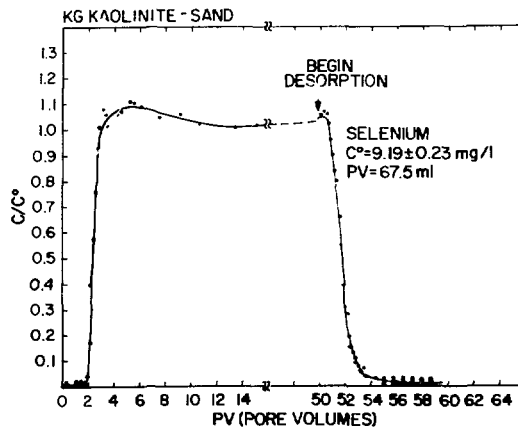
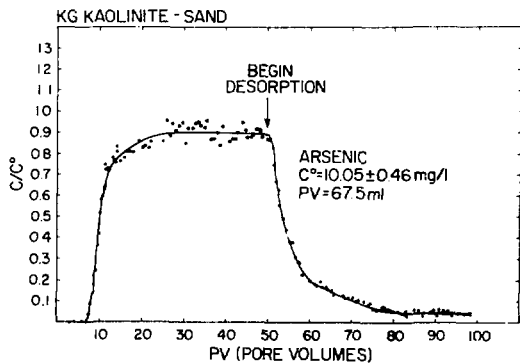
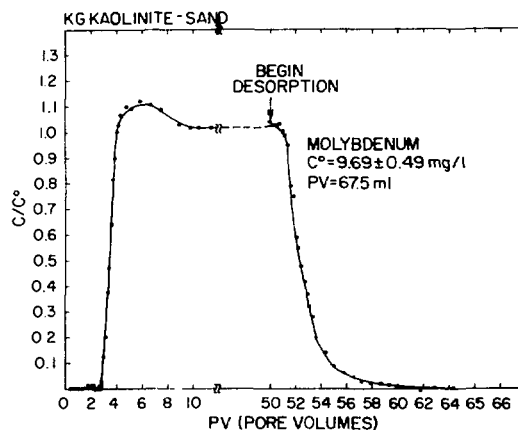
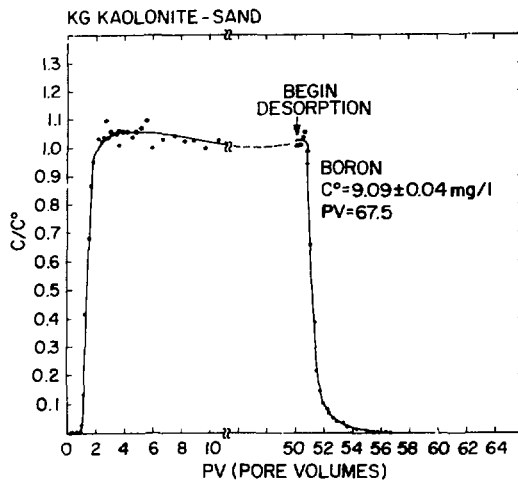
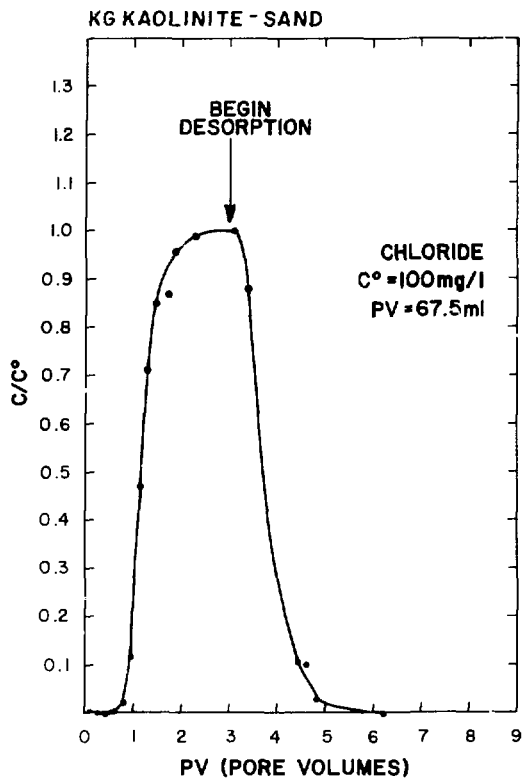


Fig. 7. Breakthrough curves for  $\text{Cl}^-$ , As, B, Mo, and Se in a dual sand.

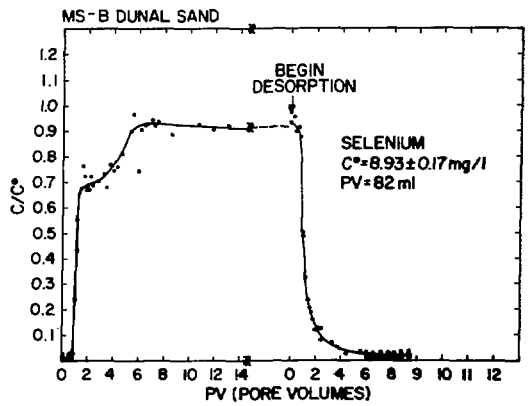
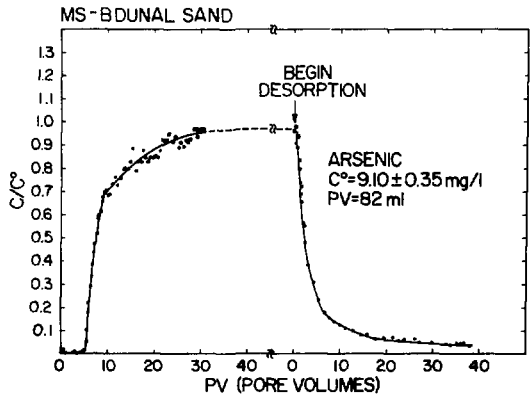
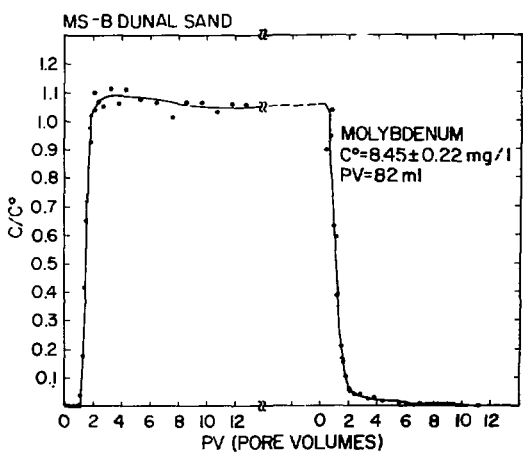
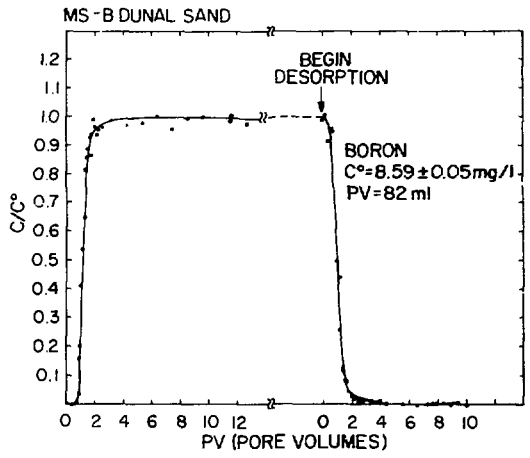
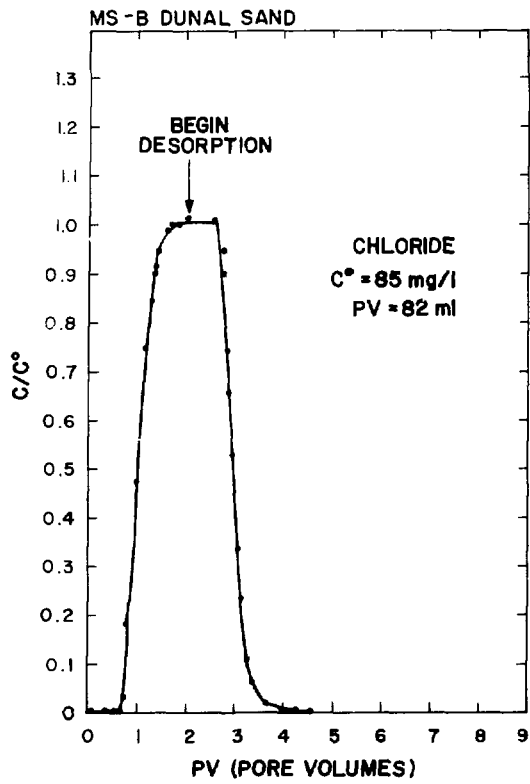


Fig. 8. Breakthrough curves for  $\text{Cl}^-$ , As, B, Mo, and Se in a dunal sand.

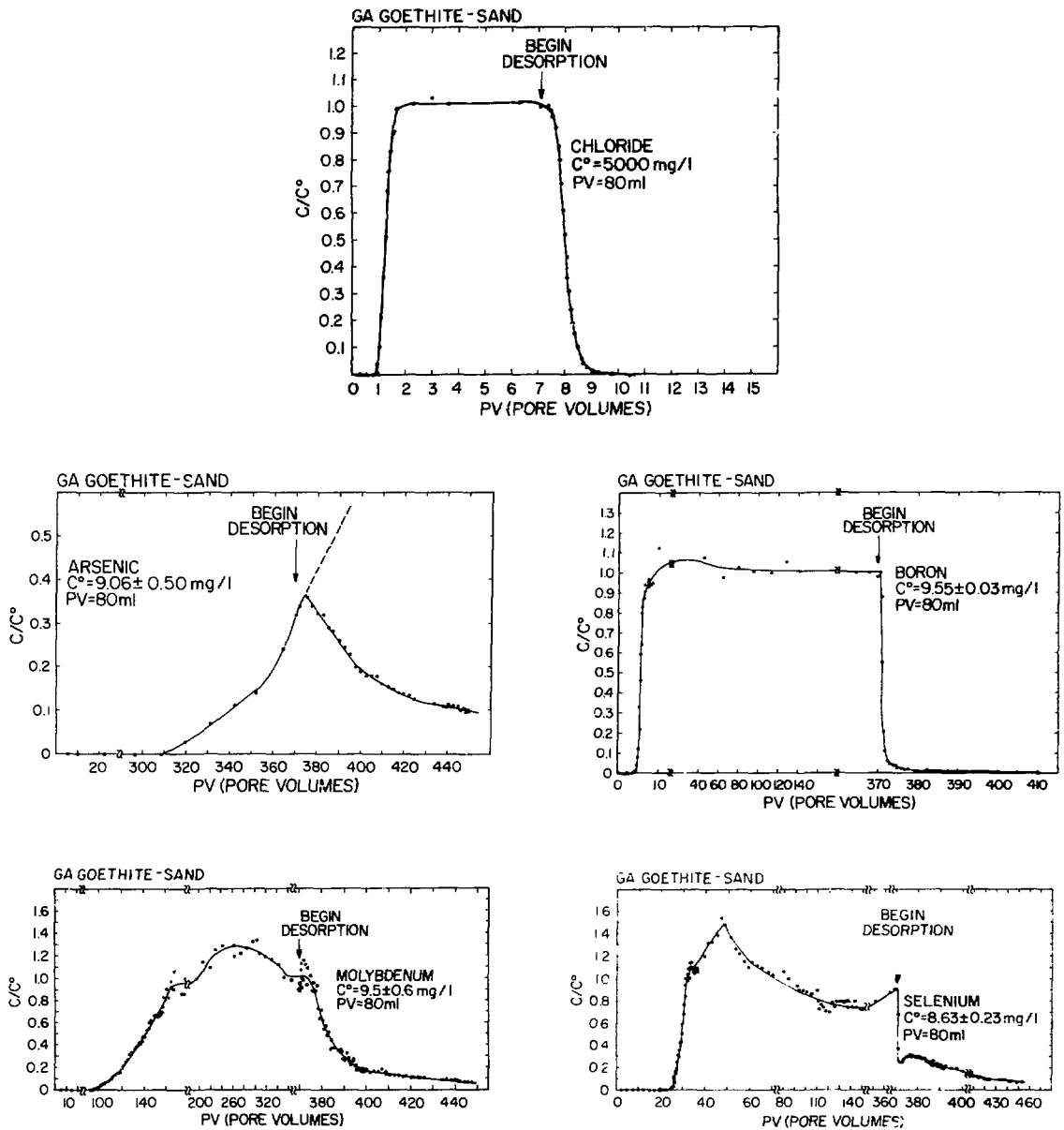


Fig. 9. Breakthrough curves for  $\text{Cl}^-$ , As, B, Mo, and Se in goethite coated onto sand.

by the dunal sand. Adsorption values in mmoles/100 g for these are shown in Table VI. Eluent pH varied from about 6.9 to 7.6 during the adsorption phase of this experiment with an average value of about 7.25. The Se breakthrough curve (Fig. 8) rises rapidly to  $C/C^{\circ} = 0.7$  at 1.5 pore volumes, levels off for a couple of pore volumes, and then rises to  $C/C^{\circ} \approx 0.93$  between 4 and 6 pore volumes. Both columns showed a similar Se break-

through pattern. We do not know the cause of this peculiar breakthrough pattern, although the presence of two different oxidation states is a possibility. (Refer to Appendix D for some discussion on As and Se oxidation states.) Such a pattern has not been observed for the other materials. The molybdenum curve (Fig. 8) rises above  $C/C^{\circ} = 1.0$  and remains high. There may be a systematic high bias in these values caused either by a

low influent value or erroneously high eluent values. The arsenic curve rises rapidly to  $C/C^0 = 0.7$  at 10 pore volumes followed by a slow increase to near 100% breakthrough at 30 to 40 pore volumes. Such a breakthrough curve may be caused by competition for adsorption sites or by some nonequilibrium process.

Goethite has the greatest affinity for these anion-forming elements as demonstrated by the adsorption values in Table VI and the breakthrough patterns in Fig. 9. In fact, arsenic is so well adsorbed that it took nearly a year before any was observed in eluent from the goethite column. In units of mmoles adsorbed per hundred grams of mineral, Goethite adsorbed nearly 100 times more of each element than kaolinite. Even chloride was somewhat retained by the goethite, as evidenced by a  $C/C^0$  value of 0.05 at one pore volume. Breakthrough curves (Fig. 9) for Mo and Se exhibit some unexplained structure. Selenium reaches 100% breakthrough after passage of 35-40 pore volumes and continues to rise to  $C/C^0$  values near 1.5 between 45 and 50 pore volumes. Selenium eluent concentrations remain high until 85 pore volumes have been eluted after which they drop to substantially less than 1.0. The curve for molybdenum is somewhat similar in that it reaches  $C/C^0 = 1.0$  at 165 pore volumes, remains there for about 20 pore volumes, then rises to 1.3 at  $PV = 260$ .  $C/C^0$  values for molybdenum are greater than 1.1 (usually greater than 1.2) from 220 to 340 pore volumes. These data may indicate the presence of interactions between the elements and pH effects. The high selenium eluent concentrations return to lower than influent concentrations only after complete breakthrough of molybdenum. Similarly, the molybdenum concentrations in eluent remained high until we observed significant eluent concentrations of arsenic. Hydrogen ion activity varied throughout this experiment. The pH of eluent slowly rose from 6.4 to 8.4 and then eventually decreased to about 7.0 by the end of the experiment (365 pore volumes). These pH variations are probably related to the sorption and desorption of solute species on goethite exchange sites. The goethite results demonstrate the necessity of carefully monitoring the pH in soil column experiments if we desire to explain observed behavior. We should generally assume a possible strong relationship between adsorption and pH.

#### IV. SUMMARY OF COLUMN ADSORPTION EXPERIMENTS

Through calendar year 1981 we have completed column experiments for Ni and Cd in silica sand,

kaolinite sand, dunal sand, and goethite sand. Experiments with anion-forming elements As, B, Mo, and Se have been completed for mixtures of sand with kaolinite and goethite and a dunal sand soil. Results of these experiments are summarized in Table VII (the anionic elements were not tested with silica sand). Adsorption values in Table VII are mmoles of contaminant removed from solution per hundred grams of adsorbent. A correction for sand content is included for kaolinite and goethite. As expected, goethite has the greatest affinity for these elements and arsenic is most highly adsorbed by all adsorbents. Silica sand has very little capacity for adsorbing these species, whereas kaolinite has some capacity but much less than that of goethite. Adsorption values shown in Table VII for goethite are consistent with those obtained from the batch experiments presented in Table IV. Cation adsorption of Ni and Cd by the dunal sand appears to be about the same as by kaolinite; however, we should recall that the kaolinite experiment for Ni and Cd was done in a 0.033M  $Ca^{2+}$  solution in contrast to the dunal sand experiment being done in a 0.1M  $K^+$  solution. The affinity of exchange sites is greater for  $Ca^{2+}$  than for  $K^+$ . According to Table I, the cation exchange capacity of kaolinite is considerably greater than that of dunal sand. Thus the low removal of Cd and Ni by kaolinite compared to dunal sand (in view of their respective cation exchange capacities) is probably caused by the much greater affinity of exchange sites for  $Ca^{2+}$  than for  $K^+$  and the resulting increased competition for sites between Ca, Cd, and Ni.

TABLE VII

QUANTITIES (mmoles/100 g) OF Cd, Ni, As, B, Mo, AND Se RETAINED BY THREE SOIL MINERAL COMPONENTS AND BY A DUNAL SAND

	Silica Sand	Kaolinite	Goethite	Dunal Sand
Cd	$2.0 \times 10^{-4}$	0.020	0.31	0.013
Ni	$4.4 \times 10^{-4}$	0.039	0.98	0.020
As	ND <sup>b</sup>	0.24	20.5	0.019
B	ND	0.041	1.77	0.0019
Mo	ND	0.048	5.93	0.0010
Se	ND	0.029	1.30	0.00048

<sup>a</sup>All influent concentrations were  $\sim 10$  mg/l. pH values are given in Tables V and Vi.

<sup>b</sup>Not done.

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## APPENDIX A

### ELEMENTS SELECTED FOR STUDY

The elements selected for study form a subset of those elements identified most frequently in other studies. Some elements have not been shown to be generally problematic in a variety of energy process waste leachates. For example, Be has been identified in only one study. Water quality standards and criteria are most often used by investigators in environmental assessment studies to flag or set priorities for chemical species. Such standards are based on the best available information regarding health and environmental effects. Thus, from the larger group of potential contaminants found in energy process wastes, we have selected an initial subset for scientific and environmental, as well as practical, reasons. This list may change depending on future requirements and in response to new information. It is felt necessary to limit the list of elements to a manageable number to facilitate chemical analysis and to enable a better understanding of the chemical system being studied.

The need to understand the chemical system requires a knowledge of major system components likely to be controlling the solution chemistry of our soil-solution

systems. In many energy process waste leachates, major system components include  $\text{SO}_4^{2-}$ , Ca, and Mg. In some wastes and in alkaline subsoils, carbonate may also be an important component. Other wastes, such as high sulfur coal wastes and some coal conversion process wastes, are often acidic with high concentrations of soluble Al, Fe, and Mn in addition to sulfate. Initially we propose to focus on nonacidic leachates. Thus, Ca, Mg, and  $\text{SO}_4^{2-}$  are the expected major components. The principal reason for focusing on nonacidic wastes is a desire to investigate the effects of adsorption or exchange on transport rather than precipitation of solids. Acidic leachates are likely to undergo significant pH changes during transport through a soil material. Such pH changes would cause the precipitation of solids to override and perhaps obscure adsorption effects. We believe that the transport of acidic leachates through soils must be viewed as a two-step process involving the removal of species subject to precipitation following pH changes and the transport of those species not particularly subject to such solubility controls. It is this second phenomenon on which we will focus initially.



Precipitation is very important but is not applicable to all species and is not what generally controls water transport of trace constituents. We believe trace species transport is controlled primarily by interactions with major solid phases, or sometimes minor solid phases, in the case of solid substances with high specific surface activity (for example, free iron oxides).

Initial trace elements selected for study are the cations Ni and Cd and the anion forming elements As, B, Mo, and Se. The cations Ni and Cd seem to appear in nearly every list identifying problem elements in energy process wastes. Additionally, Cd has a stringent federal drinking water standard (DWS) of 0.01 mg/l. Nickel is known to interact with iron oxides and its adsorption on goethite has been studied by one of the participants in the studies coordinated with this one. Thus, much is known about nickel's chemical properties and it is a relatively well characterized element with which to work.

Of the anionic elements selected for initial emphasis, there are DWS for As (0.05 mg/l) and Se (0.01 mg/l). The federal EPA has proposed a Mo standard of 0.05 mg/l *vis-a-vis* leachates released from uranium mill tailings (standards for As, Cd, and Se have also been proposed for uranium tailings leachates).<sup>1</sup> Presently, there is no standard for boron, however, because of the sensitive nature of many plants to boron, a maximum concentration of 2 mg/l in irrigation waters has been recommended by the NAS committee on water quality criteria.<sup>2</sup>

Boron is generally believed to be mobile in soils whereas As (as As III and V) is not. Selenate and molybdate are believed mobile in alkaline soils, but less so or immobile in acidic soils. Additionally, As, Mo, and Se all interact with iron oxides to various extents and thus are of scientific interest with respect to their adsorptive properties. There are ample environmental and health, as well as scientific, reasons for our selection of trace species to be studied. This can be changed if conditions dictate that some other element(s) are more deserving of study. We should also mention that initial experiments with several of these species have been completed under the previous EPA contract.

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## APPENDIX B

### SOIL MINERAL COMPONENTS AND REAL SUBSURFACE SOILS

W. H. Fuller and colleagues at the University of Arizona have performed an extensive series of studies showing that attenuation of inorganic contaminants in a leachate by a soil can be statistically related to soil properties.<sup>1</sup> These authors concluded that clay content, free iron oxide content, soil pH, and solution flux through soil were the "most important factors" affecting retention of trace elements. Of these factors, solution flux (that is, flow velocity through soil) would not normally be a controllable variable because it is determined by the natural permeability of the material (although it is noted that control of permeability is attainable in the preparation of engineered liner materials).

These studies show quite conclusively that the important factors in attenuation are chemical and that the same basic set of properties is operative regardless of the origin of a particular soil. Thus a calcareous subsoil from the eastern United States is expected to attenuate chemical species much the same as a similar calcareous subsoil from the western United States. The presence of iron oxides in this list of most important factors demonstrates the desirability of studying the transport of contaminants through iron oxides and soils high in iron oxides. Such materials have mitigation potential in engineered as well as in natural disposal situations.

In another series of studies by the Illinois State Geological Survey, the attenuation of inorganic species

in a municipal landfill leachate by three clays (montmorillonite, illite, and kaolinite) was investigated.<sup>2</sup> These are all common clay mineral constituents of natural soils. The authors ranked these three clays in order of overall ability to attenuate chemical constituents in municipal leachate, as montmorillonite > illite > kaolinite. Of these, montmorillonite has the highest cation exchange capacity and kaolinite the least. Bentonites (expansible clays of volcanic origin similar to montmorillonite) are sold commercially as impermeable liners for containment of some waste materials. Thus the utility of bentonite as an engineered semipermeable liner for mitigation purposes is also of interest. At present we are studying the attenuation of potential chemical contaminants by kaolinite because it is one of the most widespread clay minerals in soils and because it has a relatively simple structure, low cation exchange capacity, and low zero point of charge (pH 4-4.5). This means that, under most natural situations, kaolinite would be negatively charged. We are also considering some work with a montmorillonite or a bentonite clay should time permit. Such clays are prevalent in western US environments, have very high cation (but not anion) exchange capacities, and are also worth considering for engineered waste disposal sites as semipermeable attenuating liners. We have developed methods for coating clays onto silica sand, which make it possible to prepare large batches of clay coated sands for use in controlled laboratory experiments.

The subsurface soils selected for initial study consist of an oxidic sandy clay loam, a dunal sand, an acidic clay loam, and a calcareous clay loam. These four subsoils span a range of properties of interest in our studies. Subsurface soils were selected to be consistent with a near-surface disposal scenario where the topsoil has been purposely removed, such as would occur during site preparation or at a strip mine. The dunal sand was selected for early study because one of the participants was involved in an ongoing field study at an electrical generating station where this soil originated. A calcareous soil will be studied to provide a material with the buffering capacity and a high mica clay (illite) content typical of western soils.<sup>1,3</sup> Acid soils are more typical of eastern US environments,<sup>3</sup> thus one acid soil was also selected for study. These two soils have cation exchange capacities of 20-25 meq/100 g, which are within the range found by others for subsurface soils.<sup>1</sup> We believe these two soils provide good extremes in terms of the pH conditions likely to be encountered in

natural soil systems. The high iron oxide soil was selected because of our decision to study goethite as one of the mineral components. Goethite is the most prevalent iron oxide in soils.<sup>4</sup> This soil has a high free iron content (2.7%) and virtually no clays other than kaolinite, thus it provides a real soil with the two major mineral components (kaolinite and iron oxide) we are studying.

Our selection of subsurface soils is subject to revision. The materials discussed are presently in our possession and have been processed and distributed to the other participants. Column studies under the previous EPA program have been completed with one of the soils and are underway with another. In addition, as indicated above, considerable characterization has been performed on these soils. We have done some preliminary evaluation of a high organic soil collected from the Savannah River Laboratory location. This soil appears to have a high humic substance content, as indicated by a yellow color in its leachate. Organic content in soils has a considerable effect on the transport of both organic and inorganic contaminants; therefore, we are considering the desirability of including such a soil in our studies. The applicability of these to subsurface disposal scenarios is not clear so a final decision has not been made.

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## APPENDIX C

### BATCH ADSORPTION TABULAR RESULTS

This appendix contains detailed results in Tables C-I through C-VI from the set of batch adsorption experiments described in Sec. III.D.1. A major difference between these experiments and the column experiments is the absence of a supporting electrolyte in these. Thus the results are not always directly comparable to the more extensive goethite batch experiments (Sec. III.D.2) or the column experiments, which were performed in

either 0.1M  $\text{KNO}_3$  or 0.033M  $\text{Ca}(\text{NO}_3)_2$ . This is particularly true for cation exchange where the exchangeable cations K or Ca are present at much greater concentrations than Cd or Ni. In contrast, for anion exchange, which, when important, is more of a chemical reaction (chemisorption), the nitrate ion provides little competition for arsenate, molybdate, or selenate.

TABLE C-I

#### BATCH ADSORPTION RESULTS FOR CADMIUM ON SEVEN SOIL MATERIALS

Adsorbent	Per Cent Adsorbed	Specific Adsorption ( $\mu\text{g/g}$ )	Equilibrium Concentration ( $\text{mg/l}$ )	Equilibrium pH
Sandy clay loam	4.6	40	83	4.8
	72	78	3.0	4.8
	90	9.8	0.11	4.7
Dunal sand	0.0	0	100	5.1
	49	53	5.5	5.4
	92	10	0.08	5.6
Silica sand	0.0	0	92	4.4
	12.0	13	9.5	4.4
	16.6	1.8	0.91	4.4
Calcareous clay loam on silica sand	80	3431	94	6.2
	94	864	5.3	6.3
	100	94	0.01	7.6
	98	9.4	0.01	7.6
Acidic clay loam on silica sand	70	3065	131	4.3
	87	801	11.6	4.4
	99	92	0.14	4.8
	99	9.4	0.01	4.7
Kaolinite on silica sand	20	870	351	4.4
	36	335	58	4.1
	90	85	0.92	4.8
	96	9.1	0.04	4.9
Goethite on silica sand	100	4370	0.44	7.5
	99	917	0.02	8.4
	100	94	0.01	9.7
	99	9.4	0.01	9.8

TABLE C-II

**BATCH ADSORPTION RESULTS FOR NICKEL  
ON SEVEN SOIL MATERIALS**

<u>Adsorbent</u>	<u>Per Cent Adsorbed</u>	<u>Specific Adsorption (<math>\mu\text{g/g}</math>)</u>	<u>Equilibrium Concentration (<math>\text{mg/l}</math>)</u>	<u>Equilibrium pH</u>
Sandy clay loam	1.5	13	86.4	4.0
	71	74	3.1	4.2
	92	9.7	0.07	4.4
Dunal sand	0	0	101	5.1
	35	36	6.86	5.4
	90	9.4	0.10	5.6
Silica sand	0	0	97.2	4.4
	0	0	10.4	4.4
	7.7	0.8	0.96	4.4
Calcareous clay loam on silica sand	83	497	10.1	6.3
	100	63	0.02	7.6
	98	5.7	0.01	7.6
Acidic clay loam on silica sand	83	495	10.1	4.4
	98	62	0.15	4.8
	97	5.6	0.02	4.7
Kaolinite on silica sand	36	217	38.1	4.1
	91	57	0.57	4.8
	93	5.4	0.04	4.9
Goethite on silica sand	100	598	0.03	8.4
	100	63	0.01	9.7
	98.3	5.7	0.01	9.8

TABLE C-III

BATCH ADSORPTION RESULTS FOR ARSENIC  
ON SEVEN SOIL MATERIALS

Adsorbent	Per Cent Adsorbed	Specific Adsorption ( $\mu\text{g/g}$ )	Equilibrium Concentration ( $\text{mg/l}$ )	Equilibrium pH
Sandy clay loam	68	830	39	4.5
	94	106	0.73	4.9
	<100	12	$\leq 0.30$	4.8
Dunal sand	4.1	50	117	4.1
	16	18	9.5	5.7
	28	3.3	0.87	6.3
Silica sand	2.5	30	119	3.5
	4.4	5	10.8	3.7
	0.0	0	1.3	4.4
Calcareous clay loam on silica sand	69	700	31.6	6.3
	95	95	0.53	7.6
	$\leq 85$	8.5	$\leq 0.15$	7.6
Acidic clay loam on silica sand	79	810	20.9	4.4
	$\leq 97$	97	$\leq 0.28$	4.8
	$\leq 85$	8.5	$\leq 0.15$	4.7
Kaolinite on silica sand	26	270	75	4.1
	60	60	3.9	4.8
	$\leq 75$	7.5	$\leq 0.25$	4.9
Goethite on silica sand	100	1020	$\leq 0.25$	8.4
	$\leq 96$	96	$\leq 0.36$	9.7
	$\leq 78$	7.8	$\leq 0.22$	9.9

TABLE C-IV

BATCH ADSORPTION RESULTS FOR BORON  
ON SEVEN SOIL MATERIALS

Adsorbent	Per Cent Adsorbed	Specific Adsorption ( $\mu\text{g/g}$ )	Equilibrium Concentration ( $\text{mg/l}$ )	Equilibrium pH
Sandy clay loam	2.6	30	113	4.5
	11.5	13	10	4.9
	27.4	3.1	0.8	4.8
Dunal sand	1.7	20	114	4.1
	3.5	4	10.9	5.7
	1.8	0.2	1.11	6.3
Silica sand	2.6	30	113	3.5
	0.9	1	11.2	3.7
	1.8	0.2	1.11	4.4
Calcareous clay loam on silica sand	2.4	21	85.5	6.3
	18.7	17	7.5	7.6
	29.0	2.5	0.61	7.6
Acidic clay loam on silica sand	2.2	19	85.6	4.4
	9.6	8.8	8.33	4.8
	3.5	0.3	0.83	4.7
Kaolinite on silica sand	2.6	23	85.3	4.1
	10.3	9.5	8.26	4.8
	10.5	0.9	0.77	4.9
Goethite on silica sand	23	205	67.1	8.4
	4	3.7	8.84	9.7

TABLE C-V

**BATCH ADSORPTION RESULTS FOR MOLYBDENUM  
ON SEVEN SOIL MATERIALS**

<u>Adsorbent</u>	<u>Per Cent Adsorbed</u>	<u>Specific Adsorption (<math>\mu\text{g/g}</math>)</u>	<u>Equilibrium Concentration (<math>\text{mg/l}</math>)</u>	<u>Equilibrium pH</u>
Sandy clay	92	1200	10.0	4.5
loam	99	130	0.045	4.9
	100	13	0.007	4.8
Dunal sand	0	0	136	4.1
	0	0	13.6	5.7
	0	0	1.38	6.3
Silica sand	0	0	138	3.5
	0	0	13.4	3.7
	0	0	1.32	4.4
Calcareous clay loam	3.8	40	102	6.3
on silica sand	18	19	8.86	7.6
	27	2.9	0.81	7.6
Acidic clay loam	87	920	14.1	4.4
on silica sand	81	87	2.07	4.8
	97	10.5	0.05	4.7
Kaolinite on	40	426	63.4	4.1
silica sand	41	44	6.41	4.8
	49	5.3	0.57	4.9
Goethite on	27	289	77.1	8.4
silica sand	26	28	7.99	9.7
	27	2.9	0.81	9.8

**TABLE C-VI**  
**BATCH ADSORPTION RESULTS FOR SELENIUM**  
**ON SEVEN SOIL MATERIALS**

<u>Adsorbent</u>	<u>Per Cent Adsorbed</u>	<u>Specific Adsorption (µg/g)</u>	<u>Equilibrium Concentration (mg/l)</u>	<u>Equilibrium pH</u>
Sandy clay loam	48	120	13	4.5
	25	6	1.8	4.9
	-	-	≤0.25	4.8
Dunal sand	0	0	25	4.1
	0	0	2.5	5.7
	0	0	≤0.25	6.3
Silica sand	0	0	18	3.5
	0	0	3	3.7
	0	0	0.8	4.4
Calcareous clay loam on silica sand	64	159	10.7	6.3
	44	11	1.4	7.6
Acidic clay loam on silica sand	-	-	≤0.25	7.6
	13	32	23	4.4
	36	9	1.6	4.8
Kaolinite on silica sand	-	-	≤0.25	4.7
	36	89	18	4.1
	20	5	2.0	4.8
Goethite on silica sand	-	-	≤0.25	4.9
	61	146	12.0	8.4
	32	8	1.7	9.7
	-	-	≤0.25	9.8



## APPENDIX D

### EQUILIBRIUM CHEMISTRY CONSIDERATIONS

#### 1. Carbonates of Ca, Cd, and Ni

The chemistry of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  in a solution of  $\sim 0.1\text{M}$   $\text{KNO}_3$  is of importance in these experiments. The only other anion of possible interest in this system is carbonate. None of the materials studied so far has contained sufficient soluble carbonate to present a potential problem regarding precipitation of Cd or Ni carbonates, however, it is likely that carbonaceous soils will present such a problem. Solubility product constants for carbonates of Ca, Cd, and Ni are listed in Table D-I, together with activity coefficients for a solution of ionic strength 0.1 and corrected solubility product constants. Assuming the presence of 10 mg/l of Cd and Ni, the maximum amount of carbonate that can be present without precipitation is determined by the solubility product constant for  $\text{CdCO}_{3(s)}$ , which is a thousandfold less soluble than  $\text{NiCO}_{3(s)}$ . Doing the arithmetic, we calculate that up to  $3.71 \times 10^{-7}\text{M}$  (0.022 mg/l)  $\text{CO}_3^{2-}$  may be present before precipitation of  $\text{CdCO}_{3(s)}$ . This is not very much  $\text{CO}_3^{2-}$ ; however, the quantity of  $\text{CO}_3^{2-}$  in solution is strongly dependent on pH. Given a  $\text{pK}_a$  for  $\text{HCO}_3^-$  of  $1.02 \times 10^{-10}$  moles/l corrected for activities of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  and assuming a total carbonate content of 10 mg/l as  $\text{CO}_3^{2-}$  ( $1.67 \times 10^{-4}\text{M}$ ), the concentration of  $\text{CO}_3^{2-}$  will remain below  $3.71 \times 10^{-7}\text{M}$  at any pH below 7.34. Assuming tenfold less total carbonate, any pH below about 8.3 will preclude precipitation of  $\text{CdCO}_{3(s)}$  from solutions containing 10 mg/l  $\text{Cd}^{2+}$ . Thus at the pH of our experiments and in the noncarbonate materials presently used, there is no need for concern about carbonate precipitation. However, future experiments with calcareous soils will require that carbonate precipitation be considered and may also require the use of lower concentrations of the cations.

#### 2. pH Dependence of Some Forms of As, B, Mo, and Se

To prepare  $\sim 10$  mg/l solutions of the elements As, B, Mo, and Se we are using the salts or acids in the highest common oxidation states, V, III, VI, and VI, respectively. These species all occur as oxyacids in water under the conditions of these experiments. The relevant acidity constants shown in Table D-II, when corrected to an

ionic strength of 0.1, enable the determination of the particular protonated forms present at a given pH.

##### Boric acid.

$$\log \left( \frac{[\text{H}_2\text{BO}_3^-]}{[\text{H}_3\text{BO}_3]} \right) = -9.11 + \text{pH}$$

At a pH of 8 this gives a ratio ( $[\text{H}_2\text{BO}_3^-]$  to  $[\text{H}_3\text{BO}_3]$ ) of 0.078 and at a pH of 5 a ratio of  $7.8 \times 10^{-5}$ . Thus boron occurs in our solutions predominantly as the undissociated or uncharged acid  $\text{H}_3\text{BO}_3$ . Only at  $\text{pH} > 8$  does  $\text{H}_2\text{BO}_3^-$  begin to make up a large fraction of the total boron present.

##### Arsenic acid.

$$\log \left( \frac{[\text{H}_2\text{AsO}_4^-]}{[\text{H}_3\text{AsO}_4]} \right) = -2.10 + \text{pH}$$

$$\log \left( \frac{[\text{HAsO}_4^{2-}]}{[\text{H}_2\text{AsO}_4^-]} \right) = -6.67 + \text{pH}$$

$$\log \left( \frac{[\text{AsO}_4^{3-}]}{[\text{HAsO}_4^{2-}]} \right) = -11.03 + \text{pH}$$

At  $\text{pH} > 5$ ,  $[\text{H}_2\text{AsO}_4^-]/[\text{H}_3\text{AsO}_4] > 800$  and at  $\text{pH} < 8$   $[\text{AsO}_4^{3-}]/[\text{HAsO}_4^{2-}] < 9.3 \times 10^{-4}$ , so in the pH range of our experiments (5-8), arsenic is present as  $\text{HAsO}_4^{2-}$  or  $\text{H}_2\text{AsO}_4^-$ , depending on the particular pH.

##### Molybdic acid.

$$\log \left( \frac{[\text{HMoO}_4^-]}{[\text{H}_2\text{MoO}_4]} \right) = -3.44 + \text{pH}$$

$$\log \left( \frac{[\text{MoO}_4^{2-}]}{[\text{HMoO}_4^-]} \right) = -3.59 + \text{pH}$$

At pH 5 the first ratio is 36 and the second is 26, thus  $\text{MoO}_4^{2-}$  is the dominant form of molybdenum because pH values of our solutions are consistently greater than 5 and usually greater than 6.

TABLE D-I

SOLUBILITY PRODUCT CONSTANTS  
FOR CARBONATES OF  
CALCIUM, CADMIUM, AND NICKEL

	K <sub>sp</sub>	Activity Coefficient (I=0.1)	K <sub>sp</sub> Corrected to I=0.1
Ca	$5.01 \times 10^{-9}$	0.40	$3.30 \times 10^{-8}$
Cd	$5.01 \times 10^{-12}$	0.40	$3.30 \times 10^{-11}$
Ni	$6.31 \times 10^{-9}$	0.40	$4.15 \times 10^{-8}$

$\gamma_{\text{CO}_3^{2-}} = 0.38, \gamma_{\text{HCO}_3^-} = 0.77, \gamma_{\text{H}^+} = 0.83.$

I is ionic strength.

TABLE D-II

ACID DISSOCIATION CONSTANTS FOR ACIDS  
PRESENT IN EXPERIMENTAL SOLUTIONS

		I=0	I=0.1
Boric Acid	H <sub>3</sub> BO <sub>3</sub>	K <sub>1</sub> = $5.89 \times 10^{-10}$	$7.77 \times 10^{-10}$
Arsenic Acid	H <sub>3</sub> AsO <sub>4</sub>	K <sub>1</sub> = $6.03 \times 10^{-3}$	$7.98 \times 10^{-3}$
		K <sub>2</sub> = $1.05 \times 10^{-7}$	$2.13 \times 10^{-7}$
		K <sub>3</sub> = $3.0 \times 10^{-12}$	$9.25 \times 10^{-12}$
Molybdic Acid	H <sub>2</sub> MoO <sub>4</sub>	K <sub>1</sub> = $2.82 \times 10^{-4}$	$3.66 \times 10^{-4}$
		K <sub>2</sub> = $1.26 \times 10^{-4}$	$2.55 \times 10^{-4}$
Selenic Acid	H <sub>2</sub> SeO <sub>4</sub>	K <sub>2</sub> = $1.2 \times 10^{-2}$	$2.43 \times 10^{-2}$
Selenious Acid	H <sub>2</sub> SeO <sub>3</sub>	K <sub>1</sub> = $2.4 \times 10^{-3}$	$3.12 \times 10^{-3}$
		K <sub>2</sub> = $4.79 \times 10^{-9}$	$9.7 \times 10^{-2}$

\*Acidity constants at I = 0.1 are corrected for activities of the anions but not corrected for hydrogen ion activity.

### Selenic acid.

$$\log\left(\frac{[\text{SeO}_4^{2-}]}{[\text{HSeO}_4^-]}\right) = -1.61 + \text{pH}$$

At pH > 5, the ratio of  $[\text{SeO}_4^{2-}]$  to  $[\text{HSeO}_4^-]$  > 2450, so selenium is present as the doubly charged anion.

The acid dissociation constants for selenious acid ( $\text{H}_2\text{SeO}_3$ ) are also included in Table D-II because of the possible reduction of Se(VI) to Se(IV) at the Eh and pH of our experiments. An analogous, but less likely, possibility exists for As(V) to As(III) reduction. These are discussed below.

### 3. The Eh-pH Behavior of Arsenic and Selenium

An Eh-pH diagram for the system As, As(III), and As(V) is given in Fig. D-1. The equations used to construct this diagram are given in Tables D-II and D-III. Boundaries are defined by the stability of water and, where appropriate,  $10^{-4}\text{M}$  activities of arsenic in solution are assumed. No corrections have been made for effects of ionic strength on equilibrium expressions. The shaded

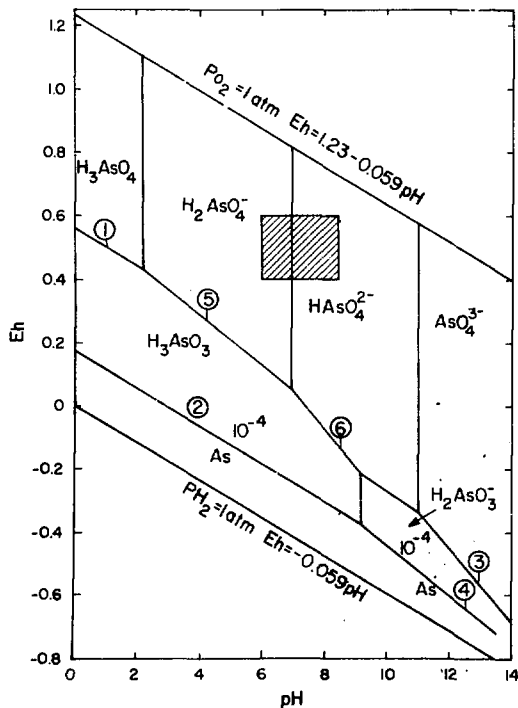


Fig. D-1. Eh-pH diagram for aqueous solution of arsenic ( $10^{-4}\text{M}$  assumed for concentration of aqueous species).

area in Fig. D-1 shows the Eh-pH regime indicated for our experimental solutions by our measurements. Thus we should not concern ourselves about reduction of As V to As III in this system.

The selenium Eh-pH diagram is shown in Fig. D-2. Equations used to construct this diagram are in Tables D-II and D-IV. Boundaries again are those of water stability and  $10^{-4}\text{M}$  activities of selenium were assumed with no corrections for ionic strength applied to the equilibrium expressions. The area in which our experiments have been performed is shown by the shaded area in Fig. D-2. Thus there is a possibility for reduction of Se VI to Se IV in our system. We are presently doing speciation studies to check out this possibility.

### 4. Calcium Salts of Arsenic, Molybdenum, and Selenium

Solubility product constants for the calcium salts with arsenate, molybdate, and selenate corrected to an ionic strength of 0.1 are in Table D-V. We recall from the above (Part 2) that arsenic is present either as  $\text{HAsO}_4^{2-}$  or  $\text{H}_2\text{AsO}_4^-$  and not as  $\text{AsO}_4^{3-}$ . However, Mo and Se

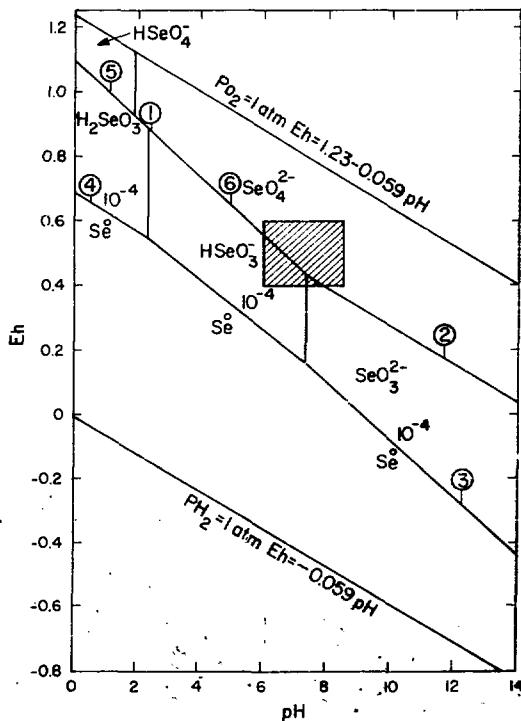
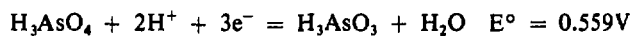


Fig. D-2. Eh-pH diagram for aqueous solution of selenium ( $10^{-4}\text{M}$  assumed for concentration of aqueous species).

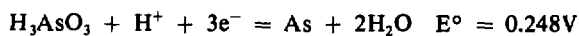
TABLE D-III

OXIDATION-REDUCTION EQUATIONS USED FOR  
THE CONSTRUCTION OF ARSENIC Eh-pH DIAGRAM



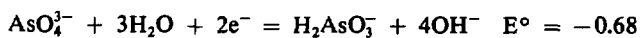
$$\text{Eh} = 0.559 - 0.059 \text{ pH} - 0.0295 \log\left(\frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_3\text{AsO}_4]}\right)$$

$$\text{if } \left(\frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_3\text{AsO}_4]}\right) = 1.0 \rightarrow \text{Eh} = 0.559 - 0.059 \text{ pH} \quad (1)$$



$$\text{Eh} = 0.248 - 0.059 \text{ pH} - \frac{0.059}{3} \log\left(\frac{1}{[\text{H}_3\text{AsO}_3]}\right)$$

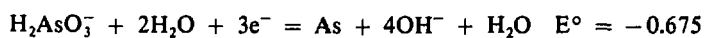
$$\text{if } [\text{H}_3\text{AsO}_3] = 10^{-4} \text{ M} \rightarrow \text{Eh} = 0.169 - 0.059 \text{ pH} \quad (2)$$



$$\text{Eh} = 0.972 - 0.118 \text{ pH} - \frac{0.059}{2} \log\left(\frac{[\text{H}_2\text{AsO}_3^-]}{[\text{AsO}_4^{3-}]}\right)$$

$$\text{if } \left(\frac{[\text{H}_2\text{AsO}_3^-]}{[\text{AsO}_4^{3-}]}\right) = 1.0 \rightarrow \text{Eh} = 0.972 - 0.118 \text{ pH} \quad (3)$$

TABLE D-III (cont)



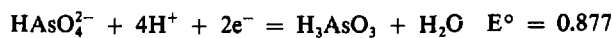
$$\text{Eh} = 0.426 - 0.079 \text{ pH} + \frac{0.059}{3} \log [\text{H}_2\text{AsO}_3^-]$$

$$\text{if } [\text{H}_2\text{AsO}_3^-] = 10^{-4}\text{M} \rightarrow \text{Eh} = 0.347 - 0.079 \text{ pH} \quad (4)$$



$$\text{Eh} = 0.660 - \frac{0.059}{2} \log \left( \frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_2\text{AsO}_4^-]} \right) - 0.089 \log \frac{1}{[\text{H}^+]}$$

$$\text{if } \left( \frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_2\text{AsO}_4^-]} \right) = 1.0 \rightarrow \text{EH} = 0.660 - 0.089 \text{ pH} \quad (5)$$

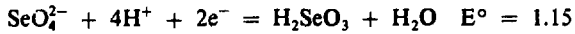


$$\text{Eh} = 0.877 - \frac{0.059}{2} \log \left( \frac{[\text{H}_3\text{AsO}_3]}{[\text{HAsO}_4^{2-}]} \right) - 0.118 \text{ pH}$$

$$\text{if } \left( \frac{[\text{H}_3\text{AsO}_3]}{[\text{HAsO}_4^{2-}]} \right) = 1.0 \rightarrow \text{Eh} = 0.877 - 0.118 \text{ pH} \quad (6)$$

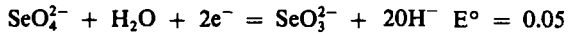
TABLE D-IV

OXIDATION-REDUCTION EQUATIONS USED FOR  
THE CONSTRUCTION OF SELENIUM Eh-pH DIAGRAM



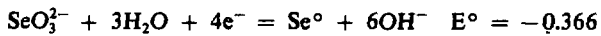
$$\text{Eh} = 1.15 - 0.118 \text{ pH} - \frac{0.059}{2} \log \left( \frac{[\text{H}_2\text{SeO}_3]}{[\text{SeO}_4^{2-}]} \right)$$

$$\text{if } [\text{H}_2\text{SeO}_4] = [\text{SeO}_4^{2-}] \rightarrow \text{EH} = 1.15 - 0.118 \text{ pH} \quad (1)$$



$$\text{Eh} = 0.876 - 0.0295 \log \left( \frac{[\text{SeO}_3^{2-}]}{[\text{SeO}_4^{2-}]} \right) - 0.059 \text{ pH}$$

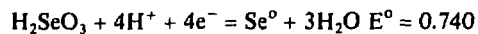
$$\text{if } [\text{SeO}_3^{2-}] = [\text{SeO}_4^{2-}] \rightarrow \text{Eh} = 0.876 - 0.059 \text{ pH} \quad (2)$$



$$\text{Eh} = 0.873 - 0.0885 \text{ pH} + \frac{0.059}{4} \log [\text{SeO}_3^{2-}]$$

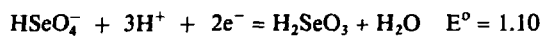
$$\text{if } [\text{SeO}_3^{2-}] = 10^{-4} \text{ M} \rightarrow \text{Eh} = 0.814 - 0.0885 \text{ pH} \quad (3)$$

TABLE D-IV (cont)



$$\text{Eh} = 0.740 + \frac{0.059}{4} \log [\text{H}_2\text{SeO}_3] - 0.059 \text{ pH}$$

$$\text{if } [\text{H}_2\text{SeO}_3] = 10^{-4}\text{M} \rightarrow \text{Eh} = 0.681 - 0.059 \text{ pH} \quad (4)$$



$$\text{Eh} = 1.10 - \frac{0.059}{2} \log \left( \frac{[\text{H}_2\text{SeO}_3]}{[\text{HSeO}_4^-]} \right) - 0.0885 \text{ pH}$$

$$\text{if } [\text{H}_2\text{SeO}_3] = [\text{HSeO}_4^-] \rightarrow \text{Eh} = 1.10 - 0.0885 \text{ pH} \quad (5)$$



$$\text{Eh} = 1.07 - 0.0885 \text{ pH} - \frac{0.059}{2} \log \left( \frac{[\text{HSeO}_3^-]}{[\text{SeO}_4^{2-}]} \right)$$

$$\text{if } [\text{HSeO}_3^-] = [\text{SeO}_4^{2-}] \rightarrow \text{Eh} = 1.07 - 0.0885 \text{ pH} \quad (6)$$

TABLE D-V

**SOLUBILITY PRODUCT CONSTANTS FOR CALCIUM SALTS  
WITH ARSENATE, MOLYBDATE, AND SELENATE**

	$K_{sp}^{a,b}$	
	$I = 0$	$I = 0.1$
$Ca_3(AsO_4)_2(s) = 3Ca^{2+} + 2AsO_4^{3-}$	$6.31 \times 10^{-19}$	$6.83 \times 10^{-17}$
$CaMoO_4(s) = Ca^{2+} + MoO_4^{2-}$	$4.17 \times 10^{-8}$	$2.74 \times 10^{-7}$
$CaSeO_4(s) = Ca^{2+} + SeO_4^{2-}$	$7.94 \times 10^{-4}$	$5.22 \times 10^{-3}$

<sup>a</sup>Assuming an activity coefficient of 0.40 for  $Ca^{2+}$  and 0.38 for the 3 anions.

<sup>b</sup>Solubility product constant at 25°C, 1 atm pressure, ionic strengths (I) are 0 and 0.1.

are both present as the completely deprotonated anions  $MoO_4^{2-}$  and  $SeO_4^{2-}$ . Thus we must consider the maximum allowable concentrations of Ca under the conditions of our experiment, for example, Mo and Se concentrations of  $\sim 10$  mg/l ( $\sim 10^{-4}$ M). At 10 mg/l Mo, it would take a  $2.74 \times 10^{-3}$ M (110 mg/l) calcium to exceed the solubility of  $CaMoO_4(s)$ . For the much more

soluble selenate salt, it takes 52.2M calcium in solution with  $10^{-4}$ M selenate before the solubility product is exceeded and precipitation of  $CaSeO_4(s)$  would occur. Thus, unless calcium concentrations get unusually high, such as might occur in a calcareous soil at low pH, precipitation of calcium molybdate will not occur.



