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HYDRODYMANIC AND CHEMICAL
MODELING OF HEAVY METALS
IN ASH POND LEACHATES

MASTER

Progress Report
for period July 1, 1979 - April 1, 1980

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Abstract

This report details activities through April 1, 1980 on the development of a finite element/chemical equilibrium subsurface flow model for application to inorganic transport around waste disposal sites. Included is an outline of the cooperative effort among several investigators from other research facilities on various aspects of the problem. These tasks include soil column studies for use with the one-dimensional model, laboratory batch studies to define the necessary thermodynamic constants, soil chemistry characterization studies, organic studies, leachate composition evaluation, and assessment of available field data.

With respect to modeling activities both the finite element and chemical equilibrium models are described. The basic mathematical problem is reviewed and the proposed coupling algorithm is presented in greater detail than previously.

I. Research Objectives

The objectives of this research as stated in the original proposal,¹ are twofold:

- 1) to develop a series of mathematical models for soil-water systems which couple the features of a finite element approach for describing the hydrodynamic flow regime and conservative solute transport with an equilibrium description of the sorption, ion exchange, precipitation, and complex formation reactions which non-conservative solutes undergo in such an environment, and
- 2) to exercise such a model, initially in one-dimensional laboratory soil columns, and subsequently on various field sites for which suitable data have been collected.

Funding for this effort became available July 1, 1979; work commenced during September of 1979. This report will detail activities during the first six months of the investigation which are directed towards achieving the stated objectives.

II. Cooperative Activities Among Other Researchers

A significant effort has been made to enlist the cooperation of other researchers, in a rather formal way, who have interests and expertise in areas complementary to those of the researchers at Notre Dame. At the present time these researchers are Dr. Lawrence Wangen of Los Alamos Scientific Laboratory, Dr. Florence Harrison of Lawrence Livermore Laboratory, and Dr. David Evans of Savannah River Ecology Laboratory. The possibility exists that Dr. Marc Anderson of the University of Wisconsin will join in the effort at a later date. A breakdown of tasks is indicated in Table 1 and an approximate timetable for achieving

these tasks is indicated in Table 2. A copy of the meeting notes from which these tables are derived is included in the Appendix. The duration of Table 2 must, at this early date, be considered plus or minus three months. Meetings among the cooperating researchers take place regularly as the need for experimental planning and data review arise.

III. Progress on a One Dimensional Model

As indicated in Table 2, the initial effort at Notre Dame is the development of a one-dimensional model. This model will be used in conjunction with column data being collected at Los Alamos, and will have limited application to multidimensional field sites. At the present time both a finite element and a chemical equilibrium model are working and being separately tested on the computational facilities at Notre Dame.

A. Finite Element Model

(1) Introduction. The development of the one dimensional contaminant transport model can be accomplished in several steps. These steps might be identified as; a) the development of a finite element computer program to solve the one dimensional advection-dispersion equation, b) the development of a computer program to solve the chemical equilibrium equations, c) modification of the finite element program to handle several species, and d) the coupling of the finite element and chemical equilibrium programs. This section of the report will detail progress in the finite element aspects of the project.

(2) Description of FEAP. There are several ways to acquire the capability to solve one-dimensional advection-dispersion problems by the finite element method (FEM). One way is to write a program from "scratch". Another way is

TABLE 1

Distribution of Tasks as Part of Research Effort

TASK	LOCATION				
	NOTRE DAME	LLL	LOS ALAMOS	SAVANNAH RIVER	WISCONSIN*
Mathematical Model	X				
Inorganic Column Studies			X		
Inorganic Batch Studies	X				X
Soil Chemistry	X				X
Organic Studies (Field, Batch, Column)		X			
Leachate Composition & Speciation				X	
+ Assessment of Field Data	X				X

* Wisconsin not currently funded.

+ The aid of TVA and other firms involved with these efforts must be sought.

TABLE 2

Approximate Timetable

- [†] a = C/dNi/As/Se, background NaNO_3 , pH = 5
 b = Cd/Ni/As/Se, background NaN_3 , pH = 10
 c = Cd/Ni/As/Se, background $\text{CaSO}_4/\text{NaNO}_3$, pH = 5
 d = Cd/Ni/As/Se, background $\text{CaSO}_4/\text{NaNO}_3$, pH = 10
 e = Real leachate

to obtain a program which already has the capability, and a third way is to modify an existing FEM program which does not presently have the capability.

If an existing FEM program is chosen it should be judged not only on its ability to solve the one dimensional equation but also on its' potential for use in the later stages of this project. Thus, attractive features would be; steady-state and transient capability, resolve capability with more than one right hand side (i.e. the ability to handle more than one species), variable number of degrees of freedom per node (the two-dimensional flow problem may require this feature), variable number of nodes per element, and the capability to handle non-linear problems. A program which has most of these features and in fact was written explicitly as a research tool, is given in reference 2. The program, called FEAP (Finite Element Analysis Program) was written by Prof. R.L. Taylor of the University of California at Berkeley. The basic structure of this program is so well suited to this project that it was decided it was easier to add to FEAP the element sub-routines required to solve a particular set of equations, rather than modify or develop a program to have the complex basic structure needed.

A detailed description of FEAP as well as a complete listing is given in reference 2. To make this report somewhat self-contained, a brief description of FEAP is given here.

Any finite element program has the following parts; data input, formation of element arrays, assembly of global arrays, solution of equations and output. The distinguishing feature of FEAP is a macro-programming language. The macro-programming language is associated with a set of compact subprograms each designed to compute one or at most a few basic steps in the FEM solution process. Examples in the macro language are commands to solve the equations, print results, increment the time step, etc. The

macro language permits the inclusion of a wide variety of solution algorithms in a single program. The basic flow of the program is shown in Figure 1. The input module consists of a set of subroutines to read in basic control information, nodal data, element data, source and boundary data, and material properties. In the solution module, macro-statements are input which set the algorithm for the problem to be solved, and direct the flow of the program to the proper subroutines to form and solve the equations according to the algorithm. A partial list of these macro-commands is given in Table 3.

The types of equations which may be solved using FEAP as given in reference 2 are, the two dimensional Laplace's equation, elasticity equations and Navier-Stoke's equations. The program has been modified to include the one-dimensional advection-dispersion equation.

TABLE 3

Macro Programming Commands

<u>Command</u>	<u>Description</u>
CHEC	Perform mesh check
CONV	Perform convergence check
DISP	Print nodal values of the unknown
DT	Set time increments
FORM	Form right hand side
LOOP	Loop N times through next instruction
MESH	Input mesh changes
NEXT	End of loop
SOLV	Solve tangent equations
TANG	Symmetric coefficient tangent matrix formulation
TIME	Advance time by DT
TOL	Set convergence tolerance
UTAN	Unsymmetric coefficient tangent matrix formulation
END	End of macro program instructions

FIGURE 1

Finite Element Analysis Program

(3) Finite Element Equations for the One Dimensional Advection-Dispersion Equation.

The one-dimensional advection-dispersion equation can be written

$$-D \frac{\partial^2 c}{\partial x^2} + u \frac{\partial c}{\partial x} + \frac{\partial c}{\partial t} = 0 \quad (\text{A.1})$$

with the variables defined as

c , solute concentration, ML^{-3}

D , dispersion coefficient, L^2T^{-1}

u , mass average velocity, LT^{-1}

x , spatial coordinate, L

t , time, T

Assuming Dirichlet boundary conditions for simplicity, the weak form of A.1 can be written

$$\int_0^L \left(-D \frac{\partial^2 c}{\partial x^2} + u \frac{\partial c}{\partial x} + \frac{\partial c}{\partial t} \right) v(x) dx = 0$$

or after integrating by parts

$$\int_0^L \left(D \frac{\partial c}{\partial x} \frac{\partial v}{\partial x} + u \frac{\partial c}{\partial x} v + \frac{\partial c}{\partial t} v \right) dx = 0 \quad (\text{A.2})$$

This assumes v satisfies the homogeneous boundary conditions. The unknown concentration is approximated by the expansion

$$C(x) = \sum_{i=1}^r \phi_i(x) C^i(t)$$

Herein ϕ_i will be the so called hat functions, Figure 2, and the C^i are the approximate nodal values of the concentration. The integral equation A.2 allows an approximation to be made if in place of any function v , a finite set of prescribed functions is used

Figure 2
Hat Functions

$$v = w_j, \quad j = 1, n$$

where n is the number of unknown parameters C^i in the problem ($n = r-2$ for Dirichlet boundary conditions). Equation A.2 becomes

$$\int_0^L \left[\frac{dw_j}{dx} \frac{d}{dx} \sum_{i=1}^r \phi_i C^i + u w_j \frac{d}{dx} \sum_{i=1}^r \phi_i C^i + w_j \frac{d}{dx} \sum_{i=1}^r \phi_i C^i \right] dx = 0$$

or

$$\int_0^L \left[\frac{dw_j}{dx} \sum_{i=1}^r \frac{d\phi_i}{dx} C^i + u w_j \sum_{i=1}^r \frac{d\phi_i}{dx} C^i \right] dx + \int_0^L w_j \sum_{i=1}^r \phi_i \frac{dC^i}{dt} dx = 0 \quad (A.3)$$

A.3 can be written in matrix notation as

$$K \quad c + C \quad c = f \quad (A.4)$$

The vector F contains Dirichlet boundary conditions in the first and last entries. The contributors to K and C from each "element" are

$$K = \sum_{e=1}^{r-1} K_e, \quad C = \sum_{e=1}^{r-1} C_e \quad (A.5)$$

where the standard finite element assembly procedure is implied and

$$K_{eij} = D \int_0^{h_e} \frac{dw_j}{dx} \frac{d\phi_i}{dx} dx + u \int_0^{h_e} w_j \frac{d\phi_i}{dx} dx \quad (A.6)$$

$$C_{eij} = \int_0^{h_e} w_j \phi_i dx$$

The element length is designated h_e . If a standard Galerkin procedure is employed then $w_j = \phi_j$ and the element matrices can be given explicitly as

$$K_{eij} = \frac{D}{h_e} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} + \frac{u}{2} \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \quad (A.7)$$

$$C_{eij} = \frac{h_e}{6} \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix}$$

The set of equations (A.4) constitute a set of coupled ordinary differential equations in time. If the equations are written as

$$(\underline{C}/\Delta t + \underline{K} \theta) \underline{c}^{t+\Delta t} + (\underline{C}/\Delta t + \underline{K} (1-\theta)) \underline{c}^t = \underline{f} \quad (A.8)$$

where the superscript indicates the times at which the vector is evaluated and Δt is the time increment, then the following time integration schemes can be obtained by varying the value of θ

θ	<u>Scheme</u>
0	Euler
1/2	Crank-Nicholson
2/3	Galerkin
1	Backward-difference

If the concentrations are known at $t = 0$, equations A.8 can be solved repetitively to march the solution through time. Note A.8 can be written

$$\hat{\underline{K}} \Delta \underline{c} = \hat{\underline{f}} \quad (A.9)$$

where the effective tangent matrix is

$$\hat{\underline{K}} = \underline{C}/\Delta t + \underline{K} \theta \quad (A.10)$$

and the effective load vector is

$$\hat{\underline{f}} = \underline{f} - \underline{K} \underline{c}^t \quad (\text{A.11})$$

and the incremental concentrations are

$$\Delta \underline{c} = \underline{c}^{t+\Delta t} - \underline{c}^t$$

$\hat{\underline{K}}$ and $\hat{\underline{f}}$ can be formulated on the element level and assembled as in (A.5).

(4) Upwind weighting functions

In a steady state condition (i.e. $\underline{c} = 0$) if equation A.4 is expanded for a typical node, the resulting equation is the same as that obtained from a centered-difference approximation to A.1. For problems where advection is significant this scheme can yield oscillatory results³. This problem is partially overcome in a finite difference formulation by using backward differences on the first derivative term. The same effect can be obtained in the finite element formulation by modifying the weighting functions, w_j as

$$w_j = \phi_j + \alpha F(x) \quad \text{A.12}$$

$$\text{Where } F(x) = 3x(x-h_e)/h_e^2 \quad \text{A.13}$$

Varying degrees of "upwinding" can be obtained by using different values of α . A zero value yields the standard Galerkin procedure and a value of one corresponds to full upwinding. In one dimension the exact answers to the steady state problem can be obtained at the nodes by using the following optimal upwind parameter³,

$$\alpha_0 = \coth \left(\frac{uh_e}{2D} \right) - \frac{2D}{uh_e} \quad (\text{A.14})$$

The use of upwinding in transient problems has also been recently studied⁴.

Using the weighting functions of A.12 the element matrices become.

$$K_{eij} = \frac{D}{h_e} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} + \frac{U}{2} \begin{bmatrix} -(1-\alpha) & (1-\alpha) \\ -(1+\alpha) & (1-\alpha) \end{bmatrix} \quad (A.15)$$

C_e is unchanged.

(5) Results

The element matrices derived in the preceding section have been incorporated into FEAP. Some preliminary steady state and transient results will be presented below.

The steady state advection dispersion equation is obtained by setting

$\frac{\partial c}{\partial t}$ equal to zero in A.1 This equation can be written in nondimensional form as

$$\frac{\partial^2 c}{\partial \xi^2} + P \frac{\partial c}{\partial \xi} = 0 \quad (A.16)$$

where $\xi = X/L$ and $P = UL/D$. The parameter P is called the Peclet number and the behavior of the solution is totally dependent on its value. The exact solution to A.16 is

$$c(\xi) = b \left(\frac{1 - e^{-P\xi}}{1 - e^{-P}} \right) \quad (A.17)$$

Which satisfies the boundary conditions

$$c(0) = 0$$

$$c(1) = b$$

Equation A.17 is plotted as the dashed line in Figure 3 for Peclet numbers of two and four. Also plotted are four element FEM solutions for each P (without upwinding). The degradation of results with increasing P is demonstrated.

An interesting phenomena is displayed in Figure 4. Reference 5 shows that the centered difference scheme yields oscillatory results if Uh_e/D is greater than two. For a Peclet number of eight, a three element mesh has Uh_e/D equal to 8/3 and the results shown are indeed oscillatory. Refinement of the mesh shows convergence to the true solution.

To demonstrate the use of the upwind parameter, Table 4 gives the values obtained from a thirty element mesh with a Peclet number of twenty and using optimal upwinding. The answers are virtually exact at the nodes.

The transient equation, A.1 can be written in non-dimensional form as

$$\frac{\partial^2 c}{\partial \xi^2} + P \frac{\partial c}{\partial \xi} + P \frac{\partial c}{\partial \tau} = 0$$

where the non dimensional time τ is ut/L . For a given P convergence now depends not only on the mesh size but the time step.

Figure 5 shows the results of two transient runs at two different times using a backwards difference scheme ($\theta=1$). Both runs used a mesh of thirteen elements. One used a time step of five minutes, the second 2.5 minutes. A third run with a time step of 1.25 minutes gave almost exact answers. The numerical results for the above runs are given in Table 5. This problem with a zero gradient at the right boundary is an approximation to the semifinite domain problem, the exact solution of which is given in reference 6.

Further numerical studies are presently underway with the transient problem including the effect of upwinding.

Figure 3

Finite Element Solution, Steady State Equation

Figure 4

Finite Element Solution Steady State Equation

Figure 5

Finite Element Solution Transient Equation

B. Chemical Equilibrium Model (C.E.M.)

The chemical equilibrium model to be used is the most current one of a series developed by various researchers largely in cooperation with the U.S. Environmental Protection Agency. The present version, known as REDEQL-EPAK, is thermodynamically rigorous (i.e., relies upon independently measured thermodynamic constants) wherein the equilibrium composition of a mixture of ionic components is computed. The approach used is to formulate the required algebraic equations in terms of component mass balances, which are solved by a multidimensional Newton-Raphson iterative technique. Further details on the numerical approach can be found in Morel and Morgan.⁷ The program is documented in the EPA user's manual⁸; and examples of the application of the equilibrium approach to a fly ash disposal site can be found in Theis et al⁹, and Theis and Richter.¹⁰

The newest version of the model allows for automatic correction of results for temperature, and the capability of computing pH from any set of input data (whether ionically balanced or not). Although oxidation-reduction reactions are included, the redox potential must be specified -- it is not presently computed. Adsorption reactions are handled by the surface complex formation model,¹¹ presently for cation adsorption only. Provisions for anion adsorption, which are not any more computationally complex, will be added upon completion of a review of anion adsorption models (see renewal proposal). A schematic flow diagram of the model is given in Figure 6. Typically running times for representative problems are on the order of 0.5 seconds of CPU time per case (IBM 370 system). This is an important consideration due to the nature of the algorithm which will be used to couple the finite element and chemical equilibrium models. (see section III.C below).

Figure 6

FLOW DIAGRAM FOR REDEQL.EPAK

C. F.E.M./C.E.M. Coupling Algorithm

The problem can be formulated as involving three mathematical operations as follows:

$$L_1(h) = \frac{\partial}{\partial x} \left(k \frac{\partial h}{\partial x} \right)$$

$$L_2(c_j) = \frac{\partial c_j}{\partial x^2} - D_x \frac{\partial^2 c_j}{\partial x^2} + \frac{q_x}{\theta} \frac{\partial c_j}{\partial x} + \rho \frac{\partial s_j}{\partial t} = 0, \quad j = 1, M$$

$$A(c_j) = \sum_{\ell=1}^P a(\ell, j) K_{\ell} \prod_{j=1}^M c_j^{a(\ell, j)} - T = s_j$$

P = # of complexes

M = # of components

In the above, c is the soluble concentration of a component, s is the particulate concentration, T is total concentration, and K is the equilibrium constant. L_1 and L_2 are differential operators (Darcy's Law and the non-conservative convection-dispersion equation, respectively) and A is an algebraic operation involving the solution of a system of M mass balance equations giving a solid form (either precipitated or adsorbed). If, for a particular set of conditions, s_j turns out to be zero, then L_2 becomes conservative and linear for those conditions. Of central importance when s_j is not zero is the estimation of the last term of L_2 .

The algorithm for coupling the two programs, as presently conceived, is given in Figure 7. The F.E.M. requires the input of coefficients of permeability for the evaluation of Darcy's Law from which a velocity profile is obtained. In addition the physical geometry of the region must be specified along with initial (soluble) component concentrations. A first guess of the solid phase concentrations must be provided; it is possible for it to be

Figure 7

Proposed Algorithm

zero. The F.E.M. will output some new soluble component concentration at each node in the element mesh. These are input to the C.E.M., along with specific soil properties and the proper thermodynamic data base, which computes the associated solid concentrations, per node, for each component. These are output to the S matrix, an $i \times k$ array of solid concentrations wherein the columns are the values for one component at all nodes and the rows are the individual nodal values for all components. This matrix is put back into the F.E.M. for correction of the c values. This iteration continues until the soluble concentrations agree within an acceptable error. Then the program progresses to the next time step. This iterative algorithm will converge to the solution of L_2 , however the rate of convergence is a matter of concern and will be investigated further (see renewal proposal).

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APPENDIX

DOE Trace Substances Transport Projects Notes of Meeting Nov. 9, 1979 (Chicago)

T.L. Theis

The effort to coordinate the research of four projects concerned with pollutant transport from fly ash and other energy residues progressed at the meeting in Chicago on Nov. 9, 1979. The attendees were the present contractors, David Evans (Savannah River), Florence Harrison (Lawrence Livermore), Thomas Theis (Notre Dame), and Larry Wangen (Los Alamos), plus Marc Anderson (Wisconsin), Ralph Turner (Oak Ridge), and Herb Allen (Illinois Institute of Technology). Among the four contractors, there is general agreement to work together to the maximum extent possible on the problem. The details of this agreement, as they are presently understood, are set out below.

A. Subsurface Transport Model

The modeling effort at Notre Dame will progress in stages. The first major output of the research will be a one-dimensional finite element hydrologic transport model in which local equilibrium is assumed for the chemical reactions which occur. At the present time, the finite element model which is at Notre Dame is being adapted to the computer. Small test runs simulating conservative substances will begin shortly. The available chemical equilibrium models are being screened to assess their suitability for coupling with the transport model. Among the more important aspects are the type of adsorption routine which is used, the manner of computation and degree of access of selected species concentrations, and the extent and quality of the thermodynamic data base.

Later stages of the effort will involve the development of a two-dimensional model in which, again, local equilibrium is assumed. It was suggested (Anderson) that a kinetic model, at least for adsorption reactions, be developed, since, particularly for the case of desorption, the reaction rate may limit the validity of the equilibrium assumption. This may well be worth doing at the appropriate time. It must be noted, however, that the numerical computations are considerably more complex and the kinetic data base is less certain. Much will depend on the resources available, for example it may be decided at some time to include a chromatographic model which can treat the data being provided by Florence Harrison on organic partitioning in soils. Ralph Turner (Oak Ridge) indicated the availability of such models, e.g., the universal transport model presently under scrutiny by EPA.

B. Experimental

Perhaps the most substantive work done at the meeting revolved around the level of understanding, down to considerable detail, on the integration of experimental needs with overall needs of the research area. The experimental approaches which were agreed upon are described below:

(1) Column studies

Data from well-designed and executed column studies will be useful for comparison with one-dimensional model outputs. There are two levels of comparison which are useful. Considering a typical breakthrough curve for a column loaded with some dissolved species at initial concentration C_0 ,

The two critical values to predict are the initial concentration of C (C_i) after the mechanisms of attenuation and dispersion take place, and the time of breakthrough, t_s . The former indicates the maximum degree of attenuation for C which is possible for a given soil/water system, while t_s is a measure of the total capacity of the soil for C in the system. It should be noted that a mirror image of the above curve can be found for the case of desorption (or, say, from a fly ash column). In this case C_i becomes the final equilibrium concentration of C in solution.

It is important that soil column experiments develop this curve for the systems studied. It suggests that, until breakthrough is reached, flameless atomic absorption would be the standard analytical technique.

Based upon previous studies, it has been tentatively decided to limit investigation to the following trace elements: arsenic (as arsenate), borate, cadmium, and nickel. The dominant electrolyte will be either NaNO_3 or $\text{NaNO}_3/\text{CaSO}_4$. The NaNO_3 is used as the background ionic species since HNO_3 and NaOH will be used for initial pH adjustments. Calcium sulfate will be used in certain runs because it is commonly associated with fly ash and scrubber sludges. The sulfate ion may form soluble ion pairs with Cd and Ni thereby enhancing their transport characteristics. In all cases it is important that ionic strength and pH be measured.

The column studies will be run with six soils and five "levels" of applied leachate, thus giving 30 separate column runs, each run in duplicate. The six soils will consist of two "model" soils, pure kaolinite and α -FeOOH (goethite); and four actual soils, an acid weathered soil, a clay soil (kaolinite), a calcareous soil, and a dunal sand (from the previously monitored Michigan City field site). The levels of applied leachate are as follows:

- a) Cd/Ni/As/^{Se}~~P~~, background NaNO_3 , pH = 5
- b) Cd/Ni/As/^{Se}~~P~~, background NaNO_3 , pH = 10
- c) Cd/Ni/As/^{Se}~~P~~, background $\text{CaSO}_4/\text{NaNO}_3$, pH = 5
- d) Cd/Ni/As/^{Se}~~P~~, background $\text{CaSO}_4/\text{NaNO}_3$, pH = 10
- e) a real ash or scrubber sludge leachate, perhaps using the Michigan City fly ash.

In order to obtain practicable flow rates, the two model soils will be attached as coatings to an inert sand material. Most probably the columns will be loaded in an upflow configuration for ease of flow control. Concentrations of trace metals will be in the 1 mg/l range. CaSO_4 will be adjusted to realistic concentrations measured in the field, ≥ 2000 mg/l. Columns will be constructed of plexiglass and have 3 or 4 side sampling ports.

The suggested timing of the experiment is to do a and c above with all soils initially, as indicative of worst-case situations. These should be completed by next summer (1980). The other runs will be made thereafter.

(2) Batch equilibrium data

It is recognized that for modeling purposes it will be necessary to perform batch studies with a given soil and each individual trace metal, i.e., Cd, Ni, As, and B. This is to determine the necessary

thermodynamic data for adsorption reactions. Some of the work has been done for model soils and is reported in the literature, e.g., Cd, Ni, As on α -FeOOH. However, for other soils the experimental work must be done. This will also serve the purpose of evaluating the degree of adequacy of the soil surface characterization studies which are described below.

Soil Chemistry Studies

For both column and batch studies, it will be necessary to achieve a high degree of surface characterization. This is not so difficult for model soils, but may prove to be a more formidable problem for heterogeneous soils. The dunal sand has already been characterized reasonably well. The extensive characterization is necessary for accurate modeling. In addition an ancillary aim of this phase of the investigation will be to define a "standard" series of tests applicable to most soils for which modeling studies are deemed desirable. The types of tests to be run have been outlined previously.

(3) Leachate composition

There remains much worthwhile investigative work on ash and sludge inorganic leachate composition that should be done. Major questions relate to the range of values of trace and macro species in different leachates, and the various associations among ionic forms, chemical speciation, which exist. For example, although arsenate will be used in batch and column studies, there is evidence for both the oxidized and reduced (arsenite) arsenic forms in fly ash leachates (Ralph Turner, Oak Ridge). Similar questions exist with respect to soluble complexes such as between Cd, Ni and SO_4^{-2} , Cl_1^- , and F^- .

It is not practical to investigate experimentally every possible set of acid-base, redox, or complexation couples which may exist in leachate streams. The column and batch studies outlined previously represent selected cases of pH and degree of complexation for the trace species used. Once it is established that the model which is being developed can describe the behavior of these systems with reasonable accuracy, it can be used to define degrees of transport for any given set of conditions. These conditions can be established through, and upper and lower concentration bounds set by a systematic study of leachate composition, concentrations and probable speciation prior to entry to the soil environment. Accordingly it is suggested that such a study be continued at Savannah River (David Evans). Ralph Turner (Oak Ridge) has collected substantial amounts of data which should be useful for this purpose and should serve as an excellent beginning. Evans will prepare an outline for this study shortly.

(5) Trace organics

The study on trace organics from ash residues as outlined by Florence Harrison is given on the next page. In addition to field work, extensive laboratory experimentation is to be done. The basic data from the lab studies will be presented in the form of partitioning coefficients. These are obtained from batch studies at equilibrium. The soils to be used will be essentially the same ones outlined previously with the possible addition of a soil characteristic of one of the field sites. Column studies will be performed in a manner similar to that already outlined. Rather than using various levels of complexity of leachate, however, the columns will be loaded with actual leachate which may be spiked with specific representative organic compounds identified from field sample analysis. Consideration will be given to the use of the Michigan City station as the alternate

field sampling site. If this is done, the leachate may be that obtained from the fly ash produced there. Columns will be made of glass rather than plastic.

The partitioning coefficients are dependent on the specific chemical and physical conditions which exist at the time of their measurement. They are the method of choice of characterizing the behavior of organic compounds in aqueous systems and are the logical input to "chromatographic" transport models. Consideration should be given to the application of such a model to the data obtained from column experiments. With respect to the modeling work at Notre Dame, it is probable that the finite-element thermodynamic model can be used as a chromatographic model with few or no modifications.

(6) Field data

The testing of the model against field data is an important aspect of the research. Although field data is best analyzed via the two-dimensional model, there may be instances where a one-dimensional model can be applied to a portion of the data. At the present time four field sites have been identified as having potential use in later aspects of the research effort.

They are:

Widows Creed (SO_2 scrubber sludge/fly ash)
Kingston
Michigan City
Columbia

There is some question as to the adequacy of the Widows Creek and Kingston trace metal data, however at the very least, macro-constituents could be modeled. Both plants are operated by TVA who are not a priori opposed to this kind of study. Both Michigan City, studied by Notre Dame, and Columbia, studied by Wisconsin, appear well characterized and have good data bases. In all cases it may be worthwhile to collect an additional

SCHEDULE OF TASKS

[illegible]

I. FIELD STUDIES

SAMPLE ANALYSIS: 4-C#1

FIELD TRIP: FOUR CORNERS #2.

SAMPLE ANALYSIS: 4-C#2

FIELD TRIP: ALTERNATE SITE

SAMPLE ANALYSES: ALT. SITE

II. LABORATORY STUDIES

A. MOBILIZATION

K_D's OF 4-C SAMPLES

COLUMN STUDIES: 4-C
SAMPLES

B. BIOLOGICAL AVAILABILITY

ESP FLY ASH-4C

WS FLY ASH-4C

set of soil borings for an "update" on species partitioning along the time axis.

There may be other sites in addition to these four which can be used. An informal search will be made for such sites. There may be a possibility of working with Oak Ridge which has recently begun a coal-fired operation and will dispose of fly ash somewhere on the grounds. This should be looked into further.

In summary there appear to be several possibilities for field data such that the undertaking of a full scale field monitoring study is not necessary. It may, however, be desirable to update the status of various sites with follow-up visits and possibly some additional sampling.