Session VI:

MONITORING AND EVALUATION

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COAL COMBUSTION BY-PRODUCTS AND CONTAMINANT TRANSPORT IN GROUNDWATER

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Abstract

Leachate from coal combustion by-products can contain elevated concentrations of boron, sulfate, trace metals, and other inorganic constituents. Contaminant transport modeling can be used to evaluate the impact of these constituents on groundwater quality. To properly evaluate the potential impact of coal combustion by-products disposal on groundwater quality, the physical and chemical properties of coal combustion by-products, transport processes in groundwater, and the solution techniques of mathematical models must be understood. Physical and chemical properties of coal combustion by-products and transport processes in groundwater are reviewed. To highlight differences in model input and output, an analytical (MYGRT) and a numerical (MODFLOW/MT3D) contaminant transport model were used to predict the transport of boron from a landfill. The concentrations predicted by the two models are slightly different 50 m downgradient from the landfill because the models handle the contaminant input differently and allow the solute to be mixed over different aquifer thicknesses.

Introduction

During the combustion of coal, bottom ash, fly ash, flue gas desulfnrization (FGD) waste, and fluidized bed boiler waste may be produced. While some of these wastes are used in building materials and as structural fill material, the majority is disposed in landfills and surface impoundments. The potential for groundwater contamination from leachate originating from these landfills and surface impoundments represents the greatest environmental concern for disposal of coal combustion by-products (USEPA, 1988). To determine the environmental impact of the leachate from coal combustion by-products in landfills and surface impoundments, modeling can be used to estimate the leachate transport via groundwater. The objective of this paper is to describe and discuss different types of models used to estimate the transport of coal combustion by-products leachate in groundwater. In this paper, we also discuss the physical and chemical characteristics of coal combustion by-products, transport processes important for coal combustion by-products, and analytical and numerical modeling of contaminant transport in groundwater. Two different models were used to model a'single case history. Differences in model input and output will be highlighted.

The significance of various transport processes depends on the leachate constituents. To focus this discussion about transport processes, the characteristics of leachate generated from coal combustion by-products will be reviewed. The three most common coal combustion by-products are fly ash, bottom ash, and flue gas desulfuization (FGD) waste. Carlson and Adriano (1993) reviewed the literature on the environmental impact of fly ash, bottom ash, and FGD waste, and noted that information on the environmental impact of FGD waste was much more limited than fly and bottom ashes. Another source of data on coal combustion by-products including FGD waste is Ainsworth and Rai (1987).

Description of Coal Combustion By-Products

The physical, chemical, and mineralogical characteristics of fly and bottom ashes depend upon several factors including the composition of the parent coal, combustion conditions, the efftciency and type of emissions control devices, and the method of ash disposal(Carlson and Adriano, 1993). Although ash characteristics are variable, certain generalizations can be made. Fly ash is composed predominantly

of silt-sized, glassy, sometimes hollow particles with specific gravities of 2.1 to 2.6. Compared with fly ash, bottom ash has a greater percentage of coarse-grained particles and has a greater specific gravity (Carlson and Adriano, 1993). Fly ash is generally considered a ferro-aluminosilicate mineral with Al, Si, Fe, Ca, K, and Na as the predominant elements. In addition, fly ash contains all naturally occurring elements and is substantially enriched in trace elements compared with the parent coal. The concentrations of major elements (Al, Ba, Fe, K, Mg, and Si) are similar in fly ash and bottom ash (Ainsworth and Rai, 1987). Fly and bottom ashes are also generally enriched in the trace elements, As, B, Ca, Mo, S, Se, and Sr. Many of these trace elements are concentrated in the smaller ash particles. Ash pH depends on the S content of the parent coal. Eastern coals produce acidic ashes because these coals generally contain higher concentrations of S. Ainsworth and Rai (1987) noted that several trace elements including As, Mo, and Zn, are more concentrated in the fly ash of bituminous coal than subbituminous or lignite coal.

Flue gas desulfurization involves the removal of SO, from the flue gas, usually by the addition of a limestone slurry to the flue gas at the smokestack (USEPA, 1988). Lime, sodium hydroxide, and sodium sulfate are also used to absorb sulfur dioxide from the flue gas (USCOTA, 1992). FGD waste is generally a combination of fly ash, Ca-S salts, and $CaCO_3$ (Carlson and Adriano, 1993). FGD waste typically contains higher concentrations of Br, Cl, and S than fly and bottom ashes (Ainsworth and Rai, 1987). Because of its higher concentrations of sulfur and other contaminants, FGD sludge may be of greater environmental concern than fly and bottom ashes (USCOTA, 1992).

Disposal of Coal Combustion By-Products

The two predominant methods for the disposal of fly ash, bottom ash, and FGD sludge are settling ponds and landfills (USEPA, 1988). Surface impoundments receive ash in slurry form. In these ponds, the ash particles settle to the bottom of the pond. The effluent water is then pumped back to the power station for reuse or is discharged to a stream or lake. Many impoundments are unlined, sometimes allowing a significant portion of the slurry water to leach through the bottom. Landfills receive dewatered ash from settling ponds and/or dry ash directly from the power plant. Landfills are currently considered the favored disposal method, although settling ponds were previously favored because of the lower cost and operational simplicity (USEPA, 1988).

The potential for groundwater contamination due to leachate from coal combustion by-products disposal sites was identified by USEPA (1988) as the primary concern, based on the elevated concentrations of soluble salts and potentially toxic trace elements including As, Ba, Cd, Cr, Pb, and Se present in coal combustion by-products. The geochemistry of As, B, Ba, Cd, Cr, Se, and SO., in groundwater was summarized by Summers et al. (1989). A limited number of field investigations has shown that the effects of ash disposal on groundwater quality depend on the physical and chemical characteristics of the ash and the hydrogeologic conditions and climate of the disposal site (Carlson and Adriano, 1993). Groundwater contamination downgradient from ash landfills and surface impoundments has been reported, but rapid attenuation limited the extent of groundwater contamination (Carlson and Adriano, 1993; USEPA, 1988). Leachate from coal combustion by-products disposal sites is generally characterized by relatively high soluble salt concentrations with Ca^{2+} and SO_4^{2-} usually the dominant cation and anion, respectively. Leachate pH varies with the ash composition (Carlson and Adriano, 1993).

Transport processes in groundwater

Leachate from disposal sites containing combustion by-products from Illinois coal will generally have an alkaline pH (Roy et al., 1981) and contain elevated concentrations of cations and anions. The important transport processes in groundwater for this type of leachate are advection, hydrodynamic dispersion, and several types of chemical reactions such as acid/base, reduction/oxidation (redox), adsorption/desorption, and precipitation/dissolution. Advection is defined as the transport of a solute with the movement of groundwater. Hydrodynamic dispersion includes mechanical dispersion and

diffusion. Mechanical dispersion is the transport of a solute resulting from minor differences in groundwater velocity as it flows through nonhomogeneous porous media. Diffusion describes the movement of a solute from an area of higher concentmtion to lower concentration, and is an important transport mechanism in geologic materials with low hydraulic conductivity. Advection and hydrodynamic dispersion simply redistribute the mass within the geologic material. Neither process changes the amount of solute mass in groundwater. However, chemical processes can alter the mass of solute by transforming the solute to another form or moving the solute from the liquid (groundwater) to solid phase (aquifer material).

Several processes including adsorption/desorption, redox, and precipitation/dissolution can change the solute mass in the groundwater. Adsorption is a general term and includes all processes where the solute bonds to a solid phase (Fetter, 1993). Adsorption includes ion exchange, which refers to the exchange of solutes (generally cations but may include some anions) with charged surfaces, such as clay minerals, due to electrostatic forces. Precipitation describes the process where solutes in the groundwater react to form a solid, while dissolution is the process where a solid dissolves in the groundwater. Adsorption, precipitation, and dissolution of inorganic solutes are controlled by pH, redox conditions, temperature, and solute concentration. These processes may be reversible if these controlling conditions change over time. Additional details on contaminant hydrogeology can be found in Fetter (1993).

Modeling of Contaminant Transport

Modeling involves three initial considerations-- model selection, solution technique, and input data. Model selection involves selection of the type of processes to be studied and included in the mathematical statement. Different solution techniques are available to solve the chosen mathematical model. Finally, input data for the model must be gathered from a literature review, field investigations, and/or laboratory studies. This discussion about modeling is limited to contaminant transport in groundwater, assuming that the leachate mixes completely with groundwater and does not change the density and/or temperature of the groundwater. This discussion also will be limited to transport through saturated, porous media. Transport through unsaturated or fractured media is beyond the scope of this introductory discussion.

Model Selection

A mathematical model of any complex natural process such as contaminant transport in groundwater may not be able to completely reproduce field observations, but a good model should reproduce the more significant field observations. Deterministic and stochastic models are used to model contaminant transport. Deterministic models provide a single result based on single input parameters. Stochastic models use statistical descriptions as input parameters and thus yield statistical descriptions as results. Because deterministic models are more widely used, this discussion will focus solely on these models.

The following differential equation describes one-dimensional, advective-dispersive transport (Fetter, 1993) and is simply a statement of one of the basic scientific principles, conservation of mass. The derivation of this equation can be found in Freeze and Cherry (1979, Appendix X).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \frac{B_d K_d}{\theta}\frac{\partial C}{\partial t} + \left(\frac{\partial C}{\partial t}\right)_{rxn} \qquad [1]$$

The first term describes the rate of change of a solute concentration, C, over time, t. The second term accounts for the dispersion of the solute, where D is the dispersion coefficient in the direction of flow. The third term accounts for the advection of the solute, where the average linear grotmdwater velocity is denoted by v. The fourth term accounts for solute adsorption, where B_d is the bulk density of the aquifer, q is the porosity of the aquifer, and K_d is the distribution coefficient. K_d accounts for the solute that adsorbs to the solid and assumes a linear and reversible adsorption model. Fetter (1993) noted that a

linear adsorption model is not always accurate because it does not limit the amount of solute that can adsorb onto the solid. However, its use allows [l] to be solved easily and is an example of the compromises made in mathematical models. The final term accounts for any solute added to or removed from solution due to any reactions. If the only type of reaction the solute experiences is radioactive decay, the fmal term in [1] can be replaced by lC(l+ B_dK_d/q), where 1 is the radioactive decay constant. As a matter of convenience, [l] is sometimes rewritten in a slightly simpler form (Javandel et al., 1984):

$$\frac{\partial C}{at} = \frac{D}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v}{R}\frac{ac}{\partial x} - \lambda RC \qquad [2]$$

The retardation factor, R, equals 1 + B&/q. This equation is suitable for modeling the transport of a single solute. Multiple, interacting solutes can be studied using multicomponent modeling, which couples grotmdwater flow and equilibrium chemistry models. Multicomponent modeling was recently reviewed by Engesgaard and Christensen (1988) and Mangold and Tsang (1991).

Solution Technique

The solution to [2] requires one initial condition for the derivative with respect to time and two boundary conditions for the derivative with respect to space (x). This equation can be solved analytically or numerically. An analytical solution is given by [3], and is based on the following assumptions:

- The system is initially free of the solute.
- The concentration gradient at a distant boundary does not change over time.
- Solute is added continuously at the concentration C_0 at the near boundary.

Mathematically, these conditions are expressed as follows:
initial condition: C(x,t) = 0 fort = 0

boundary condition 1: $\frac{\partial C(x,t)}{partialx} = 0 \quad forx = infinity$

boundary condition 2: $-D(\frac{\partial C(x,t)}{\partial x} + vC) = vC_0$

The solution to [2] is (Javandel et al., 1984):

$$\frac{C}{C_0} = \frac{v}{v+U} e^{\left[\frac{x(v-U)}{2D}\right]} erfc\left[\frac{Rx-Ut}{2\sqrt{DRt}}\right] + \frac{v}{v-U} e^{\left[\frac{x(v+U)}{2D}\right]} erfc\left[\frac{Rx+Ut}{2\sqrt{DRt}}\right] + \frac{v^2}{2DR\lambda} e^{\left[\frac{vx}{D}-\lambda t\right]} erfc\left[\frac{Rx+vt}{2\sqrt{DRt}}\right] \qquad [3]$$

where U= $(v^2 + 4DRl)^{1/2}$ and erfc is the complementary error function. This function is a special mathematical function and is tabulated in Fetter (1993, Appendix A). The concentration relative to the input concentration, C/C,,, at any time and place can be determined using [3] if the variables, D, R, v and 1, are known. These variables are assumed to remain constant over time and space.

Equation [2] also can be solved numerically using finite differences or finite elements. The finite difference method is easier to understand than finite elements, so finite differences will be used to illustrate the numerical solution of [2] As with all numerical methods, finite differences requires that the porous media under study be divided into small segments. This can be accomplished by laying a rectangular grid over the study area. At the nodes of this grid, the transport equation is solved by approximating the differential equation as a difference or algebraic equation. The difference equation is a mass balance of the solute at a node of the model. The difference equations for all nodes are grouped into a series of linear equations, which can be solved easily using a computer, Additional information on numerical methods can be found in Anderson and Woessner (1992, Chapter 2).

When solving the solute transport equation numerically, the groundwater flow equation must also be solved numerically. The flow and transport equations are linked because the head data from the flow equation are used to compute the velocity term in the transport equation. The velocity term is usually defined by Darcy's Law. A numerical solution offers several advantages over an analytical solution, which justifies the additional effort involved with using numerical methods to solve the transport equation. For numerical models, the input parameters do not have to remain constant over space, but may vary to more accurately reflect the site hydrogeology. Groundwater flow velocities are also allowed to vary over time and space. Also, numerical models allow the modeler to more accurately account for the effects of site boundary conditions, such as rivers.

Finite difference or finite element methods are not the best methods in all situations. Particle tracking is another approach adopted to numerically simulate solute transport and involves tracking imaginary particles through the modeled domain. Particle tracking models use head data from groundwater flow models to compute groundwater velocities, which are then used to determine solute transport. The two most widely used particle tracking methods are particle tracking and random walk (Wen and Gomez-Hemandez, 1996). In particle tracking, hydrodynamic dispersion is not included because transport is assumed to by dominated by advection. The random walk approach accounts for advection and hydrodynamic dispersion. Both methods are free of numerical dispersion and are well suited for determining contaminant arrival times, locations, and concentrations, but large number of particles must be tracked to obtain accurate results (Wen and Gomez-Hemandez, 1996). Numerical dispersion is the artificial spreading of the solute as a result of the numerical methods and is a common problem with finite difference or finite element methods.

Model input

Model input can be obtained from the literature (e.g., Freeze and Cherry, 1979; Summer et al., 1989), field investigations, and/or laboratory studies. Model input is often considered the most important segment of the modeling process and often dictates the type of model used and the utility of the model results.

Case History

To demonstrate the differences in model input requirements and results, two different models were used to simulate the contaminant transport from a coal combustion by-products disposal site. These models tested were MYGRT and MODPLOW/MT3D.

Description of Models

MYGRT is a code for modeling transport of inorganic and organic contaminants and includes advection, dispersion, retardation, and decay (Summers et al., 1989). MYGRT can be used to model transport in one or two dimensions. For two-dimensional simulations, the code may be used for either plan (x,y) or profile (x,z) simulations. Output is generated as a function of time and space. MYGRT assumes:

- The geologic materials are homogeneous and isotropic.
- The groundwater flow is uniform over space and time.
- Dispersion is represented by Fick's Law.
- Sorption is represented by linear equilibrium partitioning between the aqueous and solid phases.
- Solutes are not affected by chemical reactions with other solutes during transport.

The differential equation solved by MYGRT has a solution similar to [3] A new version of MYGRT is currently being developed and will allow changes in source concentration over time and changes in transport parameters over space. These changes in MYGRT will enhance modeling of the effects of site closures.

MODFLOW (McDonald and Harbaugh, 1988) is widely used and can simulate one, two or three dimensional, saturated groundwater flow under steady state or transient conditions. Head data generated by MODFLOW are used by transport models such as MT3D (Zheng, 1990) to compute groundwater velocities and contaminant transport throughout the modeled domain. The major assumptions of MODFLOW are:

- Fluid flow is governed by Darcy's law.
- Flow is not affected by thermal, chemical, or density gradients.
- The fluid is slightly compressible and homogeneous.
- The principal components of hydraulic conductivity are aligned with the model axes.

The major assumptions of MT3D are:

- Single species, miscible contaminants are transported by advection and dispersion, and may be affected by simple chemical reactions.
- Chemical reactions are equilibrium controlled, linear and non-linear sorption or first-order, irreversible rate reactions (e.g., radioactive decay and biodegradation).
- The contaminant does not significantly impact the flow field.

Description of Coal Combustion By-Products Disposal Site & Model Input

The case study site was an actual unlined coal ash landfill where fly ash and bottom ash was dry-disposed. Because the landfill owner requested anonymity, the site description has been generalized. The landfill covers an area 300 m by 300 m (22 acres). The ash was about 10 meters thick. Ash was disposed in this facility from 1970 to 1995, when it was closed and capped. The facility was located on the floodplain, approximately 100 meters from a major river. Underlying sediments consisted of highly permeable sand and gravel with hydraulic parameters given in Table 1. The data for this case study were obtained from field investigations and the literature. Because boron is an indicator constituent for coal combustion by-products leachate and is mobile in sand and gravel aquifers, it was selected for modeling. Boron was modeled using an initial relative concentration of 1.0 rather than an absolute concentration. The modeling results can be considered as relative concentration (C/C,) or percent change from the source concentration.

The alluvial aquifer in this case study was relatively homogeneous, with no pumping-well effects near the disposal facility. Furthermore, the river stage was controlled by a nearby lock and dam, so the groundwater gradient did not fluctuate much. Finally, groundwater did not mound beneath the landfill because of the high hydraulic conductivity of the aquifer combined with the relatively low leachate flux from the active landfill.

Model Results

MYGRT simulation: Because the modeled aquifer was relatively thick, MYGRT was used in the profile mode, which more accurately represents solute concentrations in thick aquifers. Transverse dispersion was ignored in the profile model; however, it had a negligible effect on concentration along the centerline of this plume due to the large width of the facility relative to the short distance to the groundwater discharge point.

MYGRT offers two possible boundary conditions for solute input. One boundary condition allows the user to set the initial concentration in the aquifer. This concentration is evenly distributed throughout the depth of plume penetration. Plume penetration depth is the thickness of the plume at the downgradient edge of the landfill. This depth can be based on monitoring data or estimated using an equation (Summers et al., 1989). If the monitoring data are sufficient to estimate leachate concentration and plume penetration depth, this first boundary condition should be used. The second boundary condition calculates the initial concentration in the aquifer from the concentration of the leachate, the flux rate of leachate into the aquifer, and the velocity of groundwater flow and was the boundary condition used here. The solute concentration is calculated assuming complete mixing throughout the

plume penetration depth.

Model input parameters for MYGRT are listed in Table 1. Because MYGRT does not calculate a groundwater flow field, groundwater velocity (v) is input rather than hydraulic conductivity (K). Groundwater velocity can be calculated as the product of K and i divided by n_e, where i is the hydraulic gradient and n_e is the effective porosity. Rather than total porosity, effective porosity is used. Effective porosity is that portion of the pore space in the aquifer through which groundwater flows. By definition, effective porosity is less than total porosity. In coarse-grained aquifers, it is only slightly less than total porosity; however, it may only be a small fraction of total porosity in clays.

Two MYGRT simulations were used to model transport before and after the landfill was capped. The first simulation assumed a leachate flux rate of 10 cm per year from 1970 through 1995. The second simulation assumed a leachate flux rate of 1.3 cm per year after 1995. The analytical solution allows these results to be added together to simulate a decreasing source term, as illustrated in Figure 1. The model results suggested that concentrations 50 m downgradient from the landfill increase for approximately 15 years and then level off at a relative concentration of approximately 0.23. After the landfill was capped in 1995, the concentration 50 m downgradient from the landfill decreased rapidly from 1998 to 2010.

MODFLOW/MT3D simulation: Input for the numerical models MODFLOW and MT3D are listed in Table 1. A two-dimensional profile model was developed using 12 nodes in the z direction and 50 nodes in the x direction. The boundary conditions for the flow and transport models are shown on Figure 2. Boron enters the groundwater by recharge from the bottom of the landfill. The concentration of boron in the recharge was 1.0 within the landfill and 0.0 outside the landfill. The capping of the landfill is represented by a decrease in the recharge rate.

Modeling results for MODFLOW/MT3D (Figure 3) were generally similar to the MYGRT results. The concentration 50 m downgradient from the landfill increased from 0 after the landfill was open for 2 years to its peak concentration approximately 2 years after the landfill was capped. The concentration then declined to a new equilibrium concentration. However, the peak concentration estimated by MODFLOW/MT3D was less than the MYGRT-estimated peak concentration, 0.20 and 0.23, respectively. Also, MYGRT predicted that the concentration remained constant at the peak concentration for over 10 years, while the MODFLOW/MT3D concentration did not level off. The models also yielded different concentrations after the landfill was capped. These differences in the predicted concentrations of boron can be explained by examining how the models introduce and mix boron into the aquifer. MYGRT added boron to the aquifer using a line source perpendicular to the direction of flow at the downgradient edge of the landfill (x= 400 m, see figure 2). MT3D introduced boron using recharge over the entire area of the landfill (x= 100 to 400 m) or along the direction of flow. Also, MYGRT assumed that the solute was mixed over the plume penetration depth (set at 16.1 m), while in MT3D the solute was transported over the saturated aquifer thickness of 18 m. Both of these factors accounted for the different concentrations observed 50 m downgradient from the landfill.

Discussion

As with most analytical solutions, MYGRT requires little data input. The transport equation is not a simple expression, but MYGRT solves it in seconds. Simple data structure and presentation of results often make analytical models appealing to regulators who may not have the time or experience to thoroughly review numerical models. Because the limited data input cannot accurately reflect the actual hydrogeologic conditions of most sites, analytical models generally will produce results with a higher degree of uncertainty than results from numerical models. However, ease of application and computational speed of analytical models make it easy to conduct sensitivity tests on model parameters that lead to the high degree of uncertainty in the model results. Analytical models can be considered specialized tools, and are useful to model simple hydrogeologic settings or to provide preliminary estimates of more complicated hydrogeologic settings.

Numerical models are general purpose tools and can be applied to a wide variety of situations. Numerical models are needed where complex groundwater flow or solute transport conditions do not match the simple assumptions incorporated into analytical models, such as uniform groundwater flow. Numerical models may be preferable for cases where calibration is desired to reduce model uncertainty. However, numerical models require much more input data and more time to set up and run, Numerical models also provide other useful data including mass balance data for flow and solute transport. For example, recharge contributed 43 percent of the total flow in the case study. Also, 91 percent of the solute that entered the aquifer was transported out of the downgradient boundary.

Summary

Contaminant transport modeling of leachate from coal combustion by-product landfills and surface impoundments allows one to assess the environmental impact on groundwater quality. However to properly assess this environmental impact, the modeler must have comprehensive knowledge of the physical and chemical properties of the coal combustion by-products disposed at the site, the significance of groundwater transport processes, and the inherent assumptions of and the solution techniques of the software used for contaminant transport modeling. The case study illustrated differences in the predicted concentration of boron 50 m downgradient from a landfill. While these differences may seem trivial, they could become quite significant in a regulatory setting.

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Table 1. Input data used for the case study

Parameter	Value (units)	Parameter used in the following models		
		MYGRT	MODFLOW	MT3D
Definition of the source				
length	300 m	X	X	X
width	300 m	X	X	X
thickness	10 m			
date opened	1970	X	X	X
date closed	1995	X	X	X
infiltration rate, pre-closure	10 cm/yr	X	X	X
infiltration rate, post-closure	1.3 cm/yr	X	X	X
distance to river	100 m	X	X	X
unsaturated zone thickness	2 m			
Hydrogeology				
aquifer thickness	20 m	X	X	X
hydraulic conductivity	0.010 cm/sec		X	X
hydraulic gradient	0.002		X	X
effective porosity	0.20	X		X
groundwater velocity	31.5 m/yr	X		
bulk density	1.6 g/cm^3			X
recharge rate	25 cm/yr		X	X
Contaminant transport				
modeled solute	Boron	X	X	X
longitudinal dispersivity	10 m	X		X
vertical dispersivity	0.063 m	X		X
R	2.0	X		X
plume penetration depth	16.1	X		

Figure 1. MYGRT predicted concentrations for boron 50 m downgradient from the landfill

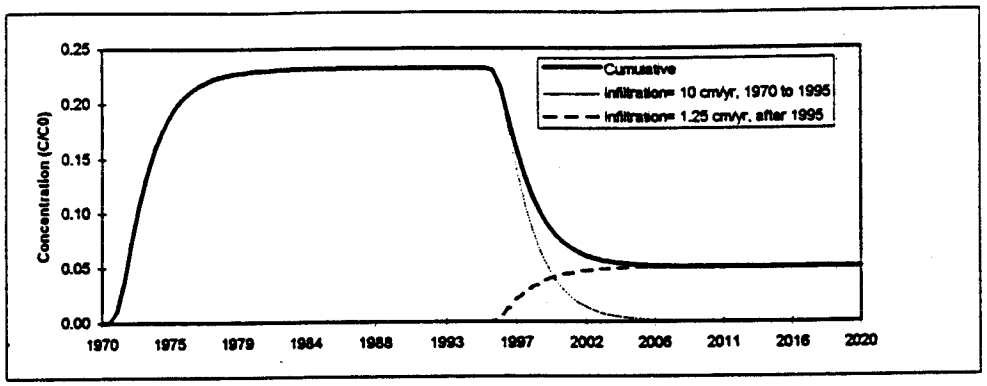


Figure 2. Boundary conditions for MODFLOW and MT3D for the case study

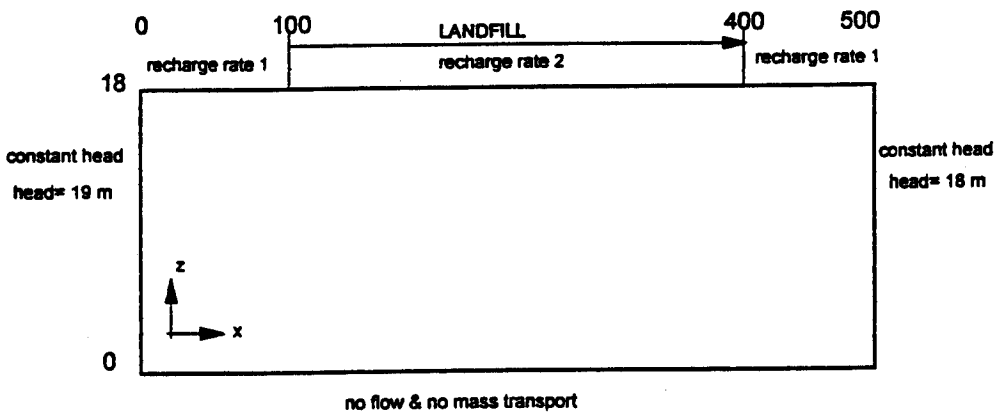
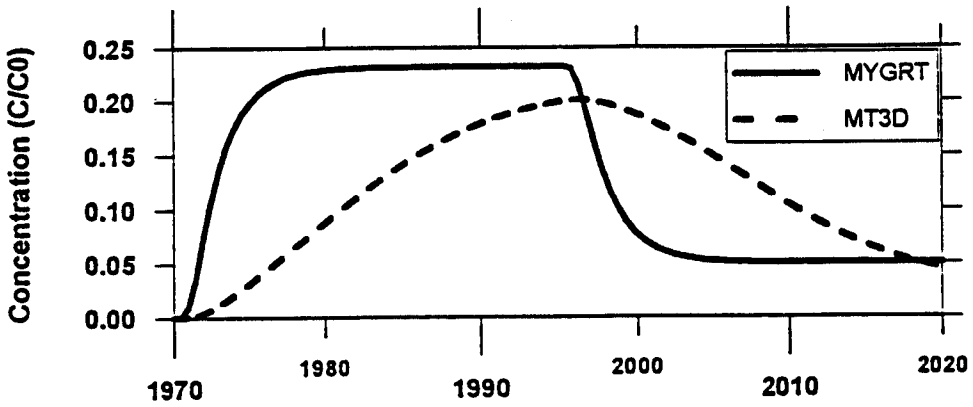


Figure 3. MYGRT and MT3D predicted concentrations for boron 50 m downgradient of the landfill



ELEMENTS OF COMPUTER-ASSISTED THERMODYNAMIC CHEMICAL EQUILIBRIUM MODELING AS APPLIED TO WASTE TREATMENT AT COAL MINES

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Abstract

Computer-assisted thermodynamic chemical equilibrium models are useful tools for describing and understanding the reactions that occur in a chemical system. Several models are available either free or at nominal cost. The models presently available generally are designed to compare the ion activity product with the equilibrium constant for a particular reaction. Understanding how models calculate total dissolved activities from solute concentrations and then calculate the activities and concentrations of various aqueous species and solids is essential for selecting the best model for a particular application. Models are limited by the quality of the data in their databases and by the state of theoretical understanding of nonideal solutions. Therefore, results from computer models must be validated through field or laboratory experiments before being accepted and used for making decisions.

Introduction

Many computerized models have been written over the years but many of these are designed for a narrow purpose. Of the many models developed, only a few are in general use by the scientific community. Acceptance of a chemical thermodynamic equilibrium model seems to be governed by its ease of use, the extensiveness of its thermodynamic database, the breadth of the capabilities of the model, and the ease of modifying the code to suit a particular need (Mattigod, 1995).

Chemical Fundamentals

Most simply states, a model is a representation of an object or an event. A chemical equation is a model for a chemical reaction. For example, equations l-4

$$CO_{2(g)} = CO_{2(aq)} \quad (1)$$
$$CO_{2(aq)} + H_2O = H_2CO_3 \quad (2)$$
$$H_2CO_3 = H^+ + HCO_3 \quad (3)$$
$$HCO_3^- = H+ + CO_3^{2-} \quad (4)$$

represent the dissolution of gaseous carbon dioxide in water.

These equations indicate that (1) carbon dioxide gas will dissolve to some extent in water, (2) an amount of aqueous carbon dioxide will combine with an equimolar amount of water to form an equimolar amount of carbonic acid, (3) carbonic acid will dissociate in water to form hydronium and bicarbonate ions, and (4) bicarbonate ion will further dissociate (equation 4) to form another hydronium ion and carbonate ion. When no additional information is provided, a set of chemical equations is primarily descriptive. These equations tell us what happens when carbon dioxide dissolves in water, but they don't tell us how much of each species will be present.

To determine quantities of species requires additional information, namely, an equilibrium constant for each reaction, that is, the ratio of the mathematical product of each product species activity raised to the power of the coefficient of that species in the chemical equation divided by the mathematical product of each reactant species raised to the power of its coefficient. For example, for the hypothetical reaction

$$aA+bB=cC+dD \tag{5}$$

the equilibrium constant is

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{6}$$

Equilibrium can be defined as the equality of the rates of opposing reactions. In other words, the rate of production of C and D in equation 5 by the reaction of A and B is equal to the rate of production of A and B by the reaction of C and D.

Another defmition of equilibrium can be formulated on the basis of free energy. Any system which is not at equilibrium will change spontaneously with the release of energy. At equilibrium, when the reactants and products are at the same temperature and pressure, the sum of the free energy of the products equals the sum of the free energy of the reactants. Or,

$$\Sigma \Delta G_{prod} - \Sigma \Delta G_{react} = 0 \tag{7}$$

The standard free energy of formation of a substance is defined as the free energy change resulting from the formation of one mole of the substance from the stable elements under standard state (25°C and 1 atm) conditions.

The equilibrium constant for a reaction can be calculated from the standard free-energy change of the reaction (A G_r^o), the difference between the sum of the free energies of formation of the products less the sum of the free energies of formation of the reactants:

$$\Delta G_r^o = \Sigma \Delta G_{r\,(prod)}^o - \Sigma \Delta G_{r\,(react)}^o \tag{8}$$

At 25°C and 1 atm pressure, the equilibrium constant is related to the standard free-energy change (in kcal) of the reaction by

$$\log K = \frac{-\Delta G_r^o}{1.364} \tag{9}$$

One cau calculate equilibrium constants from standard free energies of formation, which have been tabulated by several authors.

We are now in a position to calculate the activities of the various species that are formed with the dissolution of carbon dioxide. The equilibrium constants for reactions 1 through 4 are as follows:

$$CO_{2(gas)} = CO_{2(aq)} \qquad K_1 = 3.89\text{x}10^{-2} \tag{1}$$
$$CO_{2(aq)} + H_2O = H_2CO_3 \qquad K_2 = 2.40\text{x}10^{-3} \tag{2}$$
$$H_2CO_3 = H^+ + HC03 \qquad K_{a1} = 1.74\text{x}10^{-4} \tag{3}$$
$$HCO_3^- = H^+ + CO_3^{2-} \qquad K_{a2} = 5.62\text{x}10^{-11} \tag{4}$$

By substituting the atmospheric partial pressure of carbon dioxide, 0.0003 atm, into equation 1, and solving the four equations, the concentrations of CO,,,,,, H_2CO_3, HCO_3^-, and CO_3^{2-} are found to vary with pH as shown in Figure 1.

These calculations yield activities rather than concentrations. The activity of a species is a

measure of its effective concentration, and is usually smaller than concentration, Activity is related to concentration through the equation

$$act_i = \gamma c_i \tag{10}$$

where act_i is the activity of the ith species, γ is the activity coefficient, and c_i is the concentration of the ith species. The difference between activity and concentration arises because in a solution, each ion is surrounded by a shell of oppositely charged ions, which decreases the ability of the central ion to enter into chemical reactions.

In an ideal solution, the activity coefficient is equal to 1 and activity equals concentration. Real solutions are not ideal, however, so activity coefficients must be calculated for different solutes. An equation commonly used used to calculate activity coefficients is the extended **Debye-Hückel** equation,

$$-\log\gamma_i = \frac{Az_i^2\sqrt{I}}{I + Ba_i\sqrt{I}} \tag{11}$$

where $A = 1.82x10^6(\epsilon T)^{-3/2}$, $B = 50.3(\epsilon T)^{-1/2}$, and e signifies the dielectric constant of the solvent, and T is the absolute temperature of the solution.

The quantity a_i is dependent on the "effective diameter" of the ion. Values of a_i have been determined experimentally and are available in tabulated form. The symbol z_i is the ionic charge, and I is the ionic strength of the solution. The ionic strength is calculated from

$$I = \tfrac{1}{2}\Sigma m_i z_i^2 \tag{12}$$

where m_i is the molal concentration (mole/kg) of the ith ion in solution.

The extended Debye-Htickel equation is valid for ionic strengths up to about 0.05m. Other equations, such as the Guntelberg equation or the Davies equation have been developed for higher ionic strengths (Butler, 1964). The Davies equation is useful for ionic strengths up to approximately 0.5m. This ionic strength limit is satisfactory for most environmental work. Figure 2 shows a comparison of activity coefficients calculated from the Debye-Htickel, Guntelberg, and Davies equations with experimental data for several solutes. Figure 2 shows that none of the three equations matches the experimental data entirely adequately. The Pitzer equation (not shown in Figure 2) is useful for calculating activity coefficients in solutions in which the ionic strength is greater than0.5m.

Typically, in a thermodynamic chemical equilibrium model, the activities of solutes are compared with the solubility of each potential mineral in the database. If the solubility product of some mineral in the model's database is exceeded by the ion activity product (IAP) of the dissolved constituents in the solution being modeled, the model allows the mineral to precipitate until the IAP equals the solubility product. Conversely, if a mineral is present in the solid phase and the IAP of the dissolved constituents in the model solution is less than the solubility product of the mineral, the model allows the mineral to dissolve until the IAP and the solubility product are equal.

For example, the solubility product, K_{sp}, of calcite at 25°C is $0.87x10^{-8}$ and is simply an equilibrium constant for the chemical reaction

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \qquad K_{sp} = 0.87x10^{-8} \tag{13}$$

By definition, the activity of any solid is equal to 1, so the equilibrium constant for the above reaction is

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \quad (14)$$

The IAP is calculated from the activities of the dissolved mineral constituents. The saturation index is defined as $\log(IAP/K_{sp})$ for the mineral. If the saturation index is positive, the solution is supersaturated with respect to that mineral, and precipitation of the mineral is allowed by the model. If the saturation index is negative, the solution is undersaturated with respect to that mineral, and dissolution of the mineral is allowed.

Thermodynamic equilibrium models generally are organized around two major approaches. The most common approach is to base the calculations on equilibrium constants (Mattigod, 1995), as illustrated above. The second approach is called the free energy minimization approach. The second approach is not commonly used because the data required are neither as readily available nor as reliable as equilibrium constants. However, the two methods produce mathematically equivalent results.

Limitations of Chemical Equilibrium Models

Assumption of Equilibrium

Thermodynamic chemical equilibrium models assume that equilibrium has been attained in the system of interest. This may be the case in a well-stirred solution in a beaker, but it is not necessarily true for a natural system. Natural systems are subject to slow changes in solution composition due to the diffusion of solutes into or out of the system, the diffusion of gases such as oxygen or carbon dioxide into or out of the system, transport of solutes through the system because of groundwater flow, oxidation-reduction reactions, acid-base reactions, microbial activities, adsorption-desorption, and other processes which cause changes in solute concentrations.

Limitations of Thermodynamic Data

Models require thermodynamic data such as equilibrium constants, solubility product constants, and enthalpy values, in their calculations, but not all thermodynamic data are of equal accuracy and precision. If a model's developer chose inaccurate thermodynamic data for the database, then the modeling results will also be inaccurate.

If experimentally determined thermodynamic data are not available for each solute of interest, then estimated or indirectly calculated values must be used. However, an equilibrium constant can be calculated for the reaction only when the free energy of formation is known for each desired component in a reaction. Enthalpy data are required in the model to correct equilibrium constants if the modeled solution's temperature differs from the standard state, usually 25°C.

Required User Input

The user of a model must supply chemical information specific to the problem to be modeled. The data required usually include temperature, pH, Eh, and the concentration of each cationic and anionic component in the system to be modeled. Depending on the model, the data must be written to a file with specific formatting requirements or into a preprocessor which writes the properly formatted input file.

Models require that the concentration of some form of inorganic carbon, such as the partial pressure of CO*, dissolved inorganic carbon, or the inorganic carbon portion of alkalinity be supplied. None of these is completely straightforward While the atmospheric partial pressure of carbon dioxide is approximately 0.0003 atm at the earth's surface, the partial pressure of CO_2 in soils can range up to about 0.01 atm (Hassett and Banwart, 1992), due to microbial respiration. Knowledge of the specific soil CO_2 content is needed. Dissolved inorganic carbon is the total of all inorganic carbon species in solution, which includes all dissolved species of carbon dioxide plus ion pairs that include carbonate or

bicarbonate. Total dissolved inorganic carbon can be determined by the acidic evolution of CO_2.

Generally, the pH and Eh can be fixed in the model or allowed to vary as solution conditions change during the calculation.

If the user wishes to include minerals in the calculation, then data for the concentration of each mineral must be entered in the model. The database will usually include data for end-member compositions only. This is not a problem for minerals such as calcite ($CaCO_3$) or hematite (Fe_2O_3) which generally do not enter into solid solution or ionic substitution, but can become a significant source of error for clay minerals, such as smectites and mixed layer clays with variable composition. For example, the smectite mineral beidellite has an ideal composition of $Ca_{0.25}Al_2(Si_{3.5}Al_{0.5})O_{10}(OH)_2 \times nH_2O$. However, in nature, the chemical composition generally will be somewhat more complicated and unpredictable due to polymorphic substitution and inclusion of impurities. A more representative, but less exact chemical formula for beidellite might be $(Na,K,Ca)_{0.25}(Al,Mg,Fe^{3+},Fe^{2+})_2$ $(Si_{4-x}Al_x)O_{10}(OH)_2 \times nH_2O$. It is not possible to determine a general equilibrium constant for real smectites because of the large range of possible compositions.

Information Available From Models

The information returned by models typically includes the input data set, the charge balance for the initial solution, the distribution of species in solution, the distribution of components in various species, minerals dissolved or precipitated, the mass of each solid phase remaining at equilibrium, the concentrations of solutes at equilibrium, and the saturation indices of all possible solids.

Available Models

Several models are available free on the Internet or for a fee from the authors. Among the more widely used are MINTEQA2 and its preprocessor, PRODEFA2; ALCHEMI; PHREEQC; and PHRQPITZ. Other available models are C SALT, EQ3/6, GEOCHEM-PC, HYDROGEOCHEM, LEACHM, REACT, SOlLCHEM, and SOLMINEQ.

MINTEQA2 (Allison et al., 1991) is a chemical equilibrium model for dilute solutions with ionic strengths up to about 0.5m. The program was originally developed by Battelle Pacific Northwest Laboratory (Felmy et al., 1984) in the mid-80s as MJNTEQ. MINTEQA2 was derived from MINTEQ. MJNTEQA2 has 6 1 inorganic and 28 organic components available to describe the chemical system. The components are used as reactants in over 900 dissolved species, over 500 solid species, 2 1 gas species, 42 surface complexation species relevant to adsorption on au amorphous iron oxide surface, and 13 species of complexes of trace elements with dissolved organic matter (Allison and Brown, 1995). MINTEQA2 includes seven options for modeling adsorption-desorption. It also has the ability to conduct “sweeps,” or titrations, in which the output data from one execution are used as input for the next execution of the program.

ALCHEMI (Schecher and Driscoll, 1995) is a specialized program that was designed to evaluate the chemistry of Al as it reacts with OK, F, H_4SiO_4, and SO_4^{2-} in natural waters. It can be used to calculate the speciation of Al in water affected by acidic deposition and thereby assess the potential toxicity of Al in the water. ALCHEMI can also be used to calculate the saturation indices of well-defined mineral phases so that the solubility of Al can be evaluated, but is limited in its array of chemical reactions in acidic, low ionic strength waters.

PHREEQC (Parkhurst, 1995) is a program distributed by the U.S. Geological Survey. This program provides for the aqueous speciation of elements, dissolution and precipitation of solid phases, reaction path modeling (in which the progress of a reaction is followed), advective-transport calculations, and so-called inverse modeling. In inverse modeling, the amounts of solids and gases that must be removed from or added to a system to account for specified differences between beginning and final

compositions of a system are calculated. PHREEQC is appropriate for solutions of low ionic strength, but the results must be interpreted with care. The thermodynamic data in the database are not internally consistent because they were taken from various sources and the author did not attempt to determine whether the data were obtained in similar aqueous solutions (Parkhurst, 1995).

PHRQPITZ (Plummer et al., 1988) incorporates the Pitzer virial-coefficient equation to adapt the model PHREEQE, the predecessor of PHREEQC, to use for high ionic strength aqueous solutions. PHRQPITZ is capable of calculating aqueous speciations, mineral saturation indices, mineral solubilities, mixing and titration of aqueous solutions, irreversible reactions, and reaction paths, but PHRQPITZ does not calculate oxidation-reduction reactions.

The capabilities of other generally available geochemical models are listed in Table 1. All can calculate aqueous speciation and dissolution and precipitation of solid phases. Beyond that, the models differ in their other capabilities. REACT (Bethke, 1996) appears to be unique in its ability to integrate simple kinetic rate laws.

Application of Thermodynamic Chemical Equilibrium Models

Chemical equilibrium models can be used to aid our understanding or predict the behavior of a chemical system. For example, Schwab (1995) used the model MINTEQA2 to help in understanding which minerals were responsible for controlling aqueous elemental concentrations in leachates from coal combustion residues. Schwab (1995) used analytical data for leachates as input to the model. In initial executions of the program, solids were not allowed to precipitate. In this mode, the speciation of components and the saturation index of each potential solid phase were calculated. In a subsequent execution of the program, solids were allowed to precipitate in order to calculate changes in solution composition upon precipitation of the solids.

The potential solids suggested by the model and the solution analytical data were plotted in activity diagrams (Figure 3) to indicate visually the degree of saturation of the solutions with respect to certain minerals.

The effects of changing parameters in a chemical system can be predicted by using chemical equilibrium modeling. For example, one might wish to know the effect on leachate chemistry when gob is amended with limestone. The user would input leachate chemistry and gob mineralogy to the model. An initial execution would be made to establish equilibrium conditions, then the desired amount of calcium carbonate would be included in the input data, either as the solid or as equivalent amounts of dissolved species. Several executions of the model could be made with varying amounts of calcium carbonate. Other parameters, such as Eh or temperature, can be changed to determine their influence on chemistry and mineralogy.

If one of the models designed for use with solutions of high ionic strength is used, the user can simulate the evaporation of water in a reaction path model. The model will indicate the precipitation of various solids as water is removed from the system.

Another important ability of some models, such as EQ3/6, is that volume changes can be calculated as changes occur in the mineralogy of a deposit. This function could be applied to calculate the potential volume change in an area used for the storage of fluidized-bed combustion **(FBC)** ash as calcium oxide is hydrated to calcium hydroxide, then as it reacts with carbon dioxide to form calcium carbonate. Other mineralogical changes can occur as the FBC ash weathers. If the overall effect is that the ash will swell on weathering, will it damage a confining structure? A user might want to know whether a material to be disposed of in an impoundment is expected to cause adverse reactions in a liner material. A chemical equilibrium model could serve this purpose. In this type of application, the user could model the reaction of leachate from the disposed material with different minerals in the liner material and check for mineralogical and volumetric changes that could weaken the liner or induce

fractures, that would allow leakage of the leachate.

Other applications might include modeling the solubility of fertilizer components, such as phosphates, under different conditions of mine soil amendment, or calculating the concentration of a particular chemical form in an isolated location.

A Note of Caution

There is a tendency to give more credence than is warranted to almost anything that comes from a computer. Chemical equilibrium models are meant to help our understanding of the chemical processes that occur in a system, not to define them. Each system will define its own chemical processes. The model serves to help us recognize and understand those processes. Models do not predict, future behavior, they merely suggest the reaction paths that are expected for a specified system. Lastly, the results of modeling must be verified by field or laboratory experiments and by observations.

Conclusions

Thermodynamic chemical equilibtium models can be very beneficial for understanding rock-water interactions and "predicting" the effects of on a reaction system of changing chemical parameters. The limitations of models must be recognized. To be accepted as valid, the results of modeling must be verified by laboratory or field observations.

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Table 1. Capabilities of some available thermodynamic chemical equilibrium models

Model name	Low ionic strength	High ionic strength	Aqueous speciation	Dissolution/precipitation	Oxidation-reduction	Surface adsorption	Ion exchange	Titration	Reaction path	Simple kinetics	Saturation index	Solute transport	Inverse modeling	Temperature correction	Gas phase
ALCHEMI	✓		✓	✓		✓					✓				
C SALT	✓	✓	✓	✓										✓	✓
EQ3/6	✓		✓	✓	✓				✓		✓			✓	✓
GEOCHEM-PC	✓		✓	✓	✓										
HYDROGEOCHEM	✓		✓	✓	✓	✓	✓					✓		✓	
MINTEQA2	✓		✓	✓	✓	✓		✓			✓			✓	✓
PHREEQC	✓		✓	✓	✓	✓	✓		✓		✓	✓	✓		✓
PHRQPITZ		✓	✓	✓				✓	✓		✓			✓	
REACT	✓		✓	✓	✓	✓		✓	✓	✓	✓			✓	✓
SOILCHEM	✓		✓	✓		✓									
SOLMINEQ		✓	✓	✓	✓	✓	✓	✓			✓			✓	✓

Figure 1. Carbonate species in aqueous solutions as a function of pH

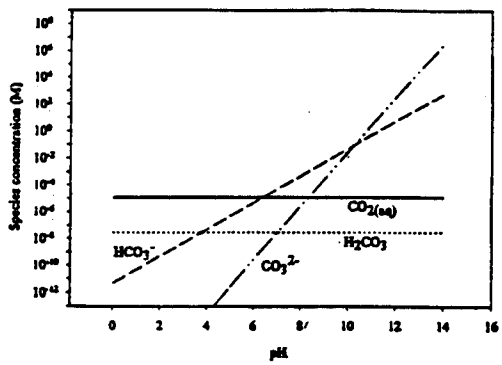


Figure 2. Comparison of emperical activity coefficient expressions with experimental data for HCL, HNO_3, $NACLO_4$, and KCL. (From Butler , 1964. Used with permission from author.)

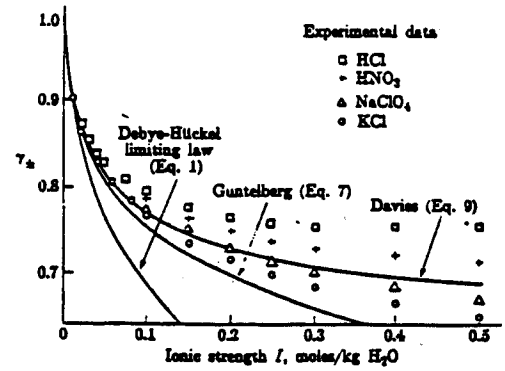
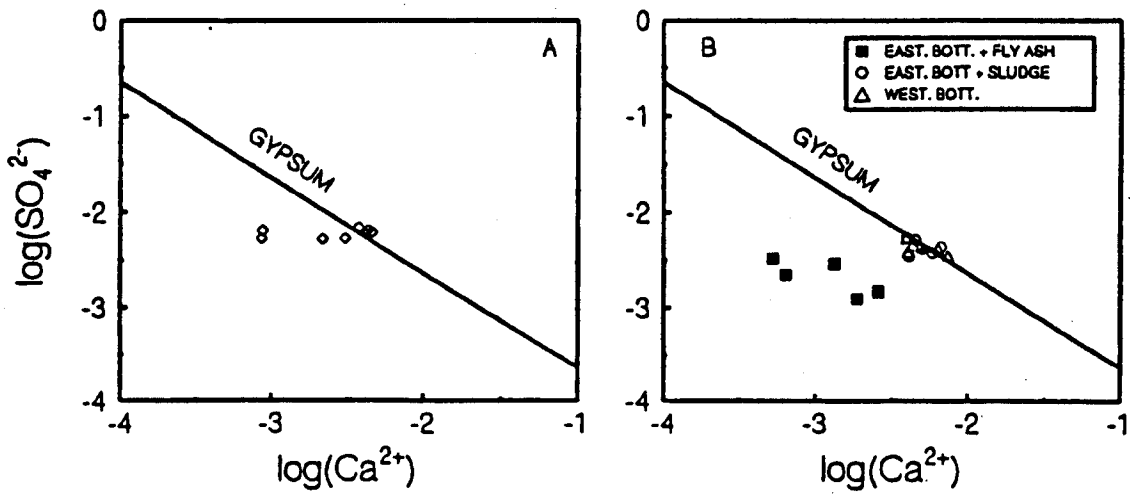


Figure 3. Activites of Ca^{2+} and SO_4^{2-} in (A) field and (B) laboratory samples. (From Schwab, 1995. Used with permission from author.)



INSTRUMENTS FOR MONITORING THE VADOSE ZONE OF SITES RECLAIMED WITH COAL COMBUSTION BY-PRODUCTS

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Abstract

Today, excess production of coal combustion by-products is either buried near the surface or pumped into slurry ponds, practices that take land suited for other purposes out of production. Mine reclamation with combustion by-products offers a significant beneficial use outlet for these materials. The by-products produce a leachate, however, and their future acceptance in reclamation requires a detailed analysis of environmental impacts. This paper describes instruments for monitoring the movement and quality of water in the vadose zone in mines reclaimed with coal combustion by-products; including the free drainage lysimeter, time domain reflectometer, tensiometer, suction lysimeter, infiltrometer, and a low-cost rain gauge. Two examples from recent research on the hydrology of areas disturbed by mining suggest that these instruments working together have greater value for monitoring vadose zone hydrology than any single instrument. The multi-instrumented site can provide significant data for evaluating the effectiveness of different reclamation strategies.

Introduction

In an effort to meet new federal emission standards, power companies rely on scrubbers or employ new coal burning technologies, both of which lead to increased production of coal combustion by-products. Although these materials have numerous applications, production will exceed demand for the foreseeable future. Today, most excess by-products produced from coal combustion are either buried near the surface in a relatively dry state (landfill) or pumped into slurry ponds (Bahor and others, 1981), both of which take land suited for other purposes out of production, at least temporarily. Reclaiming both surface and underground mines with combustion by-products in new and innovation ways may provide a real alternative to current expensive disposal practices.

Coal combustion by-products, however, may produce a leachate containing hazardous substances (see for example Le Seur Spencer and Drake, 1987; Beaver and others, 1987; Cherkauer, 1980; Fruchter and others, 1988; Hardy, 1981; Rai and others, 1989; Simsiman and others, 1987; Theis and others, 1978; Gerber, 1981; U.S. Waterways Experiment Station, 1979). Adriano and others (1980) Ferraiolo and others (1990), Theis and Marley (1979), and Theis and Gardner (1990) provided general reviews on environmental impacts associated with the disposal of coal combustion by-products. Leachate generated by these materials is distinctly different than that generated by coal, spoil, or coal processing waste.

The acceptance of reclamation with coal combustion by-products hinges on an analysis of long-term environmental impacts. Methods and the instrumentation for evaluating these impacts must withstand the rigorous requirements established by regulatory agencies. This paper describes instrumentation applied in recent research on the reclamation of surface mine and coal processing waste sites with coal combustion by-products.

Monitoring Instrumentation

Coal combustion by-products have two qualities that make them attractive materials for reclaiming areas producing acid drainage. First, they have geochemical properties that can neutralize acidic groundwater. Second, the by-products have a lower hydraulic conductivity than most spoil or coal processing waste. Therefore, not only can they improve groundwater quality, but they can retard

infiltration to acid producing materials. The monitoring well is the basic tool for conducting hydrologic tests and sampling groundwater in saturated materials. In many reclamation projects, however, the coal combustion by-products are incorporated into or layered with unsaturated materials. Because of this, research must also employ hydrologic instruments for assessing unsaturated zone (vadose zone) hydrology.

Most of this paper describes the free drainage lysimeter, a promising research instrument for determining infiltration and water quality in the vadose zone. Those instruments that can offer insight into the performance of the free drainage lysimeter, such as the tensiometer, time domain reflectometer, suction lysimeter, and rain gauge are also discussed.

Rain Gauge

Although often neglected, a detailed analysis of site hydrogeology requires an on-site measurement of precipitation. Several kinds of gauges, including the weighing and tipping types, are readily available. The commercial units, however, may not function well in open, unvegetated terrain, like that found in disturbed areas like mines. In one study (Esling and others, 1995), a commercially available weighing-type rain gauge (Belfort Instrument Company Rainfall Transmitter (Model 5915-20), with an accuracy of i0.25 cm (0.1 inch) of rain, was installed on a coal refuse pile. A comparison of rainfall amounts collected with the commercial rain gauge at the site to local records of precipitation suggest that the rain gauge significantly underestimated total precipitation. Most reclamation sites are barren, lacking trees and shrubs or other barriers to the wind. Wind striking the side of an unprotected rain gauge can create updrafts which divert precipitation from the rain gauge receiver. Wind striking the side of the weighing-type gauge rain gauge can also cause vibration which can yield erratic readings. The effects of the wind can be diminished with an artificial wind shield, but Esling and others (1995) developed a different approach, one that provides more reliable rainfall data at a lower cost than commercially available gauges.

The rain gauge (Figure 1) developed for research in reclamation sites minimizes the effects of the wind. This gauge consists of two components; a 20.3 cm (8 in) ID PVC receiver and a 3 m long 5.1 cm (2 in) ID PVC pipe (herein referred to as the reservoir). Rain enters the receiver and collects in the reservoir. The new rain gauge is installed by drilling a borehole to a depth of about 3 m. The accuracy of a rain gauge increases the closer the opening of the receiver is to the ground surface (Landsberg, 1983). This design can be installed such that the top of the receiver is at grade, if desired. Esling and others (1995) installed it approximately 15 cm above grade to prevent rain splash from entering the gauge. The rain gauge capacity is a function of reservoir length. The 3 m long gauge can hold just over 18 cm of rain. Installation of the gauge below grade prevents freezing of trapped water during winter months.

Esling and others (1995), installed a vibrating wire pressure transducer (Geokon type 4500AL) in the reservoir of the rain gauge that had a resolution of about ± 0.35 cm of water. The cross-sectional area of the receiver and the reservoir differ by a factor of 16. Therefore, one centimeter of rain translates to a change in water level within the reservoir pipe of 16 cm, suggesting that the rain gauge can resolve ±0.02 cm of rain. Other factors can affect the theoretical resolution and the range in points on Figure 1 suggest a resolution of ± 0.08 cm of rain, a value that is better than the ±0.25 cm resolution of the weighing-type rain gauge initially installed at the site (Esling and others, 1995). Figure 1 also includes a typical plot of rainfall collected by the ram gauge. Periodically, the rain gauge must be emptied and this is indicated on graphical plots by a sudden drop in water level. The design presented here costs significantly less than the commercially available weighing type rain gauge and the added cost of a wind shield is also avoided. It has served well in studies of disturbed areas for over five years.

Free Drainage Lvsimeters

A free drainage lysimeter is a device installed below the surface which traps infiltrating water. A pan buried in soil is an example of a type of free drainage lysimeter. The principle is simple; infiltrating water on its way to the groundwater system collects in the pan. Installing the pan beneath the surface, however, disturbs the original fabric of the soil altering many of its properties, including the capacity to transmit water. In addition, the natural attraction of water to the surface of particles will hold and keep infiltrating water from entering a cavity. In fact, water enters a subsurface cavity only after a saturated zone (perched system) develops and the pressures in this perched zone exceed the pressure in the cavity (the pressure in the cavity will be equivalent to atmospheric pressure if the cavity is vented to the surface). Before the pressures in the perched zone above the lysimeter cavity exceed the pressure in the cavity, water may actually flow laterally, bypassing the lysimeter.

The monolith lysimeter is a type of free drainage lysimeter designed to avoid many of the problems described above. The term monolith refers to the undisturbed block of sediment that collects infiltrating water. Monolith lysimeters have traditionally been used to measure both infiltration and evapotranspiration directly in agricultural studies. In a study of the impact of surface mining on the groundwater of small drainage basins in eastern Ohio, Helgesen and Razem (1980) assumed infiltration was equivalent to that measured with monolith lysimeters (Harrold and Dreibelbis, 1967) on similar materials. Monolith lysimeters are expensive to install and operate, a significant disadvantage.

The free drainage lysimeter described here has many of the features of a monolith lysimeter without the installation and operation costs. The lysimeter has three components, a receiving section, a drain, and a reservoir (Figure 2). The receiving section is composed of any nonporous cylindrical material with a diameter in excess of 25 cm. Previous studies have used plastic buckets or PVC pipe (10 in; 25.4 cm). A PVC cap seals the base if PVC pipe is used. An interval at the base of the receiving section (5 to 10 cm) is filled with coarse quartz silica sand. The remainder of the receiving section is filled with compacted soil (spoil or other native materials) from the study area. The sand acts as a filter between the compacted soil in the receiving section and the reservoir. The length of the receiving section is selected to contain the perched system that will develop above the interval filled with quartz sand, thereby preventing lateral flow around the lysimeter. The height of the iysimeter is a function of the particle size distribution of the soil, but a height of 30 cm should work under most conditions. Water infiltrating through the soil enters the lysimeter and saturates the compacted soil in the receiving section. Once sufficient pressure develops, water will seep into the sand, then move through the drain and into the 5.1 cm (2 in) diameter reservoir. In laboratory tests with coal refuse, this type of lysimeter collected 93% of applied artificial rainfall (Brammer and Esling, 1989). Lysimeters with smaller diameter receiving sections collected significantly less of the applied rainfall. The free drainage lysimeter samples a representative area and allows continuous passive monitoring of natural seepage through the vadose zone.

The lysimeter should monitor soil in the study area that reflects ambient conditions. In disturbed ground this means soil compacted by heavy equipment. One option is to install the lysimeters prior to reclamation in large diameter auger holes or trenches dug with a backhoe. The soil above the receiving section then reflects actual site conditions. Installation after reclamation requires a different approach. In this case, the lysimeters are installed in the sidewalls of access pits dug into the soil to the desired depth (Figure 2). The soil directly above the lysimeter receiving section will remain relatively undisturbed with this method of installation. The void space around the lysimeters is packed with soil and the access pit is backfilled. Only the standpipe for the reservoir is apparent at the surface. Care must be taken to ensure that the soil in the lysimeter receiving section contacts the soil above the lysimeter. If gaps exist, a perched system may develop possibly diverting flow away from the lysimeter receiving section. In laboratory tests, perched conditions actually prevented any water from entering the lysimeter reservoir (Brammer and Esling, 1989).

At the end of an infiltration event, a significant quantity of water will remain in the lysimeter receiving section, water held by capillary tension that would have continued to flow downward if the

lysimeter was not installed. As drier conditions return, this water may move up and out of the receiving section, a phenomenon known as wicking. The amount of water that the receiving section could absorb at any one time will depend on the initial moisture content. The total volume of water needed to create saturated conditions to drive water into the basal reservoir of a 25.4 cm diameter lysimeter ranged from 1583 to 2350 ml, equivalent to 3.1 to 4.6 cm of infiltration (Esling and others, 1995). Wicking of this water out of the receiving section would lead to a substantial difference between actual infiltration and that measured by the lysimeter.

Esling and others (1995), however, showed that the wicking error does not occur with each infiltration event. They installed gypsum blocks (7/8 in (2.2 cm) diameter Soil Moisture Equipment Corporation Model 5201) within the receiving section of the lysimeters to monitor wicking in the field. In an environment producing acid drainage, gypsum blocks have only a short life span. The blocks indicated relatively consistent moisture contents before they failed, however, suggesting that the coal refuse in the receiving section remained saturated or near saturated for extended periods of time. These stable moist conditions suggest that wicking may not be a large source of error during the late fall and winter, when recharge is more common.

Esling and others (1995) equipped the reservoir with a vibrating wire transducer for monitoring water level continuously. The transducer has an accuracy of ± 0.35 cm of water. The cross-sectional 10.8 of the lysimeter receiving section and the standpipe differ by a factor of 25. Therefore, one centimeter of infiltration translates to a change in water level within the reservoir pipe of 25 cm, suggesting that the lysimeters can resolve ±0.014 cm of infiltration. Other factors can affect the theoretical resolution and a typical plot of data (Figure 2) suggest a resolution off 0.06 cm of infiltration, which is excellent.

In some cases, lysimeters have collected anomalous high levels of infiltration, values in excess of rainfall (Esling and others, 1995). One possible explanation is that the backfill to the installation pit was not compacted properly and a perched water system developed in the disturbed ground. Saturated conditions in the pit till could discharge water into the lysimeter. Esling and others (1995) discussed this possibility and noted that with time the fill compacted to a density comparable to that of the undisturbed coal refuse, yet infiltration in excess of rainfall continued for shallow lysimeters. They suggested that subsurface saturated flow as a perched system at some level above the top of the lysimeter delivered water to the receiving section. This observation, although unexpected, is still valuable information on site hydrology.

It is important to clarify one very important point about the lysimeters described above. They are inexpensive, with costs of materials and installation comparable to that of a shallow groundwater monitoring well. To function, the lysimeter standpipe does not need to be equipped with a pressure transducer connected to a data logger. Field personnel can retrieve data from the lysimeter in the same way and at the same time that data are retrieved from groundwater monitoring wells. Vibrating wire pressure transducers are only necessary in order to monitor infiltration remotely over short intervals. Only one additional piece of field equipment is required, some type of pump to drain the lysimeter stand pipe.

Free drainage lysimeters can also provide samples of water that has moved through the vadose zone. The small volumes often collected, however, can make analysis difficult. In addition, the quality of the trapped water may change now that it is in contact with plastic and the atmosphere and no longer in contact with soil particles. Therefore, samples must be retrieved soon after accumulating in the reservoir.

In spite of their deficiencies, free drainage lysimeters are the only instruments that passively trap natural infiltration under ambient moisture conditions. Other vadose zone instruments, described below, can provide data on the performance of the free drainage lysimeters; data that can verify lysimeter results or warn of particular problems.

Ring Infiltrometer

Infiltrometers artificially induce infiltration. Therefore, they cannot measure natural infiltration as a result of precipitation. They can, however, test the performance of a free drainage lysimeter. ASTM (1991) procedures recommend driving the ring of au infiltrometer into the ground to a depth of several centimeters. With this method of installation, however, water in the infiltrometer can flow through macropores and erode non-cohesive disturbed soil along the intiltrometer edge, a problem common to coal refuse sites and spoil in surface mines. A better method of installation is to set the infiltrometer 18 cm deep into an 8 cm wide and 20 cm deep trench filled with a cement/bentonite slurry, and then left to set for several days.

In intiltrometer tests, water is regularly added so that the refuse bounded by the infiltrometer walls remain below water level. A plastic tarp covers the ring to minimize evaporation losses and to prevent precipitation influx. A small hole in the tarp allows pressures inside the infiltrometer to adjust as the atmospheric pressure changes. A pau of water under the tarp can monitor evaporation. In testing free drainage lysimeters, the infiltrometer should lie directly above the receiving section of the lysimeter. The lysimeter standpipe must remain outside of the infiltrometer, however, because the interface between the pipe and soil may act as a preferred pathway for water that could by-pass the lysimeter.

Time Domain RefIectometry

Esling and others (1995) reviewed time domain reflectometry theory, summarized here. Since the early 1940's, scientists have recognized that there is a relationship between the dielectric properties of soil, rock and other materials and their moisture content. In essence, the propagation of an electromagnetic wave is a function of the dielectric constant. Time domain reflectometry, a technique that evolved primarily from radar research in World War II, is a way of defming the dielectric relationships by measuring the transit time of electromagnetic waves along a probe placed in the soil. The theory behind the determination of the constant has been discussed by several authors (Ledieu and others, 1986; Smith and Tice, 1988a, 1988b). Topp and others (1980, 1982) and Topp and Davis (1982, 1985) described early applications of the technique.

The complex dielectric is a function of the different materials through which the electromagnetic wave passes. The velocity (V) of the waves in soil is related to the velocity in free space by the relationship:

$$V = C/\tilde{A}K \qquad (1)$$

where:

K = permittivity
C = velocity of light

For soil, consisting of three components; air (K = l), soil grains (K = 3 to 5) and water (K = 81), the wave velocity is a function of the relative proportions of each. Since the dielectric constant of water is so much larger than either soil or air, the existence of water in the soil column is easily detectable (Ledieu and others, 1986). It should be noted that temperature corrections do need to be applied since the dielectric constant of water is temperature dependent. Ledieu and others (1986) discussed this correction.

The source generates a high-frequency electromagnetic pulse which travels down a parallel set of wave guides which are inserted into the soil (the Trase System from Soil Moisture Corporation is one system available). The reflectometer measures the time it takes the wave to travel down the guides, reflect off the open ends of the guides and return along the original path. This travel time is then used to directly calculate the dielectric constant of the soil and subsequently the volumetric water content of the soil, since the water content is the primary control on the velocity of the wave propagation.

The wave guides (Soil Moisture Equipment type) have three parallel steel probes with lengths of 30 cm. Ledieu and others (1986) and De Clerck (1985) demonstrated that the electromagnetic energy is confined to a cylinder around the rods with a diameter equal to approximately twice the distance between the outer rods. For the 30 cm probes, the distance between the outer probes is 5 cm. Hence each probe can monitor the moisture content in a horizontal cylinder 10 cm in diameter and 30 cm long.

The measurement of volumetric soil moisture by time domain reflectometry is apparently not affected by relatively large variations in soil texture (Topp et al, 1980). This makes the method particularly applicable for measurements in heterogeneous coal refuse. If measurements of moisture content are taken at regular time intervals and at a series of depths, the change in moisture content can be converted into an infiltration rate.

Time domain reflectometry does suffer from one drawback; high total dissolved solids in the water flowing through the soil can attenuate the pulse, providing suspect readings or no readings at all. Obviously, sites producing acid drainage suffer from this problem. Work in one reclamation project, however, indicates that signal loss only occurs during a first flush (Esling and others, 1995). As infiltration continues, the level of total dissolved solids declines and the reflectometer again records successful readings.

Tensiometers

Hydraulic head has two components; elevation head and pressure head. Under saturated conditions, the pressure head exceeds atmospheric pressure. This is why water will flow into a void space in saturated materials. In the vadose zone, however, the pressure head is less than atmospheric. If atmospheric pressure is the datum, the pressure head under saturated conditions is positive, whereas in the vadose zone the pressure head is negative. This negative pressure, also known as tension, suction, or matric potential, actually develops because water is attracted to the surface of the soil grains.

The tensiometer can measure pressure head in the vadose zone. This instrument is composed of some length of plastic pipe (about 2.2 cm or 0.85 in diameter for the Soil Moisture Equipment type), attached to a porous ceramic cup. A vacuum gage is attached to the side of the tensiometer through an inverted "Y" connection molded into the sidewall of tensiometer. The tensiometer is filled with colored water to prevent algae growth and for easy detection of trapped air, then the tensiometer is sealed at the top. Water will seep through the ceramic tip, creating a vacuum in the tensiometer, until the tensiometer and soil in contact with the ceramic tip share the same pressure head. Water will flow into the tensiometer under moist soil conditions, when pressure head outside the ceramic tip exceeds that in the tensiometer.

The ceramic tip of the tensiometer must completely contact the soil in order to function properly. In spoil or coal refuse, large clasts are often dispersed in a fine matrix. The rock clast may keep the ceramic tip from completely contacting the fine-grained matrix. In these conditions, a hole is augured to the desired depth. The augured soil is screened to remove coarse clasts, then mixed with water to form a slurry which is then placed in the base of the hole. The tensiometer is pushed into the slurry so that the ceramic tip is completely covered. The remaining annular space is sealed to prevent leakage from the surface from reaching the base of the tensiometer. Well tamped soil may be sufficient, but an added seal well above the ceramic tip composed of bentonite slurry can further minimize leakage. Several hours may pass before the tensiometer and soil equilibrate.

Nested tensiometers, providing head data an different depths, can indicate the direction of water movement through the vadose zone. They can thus monitor wicking above a lysimeter. Limits on the tensile strength of soil water and physical limitations of the tensiometer, yields a lower operating limit of about 85 centibars. Therefore, under very dry conditions, tensiometers cease to function.

Suction Lvsimeters

A free drainage lysimeter passively collects water seeping though the vadose zone. In contrast, under a vacuum, the suction lysimeter actively extracts vadose zone water samples. The device has a simple design; composed of a porous ceramic tip connected to some length of 4.8 cm (1.9 in OD) plastic pipe (up to 1.8 m long for the Soil Moisture Equipment type). Only a short length of the suction lysimeter (5 cm), is evident at the surface. A stopper assembly, which includes a hose and valve, seals the top of the lysimeter. A vacuum, on the order of 50 to 85 centibars, is established by removing air with a hand pump though the hose. Water flows through the vadose zone, through the ceramic tip, to collect in the lysimeter. In soils having low permeability such as spoil or coal processing waste, sufficient sample may take days to accumulate. The sample collected is removed through a simple apparatus with a pump.

The suction lysimeter is installed in a hole augured to a diameter of 5 to 10 cm. Larger diameter holes are necessary in coarse refuse. Like the tensiometer, the key is to establish a complete contact between the soil and the ceramic tip of the suction lysimeter. As with tensiometer installation, the material removed from the auger hole is screened to remove large clasts, then mixed with water to produce a slurry Sufficient slurry is first placed in the base of the hole to cover the ceramic tip. The suction lysimeter is pushed into the slurry Finally, the annular space between the lysimeter walls and hole are sealed to prevent surface water from seeping along the casing to the base of the lysimeter. Again, a bentonite slurry plug well above the ceramic tip can minimize leakage.

Samples collected with the both free drainage and suction lysimeters can provide a better understanding of vadose zone water chemistry. Both instruments suffer from the same drawback; water often remains in the free drainage lysimeter reservoir or suction lysimeter casing for days, where its quality may change.

Applications

This section presents two examples of multi-instrumented studies of vadose zone hydrology in areas disturbed by mining. In the first case, a single, rare, precipitation event (herein called the event) over a two day period totaling 19.37 cm, with three separate precipitation episodes of 1.97, 1.35, and 16.05 cm, impacted the study area (Esling and others, 1995). Figure 3 presents data from time domain reflectometty, an infiltrometer, one of the lysimeters, and a rain gauge at the site. Note that prior to the event, the lysimeters and rain gauge provided stable readings.

Over the duration of the event, lysimeters LIB, L2A, and L2B captured about 4.4, 2.0, and 2.6 cm of infiltration, respectively. The two shallow lysimeters, L2A and L2B, with receiving sections at depths of only 20 cm, captured a small amount of infiltration from the first two precipitation episodes (Figure 3). These lysimeters responded immediately after the onset of the third and largest precipitation episode, collecting infiltration at a constant maximum rate until precipitation ended. They continued to trap infiltration for a period of about four days after the precipitation ceased, but at a much lower rate. The maximum rate of infiltration was unique to each lysimeter with rates of 2.6, 4.8, and 5.2 cm/day for L2A, L2B, and LlB, respectively.

The infiltrometer test was conducted before and during the hydrologic event. Although the rate of infiltration as measured by the infiltrometer changed as a consequence of the event, the lack of continuous data collection precluded a detailed analysis. The moisture content beneath the infiltrometer as determined by time domain reflectometry, however, showed interesting temporal trends. At 0.6 m below the ring, just after the onset of the last precipitation episode, the moisture content suddenly jumped from 29.7% to 45.4%. This elevated moisture content was sustained until just after precipitation ended, at which time the moisture content dropped to 33.5%. Prior to the hydrologic event, moisture content

beneath the infiltrometer increased gradually and after precipitation ended, the moisture content appeared to follow a trend similar to the one that existed before the event.

The infiltrometer provided a continuous source of water for seven days prior to the hydrologic event, yet moisture content increased gradually and appeared to be leveling off just prior to the onset of the last precipitation episode. What could lead to elevated moisture contents at a depth of 0.6 m if a continuous source of ponded water could not? Lateral water movement under saturated conditions from farther upslope is the most likely explanation, although other interpretations are possible. Hillel (1980) described a unique phenomenon occurring at sites with alternating coarse and fine-grained layers. Water would not move into certain portions of the unsaturated zone until pore pressure greatly increased, as may occur with a large infiltration event. Coal refuse texture was noted while excavating the pit for the installation of the time domain reflectometry probes. The probe at 0.6 m was installed within matrix-dominated refuse about 7.5 cm above a clast supported gravel and 20.3 cm below a coarse-grained matrix-supported layer. Increased infiltration during the rainfall period indicates that increased moisture content outside the ring facilitated greater water movement through the refuse beneath the ring. Natural infiltration rates are often inferred from infihrometer tests, but the results of this study suggest that infiltrometers do not simulate natural infiltration through heterogeneous material such as coal refuse.

The shallow time domain reflectometry probe, installed at a depth of about 0.3 m, showed a somewhat different response to the fmal precipitation episode. During the first seven days of the ring infiltrometer test, as the moisture content rose, the occurrence of failed readings from time domain reflectometry increased. The high acidity associated with the coal refuse leads to high ion concentrations, a condition that may cause a dissipation of energy from time domain reflectometry. During the fmal high intensity precipitation episode, the shallow probe again yielded successful readings, possibly because flushing by fresh rainwater decreased the ion concentration.

In the second example, Esling and others (1995) conducted an 1.8 m diameter infiltrometer test over two lysimeter receiving sections, both at depths of 0.6 m. A one meter deep access pit was excavated adjacent to the infiltrometer, outside of the cement/bentonite seal. They installed two 30 cm long wave guides horizontally in the side walls of the access pit beneath relatively undisturbed refuse, at two different horizons between the infiltrometer and the lysimeters. The wires to the wave guides were routed through a 5.1 cm (2 in) ID PVC pipe to the surface. This pipe was sealed with a cement/bentonite mixture to prevent infiltration through the loose fill of the access pit from reaching the wave guides. The pit was carefully refilled back to grade. A small channel around the pit and a plastic cover prevented runoff or precipitation from eroding the disturbed loose backfill.

Figure 4 summarizes time domain reflectometry, lysimeter, and infiltrometer data collected over a seven hour test (Esling and others, 1995). No natural precipitation fell during this time. All data were collected manually. Early in this project, lysimeter LlA provided data distinctly diierent than the other lysimeters, generally collecting little or no infiltration during events when the others captured significant infiltration. During the infiltrometer test, however, lysimeter LlA collected water at a rate higher than that provided by the infiltrometer. LlA collected 16.1 cm of infiltration during the first four hours of the test, whereas LIB collected only 2.6 cm and the infiltrometer delivered less than 8 cm for the same time period. What could cause such contradictory data? Leakage along the casing of the lysimeter standpipe can be discounted; the infiltrometer was not installed over the standpipes. A macropore connecting the surface to the receiving section of **Ll A** could have transferred a quantity of water greater than that yielded through intergranular flow to LIB. The behavior of the lysimeters offers important insight into the hydrology of this particular site; information that a single instrument could not have provided.

The response of LIB to the infiltrometer test suggests that the lysimeters can be effective tools for monitoring infiltration. Early in the infihrometer test, water seeping into the refuse increases the moisture content to field saturation. Only then can water flow into lysimeter LIB, which began capturing infiltration about 2 hours into the test. The rate of infiltration into LlB and that of the infiltrometer, just under 3 hours into the test were approximately the same. Time domain reflectometry, as a tool for

monitoring moisture content in coal refuse piles has some deficiencies. The lower probe failed to return readings on moisture content because of time measurement errors, apparently because of high total dissolved solids content in the infiltrating water. The upper wave guides (Figure 4) showed the gradual increase in moisture content as a consequence of the intiltrometer test.

Conclusions

This paper describes instruments for monitoring the vadose zone in studies on the environmental impact of different reclamation methods. Even with its deficiencies, the free drainage lysimeter shows promise as a tool for monitoring natural infiltration under ambient moisture conditions through reclaimed areas. Data collected by other vadose zone instrumentation, such as time domain reflectometry, tensiometers, or suction lysimeters, can verify lysimeter results or warn of particular problems.

The instruments discussed here represent only part of the instrumentation necessary to conduct detailed study on the impact of a particular reclamation method. Other instruments for monitoring the vadose zone may also have application in reclamation research. In addition, research should also monitor groundwater conditions in the saturated zone. Readers should consult procedures for the proper installation and sampling of groundwater monitoring wells to guarantee reliable data. In particular, a sampling plan appropriate for new statistical procedures designed to confirm a detection of some contaminant downgradient, is essential.

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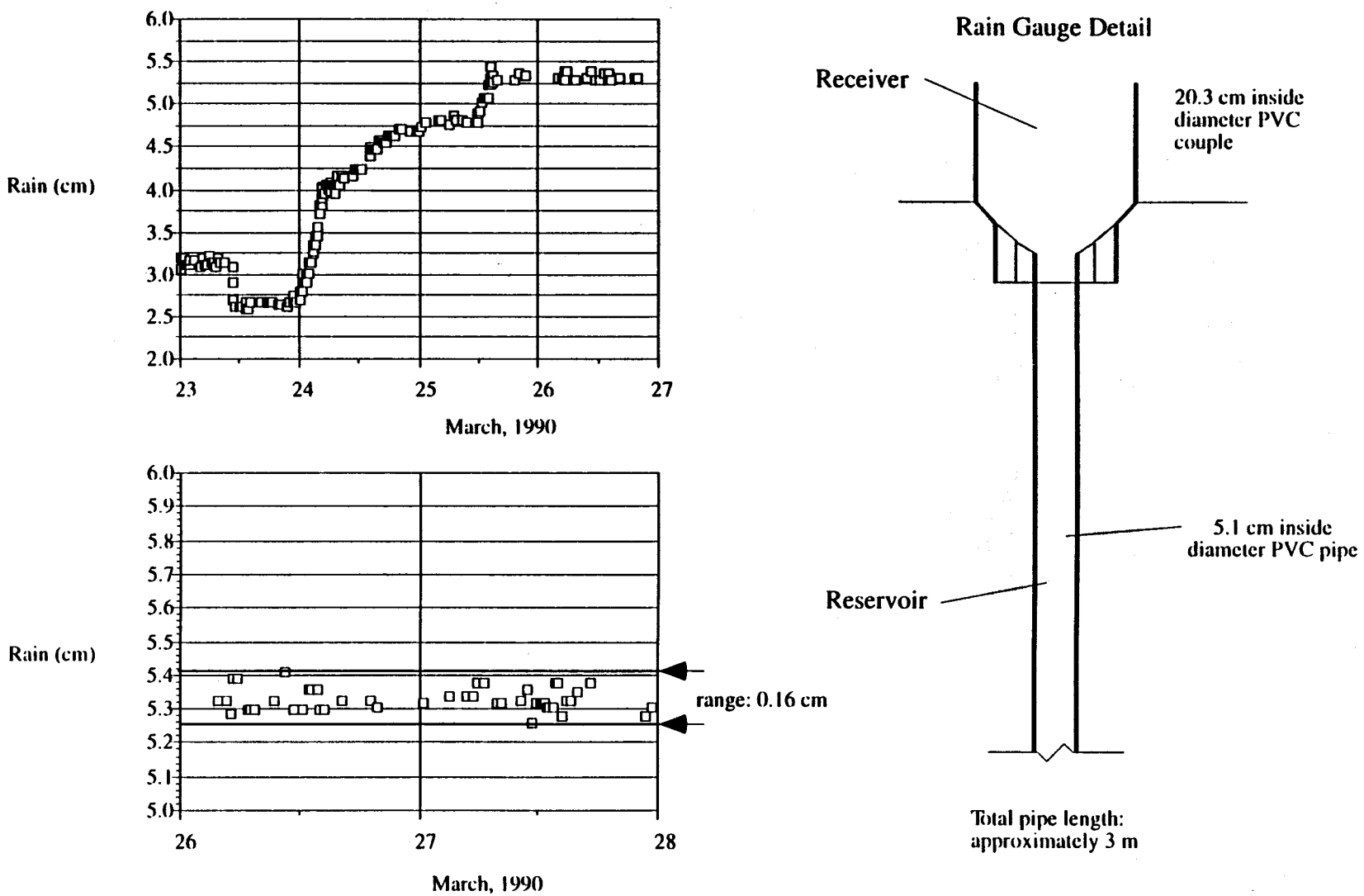
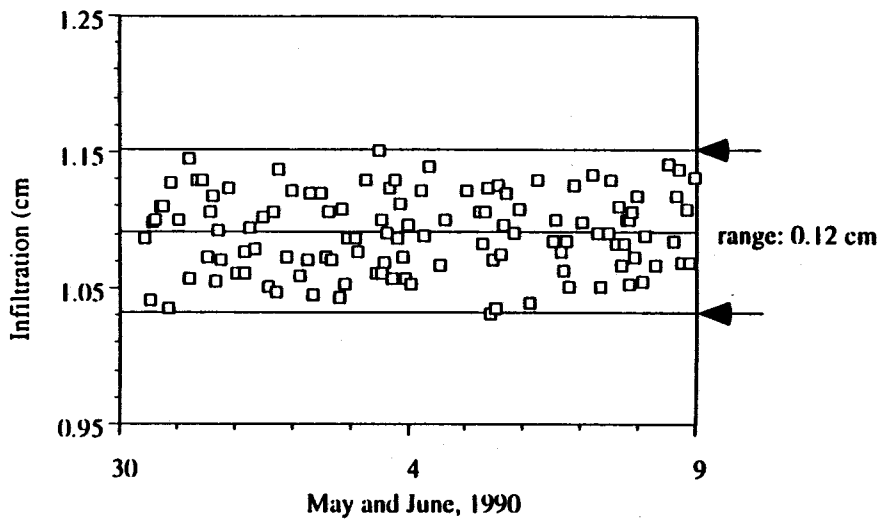


Figure 1. Schematic diagram of the rain gauge. The range in values suggest a practical resolution for the rain gauge of approximately ±0.08 cm. The figure also shows a typical graph of rainfall data through time. A drop in water level in the rain gauge indicates a time when it was emptied. (Data from Esling and others, 1995)



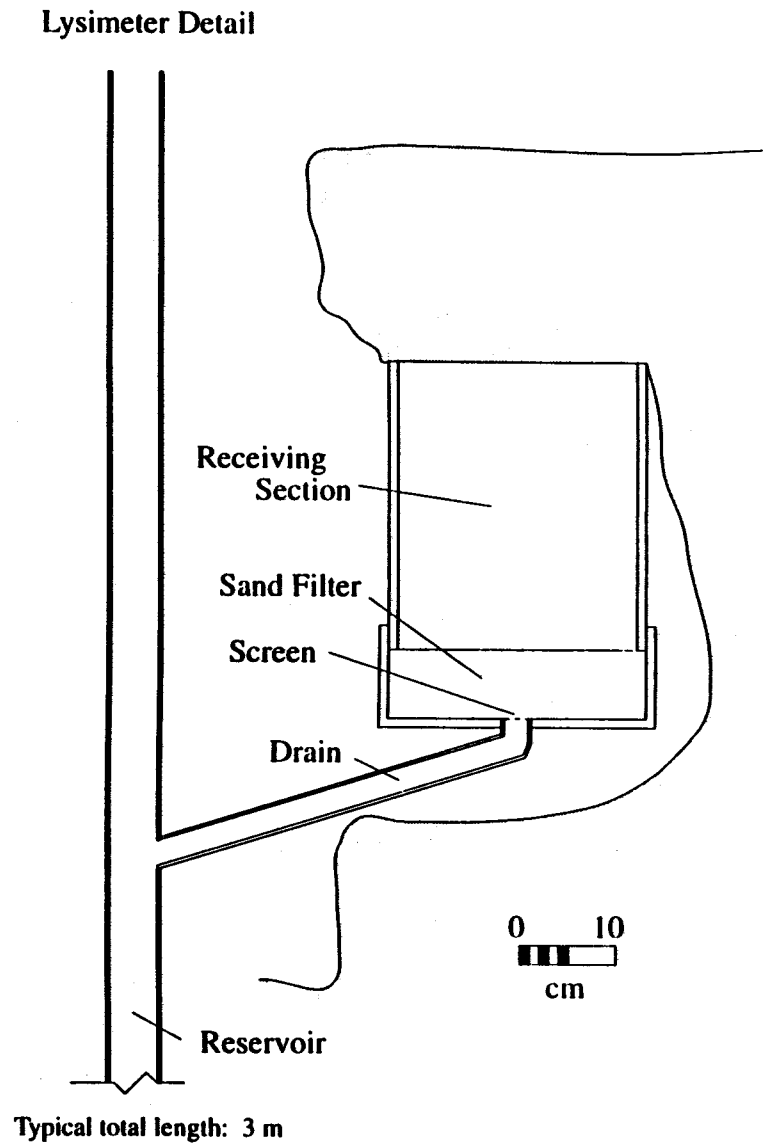


Figure 2. Lysimeter detail and data plot. The range in values (Esling and others, 1995) suggest a practical precision for the lysimeter of approximately ±0.06 cm.

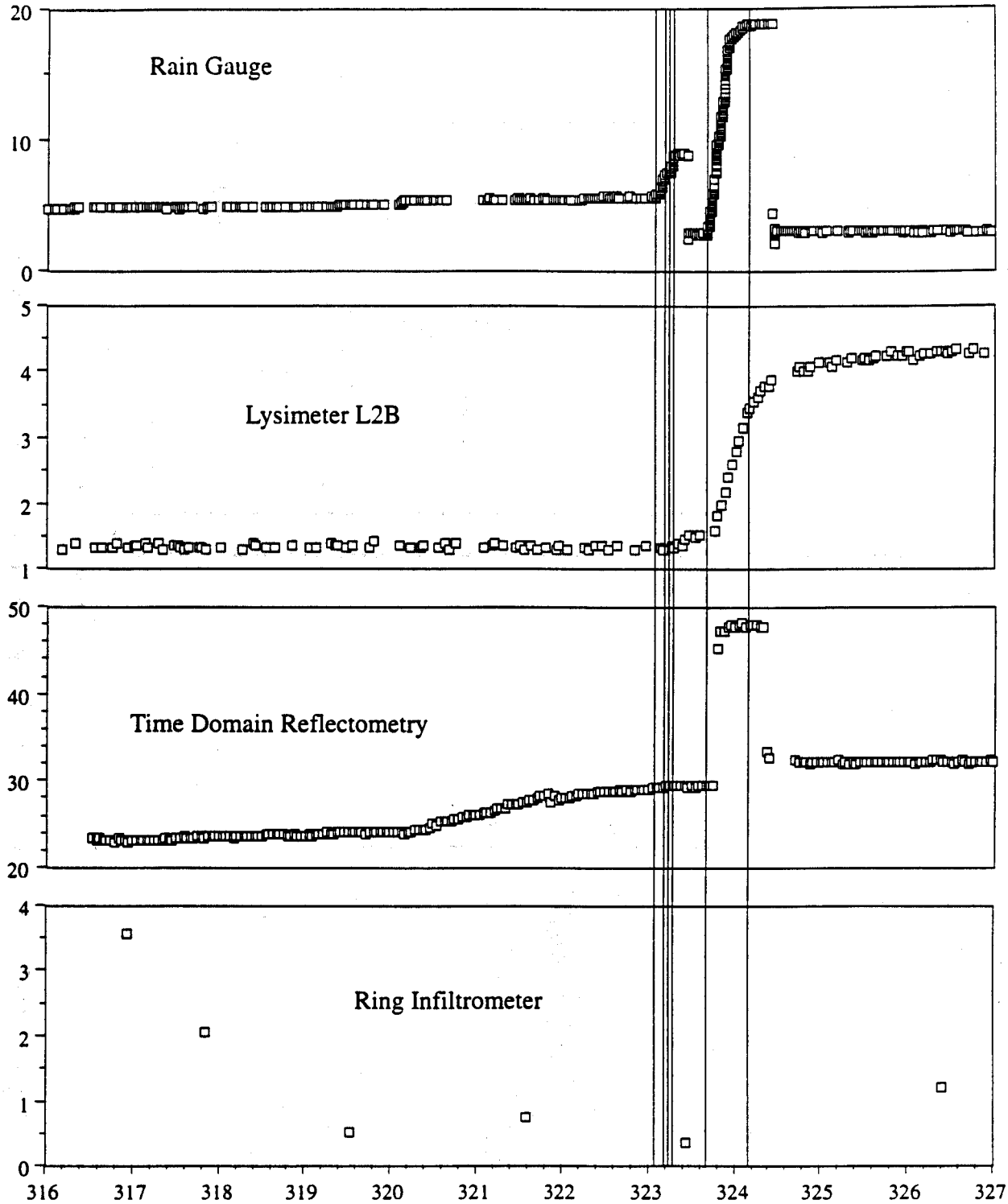


Figure 3. Hydrologic data collected from the vadose zone during a single precipitaiton event. Horizontal axis is in days. Vertical axis for the infiltrometer is in milliliters per day. Vertical axis for the rain gauge and lysimeter is in volume of water per unit area (centimeters). Vertical axis for the TDR data is in percent by volume moisture content. (Data from Esling and others, 1995).

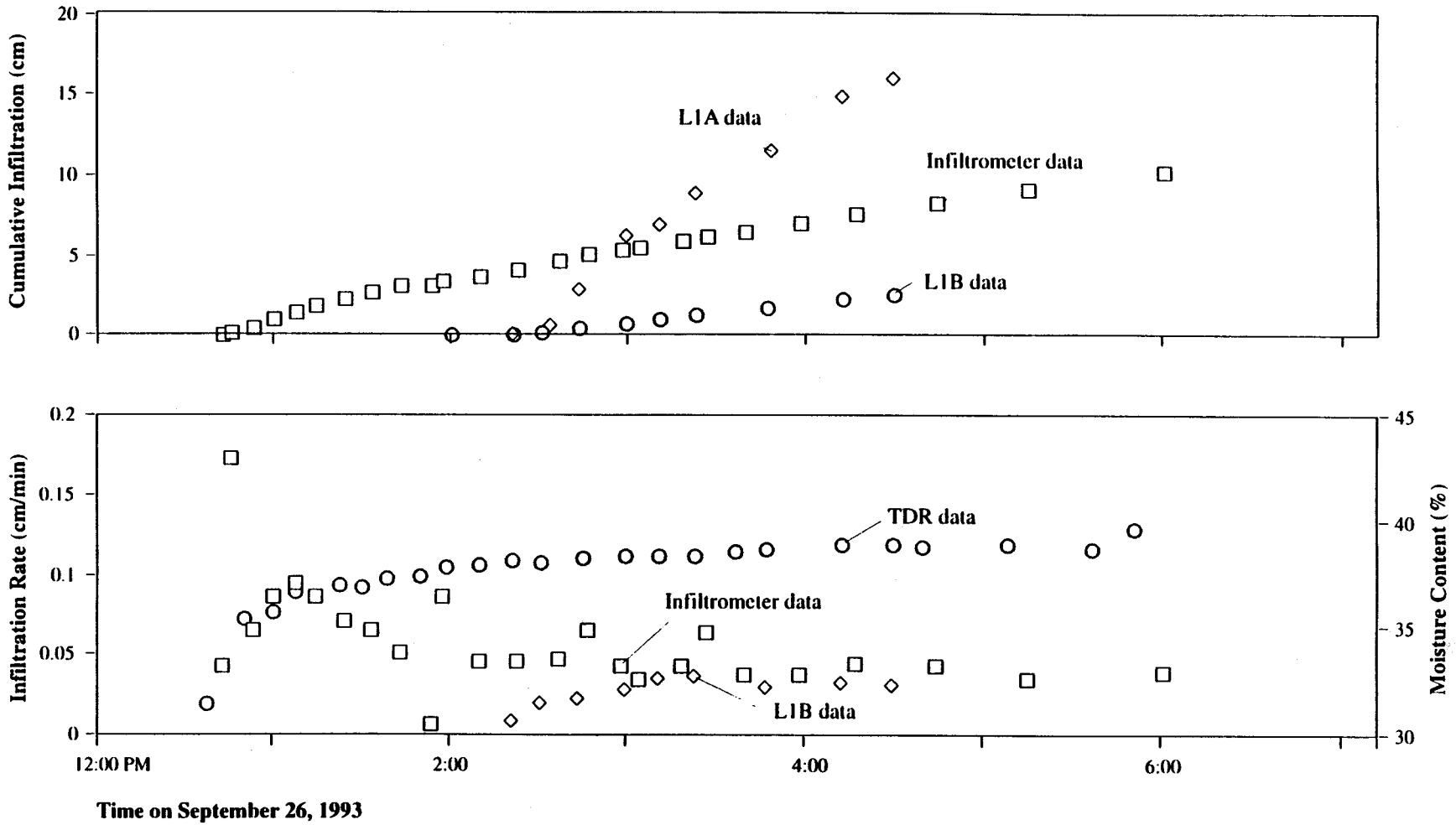


Figure 4. Plots of cumulative infiltration, infiltration rate, and moisture content for the first seven hours of an infiltrometer test (Data from Esling and others, 1995).