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**Physical model for transport of a contaminant through porous
media**

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PHYSICAL MODEL FOR TRANSPORT
OF A CONTAMINANT THROUGH
POROUS MEDIA

by

Gordon Leroy Haws

A Thesis Submitted to the Faculty of the
DEPARTMENT OF CIVIL ENGINEERING AND ENGINEERING MECHANICS
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
WITH A MAJOR IN CIVIL ENGINEERING
In the Graduate College
THE UNIVERSITY OF ARIZONA

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This thesis has been approved on the date shown below:

Desai
Dr. C.S. Desai
Regents Professor and Head

12/10/50
Date

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ABSTRACT

This thesis presents the results of two-dimensional, transient flow/chemical transport experiments. The porous medium consisted of glass beads mixed with resin pellets. The simulated chemical contaminant is a fluorescent dye, Rhodamine WT, which is adsorbed by the resin pellets. The concentration of the dye in solution is measured using a fluorometer. By varying the resin/glass beads weight ratio, porous media of various adsorptive capacities were created. Adsorption is the primary property that was studied.

The reported results of these experiments include the densities and permeabilities of the porous media, the location of the two-dimensional phreatic surface, the downstream flow-rate and the output concentration under transient conditions. These results are significant and contribute to the understanding of chemical transport and adsorption effects, and provide a methodology for laboratory simulation of pollutant transport in granular porous media.

PHYSICAL MODEL FOR TRANSPORT
OF A CONTAMINANT THROUGH
POROUS MEDIA

1.0 INTRODUCTION

The intent of this research is to model a chemical transport process using a fluorescent dye as the simulated chemical contaminant and glass beads as the porous medium. Ion exchange resin pellets capable of adsorbing the dye were mixed with the glass beads to simulate the adsorption properties of soil. The porous medium was placed in an arrangement to simulate two-dimensional flow through a dam or dike wall into a nearby "river", Figure 1. The input or inflow dye concentration (C_i) was held constant. The outflow dye concentration (C_o) was measured under transient conditions and compared to the input value.

No attempt was made to exactly model what happens in the real world. Rather, the model itself is a valid physical simulation of chemical transport. Measurements were made of 1) the location of the phreatic surface as a function of time with a variable head on the upstream face; 2) the variation of the downstream dye concentration as a function of time due to adsorption on the glass beads and the resin pellets; 3) the variation of the downstream flowrate with time, and; 4) other parameters such as permeability and dry density of the porous

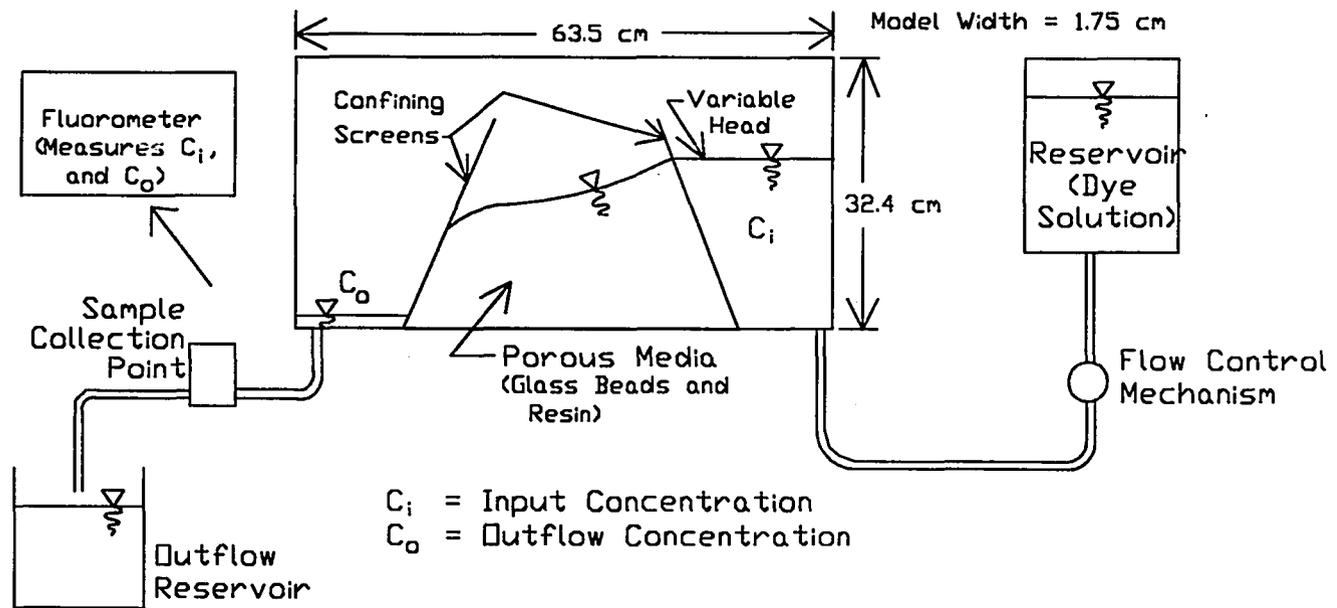


Figure 1- Experimental Setup

media which must be known to adequately model this arrangement using numerical solution procedures.

The primary objective of this research is to develop a laboratory methodology for simulation of pollutant transport in granular porous medium. In performing these experiments, much was learned about the glass beads, the resin pellets, the dye, the model and their interactions. Comments regarding improvements that can be made to the existing model and the most efficient operation of the model are presented herein.

Measurements and observations made during this research can also be used to: 1) calibrate new computer and numerical models or test how well they can predict the results observed in these experiments, and; 2) to reveal certain basic properties of chemical transport.

2.0 PREVIOUS STUDIES

A number of physical models--two-dimensional or three-dimensional and steady-state or transient--have been developed to study flow and flow patterns. Some of these models are parallel plate, viscous flow models for two-dimensional flow (e.g.- Desai, 1970; Desai & Sherman, 1971; Desai, 1972; Desai, 1973 and Homma, 1983). Many others use sand or a simulated porous medium for two and some three-dimensional experiments. Two-dimensional physical flow models are reported in works by Desai & Kuppusamy (1980), Desai & Li (1983), Desai, Lightner & Somasundaram (1983) and many others. Results of three-dimensional experiments are reported by Desai, Lightner & Somasundaram (1983) and Baseghi & Desai (1990).

Baseghi and Desai (1990) performed three-dimensional, flow experiments using glass beads as the porous medium to verify the Residual Flow Procedure (RFP) they had developed. (See also Baseghi, 1987 and Desai & Baseghi, 1988.) The permeating fluid was glycerin mixed with 20% water to minimize capillary effects. Their work presents observations of the free surface during rise, steady-state and drawdown in homogeneous and nonhomogeneous, simulated, 3-D dam cross-sections. Experimental observations are compared with the results of numerical calculations and showed good agreement.

Contrary to what is true of flow models, most of the physical models which have been developed to simulate chemical transport have been one-dimensional. A typical example is the work done by Nielsen and Biggar (1962). They present breakthrough curves from one-dimensional, miscible displacement experiments using the chloride ion and tritium as tracers. The porous media they used were glass beads, sieved aggregates and natural soils.

The same two experimenters (Biggar and Nielsen, 1964) studied the dependence of the diffusion coefficient upon the solution's concentration using glass beads as the porous medium, salt (NaCl) solutions of various concentrations as the permeating fluids and a radioisotope of salt (chloride-36) as a tracer.

Wierenga and Van Genuchten (1989) performed one-dimensional, unsaturated solute transport experiments in columns packed with a sandy soil using chloride and tritium as tracers. They examined the effectiveness of a four-parameter transport model which assumes a portion of the water to be immobile in predicting the experimentally-observed results and found that its predictive capabilities were superior to models that do not make such an assumption.

Herr, Schafer and Spitz (1989) performed one-dimensional, chemical transport experiments in sand, studying the effects of local heterogeneities in the form of ceramic cubes with

permeabilities that were different from the surrounding sand upon transport behavior. The chemical contaminant was salt.

Perhaps the most relevant one-dimensional, solute transport experiments were done by Everts, et al (1989). They studied the transport of Rhodamine WT dye and three ionic tracers through a soil column. The delay of Rhodamine WT in the breakthrough curve due to adsorption on soil particles was observed. Field experiments involving a tile drain in a cropped field were also performed.

Adsorption resins were used in one-dimensional column experiments done by Yunker, et al (1989). The resins they used were not the same resin used in these experiments. The chemical contaminants were general hydrocarbons, not fluorescent dyes. The experiments, intended for application in the water treatment field, focus solely on the efficiency of the resins in removing the hydrocarbons and not on more general transport phenomena.

Many other one-dimensional chemical transport experiments are reported in the literature, but very few two-dimensional physical models simulating chemical transport have been developed.

Stauffer and Dracos (1986) performed two-dimensional chemical transport and flow experiments using salt as the tracer. Flow was two-dimensional infiltration into layered sands, and the experiments were restricted to the vertical

plane. The experiments examined such phenomena as advection, hysteresis, instability of the wetting front, effects of sand layering, etc.

The author with others performed similar infiltration experiments (Haws, El-Shinnawy and Tang, 1990), studying longitudinal and lateral dispersivities of the chloride ion in a homogeneous sand with flow restricted to the vertical plane. The experiments were unsaturated and steady-state with respect to flow. The chloride ion was introduced as a pulse input.

Other infiltration experiments were performed by Glass, Oosting and Steenhuis (1989). Flow was two-dimensional in the vertical plane. A blue dye was used to study dispersion effects.

The present experiments are unique in that few two-dimensional physical models of both flow and chemical transport have been developed and none have used Rhodamine WT dye as the tracer with resin pellets as an adsorbing substance mixed into the porous medium. Few studies allow the researcher to vary the adsorption capacity of the porous medium as this model does, and in that way to nearly isolate the adsorption effect for close scrutiny.

The present experiments also differ from the other two-dimensional chemical transport experiments that were cited above because the other experiments were infiltration experiments with vertical flow. The present experiments involve horizontal and vertical flow in a simulated dam with a free surface.

3.0 EXPERIMENTAL SETUP AND PROCEDURE

Figure 1 (presented in Chapter 1) shows the experimental setup. The simulated dam with its associated reservoirs was developed and used by earlier researchers, Desai & Kuppusamy (1980), Desai & Li (1983) and Desai, Lightner & Somasundaram (1983), for two-dimensional transient flow experiments. The experimental setup consists of reservoirs, head/flow control mechanisms, the porous medium in the simulated dam, the outflow structure, the sample collection point and the fluorometer.

The experimental procedure that was followed is presented next. The glass beads and the resin pellets were mixed in the desired weight ratio. The glass beads/resin mixture was then poured into the model in three centimeter layers and each layer was compacted to a uniform density by raising the model approximately five centimeters off of its base and letting it fall. The falling action was repeated seven times for each layer.

The input dye solution was prepared and its initial temperature, and fluorometer reading recorded. The fluorometer reading is related to the dye solution's concentration by an empirically-derived relationship which will be presented in the next chapter. The dye solution was

poured into the upstream reservoir to be used as the inflow fluid source. The input solution's concentration (C_i) was held constant throughout the experiment. With the upstream reservoir full, the experiment officially began.

The head on the upstream face was varied during the experiments. Figure 2 shows the general manner in which the head was varied. Observations of the upstream head, the shape and position of the phreatic surface, the downstream dye concentration (C_o), and the downstream flowrate were recorded as the experiment proceeded.

The position of the phreatic surface was visually observed and marked directly on a transparent sheet taped to the front of the model. The actual phreatic surface may have been somewhat obscured by the capillary fringe of the porous medium in some instances.

The downstream concentration (C_o) was measured by collecting samples at discrete times and inserting them into the fluorometer. The fluorometer reading is related to the solution's concentration through the use of a calibration curve that will be presented in the next chapter.

The downstream flowrate was measured using a graduated cylinder and a stopwatch. The results of the experiments are presented subsequently.

After each experiment, the model was emptied of the porous medium and rinsed to prevent permanent contamination of

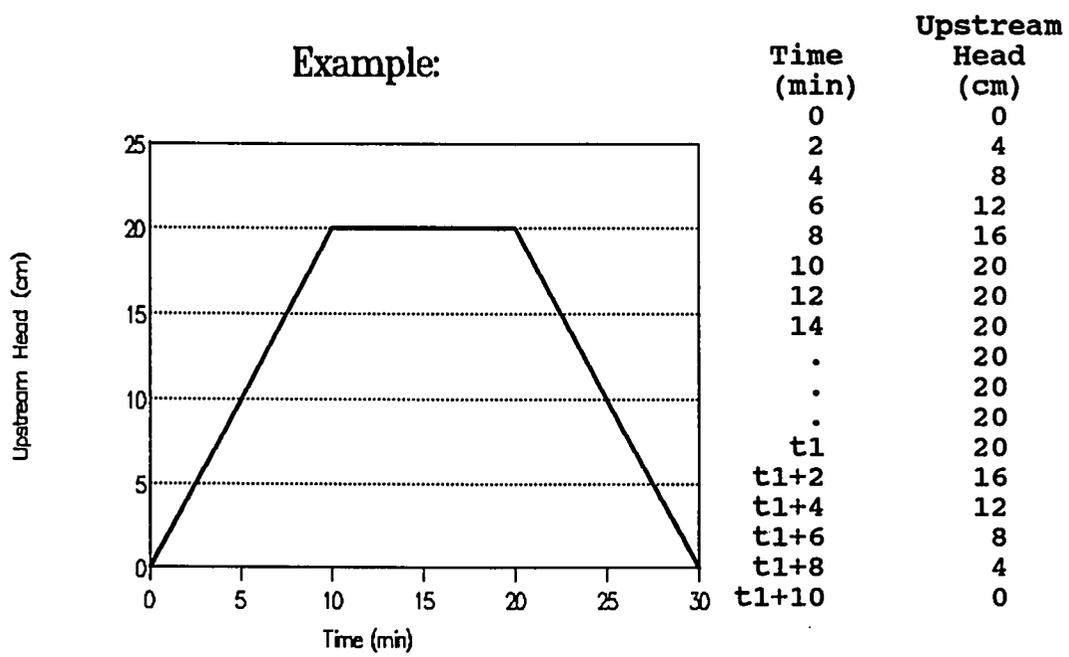


Figure 2- General Head Variation vs. Time

the model's surfaces by the dye. The dye solution recovered in the outflow reservoir was discarded after each run. Water used to rinse the model before each experiment was checked for background fluorescence by collecting samples and inserting them into the fluorometer. In all cases the fluorescence (i.e.-dye concentration) was negligible.

After each experiment, the used porous medium was washed on a sieve (US Sieve No. 40) that allowed the resin pellets to pass but retained the glass beads. Washing was done very carefully to ensure that all dye and resin pellets were completely washed away. After washing, background levels of adsorbed dye on the glass beads were checked by placing the glass beads in a small amount of clean water for 48 hours (allowing for desorption) and then measuring the fluorescence of the water and the glass beads. In all cases, the fluorescence, and therefore the dye concentration, was negligible.

The presence of resin pellets in the cleaned glass beads was also checked. A small sample of the cleaned beads was immersed in a dye solution of known concentration and left for 48 hours. Change in the solution's concentration, above and beyond what is expected due to adsorption on the glass beads themselves, was attributed to adsorption by contaminating resin pellets. (Adsorptive capacities of the glass beads and the resin pellets will be discussed in more detail in the next

chapter.) In all cases, the glass beads were judged to be free of resin pellets after washing.

In separate determinations, the dry density and permeability of the various mixtures of glass beads and the resin pellets were determined. These results are presented in Table 1.

The dry density was determined by recording the mass of dry porous medium, compacted using the same method employed in the experiments, in a known volume. Permeability was determined in constant head tests using a 1-meter long tube having an inner diameter of 2.62 cm. Such a long and skinny tube was required due to the high permeabilities of the porous media.

Table 1-Permeability and Dry Density
of the Porous Media
(Temperature = 25 degrees Celsius)

Resin Ratio (g/g)	Perme- ability (cm/s)	Dry Density (g/cm ³)
None	0.435	1.58
1:360	0.309	1.60
1:180	0.228	1.60
1:90	0.119	1.59
1:18	0.026	1.63

4.0 LABORATORY MATERIALS

Basic properties of the materials and equipment that were used in these experiments are discussed in the sections that follow.

4.1 FLUORESCENT DYE

A fluorescent dye, Intracid Rhodamine WT liquid (Color Index Name= C.I. Acid Red 388), of the Xanthene chemical family was used as the chemical tracer/ simulated contaminant in this experiment. The dye was obtained from Crompton & Knowles Corporation as a 20% aqueous solution (Crompton & Knowles, 1989) and was diluted to desired concentrations using very precise pipets and mass scales available in the Civil Engineering Department's Environmental Laboratory.

Fluorescent dyes have several advantages over many other tracers, including the following:

- 1) Very little dye is required to treat large volumes of water. Less than one microgram of dye per liter of water was adequate for these experiments.

- 2) The cost of the dye is very low.

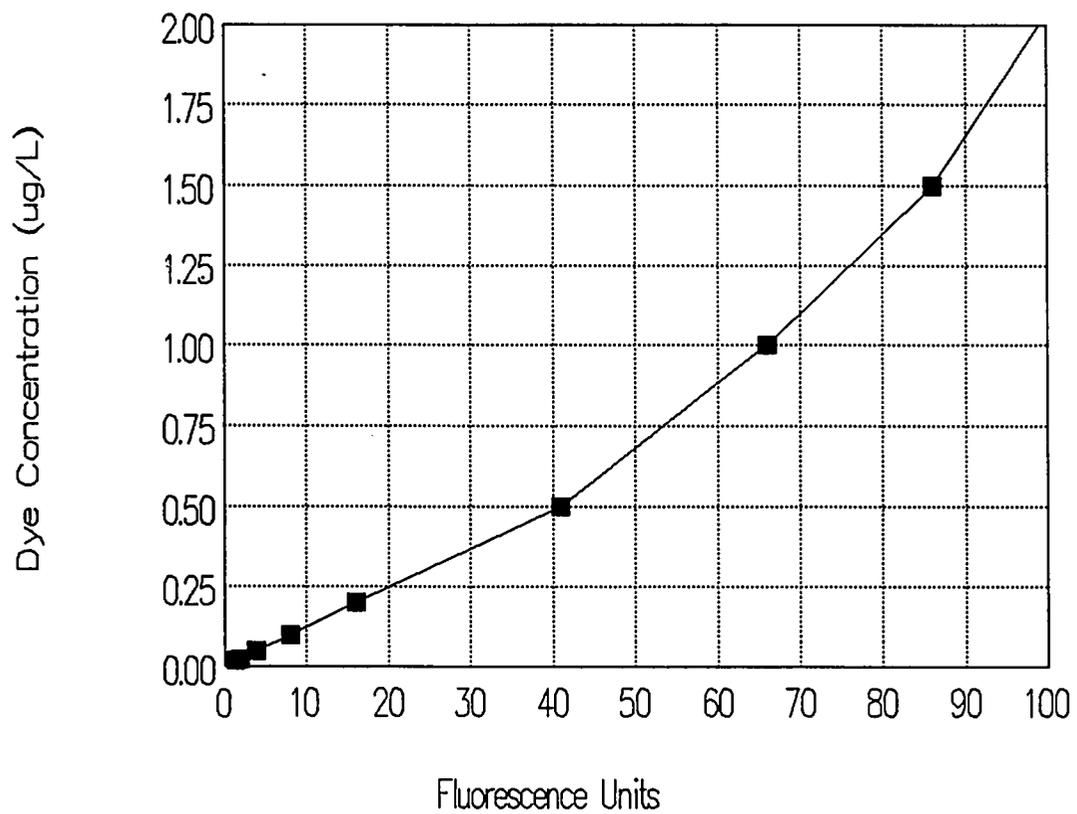
3) The dye exhibits properties of adsorption, diffusion and dispersion which mimic the behavior of chemical contaminants in natural porous media.

4) The concentration of the dye can be measured quite easily and with great accuracy using a simple, low-cost instrument known as a fluorometer. The dye's concentration is related to the fluorescence units measured by the fluorometer through an appropriate calibration curve which will be presented below. The fluorometer will be discussed in greater detail in a later section.

5) The relationship between the dye concentration and the fluorometer's reading is linear for the range of concentrations used in the experiment. Therefore, the fluorometer's readings can often be compared directly without first consulting a calibration curve.

See the article by Gaspar (1987) for a comparative study of several different types of tracers and a general discussion of the properties an ideal tracer should have.

Figure 3 shows the experimentally-derived relationship between Rhodamine WT concentration and the fluorometer reading



**Figure 3- Dye Concentration Calibration Curve
(for 25° C)**

at 25° C which was the standard temperature for the experiments. Concentration observations made at other temperatures were corrected back to 25° C using an equation that will be presented in Section 4.1.3. Note that for concentrations less than about 0.5 micrograms per liter, the relationship is linear. Concentrations used in these experiments were below 0.5 micrograms per liter.

4.1.1 GENERAL PROPERTIES OF THE DYE

An article by Smart and Laidlaw (1977) lists several other properties of Rhodamine WT which make it a good tracer for this experiment:

- 1) The fluorometer can detect differences in Rhodamine WT concentration as small as 0.013 micrograms per liter.
- 2) The fluorometer can detect a minimum concentration of Rhodamine WT of 0.013 micrograms per liter.
- 3) The background level of fluorescence in the wavelength range of Rhodamine WT is usually very small even in natural waterways. Virtually no background fluorescence was measured for the City

of Tucson tap water that was used as the diluting water in these experiments.

4) The pH of water has very little effect on the accuracy of the fluorometer's readings unless the pH drops below 6.0. City of Tucson tap water has a nearly constant pH of 7.0 (Herwehe, 1990).

5) Salinity of the water as measured by the chloride ion's presence will affect the fluorometer's readings for chloride ion concentrations greater than 0.355 g/L. The concentration of the chloride ion in City of Tucson tap water is less than 0.020 g/L (Herwehe, 1990).

6) Before the Rhodamine WT dye was mixed with the tap water, the tap water was allowed to sit uncovered so that residual chlorine gas in the water would dissipate. Even without this precaution, chlorine residuals in tap water are not great enough to affect the fluorometer's measurements (Herwehe, 1990).

7) Suspended sediment concentrations lower than 100 mg/l have very little effect on the measured

fluorescence of Rhodamine WT. Suspended sediment in City of Tucson tap water is less than 1 mg/L (Herwehe, 1990).

8) Changes in the actual dye concentration can occur due to such causes as photochemical decay, chemical decay, and biodegradation. These losses are more common when the dye is used outdoors in natural drainage course experiments. These losses are not significant for these experiments because: a) Rhodamine WT is fairly resistant to these types of decay; b) The experiments are not performed in direct sunlight which promotes photochemical decay; c) The relatively sterile laboratory environment is not conducive to biodegradation; and, d) The duration of each experiment was less than one hour. This is not enough time for significant levels of decay to occur. (See Bencala and Zellweger, 1988.)

9) Rhodamine WT is highly resistant to adsorption losses on equipment and suspended sediment surfaces. This observation is both reported in the literature and was observed in these experiments. Adsorption tests performed in conjunction with these experiments are discussed in the next section.

For further discussion of this and other fluorescent dyes, see Smart & Laidlaw (1977), Feuerstein & Selleck (1963), Wilson, Cobb & Kilpatrick (1984) and Trudgill (1987).

4.1.2 ADSORPTION PROPERTIES OF THE DYE

In adsorption tests that were performed in conjunction with these experiments, a dye solution was prepared and its initial fluorometer reading recorded. Next, weighed amounts of the 1-mm diameter glass beads, the 3-mm diameter glass beads and the resin pellets were placed in separate, small, plastic containers with known volumes of the solution and allowed to sit for 48 hours. The final fluorometer reading for the solution in each container after 48 hours was recorded. Change in the dye concentration in the container over the 48 hour period is related to the adsorption capacity of the glass beads or resin pellets, whichever was in the container.

Some adsorption of the dye can also be attributed to the container walls. The adsorption due to the container walls was measured by recording the concentration change over the 48 hour period in a container that held only the dye solution and no glass beads or resin pellets.

Knowing the initial and final dye concentrations and the volume of the solution, the mass of dye that was adsorbed was calculated. By subtracting off the dye adsorbed to the

container walls, the net amount of dye adsorbed by the resin or glass beads was calculated. The adsorption ratio was calculated as the net mass of adsorbed dye divided by the mass of the adsorbing substance (i.e.-glass beads or resin.)

The adsorption test described above was repeated for various initial dye concentrations because adsorption capacity is a function of solution concentration. The adsorption ratios for the various adsorbing substances at different concentrations are listed in Table 2. The adsorption ratios are plotted versus the initial dye concentrations in Figures 4 through 6. Adsorption data for the 3-mm diameter glass beads are presented, but that size of bead was never used in the experiments.

Dye adsorption losses on the glass beads or surfaces of the apparatus are undesirable. However, adsorption of the dye by the resin is desirable. The resin mimics the adsorption properties of real soil. By varying the resin/glass beads weight ratio, porous media having different adsorption capabilities can be created and the effect of adsorption on experimental results can be tested.

From Table 2 and Figures 4-6, the following observations can be made:

- 1) Some dye did adsorb onto the glass beads, resin pellets and the walls of the container.

Table 2- Dye Adsorption Experiments; Various Substances; 48 hours

Adsorbing Substance	Amount of Substance (g)	Volume of Fluid (ml)	Initial Dye Conc. ($\mu\text{g/L}$)	Final Dye Conc. ($\mu\text{g/L}$)	Adsorption Ratio * (nanograms/g)
Resin	1.2727	10.0	0.025	0.002	0.1801
Resin	0.4967	10.0	0.050	0.003	0.9527
Resin	0.9642	10.0	0.500	0.004	5.1396
Resin	1.0751	10.0	1.000	0.011	9.2023
Container	NA	8.0	0.025	0.025	NA
Container	NA	10.0	0.050	0.043	NA
Container	NA	10.0	0.500	0.478	NA
Container	NA	10.0	1.000	0.971	NA
1mm Beads	1.9658	10.0	0.025	0.017	0.0382
1mm Beads	2.6754	10.0	0.050	0.032	0.0667
1mm Beads	2.4776	10.0	0.500	0.433	0.2691
1mm Beads	2.7230	10.0	1.000	0.934	0.2430
3mm Beads	3.5543	10.0	0.025	0.021	0.0106
3mm Beads	2.7715	10.0	0.050	0.039	0.0412
3mm Beads	3.0747	10.0	0.500	0.467	0.1084
3mm Beads	3.6940	10.0	1.000	0.941	0.1592

* The adsorption ratio is the amount of dye adsorbed per gram of adsorbing substance.

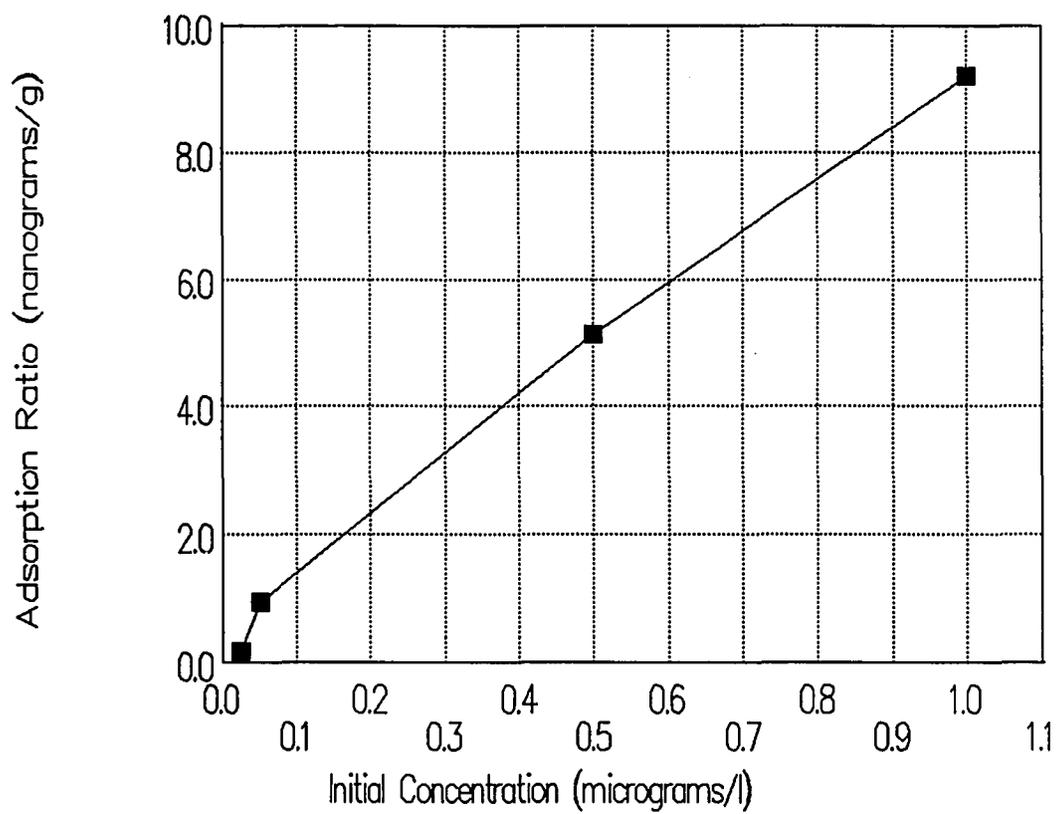


Figure 4- Adsorption Curve for the Resin

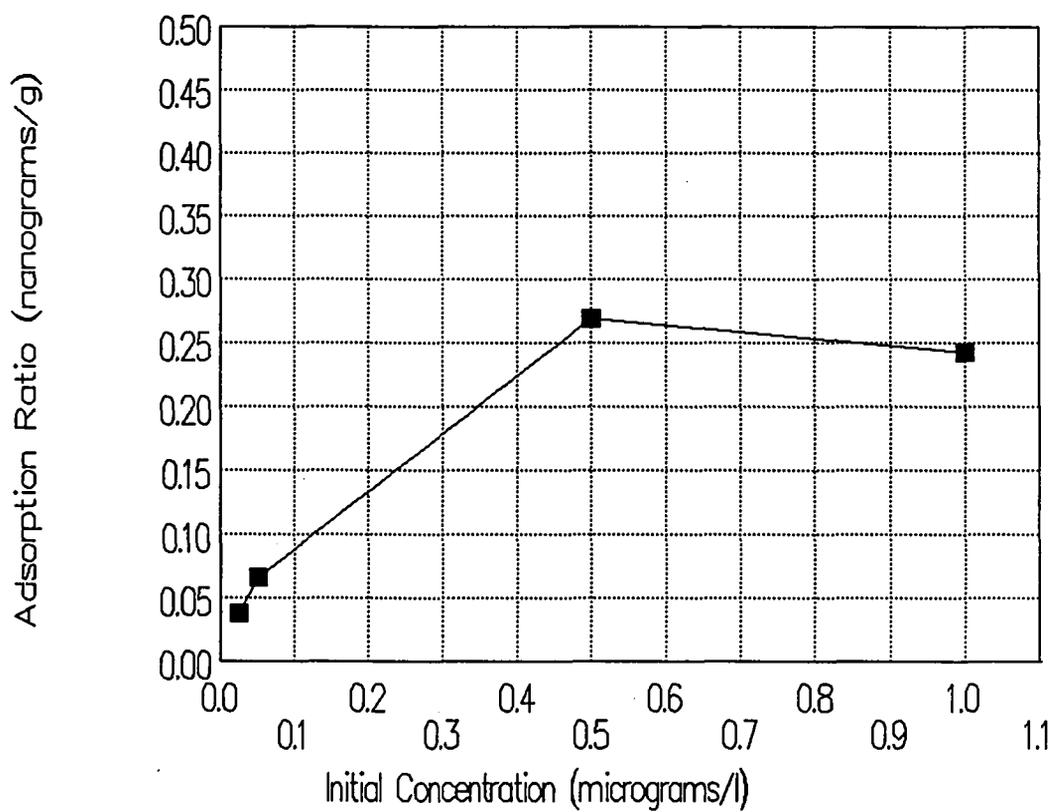


Figure 5- Adsorption Curve for the 1mm Glass Beads

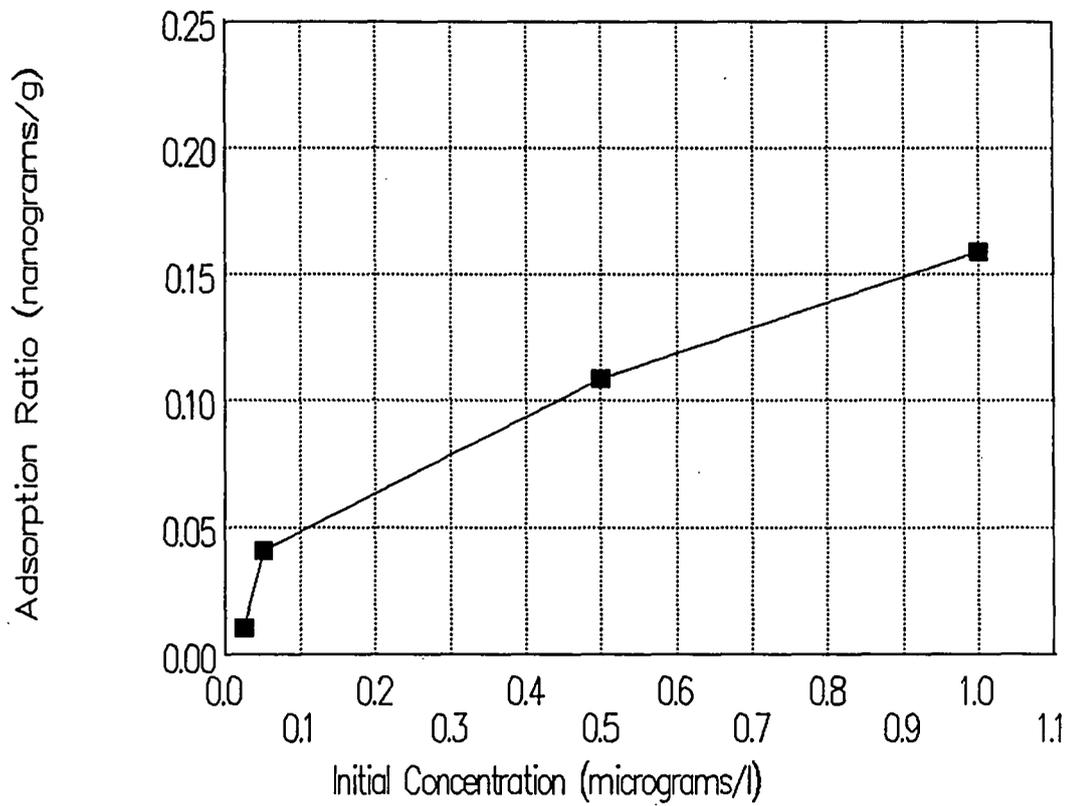


Figure 6- Adsorption Curve for the 3mm Glass Beads

2) The resin pellets had the greatest adsorption capacity by far, followed by the 1-mm glass beads, the 3-mm glass beads and the plastic container walls, respectively. These results are logical and can be explained as follows: a) The resin pellets are chemically formulated for high adsorption while the other surfaces are not. Therefore, the resin has the highest adsorption capacity. b) The small glass beads have superior adsorptive properties over the large beads due to their greater specific surface area. c) Finally, the plastic container walls represent a relatively small surface area and the plastic surfaces are fairly inert.

3) The relationship between the dye's initial concentration and the adsorption ratio is approximately linear for the resin, Figure 4.

4) As stated previously, it is desirable for the adsorption to occur on the resin pellets, but not on the glass beads or the experiment apparatus surfaces. Table 2 and Figures 4-6 show that the adsorption capacity of the resin is much greater than that of the other surfaces and that this objective is achievable.

5) Even though the adsorption tests extended over a relatively long period of 48 hours, the amount of dye adsorbed by surfaces other than the resin was small. Therefore, the amount of dye adsorbed to experiment apparatus surfaces and the glass beads during the regular experimental runs which are much shorter in duration is negligible. However, as a precaution, all equipment was washed with clean water after each experiment and background levels of fluorescence checked before each experiment.

4.1.3 TEMPERATURE DEPENDENCE OF FLUORESCENCE

One unfortunate property of Rhodamine WT dye is that its fluorescence is highly temperature dependent. Differences in temperature of a few degrees Celsius are significant. Fluorescence must be corrected for temperature effects using the following equation:

$$F_2 = F_1 \exp(n(t_2 - t_1)) \quad (1)$$

Where F_1 is the fluorescence reading at temperature t_1 ,
 F_2 is the fluorescence reading at temperature t_2 and
 $n = -0.027 \text{ } ^\circ\text{C}^{-1}$ (Smart and Laidlaw, 1977).

The standard temperature for these experiments was 25°C and fluorescence observations at other temperatures were multiplied by the correction in equation (1) to determine their equivalent value at 25°C .

4.1.4 TOXICITY OF THE DYE

Another undesirable characteristic of Rhodamine WT dye is that it is toxic to humans and other life forms. Permissible, continuous ingestion levels of Rhodamine WT for humans have been set at 0.75 milligrams per day. The U.S. Geological Survey recommends that final concentrations of the dye for tracer experiments not exceed 10 micrograms/liter (Smart and Laidlaw, 1977). In these experiments, the dye concentration was less than 1 microgram per liter. Skin contact and ingestion of the dye were avoided. Waste dye and other chemicals were handled and disposed of in accordance with University of Arizona standards for toxic waste (Department of Risk Management, 1989). Interested parties should contact the Crompton & Knowles Corporation for further guidelines regarding the handling and disposal of this dye; see also Crompton & Knowles (1989).

4.2 FLUOROMETER

The fluorometer is a moderately expensive piece of equipment that is simple to use, yet provides accurate measurements. It measures the amount of fluorescence of a fluorescent solution placed in a test tube inside its chamber. As discussed earlier, the fluorescence of the Rhodamine WT dye solution is related to its concentration.

The definition of a fluorescent material must be

understood if the operation of the fluorometer is to be comprehended. A fluorescent material (e.g.-the dye solution) is a material that absorbs light energy in a particular wavelength band and re-emits that energy in another wavelength band (Feuerstein and Selleck, 1963).

With that definition in mind, fluorometry and the basic operation of a fluorometer can be explained, Figure 7. In the fluorometer, an excitation light source such as a mercury bulb with a phosphor coating is used. Before the light strikes the sample, it passes through a primary filter that filters out all light except light within a certain wavelength band. Each dye responds differently to light in different wavelength bands. Each fluorescent dye has a wavelength band to which its response (excitation level and light emissions) is the greatest. The primary filter that is chosen for a particular dye should be the one that allows light within this optimal range to pass.

Light within the selected wavelength band is allowed to pass through the primary filter and continues on until it strikes the sample. Some of the light is absorbed by the sample and excites the fluorescent dye which then emits light in a different wavelength band.

Light emitted by the sample passes through a secondary filter which is at 90° to the incident beam. The 90° angle is to help ensure that the light passing through the secondary

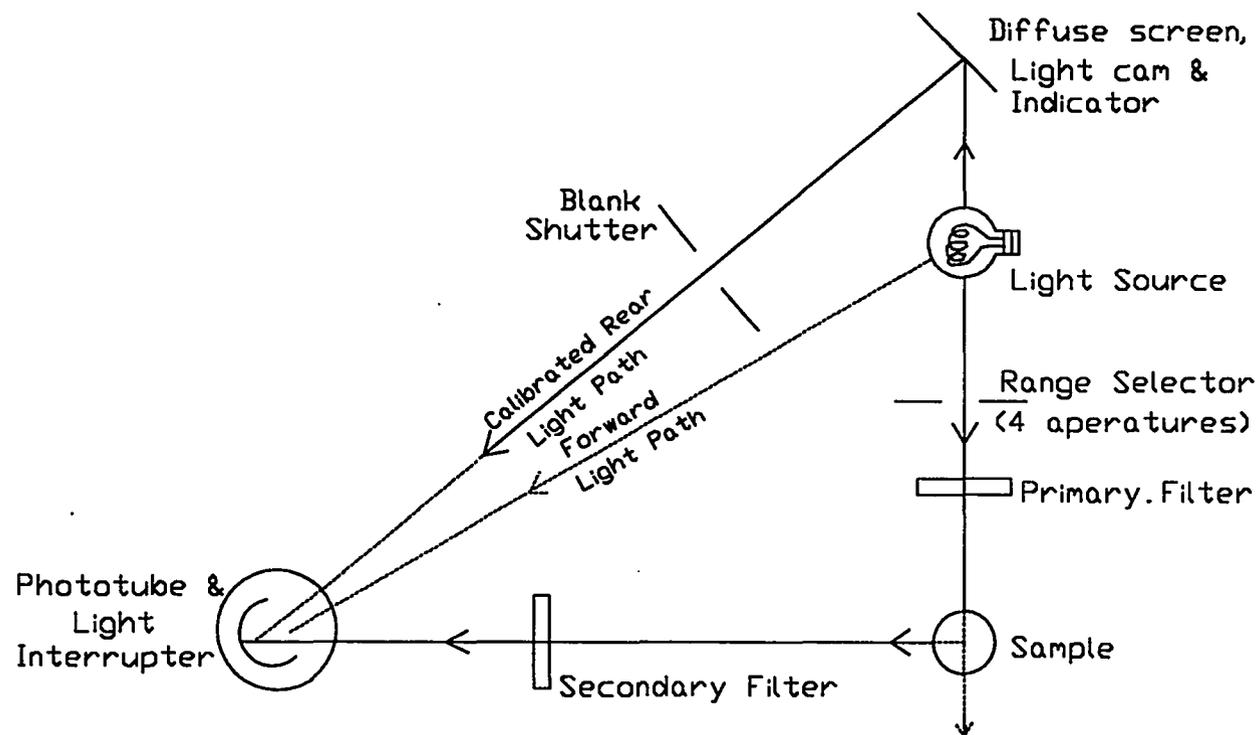


Figure 7- Optical Systems of the Fluorometer
(Feuerstein and Selleck, 1963)

filter is light emitted by the dye and not light from the mercury bulb. The secondary filter is opaque to light passing through the primary filter, but transparent to the light emitted by the dye. The amount of light passing through the secondary filter is measured by a photomultiplier and compared with a reference light path. The results are registered automatically on a dial on the exterior of the fluorometer (Feuerstein and Selleck, 1963).

By using filters of various colors (i.e.-wavelength bands) and densities, the fluorometer can be used for different fluorescent dyes at various concentrations. The sensitivity of the fluorometer can also be changed by using the range selector to adjust the amount of light that strikes the sample.

The fluorometer that was used in these experiments is a Turner-111 with a 546 nanometer (nm) wavelength primary filter and a 590 nm secondary filter.

4.3 ION EXCHANGE RESIN PELLETS

The resin pellets used for the experiment are Dowex 50W-X4, Cation H⁺ exchange resin pellets manufactured by Dow Chemical. The pellets are a sulfonated copolymer of styrene and divinylbenzene in the hydrogen form, Dow Product No. 6383687. The pellets are solid beads of mesh size 50-100, light amber in color and insoluble in water. They have a

density of 50 lb/ft³ (Dow Chemical, 1990).

For the experiments, the resin pellets were mixed with the glass beads in varying weight ratios to form homogeneous mixtures. The resin pellets are smaller than the glass beads, but are slightly moist so that they adhere to the surfaces of the glass beads.

The fact that the resin pellets are smaller than the glass beads allowed for separation of the two materials at the end of each experimental run so that the glass beads could be used again. The procedure followed in performing this separation is discussed in Chapter 3.

The property of the resin most crucial to the experiment is its ability to adsorb the Rhodamine WT dye. The greater the amount of resin in the glass bead/resin mixture, the greater the adsorptive properties of that composite porous medium. As the dye solution flows through the model, the resin adsorbs the dye until its adsorptive capacity is exceeded. A red coloration matching the dye's color was visible on individual resin pellets at the end of the experiment. The glass beads showed no such coloration. Table 2 and Figure 4, presented in an earlier chapter, give further information regarding the adsorption properties of the resin.

Dowex 50W-X4 resin is a skin and eye irritant, but its toxicity to humans is very low. Special precautions must be used when working with it or disposing of it. These

precautions are outlined in literature available from Dow Chemical (Dow Chemical, 1990). University of Arizona guidelines for the disposal of hazardous waste (Department of Risk Management, 1989) and Dow Chemical guidelines were followed in handling and disposing of this resin.

4.4 GLASS BEADS

The glass beads used in these experiments are technical quality glass spheres manufactured by Potters Industries, Incorporated. The beads used in these experiments are of the size, US Sieve No. 18-20 (1.00-1.18 mm, Potters' designation A-100) (Potters Industries, Inc., 1990). Properties of the glass beads are listed in Table 3.

Table 3- Properties of the Glass Beads
(Potters Industries, Inc., 1990)

Density	2.50 g/cc
Crush Resistance	31000-36000 psi
Poisson's Ratio	0.21
Rigidity Modulus	4.3×10^6 psi
Young's Modulus	10×10^6 psi
Hardness (Knoop 100g load)	515 kg/mm ²
Coefficient of Friction (Static)	0.9-1.0
Composition	Soda-Lime Silica Glass
Free Silica	None

5.0 PRESENTATION AND DISCUSSION OF RESULTS

Results from the experiments are shown in Tables 4 through 8 and Figures 8 through 12 in this chapter. Discussion of the results follows.

5.1 EXPERIMENTAL RUN 1

In Experimental Run 1, the porous medium consisted only of the glass beads with no resin. The initial concentration of the dye solution was about 0.40 micrograms/liter. Table 4 shows the experimental results. Figure 8a shows the variation of head and downstream flowrate with time. The variation of C_o/C_i (output concentration/input concentration) with time is plotted in Figure 8b and the position of the phreatic surface with time is shown in Figure 8c.

For the first 2.5 minutes, there was no flow at the downstream end as the wetting front moved through the section. Downstream flow began shortly thereafter and increased to a peak flowrate of 8.83 ml/s. When the head was decreased beginning at $t=15$ minutes ("t" represents time), the flow also decreased.

Figure 8b shows the variation of C_o/C_i with time. When downstream flow started at approximately $t=2.8$ minutes, the output concentration was zero. Between $t=3$ and 4 minutes, the

Table 4- Experimental Run 1

Glass Beads:	1mm size
Resin/Glass Bead Wt Ratio:	No resin
Water temperature (Celsius):	26 degrees
Initial fluorometer reading:	32.00
Corrected fluorometer reading:	32.88
Initial concentration: (microg/l)	0.401

Time (min)	Head (cm)	Fluorometer Reading	Co (microg/l)	Co/Ci
0.0	0	No Flow	--	--
0.5	1	No Flow	--	--
1.0	2	No Flow	--	--
1.5	3	No Flow	--	--
2.0	4	No Flow	--	--
2.5	5	No Flow	--	--
3.0	6	18	0.226	0.563
3.5	7	25	0.313	0.781
4.0	8	28	0.351	0.875
4.5	9	29	0.363	0.906
5.0	10	29	0.363	0.906
5.5	11	29	0.363	0.906
6.0	12	30	0.376	0.938
6.5	13	30	0.376	0.938
7.0	14	30	0.376	0.938
7.5	15	30	0.376	0.938
8.0	16	30	0.376	0.938
8.5	17	30	0.376	0.938
9.0	18	30	0.376	0.938
9.5	19	30	0.376	0.938
10.0	20	30	0.376	0.938
11.0	20	30	0.376	0.938
12.0	20	31	0.388	0.969
13.0	20	32	0.401	1.000
14.0	20	31	0.388	0.969
15.0	20	30	0.376	0.938
16.0	18	31	0.388	0.969
17.0	16	31	0.388	0.969
18.0	14	31	0.388	0.969
19.0	12	32	0.401	1.000
20.0	10	32	0.401	1.000
21.0	8	31	0.388	0.969
22.0	6	32	0.401	1.000
23.0	4.5	31	0.388	0.969
24.0	3.3	32	0.401	1.000
25.0	2.5	32	0.401	1.000
26.0	Stop	Stop	Stop	Stop

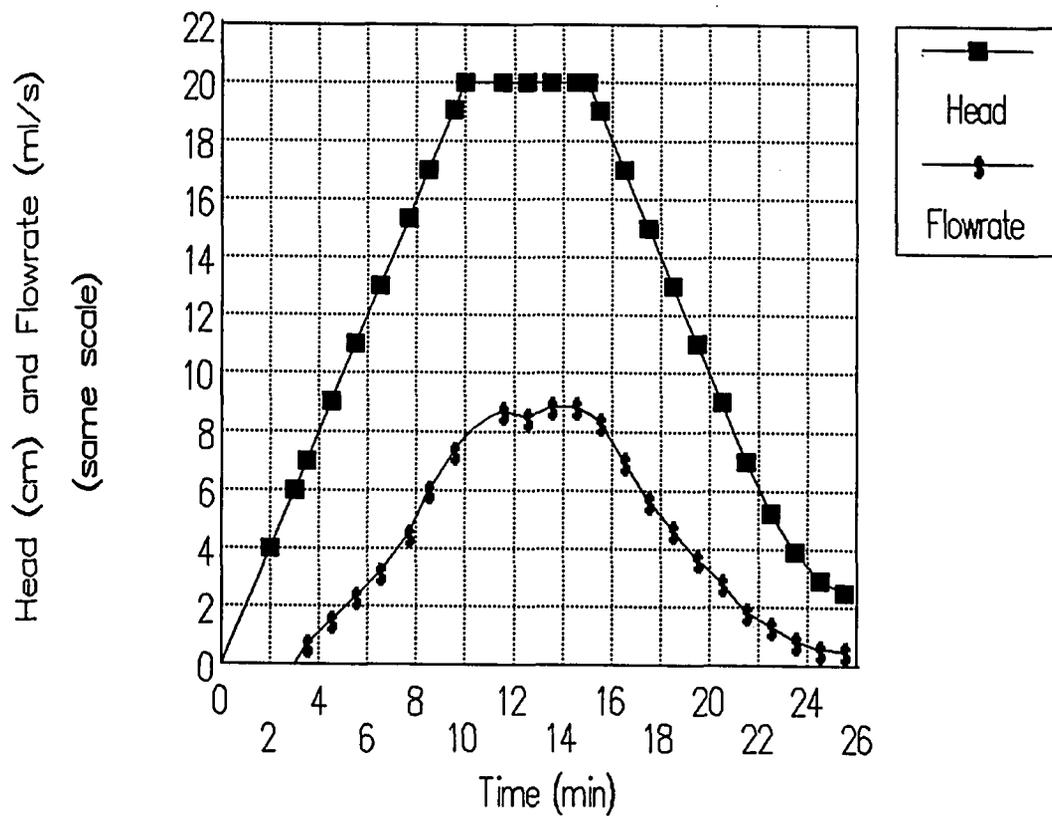


Figure 8a- Head and Flowrate vs. Time; Run 1; No resin

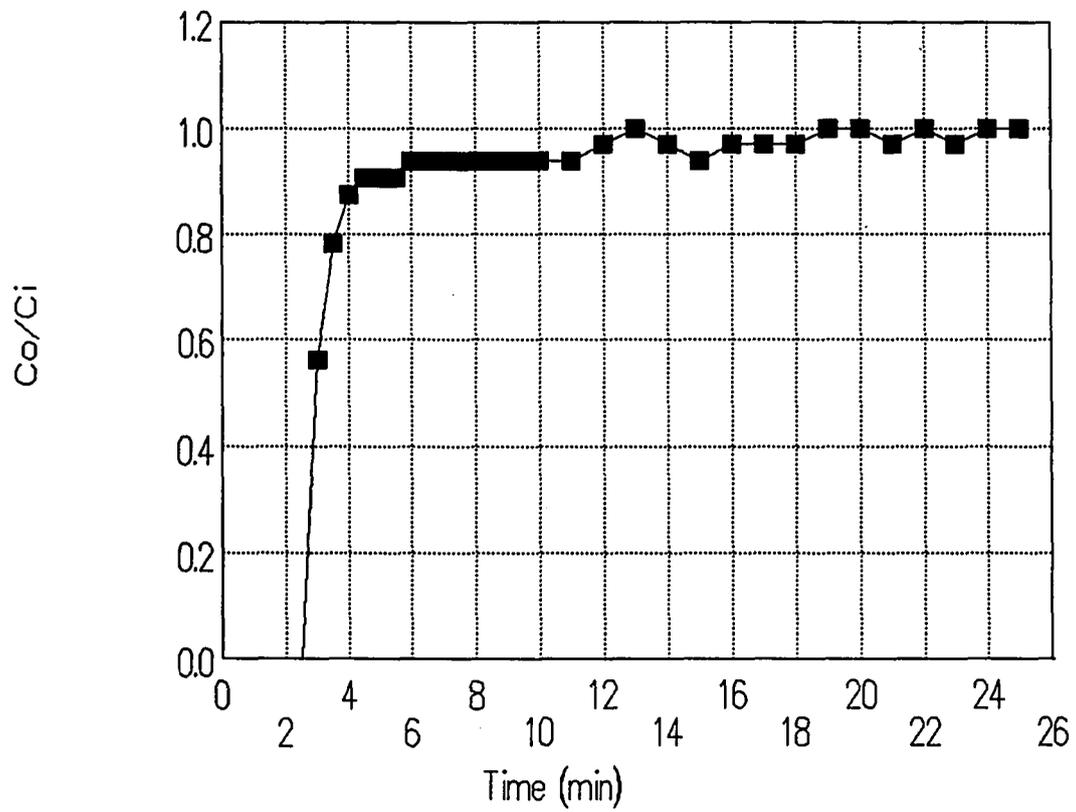


Figure 8b- C_o/C_i vs. Time; Run 1; No resin

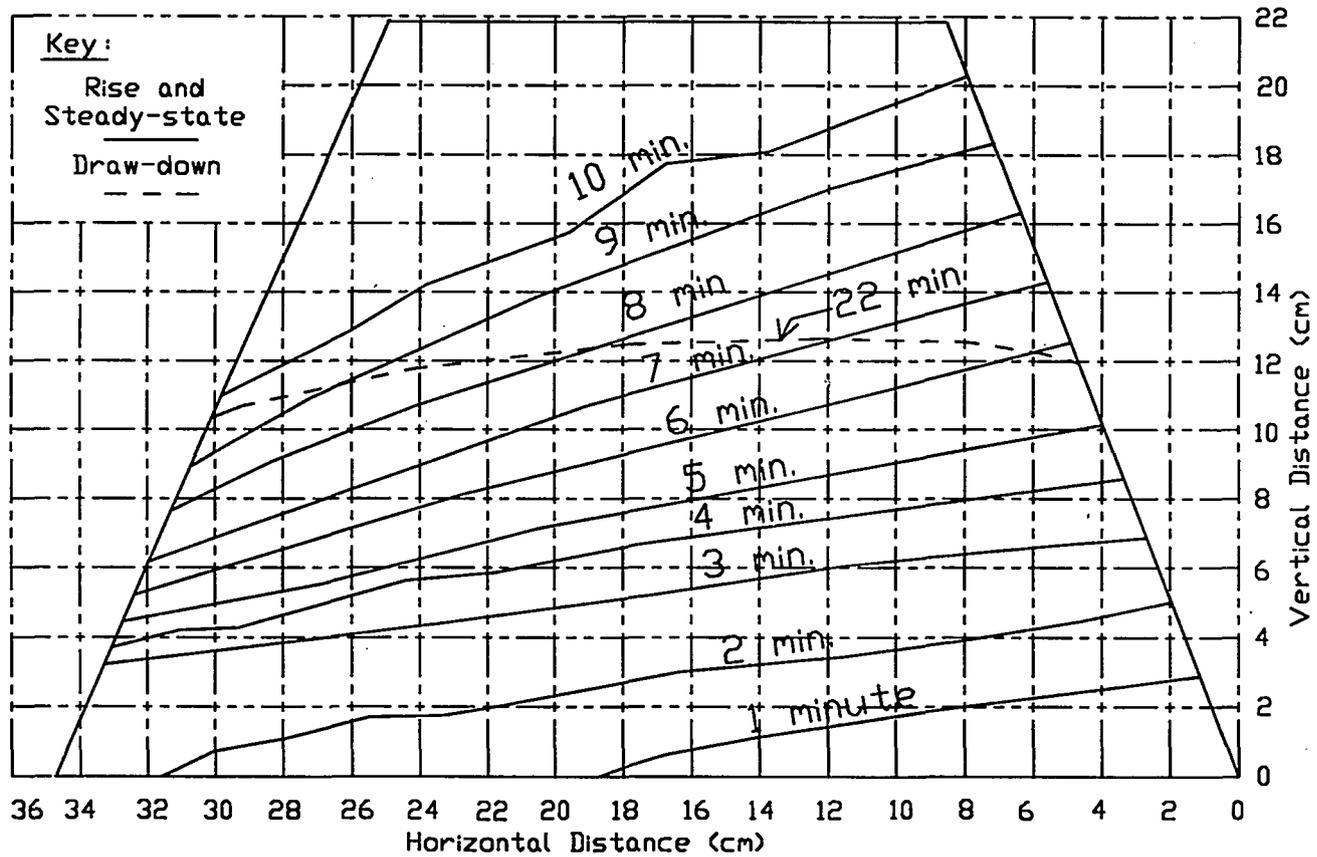


Figure 8c- Phreatic Surface vs. Time; Run 1; No resin

output concentration rapidly increased to nearly equal to the input concentration. For the next several minutes, the concentration fluctuated slightly below the input concentration, finally equalling the input concentration for the first time at about $t=13$ minutes. For all times greater than 13 minutes, the input and output concentrations were essentially equal.

The results in Figure 8b are somewhat surprising. It was anticipated that once the downstream flow began, the output dye concentration would almost immediately equal the input concentration because of the lack of resin pellets (adsorbing material) in the porous medium. The rapid (but not instantaneous) increase in the downstream concentration indicates that the glass beads have a small adsorption capacity. The adsorption capacity of the glass beads was virtually exhausted within the first five minutes.

In many instances, the shape of the phreatic surface in Figure 8c and in similar figures for other experimental runs does not perfectly match what other researchers have observed, but the observed results were closely checked and are reproducible. For instance, others have observed that the phreatic surface is perpendicular to the upstream face during rise and steady-state (Desai & Li, 1983 and Desai & Kuppusamy, 1980). In many instances during the present experiments, it was not. The phreatic surface should also bend downward at

the downstream face (Desai & Kuppusamy, 1980). This was violated in some instances. During initial stages of rise, before the phreatic surface has reached the downstream face; the leading edge of the phreatic surface should be nearly tangent to the bottom boundary (Desai & Li, 1983 and Baseghi & Desai, 1990). This condition was violated in many instances during the present experiments.

The apparent discrepancies with the observations of other researchers seem to be due to the wide capillary fringe exhibited by the porous medium. When performing these experiments, a wide capillary fringe was observed. The porous medium above the true phreatic surface became saturated due to capillary effects and the true phreatic surface was often obscured. The shapes recorded in the figures such as Figure 8c are the edges of the capillary fringe and not the true phreatic surface.

In many of the experiments performed by the other researchers, the glass beads were coated with silicon and a mixture of glycerin and 20% water was used as the permeating fluid to minimize capillary effects. For the present experiments, it was felt that silicon and glycerin would interfere with the chemical transport and adsorption effects that were the primary aim of these experiments.

5.2 EXPERIMENTAL RUN 2

In Experimental Run 2, the resin/glass beads weight ratio was 1:360. The initial concentration of the dye solution was about 0.297 micrograms/liter. Table 5 shows the experimental results. Figure 9a shows the variation of head and downstream flowrate with time. The variation of C_o/C_i with time is plotted in Figure 9b and the position of the phreatic surface with time is shown in Figure 9c.

For the first 3.0 minutes, there was no flow at the downstream end as the wetting front moved through the section. Downstream flow began shortly thereafter and increased to a peak flowrate of 8.33 ml/s. When the head was decreased beginning at $t=15$ minutes, the flow also decreased.

When downstream flow began at approximately $t=3.5$ minutes, the concentration at the downstream end was zero. The output concentration gradually increased over the next eight minutes until it equalled the input concentration at about $t=12$ minutes. The rate of increase was much more gradual than in Run 1. For all times greater than about 12 minutes, the output concentration equalled the input concentration.

The shape of the curve in Figure 9b can be explained as follows: As the flow began, the clean resin was able to adsorb almost all of the dye that flowed by it. For the first six minutes of flow, the resin adsorbed most of the dye and

Table 5- Experimental Run 2

Glass Beads: 1mm size
 Resin/Glass Bead Wt Ratio: 1/360
 Water temperature (Celsius): 25.5 degrees
 Initial fluorometer reading: 24.00
 Corrected fluorometer reading: 24.33
 Initial concentration:(microg/l) 0.297

Time (min)	Head (cm)	Fluorometer Reading	Co (microg/l)	Co/Ci
0.0	0	No Flow	---	--
1.0	2	No Flow	--	--
2.0	4	No Flow	--	--
3.0	6	No Flow	--	--
4.0	8	0.0	0.000	0.000
5.0	10	3.0	0.037	0.125
6.0	12	8.0	0.099	0.333
7.0	14	10.0	0.124	0.417
8.0	16	14.0	0.173	0.583
9.0	18	18.0	0.222	0.750
10.0	20	22.0	0.272	0.917
11.0	20	21.0	0.260	0.875
12.0	20	23.5	0.290	0.979
13.0	20	24.0	0.297	1.000
14.0	20	23.5	0.290	0.979
15.0	20	23.5	0.290	0.979
16.0	18	24.0	0.297	1.000
17.0	16	25.0	0.309	1.042
18.0	14	23.5	0.290	0.979
19.0	12	23.5	0.290	0.979
20.0	10	24.0	0.297	1.000
21.0	8	23.0	0.284	0.958
22.0	6	23.0	0.284	0.958
23.0	4.5	23.0	0.284	0.958
24.0	3.4	24.5	0.303	1.021
25.0	2.7	24.0	0.297	1.000
26.0	Stop	Stop	Stop	Stop

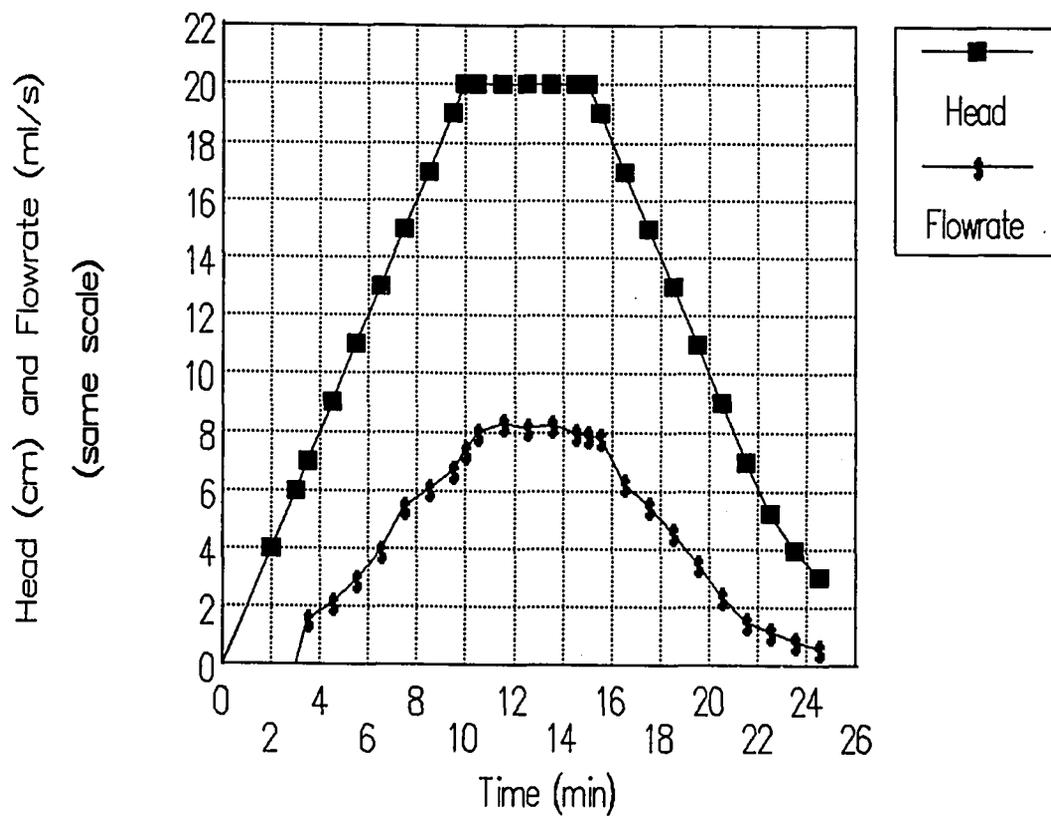


Figure 9a- Head and Flowrate vs. Time; Run 2;
Resin ratio 1:360

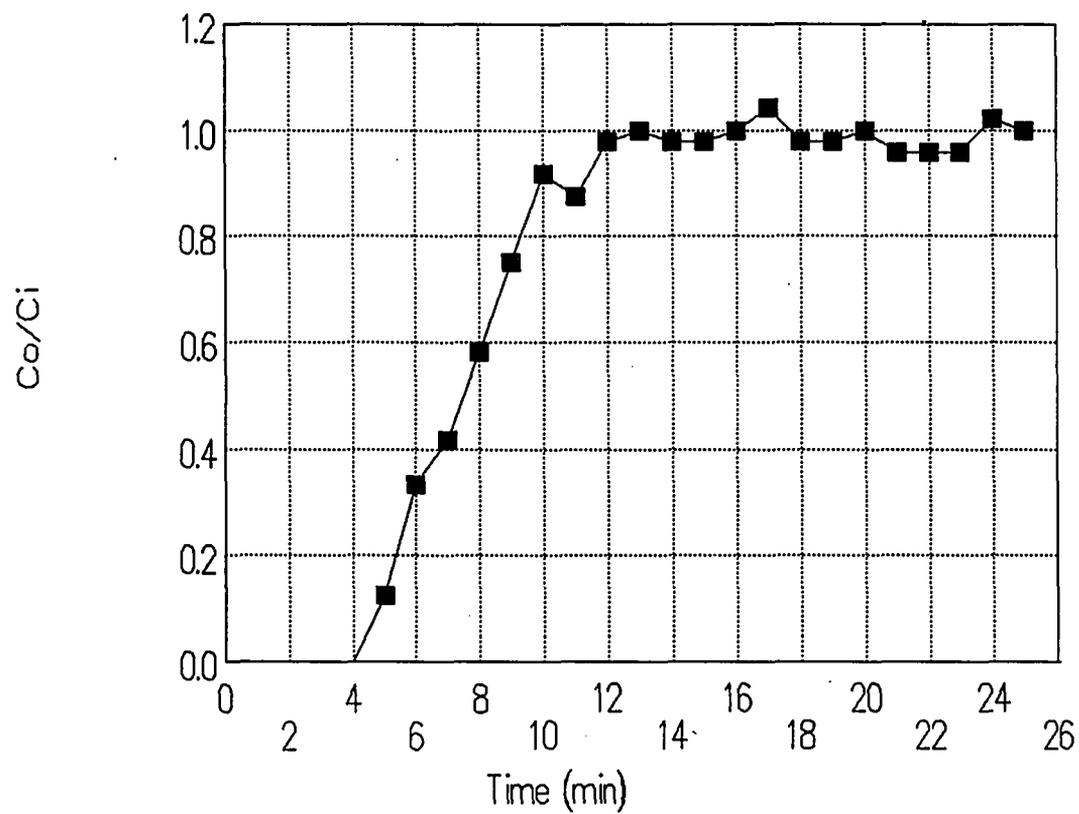


Figure 9b- C_o/C_i vs. Time; Run 2; Resin ratio 1:360

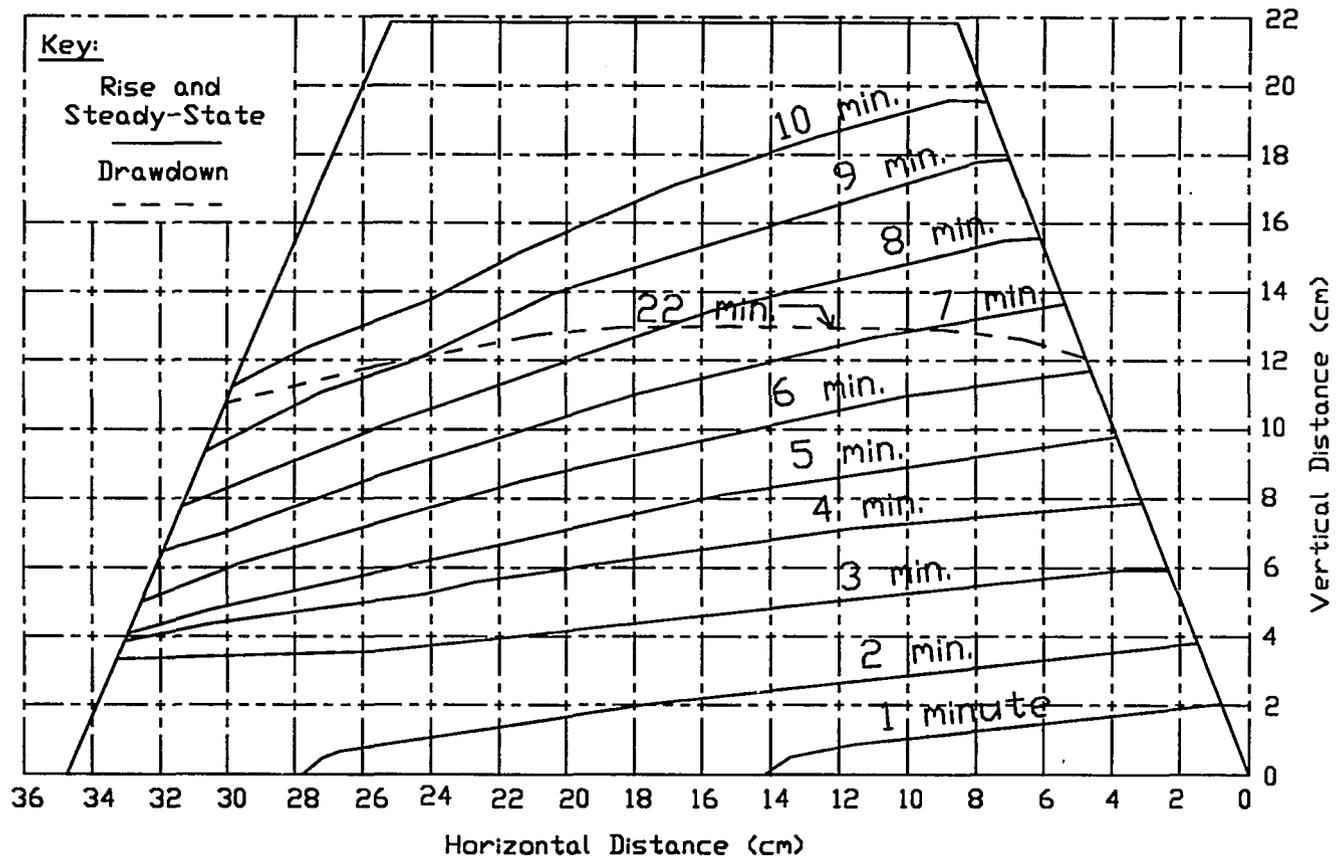


Figure 9c- Phreatic Surface vs. Time; Run 2; Resin ratio 1:360

output fluorescence levels were low. Gradually, as adsorption sites on the resin pellets were utilized, the adsorption capacity of the resin pellets decreased and less dye was adsorbed. The outflow fluorescence levels increased. Finally, the adsorption capacity of the resin was exceeded at approximately $t=12$ minutes. From that time onward, the input and output concentrations were equal.

The porous medium in Run 2 was slightly less permeable than that in Run 1 due to the presence of the small resin pellets that clog the pore spaces between the glass beads. This is evident from the fact that the peak flowrate for Run 2 (8.33 ml/s) was less than the peak flowrate for Run 1 (8.83 ml/s) under the same head conditions. (See Figures 8a and 9a in this chapter.) The permeabilities of the porous media used in Runs 1 and 2 are shown in Table 1, Chapter 3.

5.3 EXPERIMENTAL RUN 3

In Experimental Run 3, the resin/glass beads weight ratio was changed to 1:180, thereby increasing the proportion of the resin. The initial concentration of the dye solution was about 0.251 micrograms/liter. Table 6 shows the experimental results. Figure 10a shows the variation of head and downstream flowrate with time. The variation of C_o/C_i with time is plotted in Figure 10b and the position of the phreatic surface with time is shown in Figure 10c.

Table 6- Experimental Run 3

Glass Beads: 1mm size
 Resin/Glass Bead Wt Ratio: 1/180
 Water temperature (Celsius): 26 degrees
 Initial fluorometer reading: 20.00
 Corrected fluorometer reading: 20.55
 Initial concentration (microg/l): 0.251

Time (min)	Head (cm)	Fluorometer Reading	Co (microg/l)	Co/Ci
0.0	0	No Flow	--	--
1.0	2	No Flow	--	--
2.0	4	No Flow	--	--
3.0	6	No Flow	--	--
4.0	8	0.0	0.000	0.000
5.0	10	0.0	0.000	0.000
6.0	12	0.0	0.000	0.000
7.0	14	1.5	0.019	0.075
8.0	16	3.0	0.038	0.150
9.0	18	4.0	0.050	0.200
10.0	20	5.0	0.063	0.250
11.0	20	6.0	0.075	0.300
12.0	20	8.0	0.100	0.400
13.0	20	10.0	0.125	0.500
14.0	20	13.0	0.163	0.650
15.0	20	19.0	0.238	0.950
16.0	20	23.0	0.288	1.150
17.0	20	24.0	0.301	1.200
18.0	20	24.0	0.301	1.200
19.0	20	23.5	0.294	1.175
20.0	20	24.0	0.301	1.200
21.0	18	23.5	0.294	1.175
22.0	16	24.0	0.301	1.200
23.0	14	24.0	0.301	1.200
24.0	12	24.0	0.301	1.200
25.0	10	24.0	0.301	1.200
26.0	8	24.0	0.301	1.200
27.0	6	24.0	0.301	1.200
28.0	4	24.0	0.301	1.200
29.0	4	24.0	0.301	1.200
30.0	4	25.0	0.313	1.250
31.0	4	Stop	Stop	Stop

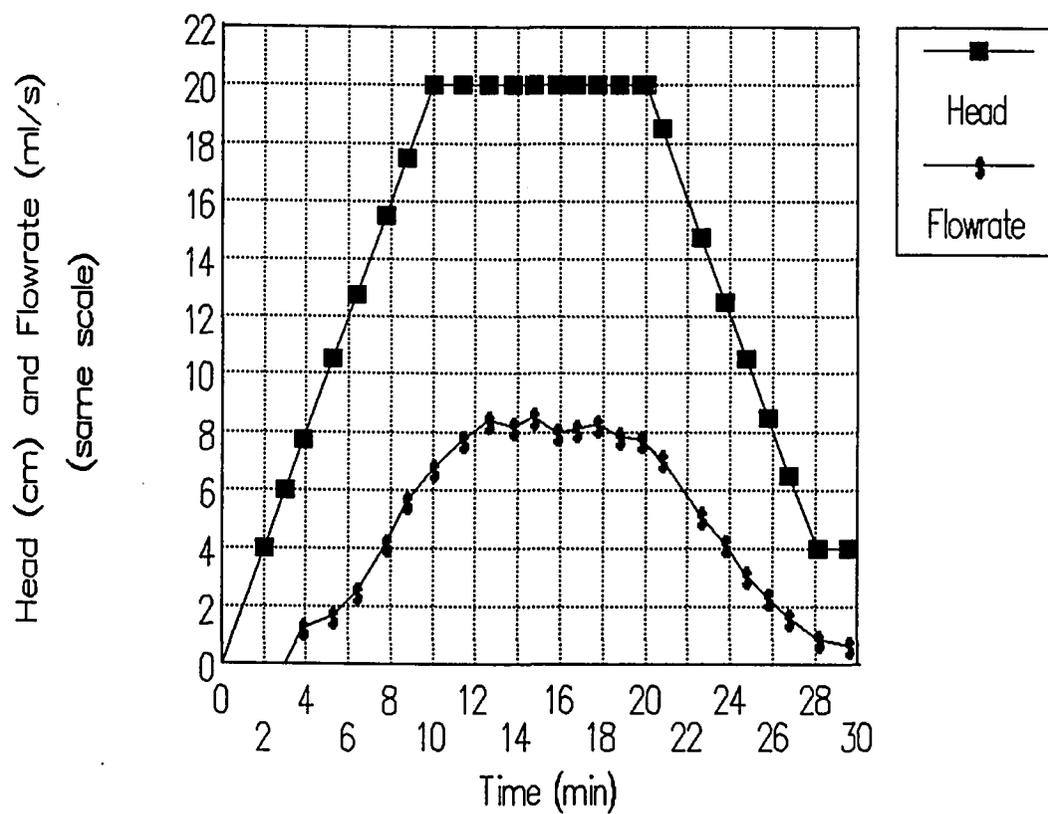


Figure 10a- Head and Flowrate vs. Time; Run 3;
Resin ratio 1:180

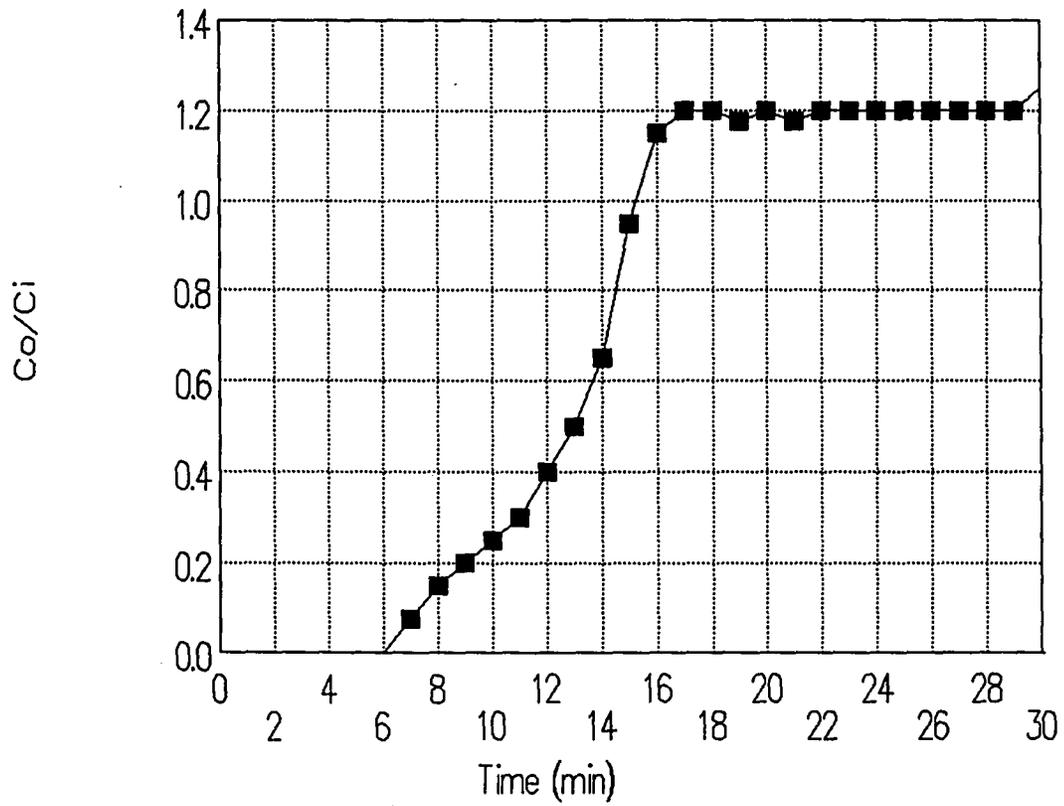


Figure 10b- C_o/C_i vs. Time; Run 3; Resin ratio 1:180

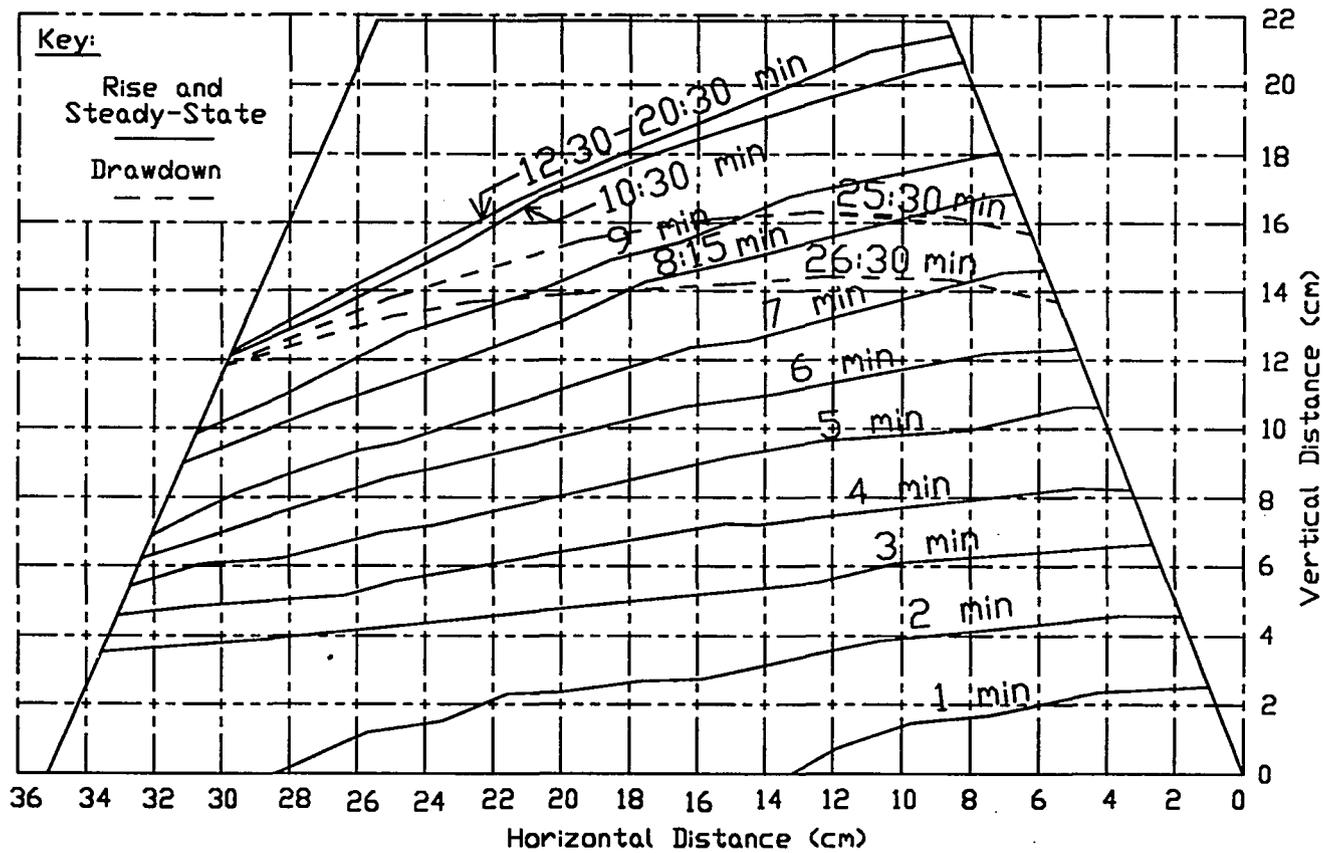


Figure 10c- Phreatic Surface vs. Time; Run 3; Resin ratio 1:180

For the first 3.0 minutes, there was no flow at the downstream end as the wetting front moved through the section. Downstream flow began shortly thereafter and increased to a peak flowrate of approximately 8.3 ml/s. When the head was decreased beginning at $t=20$ minutes, the flow also decreased.

Figure 10b shows the relationship of C_o/C_i versus time. When downstream flow began at approximately $t=3.8$ minutes, the concentration at the downstream end was zero and remained so until about $t=6$ minutes. From $t=7$ minutes to $t=11$ minutes, the curve has a gentle slope as the output concentration increased. The slope changes at about $t=11$ minutes, becoming steep and increasingly more so until about $t=15$ minutes, when the output concentration approximately equalled the input concentration. The output concentration continued to increase after $t=15$ minutes until the ratio C_o/C_i reached an equilibrium value of 1.2 for times greater than about 17 minutes. Great care was taken in measuring, checking and recording these results to make sure that the observations of the upstream and downstream concentrations were not in error.

The shape of the curve in Figure 10b can be explained as follows: As flow began, the clean resin was able to adsorb almost all of the dye that flowed by it. Thus the outflow exhibited no fluorescence for $t=4$ minutes to about $t=6$ minutes. Gradually, available adsorption sites on the resin

pellets were utilized and some dye began to break through. Outflow fluorescence continued to increase with time as the adsorption capacity of the resin was exhausted.

The final C_o/C_i ratio of 1.2 must be explained. Initially, it was thought that the output concentration in excess of the input concentration was due to dye-covered resin pellets being washed out of the dam and entering the outflow stream. Separate tests showed that dye-covered resin pellets can increase the fluorescence of the outflow stream if they remain suspended in the solution. This is because they increase the solution's response to the fluorometer's light beam. (See Section 4.2.) However, further tests showed that the Dowex resin pellets used in these experiments are large and dense enough that they quickly settle out of solution and do not make a significant contribution to the fluorescence of the outflow stream. When Run 3 was repeated and the outflow stream was filtered to remove resin pellets that washed out from the dam, the results were the same.

The primary cause of the outflow concentration being in excess of the input concentration is due to displacement of the dye from certain adsorption sites on the resin pellets by other cations (James M. Montgomery, Consulting Engineers, Inc., 1985). The other cations are found in the City of Tucson tap water that was used as the dilution water for these experiments. These cations, such as Ca^{2+} and Mg^{2+} , are

preferred by the adsorption sites on the resin, but are at much lower concentrations in the bulk solution. As a result, the available adsorption sites are initially claimed by the more abundant dye cations. However, as the experiment proceeds, the preferred ions come into contact with the resin and displace the dye from some locations. This sends the dye back into solution, increasing the output stream's concentration.

If the experiment were continued for a sufficiently long period of time, an equilibrium would be established. Dye cations would occupy some adsorption sites on the resin, while the more highly preferred cations would occupy other sites. The ratio of the dye to the other cations on the resin would be a function of the concentrations of the various cations in the bulk solution and of the affinity of the resin for each species. After equilibrium was established, the output dye concentration would once again equal the input dye concentration (James M. Montgomery, Consulting Engineers, Inc., 1985).

The question may arise: Why wasn't the output concentration in Run 2 greater than the input concentration? This did not occur because of the low amount of resin that was used in Run 2. Because of the low amount of resin, the dye that was displaced back into solution was small enough that it apparently did not affect the output concentration.

5.4 EXPERIMENTAL RUN 4

The resin/glass beads weight ratio was changed to 1:90 for Experimental Run 4, thereby increasing the proportion of the resin. The initial concentration of the dye solution was about 0.356 micrograms/liter. Table 7 shows the experimental results. Figure 11a shows the variation of head and downstream flowrate with time. The variation of C_o/C_i with time is plotted in Figure 11b and the position of the phreatic surface with time is shown in Figure 11c.

For the first 3.0 minutes, there was no flow at the downstream end as the wetting front moved through the section. Downstream flow began shortly thereafter and increased to a peak flowrate of approximately 6.9 ml/s. When the head was decreased beginning at $t=27$ minutes, the flow also decreased.

Figure 11b shows the relationship of C_o/C_i versus time. When downstream flow began at approximately $t=4$ minutes, the concentration at the downstream end was nearly zero and remained so until about $t=9$ minutes. From $t=9$ minutes to $t=18$ minutes, the output concentration gradually increased with a very gentle slope. The slope of the curve increases at about $t=20$ minutes and continues to increase until about $t=24$ minutes when the output concentration was much greater than the input concentration ($C_o/C_i=1.2$). The output concentration remained constant at $C_o/C_i=1.5$ from $t=28$ to about $t=32$ minutes

Table 7- Experimental Run 4

Glass Beads: 1mm size
 Resin/Glass Bead Wt Ratio: 1/90
 Water temperature (Celsius): 26.5 degrees
 Initial fluorometer reading: 28.00
 Corrected fluorometer reading: 29.16
 Initial concentration:(microg/l) 0.356

Time (min)	Head (cm)	Fluorometer Reading	Co (microg/l)	Co/Ci
0.0	0.0	No Flow	--	--
1.0	2.0	No Flow	--	--
2.0	4.0	No Flow	--	--
3.0	6.0	No Flow	--	--
4.0	8.0	0.0	0.000	0.000
5.0	10.0	0.0	0.000	0.000
6.0	12.0	0.5	0.006	0.018
7.0	14.0	0.5	0.006	0.018
8.0	16.0	0.0	0.000	0.000
9.0	18.0	1.0	0.013	0.036
10.0	20.0	1.0	0.013	0.036
11.0	20.0	2.0	0.025	0.071
12.0	20.0	2.5	0.032	0.089
13.0	20.0	3.0	0.038	0.107
14.0	20.0	4.0	0.051	0.143
15.0	20.0	4.5	0.057	0.161
16.0	20.0	6.0	0.076	0.214
17.0	20.0	7.0	0.089	0.250
18.0	20.0	8.5	0.108	0.304
19.0	20.0	10.5	0.133	0.375
20.0	20.0	12.0	0.152	0.429
21.0	20.0	15.5	0.197	0.554
22.0	20.0	19.5	0.248	0.696
23.0	20.0	24.0	0.305	0.857
24.0	20.0	33.0	0.419	1.179
25.0	20.0	37.0	0.470	1.321
26.0	20.0	40.0	0.508	1.429
27.0	20.0	40.5	0.514	1.446
28.0	18.0	42.5	0.540	1.518
29.0	16.0	42.5	0.540	1.518
30.0	14.0	42.0	0.533	1.500
31.0	12.0	42.5	0.540	1.518
32.0	10.0	43.0	0.546	1.536
33.0	8.0	44.5	0.565	1.589
34.0	6.2	46.0	0.584	1.643
35.0	5.0	48.0	0.610	1.714
36.0	4.0	52.0	0.660	1.857
37.0	3.5	54.0	0.686	1.929
38.0	Stop	Stop	Stop	Stop

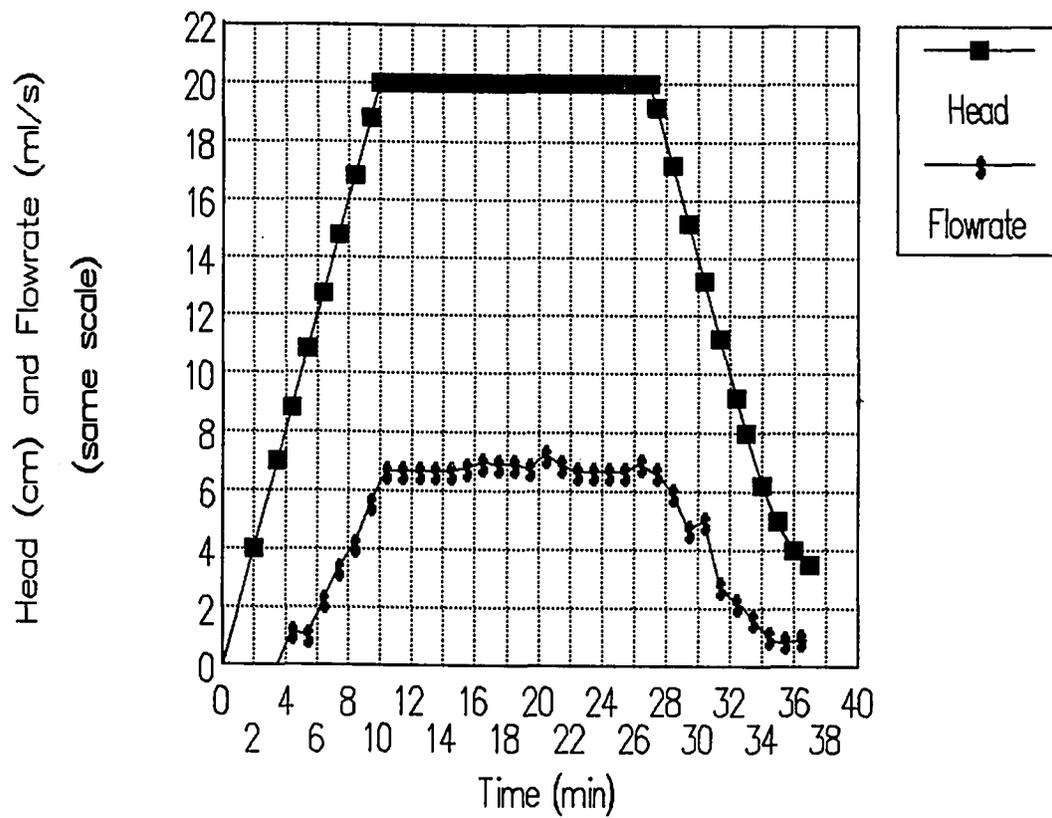


Figure 11a- Head and Flowrate vs. Time; Run 4;
Resin ratio 1:90

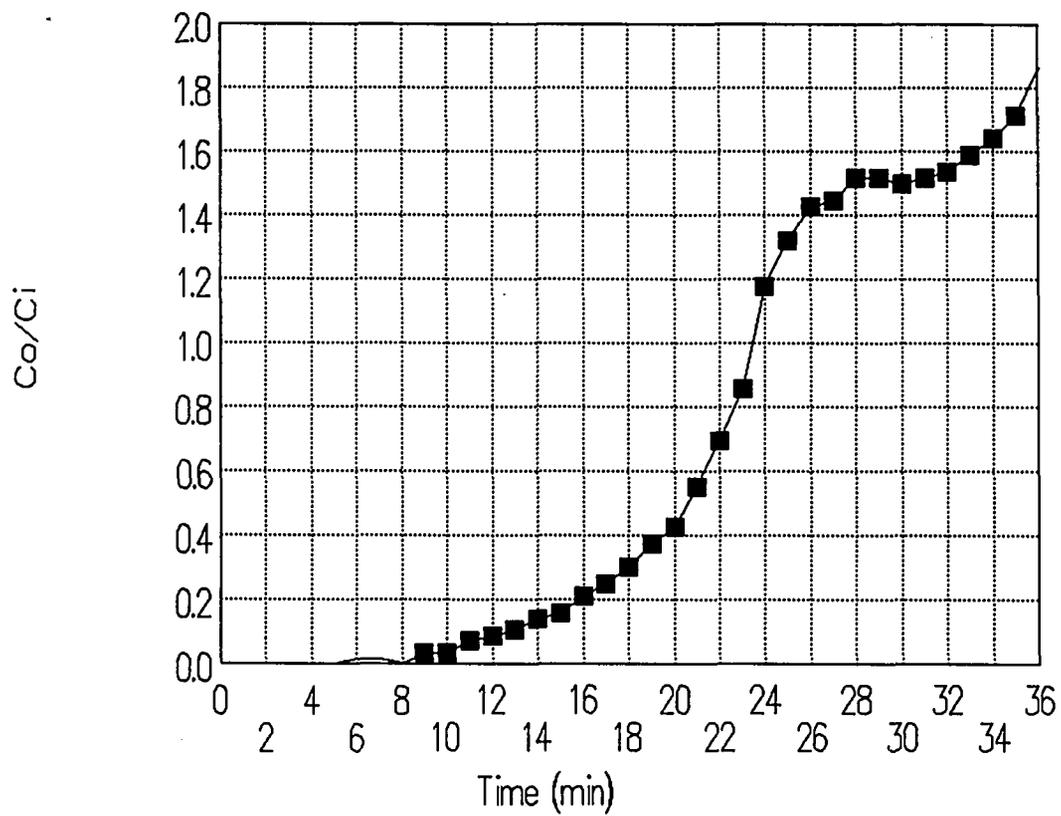


Figure 11b- C_o/C_i vs. Time; Run 4; Resin ratio 1:90

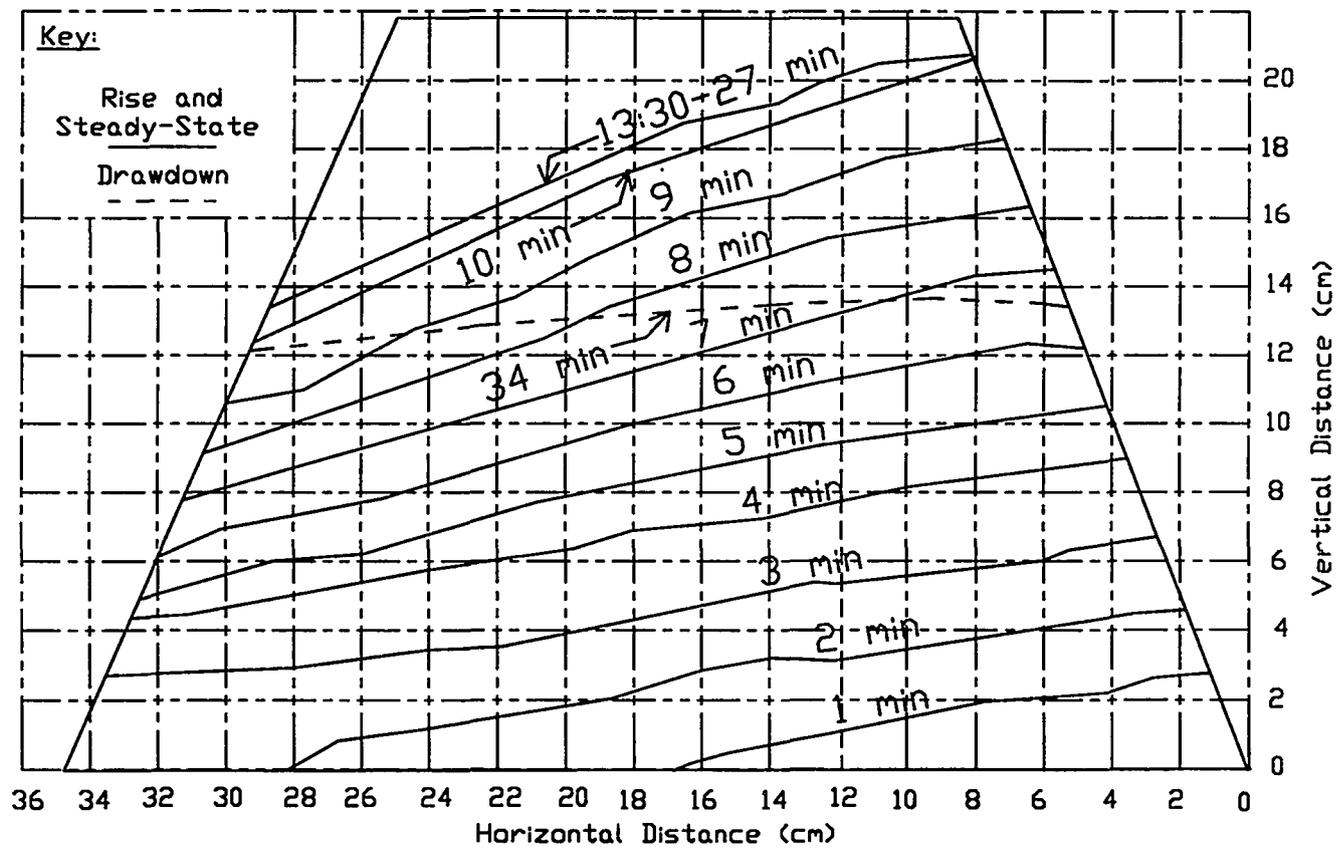


Figure 11c- Phreatic Surface vs. Time; Run 4; Resin ratio 1:90

before increasing again. By the end of the experiment, the output concentration was about 1.9 times greater than the input concentration.

The shape of the curve in Figure 11b can be explained as follows: Initially, the resin pellets' adsorption sites are free and almost all of the dye is adsorbed. At later times, the adsorption sites are utilized; and, in addition, the dye is displaced from some of the adsorption sites by cations which are more strongly preferred by the resin. Both of these phenomena lead to higher fluorescence levels at later times. (See Section 5.4 for further discussion.)

The changes in slope and the plateau in Figure 11b are probably due to different cations in the solution (Ca^{2+} , Mg^{2+} , etc.) displacing the dye at different times. Because the amount of resin used in this run is greater than in earlier runs, the amount of dye that is displaced back into solution is also much greater. This explains the larger C_o/C_i ratios.

5.5 EXPERIMENTAL RUN 5

The proportion of the resin in the porous medium was substantially increased in Run 5 to a resin ratio of 1:18. The initial concentration of the dye solution was about 0.532 micrograms/liter. Experimental results are shown in Table 8. Figure 12a shows the variation of head and downstream flowrate with time. The variation of C_o/C_i with time is plotted in

Table 8- Experimental Run 5

Glass Beads: 1mm size
 Resin/Glass Bead Wt Ratio: 1/18
 Water temperature (Celsius): 26 degrees
 Initial fluorometer reading: 42.50
 Corrected fluorometer reading: 43.66
 Initial concentration:(microg/l) 0.532

Time (min)	Head (cm)	Fluorometer Reading	Co (microg/l)	Co/Ci
0.0	0	No Flow	--	--
1.0	2	No Flow	--	--
2.0	4	No Flow	--	--
3.0	6	No Flow	--	--
4.0	8	No Flow	--	--
5.0	10	No Flow	--	--
6.0	12	No Flow	--	--
7.0	14	No Flow	--	--
8.0	16	1.0	0.013	0.024
9.0	18	1.0	0.017	0.031
10.0	20	2.0	0.033	0.063
11.0	20	1.0	0.017	0.031
12.0	20	1.0	0.017	0.031
13.0	20	0.0	0.000	0.000
14.0	20	1.0	0.017	0.031
15.0	20	0.5	0.008	0.016
16.0	20	0.0	0.000	0.000
to	20	0.0	0.000	0.000
25.0	20	0.0	0.000	0.000
26.0	20	0.0	0.000	0.000
27.0	20	0.0	0.000	0.000
28.0	20	0.0	0.000	0.000
29.0	20	0.0	0.000	0.000
30.0	20	0.0	0.000	0.000
31.0	19	0.0	0.000	0.000
32.0	18	0.0	0.000	0.000
33.0	17	0.0	0.000	0.000
34.0	16	0.0	0.000	0.000
35.0	15	0.0	0.000	0.000
36.0	14	0.0	0.000	0.000
37.0	13	0.0	0.000	0.000
38.0	12	0.0	0.000	0.000
39.0	11	0.0	0.000	0.000
40.0	10	0.0	0.000	0.000
41.0	9	0.0	0.000	0.000
42.0	8	0.0	0.000	0.000
43.0	7	0.0	0.000	0.000
44.0	6	0.0	0.000	0.000
45.0	Stop	Stop	Stop	Stop

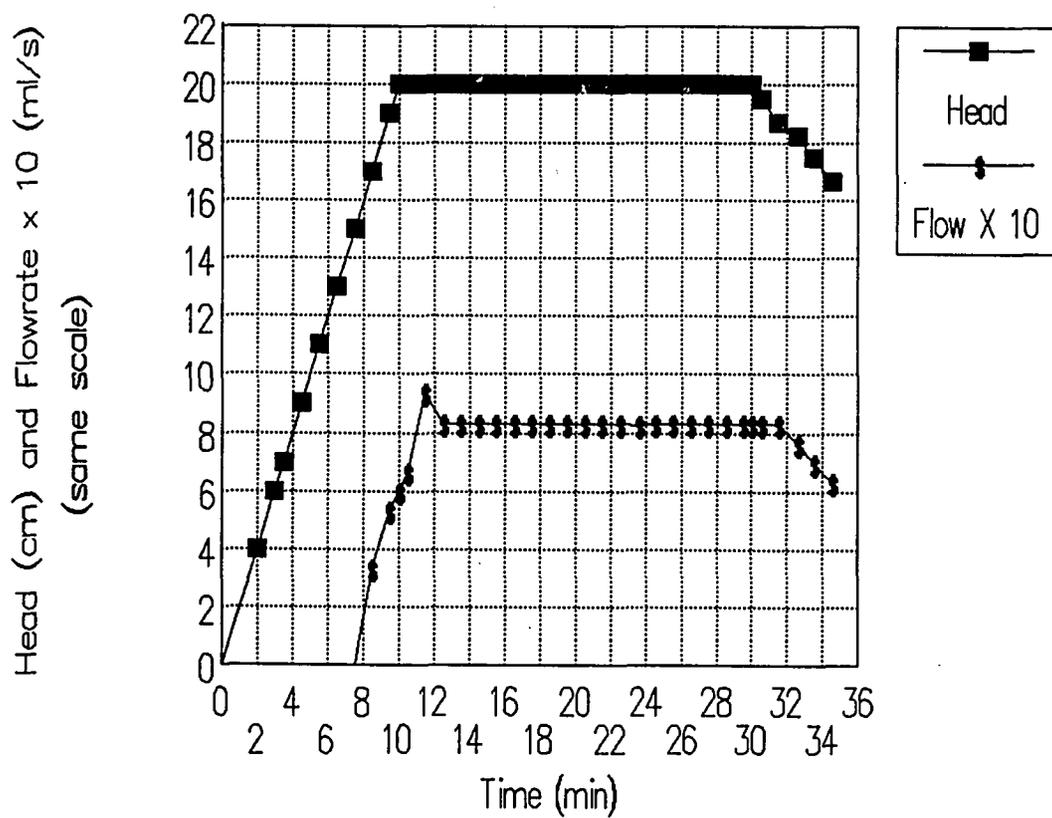


Figure 12a- Head and Flowrate vs. Time; Run 5;
Resin ratio 1:18

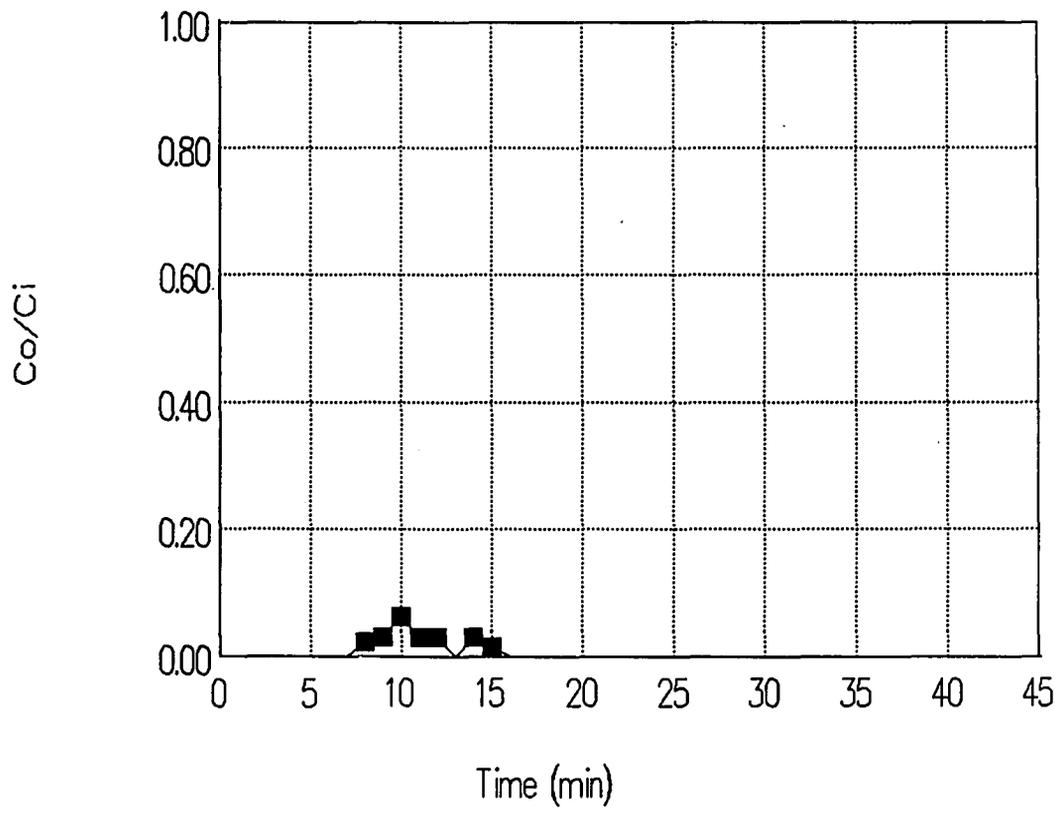


Figure 12b- Co/Ci vs. Time; Run 5; Resin ratio 1:18

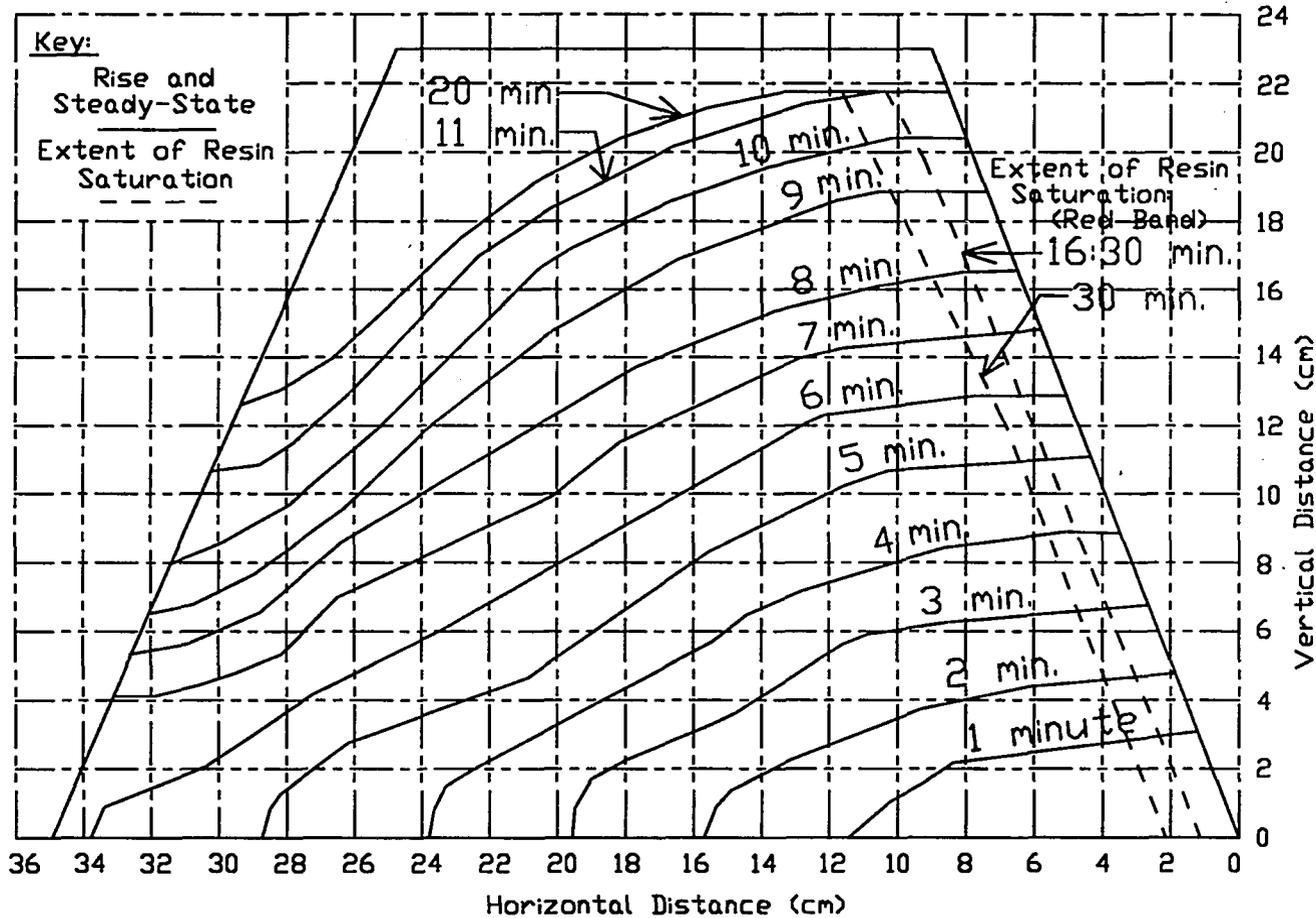


Figure 12c- Phreatic Surface vs. Time; Run 5; Resin ratio 1:18

Figure 12b and the position of the phreatic surface with time is shown in Figure 12c.

For the first 7.5 minutes, there was no flow at the downstream end as the wetting front moved through the section. Downstream flow began shortly thereafter and increased to a peak, constant flowrate of 0.83 ml/s. When the head was decreased beginning at $t=30$ minutes, the flow also decreased after a lag period of almost 2 minutes. The lag time, the fact that downstream flow does not even begin until 7.5 minutes, and the very low peak flowrate are all reflections of the very low permeability of the composite porous medium in comparison to earlier runs. The permeability was lower because of the large amount of small resin pellets. The low permeability is also evident in the large head losses across the dam in Figure 12c and in the permeability value reported in Table 1 (Chapter 3).

During Run 5, the amount of resin was so great that no dye made it through to the downstream end. The low fluorescence measured between times 8 and 15 minutes was probably due to another source as will be explained later. The water at the downstream end during that period had a visible, light amber color similar to the color of the resin pellets. This color gradually disappeared and was only slightly noticeable at $t=20$ minutes. Color in the outflow stream was not visibly evident after $t=30$ minutes.

Owing to the efficiency of the upstream resin pellets in adsorbing the dye, the low fluorescence between $t=8$ and 15 minutes was probably not due to the dye. The low fluorescence was probably due to some of the resin being dissolved into the outflow stream. While the manufacturer lists the resin pellets as being insoluble in water, they appeared to be slightly soluble. The coloration in the outflow stream matched the coloration of the resin pellets.

It was verified in separate experiments that if enough clean resin pellets (i.e.-pellets to which no dye had adsorbed) are dissolved and/or suspended in a water sample, the sample will show a slight fluorescence similar to what was observed in this run. The results of these separate experiments using clean resin pellets partially dissolved and/or suspended in water are shown in Figure 13.

The concentration of resin pellets in a water sample is plotted versus the fluorescence that sample exhibits. The lower curve in Figure 13 shows the fluorescence of quiescent samples whose fluorescence is probably primarily due to dissolved resin. The upper curve shows the fluorescence of a sample that is vigorously shaken right before placement in the fluorometer. The difference between the two curves is due to suspended resin pellets. The fluorescence of a sample taken during the regular experimental runs would likely lie somewhere between the two curves. Figure 13 clearly shows

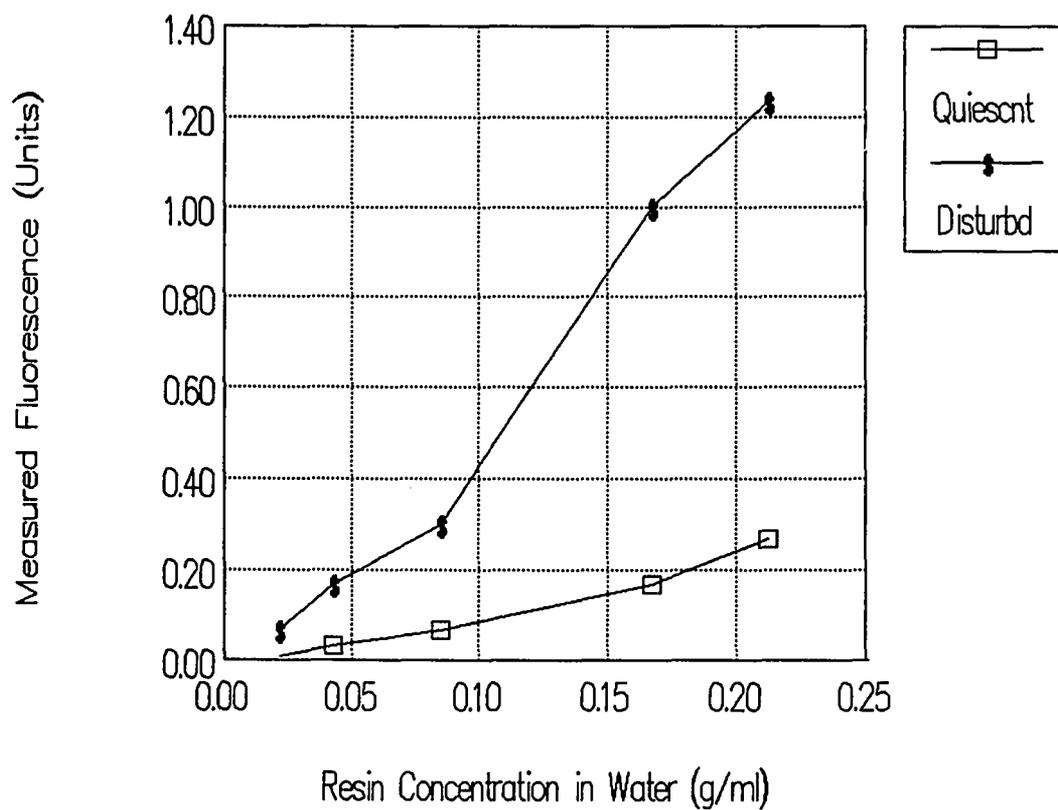


Figure 13- Fluorescence of the Resin in Water

that dissolved or suspended resin pellets entering the outflow stream could account for as many as two fluorescence units. Two fluorescence units was also the maximum fluorescence measured in Run 5.

As the experiment proceeded, a band of pink or red coloration was visible in the porous medium near the upstream face. (See Figure 12c.) The colored band was approximately parallel to the upstream face and was approximately 1.5-2 cm wide at $t=16.5$ minutes. The band gradually increased in width to about 2-3 cm by $t=30$ minutes. It is theorized that the amount of resin in the porous medium was so great that it adsorbed virtually all of the dye within the first few centimeters of flow. The resin pellets were colored red when they adsorbed the red dye. The density of the resin pellets in the porous medium was high enough in Run 5 that this coloration was highly visible. After the experiment was terminated, visual inspection revealed that the resin pellets near the upstream face were red in color, but the glass beads remained colorless.

Individual resin pellets in the other experimental runs also became colored, but the coloration was not as evident due to the lower resin content. Coloration of the resin pellets in other experimental runs also occurred throughout the dam rather than in one single band near the upstream face as it did in Run 5. This was due to less efficient adsorption near

the upstream face in the other experimental runs due to lower resin ratios.

Experimental Run 5 was terminated at $t=45$ minutes because the resin pellets seemed to have a great amount of adsorption capacity left. It was felt that no dye would break through for several hours. Had the experiment continued, it is hypothesized that the red band would gradually have increased in width until its extreme edge would have reached the downstream face. In the meantime, the dye would gradually have begun to break through.

6.0 FINDINGS

From these experiments, several principles were learned that will be useful in conducting further experiments of this nature. These principles are enumerated below:

- 1) The Rhodamine WT dye calibration curve (Figure 3 in Chapter 4) was experimentally determined, relating a solution's fluorescence to its concentration. It was shown that the solution's fluorescence is linearly related to its concentration for the range of concentrations used in these experiments.

- 2) Adsorption curves for the resin and two sizes of glass beads were experimentally determined (Figures 4-6 in Chapter 4). The adsorption data for the resin is particularly useful when determining the proper amount of resin to use in simulated porous media to achieve the desired adsorption capacity. It is shown in Figure 4 that the adsorption ratio for the resin is linearly related to the initial concentration of the solution.

3) Downstream flowrate and the position of the phreatic surface as a function of time and variable head were experimentally determined. These data can be used to calibrate computer and numerical models, check the results of such models or to develop empirical relationships.

4) Figures showing C_o/C_i as a function of time can also be used to calibrate chemical transport numerical models which consider adsorption effects. Few physical models have included adsorption effects. However, when using the results of Experimental Runs 3-5, the user must be careful to separate out the effects of cations in the solution displacing the dye on the resin as was discussed in Section 5.3.

5) While performing the experiments, several deficiencies in the experimental setup and in the experimental procedures were discovered. Suggestions for remediation of these deficiencies are made in the next section. These suggestions and other insights gained during the current experiments will prove to be valuable to the success of future work.

7.0 SUGGESTED IMPROVEMENTS

Several improvements should be made to the existing laboratory setup:

1) The upstream, dye solution reservoir should be increased in size so that refilling is not necessary during a single experimental run and so that experiments may be extended for a longer duration. A 25 to 30-liter reservoir should be sufficient.

2) The problem presented by other cations in the solution displacing dye cations that had adsorbed to the resin was discussed in Sections 5.3 through 5.5. This problem can be avoided by using dilution water which is free of cations; or at least, free of cations that are preferred above the dye cations. High concentrations of cations that are not preferred above the dye cation should also be avoided (James M. Montgomery, Consulting Engineers, Inc., 1985).

3) Because it was observed that dye-covered resin pellets do wash out of the dam and because these resin pellets can affect the output stream's fluorescence if they become suspended, the output stream should be filtered to removed them. The washed-out resin pellets did not significantly affect the results presented in this report, but one should not ignore the potential for such deleterious effects.

4) If record of the phreatic surface is desired, a way to minimize the capillary fringe or a way to measure the true phreatic surface in spite of the capillary fringe should be devised. Some techniques that would minimize the capillary fringe such as spraying the glass beads with silicon or using glycerin as the permeating fluid would interfere with adsorption effects of the resin. Piezometers may be a suitable solution.

5) The current setup is much too labor-intensive, requiring three or more people for a single run. Tasks now performed by humans should be automated as discussed in further detail in items that follow.

6) One task that should be automated is the upstream head/flow control. At the very least, a flow control faucet or gauge requiring minimal human regulation should be installed in-line. This would be an improvement over the current "hose pinching" technique. Ideally, a fully automated system would be employed. A computer could be programmed for the desired head variation and would control electronic pumps and/or gauges. Sensors would measure the actual head and report to the computer.

7) Flowrate measurement at the downstream end should also be automated. The computer could control an in-line flowrate measuring device and record the results.

8) It would be useful to simultaneously measure concentrations at many different locations throughout the simulated dam. This is very labor-intensive and is difficult to do with current fluorometers which require discrete samples of a few milliliters and also require at least five seconds to register a reading. Continuous-flow fluorometers are available but require (for proper

operation) flowrates that are too large. They can also only measure one input stream.

To be done effectively, this task would have to be automated. Samples would be automatically collected at desired times, catalogued and set aside until such time as they could be inserted one-by-one into the fluorometer. Figure 14 presents a conceptual design for accomplishing this task and is discussed in more detail below.

The locations within the dam from which samples are collected should be permanent ports. The ports (shown in Figure 14) are small chambers which are pervious to flow, but are sealed at the outer walls.

A syringe needle is inserted through one wall of the chamber. Samples are withdrawn through the needle. On the exterior of the dam, the sample flows through the needle and into small diameter plastic tubing connected to a small pump. One sample in the tubing is separated from the next by an air gap which is introduced into the tubing by opening an air valve as the pump continues to pump. The tubing must be small enough in diameter that the samples are kept separated by capillary forces even after the pump is disconnected.

The tubing must be long enough that samples collected at the start of the experiment do not reach the pump before the

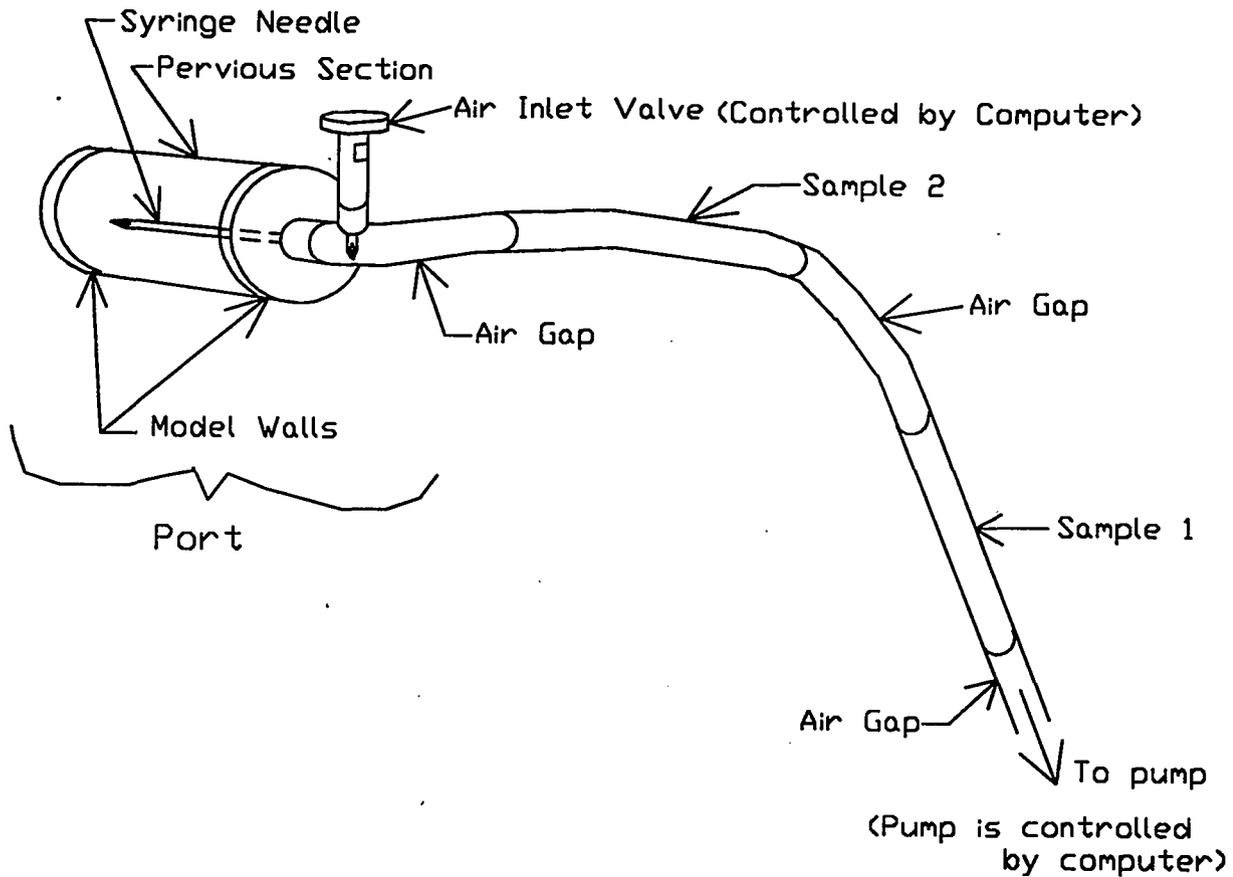


Figure 14- Conceptual Design for Sample Collection System

end of the experiment. At the termination of the experiment, the samples may be extruded one-by-one from the tubing and into test tubes for insertion into the fluorometer.

Obviously, many refinements will have to be made to this very conceptual design which is meant to serve only as a starting point. But the fact remains that some design must be developed to minimize the labor required, yet give the data desired.

Unfortunately, many of the improvements suggested in the above list require considerable capital, expertise and work. However, they will greatly improve the usefulness and ease of operating this experiment.

In addition to the improvements suggested above, the experimenter should be aware of the following operating guidelines:

- 1) The experiment operator must remember to turn on the fluorometer approximately 30 minutes before the experiment begins to allow it to "warm-up" and thus function properly.

- 2) Outflow water may be contaminated with resin pellets washed into the stream and should not be reused from one run to the next.

3) The glass beads may be reused from one run to the next if they are thoroughly washed and checked for background levels of fluorescence and contamination by resin pellets. A method for doing this is discussed in Chapter 3.

4) A method must be developed to compact the same porous medium to the same consistent and uniform dry density. A method to measure the density must also be developed.

5) The temperature of the water should always be recorded and temperature corrections be made to the measured fluorescence. The temperature correction is presented in Section 4.1.3.

6) For consistent results, the same fluorometer should be used for all experimental runs. The University of Arizona I.D. number for the fluorometer used in these experiments is A-023699.

7) The glass bead size used in these experiments seemed to work well, but it is not the only size available. (See Section 4.4 for a description of the size used.) Many other sizes are available from the same manufacturer (Potters Industries, Inc., 1990).

8.0 CONCLUSIONS

The objectives set forth in the introductory section of this report were met by this research:

1) Quantitative records of the downstream flowrate, location of the phreatic surface and the output concentration were kept that can be used to calibrate various kinds of computer and numerical models or to test such models. Models that predict flow/flow patterns and those that predict chemical transport can be used in conjunction with these results.

2) Several basic properties of chemical transport and adsorption are revealed in these results and discussed herein, such as the basic shape of the adsorption curve, ion exchange behavior, and the fluorescent nature of the dye and the resin.

3) Most importantly, a methodology for laboratory simulation of pollutant transport was developed and

tested. Several suggestions based upon what was learned from the current research were made that will improve future experiments of this nature.

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