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Predicting the movement of a radionuclide through soil

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PREDICTING THE MOVEMENT OF
A RADIONUCLIDE THROUGH SOIL

by

Phillip Alexander Plato

A Dissertation Submitted to the
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Major Subject: Sanitary Engineering

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Signature was redacted for privacy.

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INTRODUCTION

Purpose of the Thesis

Nuclear installations located in isolated areas have disposed of radioactive wastes in a variety of ways into the soil environment. Such a waste handling technique has been employed using subsurface and surface seepage pits in which significant quantities of the liquid phase of the waste material were permitted to percolate into the soil surrounding the waste pits. Ground storage has also been used for sealed containers filled with radioactive waste materials. Although the sealed containers were designed to minimize the release of their waste products into the soil, attention was nevertheless given to the possibility of an accidental leakage from such containers.

When a liquid radioactive waste enters a soil formation, either by accident or by design, the waste material may eventually find its way to man. The path to man may be relatively short such as the direct uptake of the waste by plants growing in the soil near the disposal site. However, such sites are carefully chosen so that they are not located near human food sources. A much longer path to man does exist, however, through an aquifer located beneath a radioactive waste storage area. Radionuclides with long half lives which are able to migrate through the soil to the water table may be carried long distances by ground water and eventually reach man,

either indirectly through plants and animals or directly through his ingestion of the water as part of his diet.

The 1957 report of the National Academy of Sciences' Committee on Waste Disposal concluded that radioactive wastes could be disposed of safely in a variety of ways in many locations throughout the United States (19). The conclusion was based on preliminary investigations concerned with the feasibility of disposing of radioactive wastes into shallow pits, deep wells, and salt cavities. However, the committee indicated that more knowledge was needed concerning the rate of movement of critical radionuclides through soil before ground disposal techniques could be used extensively.

The purpose of this study was the development of a reliable method for predicting the movement of ions through soil formations underlying a waste seepage pit. By developing a method for predicting the rate of movement of one ionic species through soil, it was felt that the procedure could be expanded to include several or even all of the elements which are incorporated into a typical nuclear waste. Such a prediction technique was also seen to have possible applications to non-radioactive wastes in which ionic movement through soil was of prime concern. The work done by Preul and Schroepfer (27) with ammonia ions was recognized as a good example of an application of the results obtained from this study to a problem involving ground disposal of a non-radioactive waste.

The element chosen for this study was strontium. This

element was selected for the following reasons:

- ⊙ strontium is a major constituent of many radioactive liquid wastes;
- ⊙ strontium is chemically similar to calcium which is an element that is used in the synthesis of teeth and bones.

Experimental Approach Taken

Work had been done at Iowa State University by LeBlanc (15) on the movement of ^{137}Cs and ^{90}Sr through soil. LeBlanc assumed that the soil beneath a waste seepage pit would be saturated, homogeneous, and isotropic. A liquid radioactive waste entering such a soil would then have an equal probability of moving through the soil in any radial direction from the seepage pit. Although soil is not isotropic, this assumption permitted LeBlanc to make a laboratory investigation under idealized conditions. If a truly isotropic soil existed beneath the seepage pit, then a soil sample taken at any location beneath the pit would be identical to a soil sample taken at any other location beneath the same pit. The flow through a small increment of soil was assumed to be in one direction due to the radial movement of the waste solution from the seepage pit. The soil increment was modeled in the laboratory in the form of soil columns containing disturbed soil samples obtained from the Ames Laboratory Research Reactor (ALRR) site. The soil samples were tested to determine the rate at which they adsorbed strontium from solution.

Influent solutions were fed to the soil columns from an overhead reservoir. Effluent samples were collected from the bottom of the columns for analysis. A diagram showing the apparatus used for LeBlanc's soil column experiments is shown in Figure 1.

LeBlanc attempted to correlate the velocity at which contaminated water would flow through soil with the velocity at which a waste solution would move through the same soil. If such a relationship could be found, then a relatively simple set of tests could be run on a soil through which a waste solution was to be passed. These tests would be designed to measure the permeability and adsorption capacity of the soil. From these laboratory tests, the rate of movement through the soil profile of the elements contained in the waste solution could be accurately predicted. In order to measure the rate of movement of distilled water through his soil samples, LeBlanc used fluorescein dye as a hydraulic tracer. LeBlanc arrived at an empirical equation, based on the data collected from his soil columns, for the prediction of the movement of cesium and strontium through soil.

In an effort to continue the work begun by LeBlanc, some preliminary investigations were made using his soil-strontium system. Several soil columns were tested using the apparatus and analytical techniques outlined by LeBlanc in an attempt to reproduce his results. LeBlanc's apparatus, shown in Figure 1, was assembled, and an influent solution was prepared which

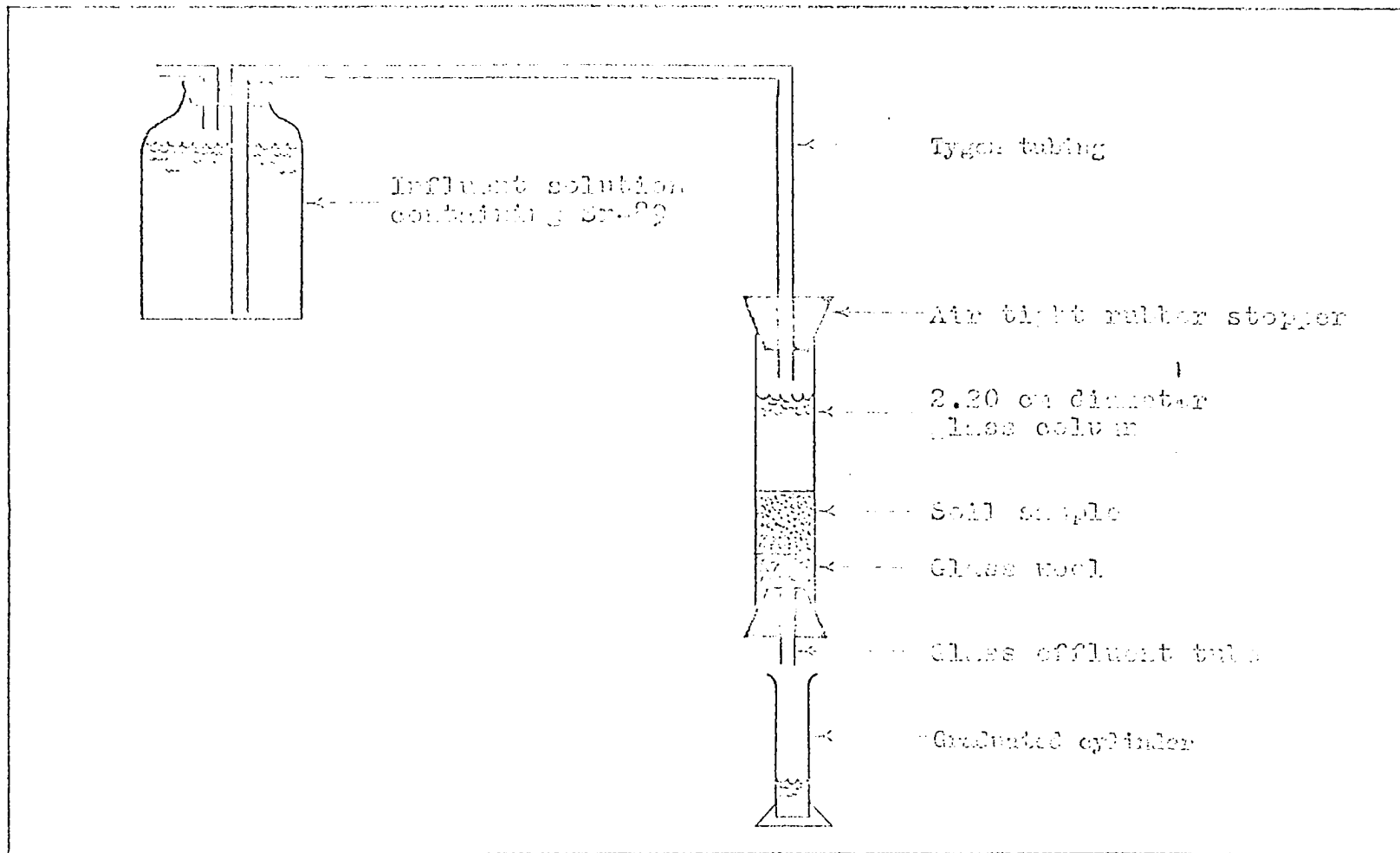


Figure 1. Apparatus used for the initial soil column experiments

consisted of a strontium carrier tagged with ^{89}Sr and approximately 50 mg/l CaCO_3 used to simulate the hardness expected from ordinary tap water. LeBlanc's prediction equation excluded the need for knowing the values of such parameters as influent concentration and flow rate. Therefore, during the initial set of experiments little attention was paid to the exact strontium concentration of the influent solution, and no effort was made to control the flow rate through the soil columns.

The data obtained from the initial set of experiments designed to reproduce LeBlanc's work were erratic and inconsistent. The data obtained from a particular soil column experiment could not be reproduced even when all of the variables were apparently held constant.

While an empirical approach is often expeditious, it does not attempt to describe the actual phenomena which govern the event being studied. In order to be able to accurately predict the movement of ^{90}Sr through a soil profile the individual and combined effects of many transport mechanisms must be understood. An attempt was made to determine which mechanisms would influence the movement of cations through soil. This would have permitted a detailed study of the exact effects of the individual mechanisms on the migration of ^{90}Sr through soil.

Properties of the soil matrix itself were found to be major contributors to ionic movement through soil. These pro-

properties included the relative volumes of air and water within the soil mass, as well as the ion exchange capacity and specific surface area of the solid particles. Collins (5) described the interrelationships among the various soil matrix properties and how those properties affected the movement of liquids through soil. Interfering ions present in the solid, liquid, and gas phases of the soil system must also be considered. Air pressure, soil suction, osmotic pressure, and temperature are other important factors. Finally, there are biotic factors such as plant and microorganism growth within the soil which influence the movement of ions through the soil.

Although the soil samples used in the laboratory soil columns were sieved to produce a more homogeneous soil, the techniques employed in the laboratory tests did not permit good control of the individual transport mechanisms. In an attempt to examine the mechanisms a cation exchange resin was used to simulate the soil, and stable calcium was used in place of the radiostrontium. The resin provided a means of insuring reproducible exchange columns, and the use of calcium resulted in a rapid analytical technique for measuring cationic concentrations in the influent and effluent samples. The resin-calcium system was used extensively throughout the research schedule as an idealized substitution for the soil-strontium system. The data collected using the resin-calcium system were consistent and reproducible. However, the resin

calcium system was only a model for the more realistic soil-strontium system. An attempt was therefore made to relate the knowledge gained from the use of the ion exchange resin and the stable calcium to the soil medium and strontium.

An equation was developed which would accurately predict the movement of calcium through the ion exchange resin. The equation incorporated the flow rate through the column, the concentration of the influent solution, and the resin bed depth. However, the equation did not prove to be successful when applied to the soil columns using influent solutions containing calcium and stable strontium. An empirical equation was developed which tended to describe the results obtained when calcium solutions were passed through the soil columns. While the empirical equation was partially successful in describing the behavior of laboratory soil columns, the equation was not evaluated to the point where field testing of the equation was considered advisable.

If an empirical equation, based on laboratory studies, could be shown to accurately predict the movement of strontium through laboratory soil models, then it might be desirable to conduct some small scale seepage pit studies in the field to further test the prediction equation. This could be done by constructing a small diameter seepage pit in the field and allowing a known volume of synthetic waste of a known concentration to percolate into the soil at a known infiltration rate. If the waste were tagged with ^{89}Sr , soil samples could

be removed from various locations beneath the pit after the flow of waste had ceased. The soil samples could then be brought to the laboratory and tested for ^{89}Sr content. If the ^{89}Sr content of the soil samples had been previously predicted based on the equation developed in the laboratory, the results from such a field study could be used to determine the desirability of using the prediction equation in the design of actual radioactive waste seepage pits.

The proposed method of field testing the results obtained from the use of laboratory models required a suitable technique for removing the ^{89}Sr from the soil samples. Several extraction techniques were tried in which ^{89}Sr was removed from batch soil samples. Some tests were conducted in which ^{89}Sr solutions were passed through large diameter soil columns. Soil samples were then removed from various depths within the columns and analysed for ^{89}Sr . The same technique was tried with ion exchange resin samples when calcium influent solutions were used. The extraction tests using soil samples indicated that field testing of knowledge gained from laboratory soil columns would be feasible using the soil sampling approach suggested.

After the successful experiments in which the movement of calcium through an ion exchange resin was accurately predicted, some work was done with a tank filled with the resin. A synthetic waste entered the resin through a modeled seepage pit and percolated into the resin in the horizontal as well as

the vertical direction. The two dimensional flow studies were done in an effort to better model the seepage conditions expected under actual field conditions. The extraction procedure previously described proved to be a useful technique in analysing the results of the two directional flow studies. Resin samples were removed from various locations beneath the artificial seepage pit. Any calcium present on the resin samples was extracted, thus enabling the movement of the calcium front through the resin to be followed.

LITERATURE REVIEW

Actual Operation of Radioactive Waste Pits

Radioactive waste pits are used with various degrees of success at several locations within the United States (29). The Hanford Atomic Products Operation (HAPO) uses three separate disposal sites in its operations. By 1958 HAPO had used these sites to dispose of approximately 3×10^9 gallons of waste products containing about 2.4×10^6 curies of beta activity. The gross beta activity of the HAPO waste was kept at 5×10^{-5} microcuries per milliliter, about 500 times the maximum permissible concentration of ^{90}Sr in public water supplies (30). The radioactive wastes at HAPO were transferred into cribs rather than open seepage pits. The solutions were then allowed to pass through the crib walls into the soil. The Ringold formation beneath the cribs consists of about 100 feet of silty clay and 200 feet of sand and silty sand. The water table lies approximately 350 feet below the surface, and the area has an average annual rainfall of seven inches. The transmissibility of the Ringold sediments is about 50,000 gal/day-ft.

At the National Reactor Testing Station at Idaho Falls, Idaho, only small quantities of low level radioactive wastes are deposited into seepage pits. This is due to the relatively high transmissibility of the underlying soil of about 10^6 gal/day-ft and the low cation exchange capacity of the

soil of about 0.015 meq/gram. The depth of the water table around Idaho Falls varies from 200 feet to 500 feet.

The relatively high cation exchange capacity of 0.20 meq/gram of the soil located around the Oak Ridge National Laboratory makes the use of open seepage pits desirable. High water tables together with low cation exchange capacities of the soils around the Savannah River Plant and Brookhaven National Laboratory have made direct disposal into the ground inadvisable at these locations. Ground disposal of radioactive wastes has also been successfully attempted at Mol, Belgium (7), and at the Chalk River site in Canada (23).

Review of LeBlanc's Work

LeBlanc attempted to predict the movement of strontium through soil by using soil columns to represent typical soil increments located beneath a waste seepage pit. His disturbed soil samples were contained in glass columns which were connected to an overhead reservoir containing a synthetic waste solution. The apparatus used by LeBlanc is shown in Figure 1. The waste solution was passed through the soil column, and effluent samples were collected at regular intervals until the strontium concentration in the effluent samples was found to equal the strontium concentration in the influent solution. When this condition was reached, it was assumed that the adsorption capacity of the soil sample for strontium had been exhausted. In addition to using strontium solutions in his soil

column models, LeBlanc also used distilled water containing only fluorescein dye as a hydraulic tracer.

Before a soil column test was begun, the reservoir was sampled to determine the concentration of the influent solution. This initial concentration was designated as C_0 . While a solution with a given initial concentration was passing through the column, effluent samples were taken to determine the concentration C leaving the column after a known volume V of solution had been passed through the column. All of the effluent was collected in the form of 50 ml samples. It was convenient when reporting the breakthrough data collected to normalize the effluent concentrations against the influent concentration being used. The normalized ratio C/C_0 was then plotted against the volume V at which the effluent concentration C was collected. If the material being passed through the soil column were in continuous chemical equilibrium with the soil, and if none of the ions present in the influent solution were to diffuse into the solution initially present in the soil pore spaces, then a plot of C/C_0 versus V , known as a breakthrough curve, would appear as a vertical line extending upward from a particular breakthrough volume. Such a plug flow breakthrough curve is shown in Figure 2. When $C/C_0 = 1.0$ the effluent concentration was equal to the influent concentration, and the column was said to have reached its maximum uptake capacity. If the material being passed through the column was not in continuous chemical equilibrium with the

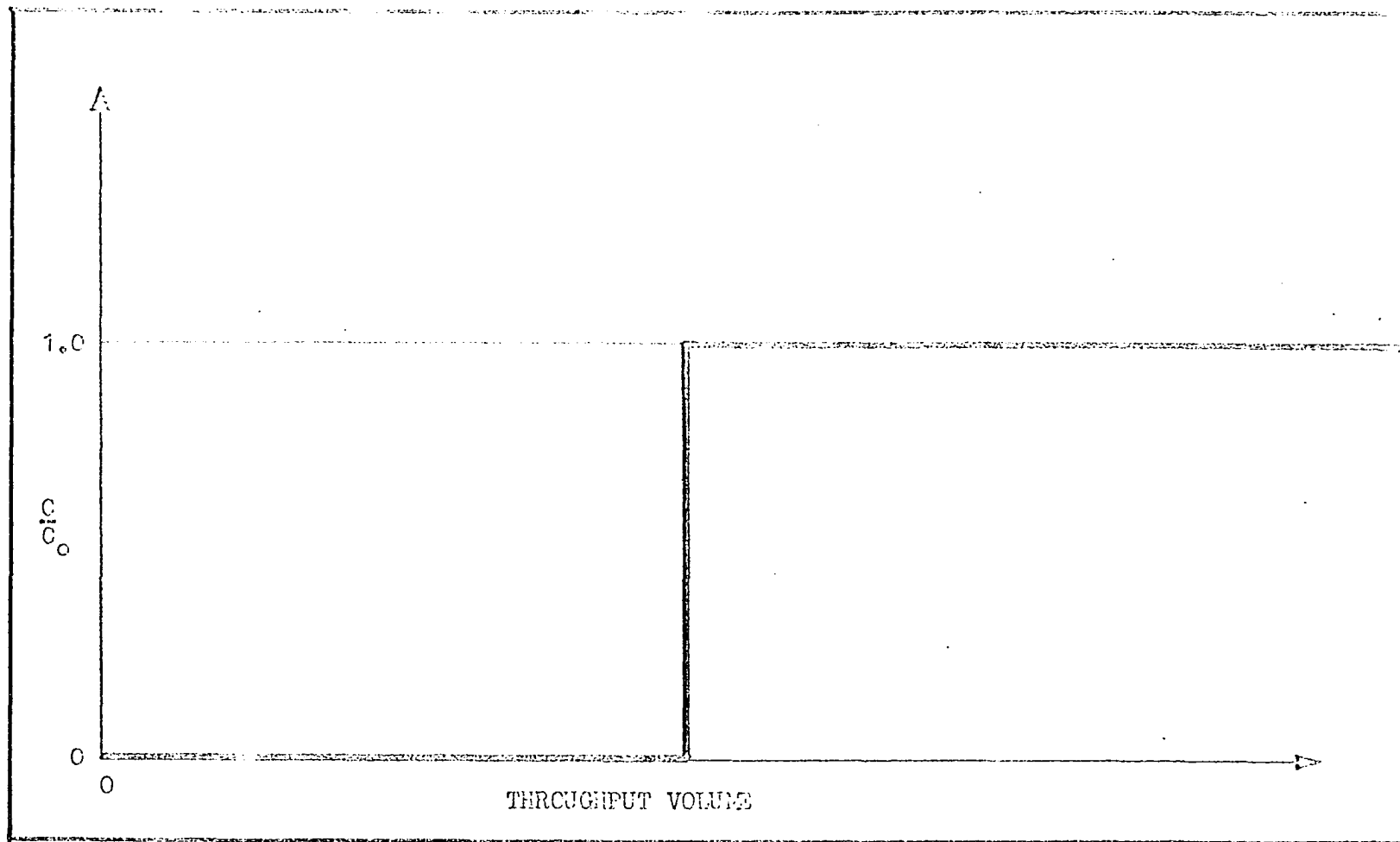


Figure 2. Typical plug flow breakthrough curve resulting from continuous chemical equilibrium between ions in the liquid and solid phases

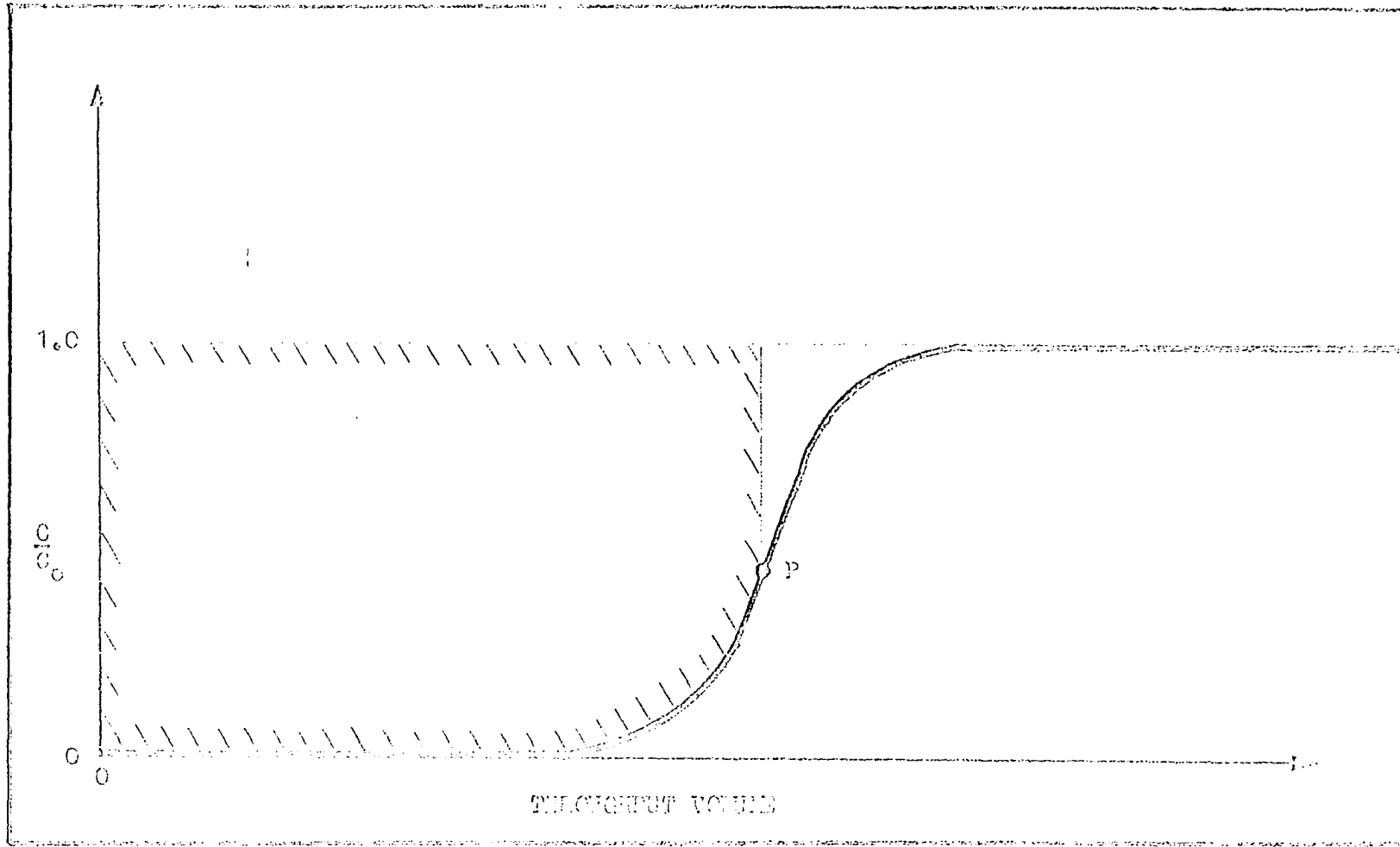


Figure 3. Typical "S-shaped" breakthrough curve

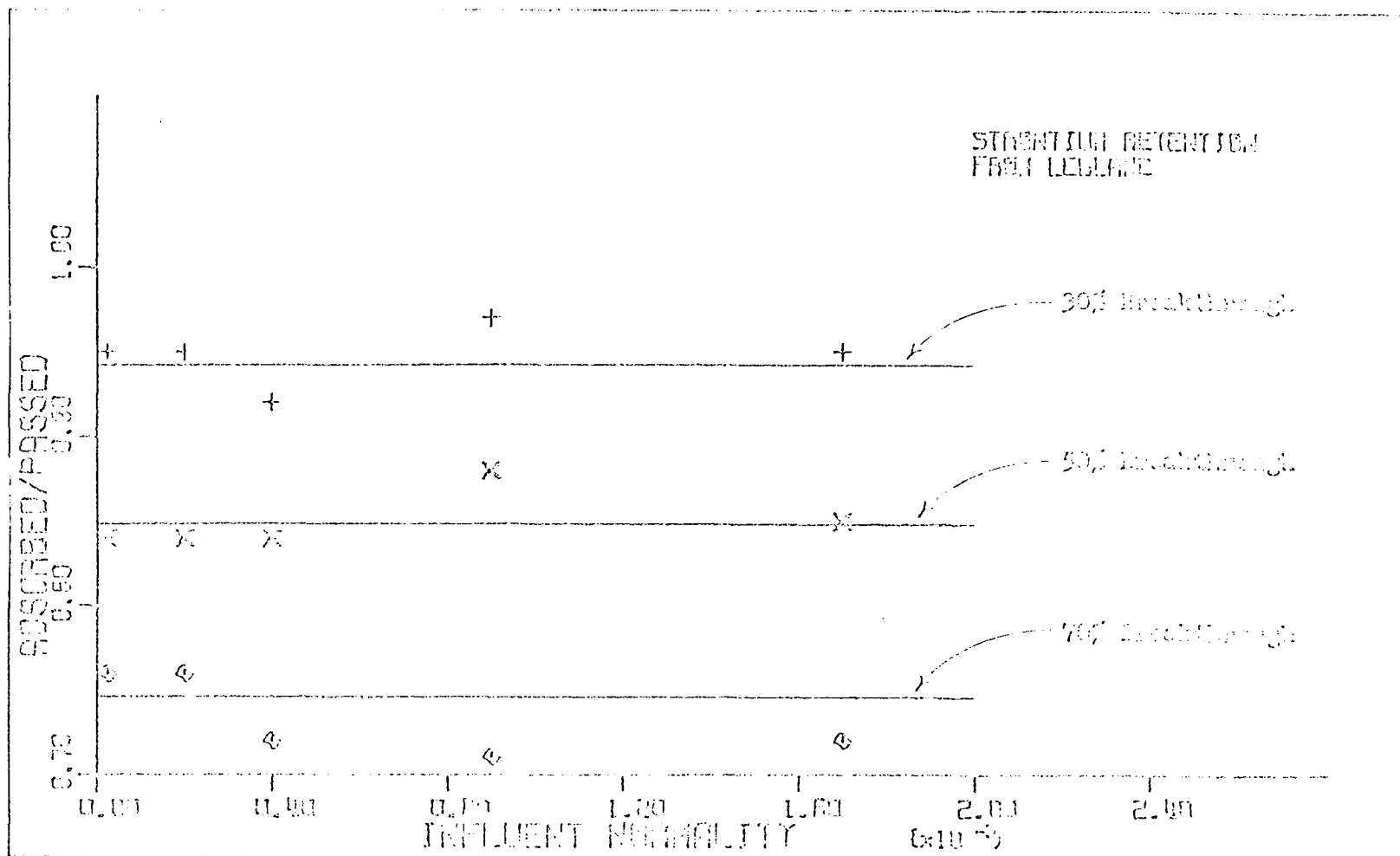


Figure 4. The ratios obtained by LeBlanc of the meq of strontium adsorbed to the meq of strontium passed by soil columns as a function of the strontium concentration in the influent solution -- ratios taken at 30%, 50%, and 70% breakthrough fractions

soil, or if diffusion were taking place at the interface of the influent solution and the soil water, the resulting breakthrough curve would be distorted from the vertical line shown in Figure 2. The breakthrough curve would then be expected to assume an "S-shape", gradually approaching $C/C_0 = 0.0$ at the lower end and $C/C_0 = 1.0$ at the upper end. Such a typical shape is shown in Figure 3. A C/C_0 value greater than unity would indicate some desorption taking place within the soil mass.

LeBlanc formulated an equation designed to predict the movement of strontium through soil. The equation was based on the conclusion that the amount of material adsorbed on the soil per unit amount of material passed by the soil was a function only of the percent breakthrough at which such an observation was made. This conclusion was deduced from the breakthrough data collected by LeBlanc. After a given breakthrough fraction had been reached, LeBlanc determined the amount of strontium which had been deposited on the soil and the amount which had passed through the soil column. The ratio of the strontium adsorbed to the strontium passed was then determined for the breakthrough fraction examined. The ratios for the 30%, 50%, and 70% breakthrough fractions for soil columns operated at various influent solution concentrations were plotted against the C_0 values used for the tests. The results, shown in Figure 4, indicated that the ratios for the breakthrough fractions considered were constant for a

given breakthrough fraction and were independent of the strontium concentration in the influent solution. LeBlanc then postulated that the ratio at a particular value of C/C_0 was a function of that C/C_0 value. LeBlanc's breakthrough prediction equation therefore became

$$Y = a(C/C_0)^b \quad [1]$$

where Y represented the fraction of cations entering the soil column which were retained by the soil. A particular value of Y for a particular breakthrough fraction of C/C_0 determined for a throughput volume of V was determined graphically.

Based on the typical breakthrough curve shown in Figure 3, the value of Y for point P was calculated as

$$Y = \frac{A}{V} \quad [2]$$

where A represented the shaded area shown in Figure 3. The area occupied by the rectangle bounded by ordinate values from zero to one and abscissa values from zero to V became V , the denominator of [2]. Once values of Y were determined for various values of C/C_0 , the constants a and b were determined by taking the logarithm of both sides of [1] and obtaining

$$\log Y = \log a + b (\log C/C_0) . \quad [3]$$

By plotting $\log Y$ versus $\log C/C_0$ on linear graph paper, values for a and b could be determined.

Application of Adsorption Isotherms

The amount of an ionic species which can be adsorbed on a given adsorbent will increase if the ionic concentration is increased. The relationship between the amount of ions adsorbed and the concentration of the ions present in solution at a given temperature is known as the adsorption isotherm. Scheidegger (28) has summarized the use of isotherms with respect to adsorption from fluids flowing under saturated conditions through porous solids.

Relationships describing adsorption isotherms have been postulated by Freundlich and Langmuir (2). The Freundlich equation was given as

$$\frac{X}{M} = KC_0^n \quad [4]$$

and the Langmuir equation was given as

$$\frac{C_0}{X/M} = \frac{1}{AB} + \frac{C_0}{A} \quad [5]$$

where X grams of adsorbate of concentration C_0 were held by M grams of adsorbent. The constants K, n, A, and B, were determined experimentally.

Theoretical Approaches

If soil had no adsorptive properties with respect to strontium ions, then the strontium solution would move through the soil by displacing any other solution which might have been in the soil. This process of miscible displacement has

been studied by Nielson and Biggar (20, 21, 22). The tracer used in their experiments appeared at the end of the soil columns in advance of the time expected had there been no mixing at the boundary of the tracer and tracer-free solutions.

Their column studies were done using a variety of soils as well as glass beads. Various flow rates and moisture contents were also incorporated into their experiments. The most successful mathematical model tested by Nielson and Biggar was their solution to a differential equation proposed by Lapidus and Amundson (14). Their solution was given as

$$C/C_0 = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{x - vt}{\sqrt{4Dt}} \right) + \exp\left(\frac{vx}{D}\right) \operatorname{erfc} \left(\frac{x + vt}{\sqrt{4Dt}} \right) \right] \quad [6]$$

where the breakthrough fraction C/C_0 was described as a function of the column depth x , the linear flow velocity v , the time lapsed t , and a diffusivity constant D . Using [6], Nielson and Biggar were able to closely predict chlorine breakthrough curves using sand and clay loam columns operated at about 30% saturation. Linear velocities were on the order of 0.1 to 3 cm/hour.

Since soil does possess both chemical and physical properties which will affect the movement of ions, it becomes necessary to carefully examine these properties. It may be necessary to view these factors individually as well as to observe how they behave collectively as a system.

McHenry et al. (18) have studied the effects of concentration, pH, other ions, total salt concentration, and the

type of soil with regard to the uptake of radionuclides on soils at the HAPO. In order to determine the equilibrium adsorption capacity at the Hanford site, samples of soil were shaken in test tubes with solutions of various concentrations of strontium. The suspensions were then centrifuged, and the cationic concentration in the supernatant was determined. The difference in concentration of the strontium in solution before and after the shaking process was taken as the adsorption capacity of the soil sample. It was found that the exchange capacity of the soil for strontium under equilibrium conditions was dependent on the hydrogen ion concentration of the suspension. Below a pH of about 3.5 virtually no strontium was removed from solution by the soil. The strontium concentration was $0.001S$, where S represented the saturation concentration of strontium for that particular soil. At a neutral pH approximately 50% of the strontium added was removed. At a pH of 10 about 95% of the strontium added was removed which represented the optimum removal. At a pH greater than 10 the strontium removal efficiency of the soil was observed to decrease.

The amount of strontium adsorbed by the soil was observed to decrease as the concentration of other cations in the strontium solution was increased. It was further observed that strontium adsorption decreased with an increase in valence of the competing cation. The addition of anions to the strontium solution had little effect on the strontium adsorp-

tion capacity of the soil except when large concentrations of anions were used or when high valent anions were used. The addition of PO_4^{-3} increased the adsorption of strontium compared to the amount adsorbed with no interfering ions. It was noted, however, that the resulting pH for the PO_4^{-3} treatments was about 9.0 which was close to the optimum strontium adsorption pH of about 10.0.

In an attempt to predict the rate of movement of strontium through soil, Orcutt et al. (24) tried soil column breakthrough studies using several different types of soil. The cation exchange capacities of their soils ranged from 0.23 meq/100 grams to 15.2 meq/100 grams. They arrived at the relationship

$$F = \frac{S}{1 + \left(\frac{\frac{K}{C}}{\left[1 + \frac{C}{C_0} (K - 1) \right]^2} \right) \left(\frac{ED}{C_0 f} \right)} \quad [7]$$

where F was the linear velocity of that portion of the breakthrough curve having a concentration of C, and S represented the linear velocity of distilled water through the soil. The soil had an exchange capacity of E, a bulk density of D, and a porosity of f. The term K was called an equilibrium quotient. Their approach required that the strontium be in chemical equilibrium with the soil. While the results of several breakthrough curves were given, no attempt was apparently made by Orcutt et al. to apply [7] in order to predict a breakthrough curve.

ALTERNATE APPROACHES

The problem of predicting the movement of radionuclides beneath a waste seepage pit may be investigated by a number of different approaches. These include the use of direct measurements, laboratory models, and mathematical models. The direct measurements approach involves the construction of a model seepage pit at the site on which the actual pit is to be built. The advantage of such an approach is that the data collected will probably represent the actual conditions which will be observed at that particular site better than any other approach. But within this advantage lies one of many disadvantages for this approach. Since this method does not involve an examination of most of the relevant transport mechanisms which govern the movement of ions through soil, it may be exceedingly difficult to relate any information gained from such a study to other geographic locations.

Such a large scale model may require a relatively large cost resulting from the construction of a test pit and drainage wells. A large area of land around a test pit may become contaminated as a result of such a study. Percolation rates through undisturbed soil tend to be low, resulting in a large amount of time required to complete one seepage study. Unforeseen difficulties may also arise from a direct study, such as the eventual wash-out of the contaminating ions present in the influent solution. In addition to the above disadvantages,

there is the possibility of a health hazard resulting from the use of very large volumes of even low level synthetic wastes.

The laboratory model approach involves the physical simulation of actual field conditions. In the case of soil adsorption studies the model may be a one directional flow column of soil or a two directional flow tank containing a soil sample. A disadvantage of such models is that they do not exactly reproduce actual field conditions. Virtually all soil samples removed from their natural environment become disturbed samples. If the samples are screened to remove such things as roots and rocks, the samples become further disturbed. Despite the disturbed nature of the samples used in the laboratory, they are still soil samples and as such are closer to reality than purely mathematical models. Laboratory conditions provide excellent control over the variables which affect the behavior of the actual field operations. It is possible to hold all of the variables constant except one. The effect of that variable on the performance of the model can then be carefully examined.

The final alternate approach considered was the construction of a purely mathematical model. A mathematical model may be derived from the physical and chemical phenomena thought to be responsible for ionic migration through soil. Such a model frequently used in connection with ion exchange columns consists of a mass balance on segmented portions of the column. The exchange column may be considered to be comprised of many

sub-columns, stacked one on top of the other with an infinitely thin membrane separating the segments. A mass balance may then be written for each of the segments which describes the fact that what ever goes into a particular segment must be accumulated within that segment or leave that segment and enter the next segment. The accumulation process may further be described by the mathematical considerations of the ion exchange process. The disadvantage of mathematical models is that they tend to become too idealized. Natural soil characteristics such as root holes and worm holes in soil are neglected.

After reviewing the advantages and disadvantages of the above three approaches, it was decided to investigate the problem of ionic migration beneath a waste seepage pit with the aid of laboratory models. Since a field study would involve much time and expense, it would be desirable to have a good understanding concerning the performance of such test pits before initiating a field study. The concentration and volume of the synthetic waste solutions as well as the dimensions of the modeled seepage pits would have to be determined before the pits could be used successfully. It was the intention of this study to provide the information required to operate a field model of a waste seepage pit. Although time did not permit the scheduling of field tests into this research program, the eventual use of field models will be required to test any results gained from this study.

Since the ultimate goal of this study was the ability to

predict the operating behavior of a waste seepage pit, some thought was given to the method in which knowledge gained from this study would be related to actual field conditions. A conventional method for studying the hydraulic behavior of field soils involves the sinking of wells around a central loading area. This loading area may be an open pit or an injection well. Effluent samples are then collected from the sampling wells.

The approach selected for the field testing of a satisfactory laboratory model was one involving the removal of soil samples for contamination analysis. A synthetic waste solution containing low levels of an ionic species such as strontium would be allowed to percolate through the ground at the testing area. After a predetermined volume of the waste solution had been injected, soil samples from beneath the waste pit would be removed from various depths and taken to the laboratory. There, any strontium present on the samples would be removed using an appropriate extraction process. This technique has the disadvantage of destroying the soil beneath the waste pit and eliminating further tests at that site. However, the necessity for effluent wells is eliminated. The soil samples taken in this manner may also be analysed for various physical and chemical properties which would be relevant to the movement of the waste solution through the soil.

Once it was decided that field tests would be conducted by analysing soil samples for strontium content, a laboratory

technique was sought which would permit the rapid and accurate extraction of strontium from soil. Butler (3) did extensive work in extracting strontium from soil as well as from milk, water, teeth, and vegetation as part of the environmental monitoring program at the Savannah River nuclear installation of the Atomic Energy Commission. Di-2-ethylhexyl phosphoric acid (HDEHP), obtained from the Union Carbide Chemical Company, was used in the Strontium extractions. Soil samples were leached with a 6N solution of HCl and strontium and calcium oxalates were precipitated. A 20% HDEHP solution diluted in toluene was then used to extract any strontium present in a separatory funnel. Using 300 gram soil samples Butler reported a ^{89}Sr sensitivity of 1 pCi/kg. The working time for each sample was approximately two hours.

In addition to his work with the liquid cation exchanger HDEHP, Butler et al. (4) has also used the liquid anion exchanger tri-isooctylamine (TIOA). TIOA extraction was used to isolate 36 different elements into either an aqueous, organic, or strip phase. Using this procedure, Butler reported recovering more than 99% of the strontium dissolved at a known concentration. The method greatly reduced the analysis time required for the separation of chemically similar elements.

The measurement of radiostrontium in soil was done using a relatively simple method by Plummer and Helseth (26). Soil samples were oven dried, screened through a #20 mesh sieve, and composited into 20 gram samples. Gamma-ray spectrometric

analysis was then used for a direct analysis. This procedure employed a 400 channel pulse-height analyser with a 3x3 inch NaI crystal. The overall accuracy of the concentration estimates was given as about $\pm 15\%$. Strontium concentrations of up to 125 pCi/gm were reported with a ^{90}Sr sensitivity of 1 pCi/gram.

In the liquid ion exchange methods of removing strontium from soil samples, large quantities of unwanted elements, especially iron and aluminum, were also extracted. These proved to be difficult to separate from any strontium present without adding additional experimental errors. The presence of high concentrations of the extracting agent was also considered undesirable.

Graham (8) has investigated the possibility of using electro dialysis as a method for removing ^{90}Sr from soil. The method involved the replacement of exchangeable cations in the soil with hydrogen ions similar to the conventional ion exchange process. The soil was placed in a submerged membrane sack made of filter paper. A platinum sheet anode was placed on one side of the sack and a stainless steel cathode was placed on the other side. The electrodes were then connected to a 200 volt D.C. power supply. The hydrolyzed ions migrated through the membrane due to the applied electrical potential. A more sophisticated apparatus was also described whereby the soil sample was placed in the center cell of a three-cell chamber. Permeable membranes were used to separate the three

cells. All three cells were filled with distilled water, and an electrical potential was applied. The cations were collected as hydroxides in the cathode chamber. Strontium recovery was reported as better than 96%.

Kahn (10) described the procedure adopted at the Oak Ridge National Laboratory for determining radionuclides adsorbed on soil. The radionuclides were leached from the soil samples using nitric acid, sulfuric acid, or a combination of oxalic and hydrochloric acids. Carriers were then added to the leach solutions. Leaching efficiencies of 97% to 99% were obtained.

An analytical procedure in which soil samples to be tested for ^{90}Sr were first leached with ammonium acetate was investigated by Martell (17). The filtrate was evaporated to dryness and ashed at 600 °C. The ashed residue was then dissolved in concentrated HCl, and any iron and aluminum present were removed by precipitation as hydroxides. Calcium and strontium were then precipitated from the filtrate as oxalates at a pH of about 6.3. After drying, the filtrate was ready for counting. A very low background counting apparatus was used which included eight inches of steel shielding and a ring of thirteen anticoincidence Geiger-Muller tubes. This resulted in a background of about 0.15 count per minute and permitted the determination of ^{90}Sr in samples with activities as low as one disintegration per minute.

Butler's approach using TIOA appeared to be a relatively

simple technique and was tried with some success. However, the time required for a complete extraction analysis, about four days, was undesirable. Modifications were made to Butler's technique which resulted in faster analyses with no detectable loss in precision.

SOIL-STRONTIUM MODEL OF A SEEPAGE PIT

Apparatus and Materials Used

The technique and apparatus used by LeBlanc was duplicated in some early experiments. It was desired to be able to take all of the soil samples from the same common soil source in order to obtain identical soil samples for successive soil column tests. Therefore, approximately five cubic feet of B-horizon soil were collected from the Ames Laboratory Research Reactor site, allowed to pass a U. S. Standard #4 sieve, and stored in a clean container.

Several soil columns were tested using fluorescein dye as a hydraulic tracer and ^{89}Sr as a tag for strontium solutions. The frequency with which effluent samples were taken varied. For column runs completed in a relatively short time all of the effluent was collected in the form of 50 ml samples. For relatively long column runs only every other sample was analysed for ^{89}Sr content. However, the volume of the samples not analysed was recorded which permitted an accurate determination of the total throughput volume at the time any sample was taken.

Hydraulic Breakthrough Curves

Following LeBlanc's approach the velocity at which uncontaminated water would flow through soil was observed using

fluorescein dye. The dye was found to be detectable at low concentrations.* The columns tested for hydraulic permeability contained 10 gram soil samples taken from the common soil container. A 2.20 cm inside diameter glass column was used. The influent fluorescein concentration was kept at about 50 mg/l. Five milliliter sample volumes were taken and diluted by a factor of 1:100. Aliquots from the diluted solution were then analysed using the fluorometer. Typical results using fluorescein dye are shown in Figure 5.

Radioisotope Breakthrough Curves

In an attempt to examine the behavior of strontium as it moved through soil, synthetic strontium waste solutions were produced using ^{89}Sr as a radioactive tag. Stable strontium in the form of strontium nitrate was also added to the synthetic waste solution, together with 50 mg/l of calcium carbonate. The CaCO_3 was added to the waste solution to simulate the hardness expected if tap water were used in the creation of a strontium waste solution at a nuclear reactor site. Since a basic assumption of the soil column models was that saturated flow conditions would exist beneath a waste seepage pit, it was decided to presaturate each soil column with a 50 mg/l solution of CaCO_3 . This was done to represent tap water which

*A Turner Fluorometer, Model 110, was used to determine fluorescein dye concentrations.

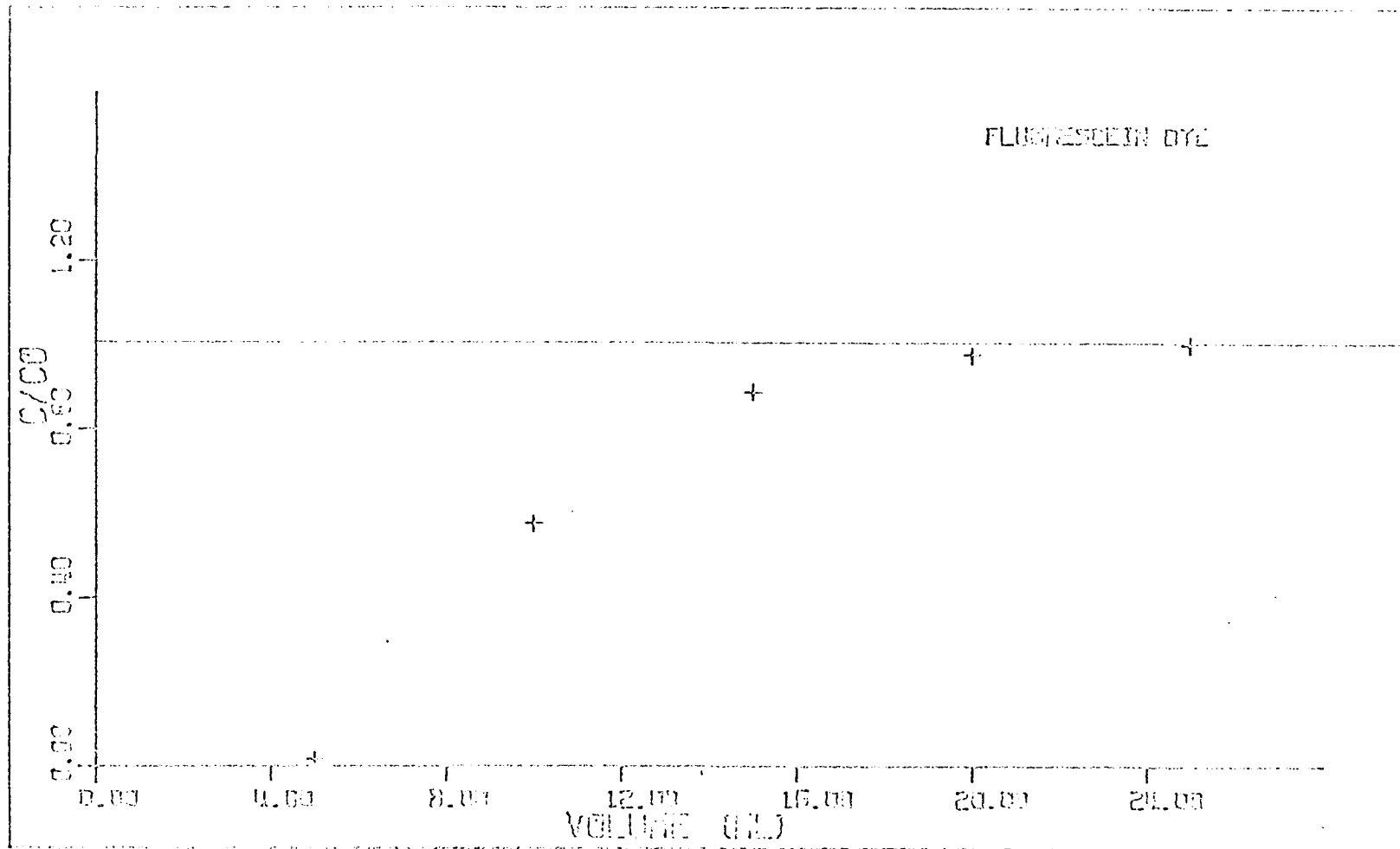


Figure 5. A typical breakthrough curve obtained by passing a 50 mg/l solution of fluorescein dye through a 2.20 cm diameter soil column with a depth of one inch

might be introduced into the seepage pit prior to the injection of a radioactive waste.

The soil columns were constructed using 10 gram soil samples taken from the same soil container used for the hydraulic breakthrough columns. This resulted in a soil depth of approximately one inch in the 2.20 cm diameter glass column. All of the soil columns were run using an apparatus similar to the one shown in Figure 1.

The concentration of the influent solution was determined by removing a 50 ml sample from the supply reservoir. The sample was transferred to a small beaker and evaporated to near dryness on a hot plate. The solution remaining in the beaker was then transferred to a planchet and evaporated to complete dryness on a hot plate. After being allowed to cool in a desiccator, the activity of residue remaining in the planchet was determined.* The high voltage was kept at 2050 volts with a sensitivity of 2.5 millivolts. During a soil column test, 50 ml effluent samples were taken. Each effluent sample was analysed in the same manner as the control sample which was taken from the supply reservoir. The C/C_0 values were then determined for each effluent sample based on the relative ^{89}Sr activities observed. Natural background activities were also taken and subtracted from both the C and C_0 values before

*All radioactivity measurements were done using a Nuclear Chicago, Model 186A, gas proportional counter.

each breakthrough ratio was computed. A typical ^{89}Sr breakthrough curve is shown in Figure 6.

Using LeBlanc's hypothesis summarized in [1], the evaluation of the constants a and b was required based on the strontium breakthrough curves obtained. A computer program was written to aid in this evaluation. Since the breakthrough data were erratic, a fourth degree equation was fitted to the data. The areas above and below this revised breakthrough curve could then be determined by integrating the fourth degree equation. In this way a logarithmic plot was made according to [3]. Theoretically, the logarithmic points should have plotted as a straight line. By fitting a least squares straight line through those logarithmic points, the computer program was able to evaluate the constants a and b of LeBlanc's equation. Figure 7 shows such a logarithmic plot and the resulting least squares fit for the breakthrough curve shown in Figure 6. In this manner the constants for the sample breakthrough curve shown were found to be:

$$\begin{aligned} a &= 0.535 \\ b &= 1.344 . \end{aligned}$$

In order to test the validity of using LeBlanc's equation a breakthrough curve was "predicted" using the computed values of a and b for the same data from which a and b were computed. The results of such a "prediction" for the sample breakthrough column are shown in Figure 8.

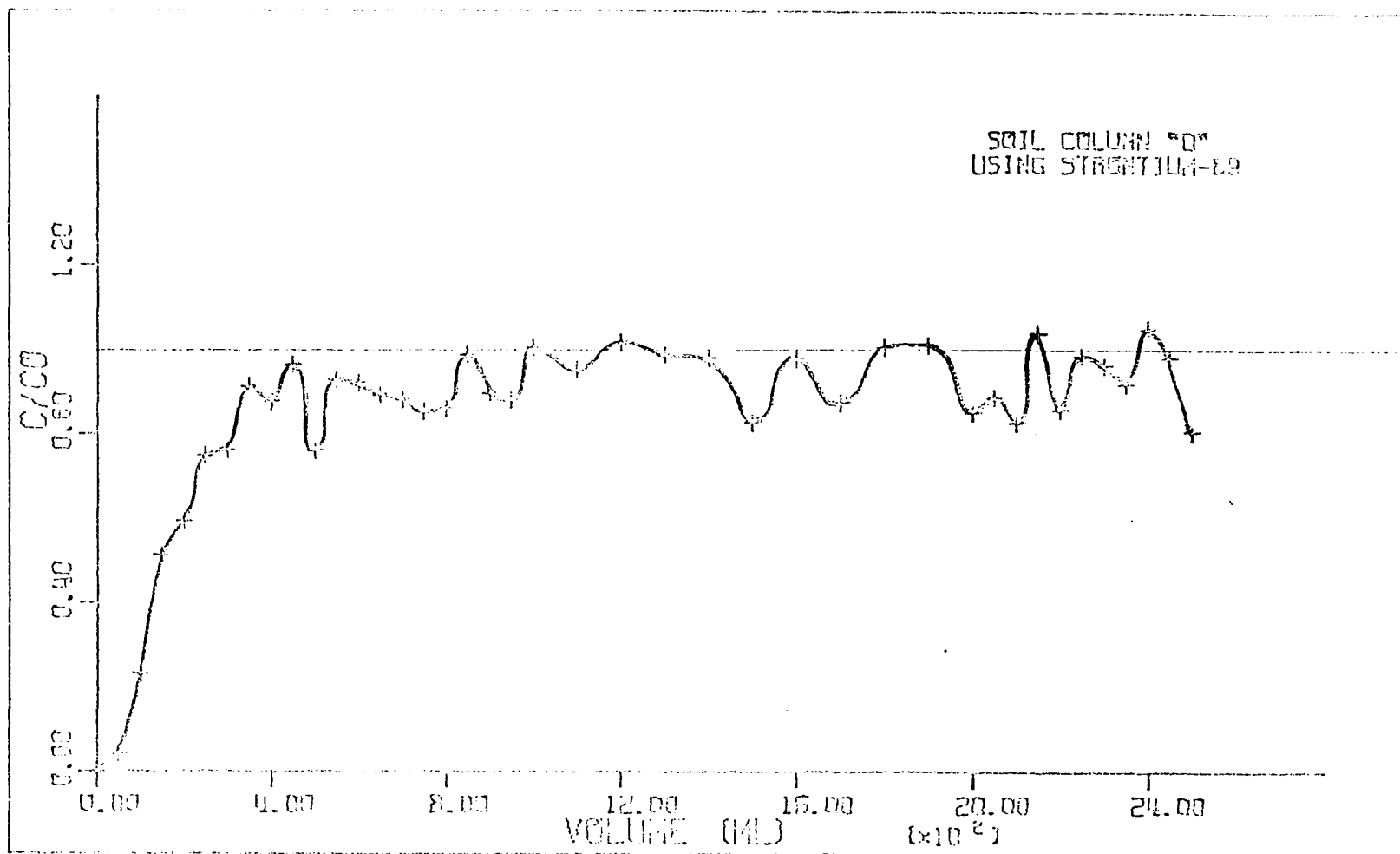


Figure 6. Breakthrough curve obtained for soil column "D" loaded with ten grams of soil and using a Sr-89 tagged influent solution

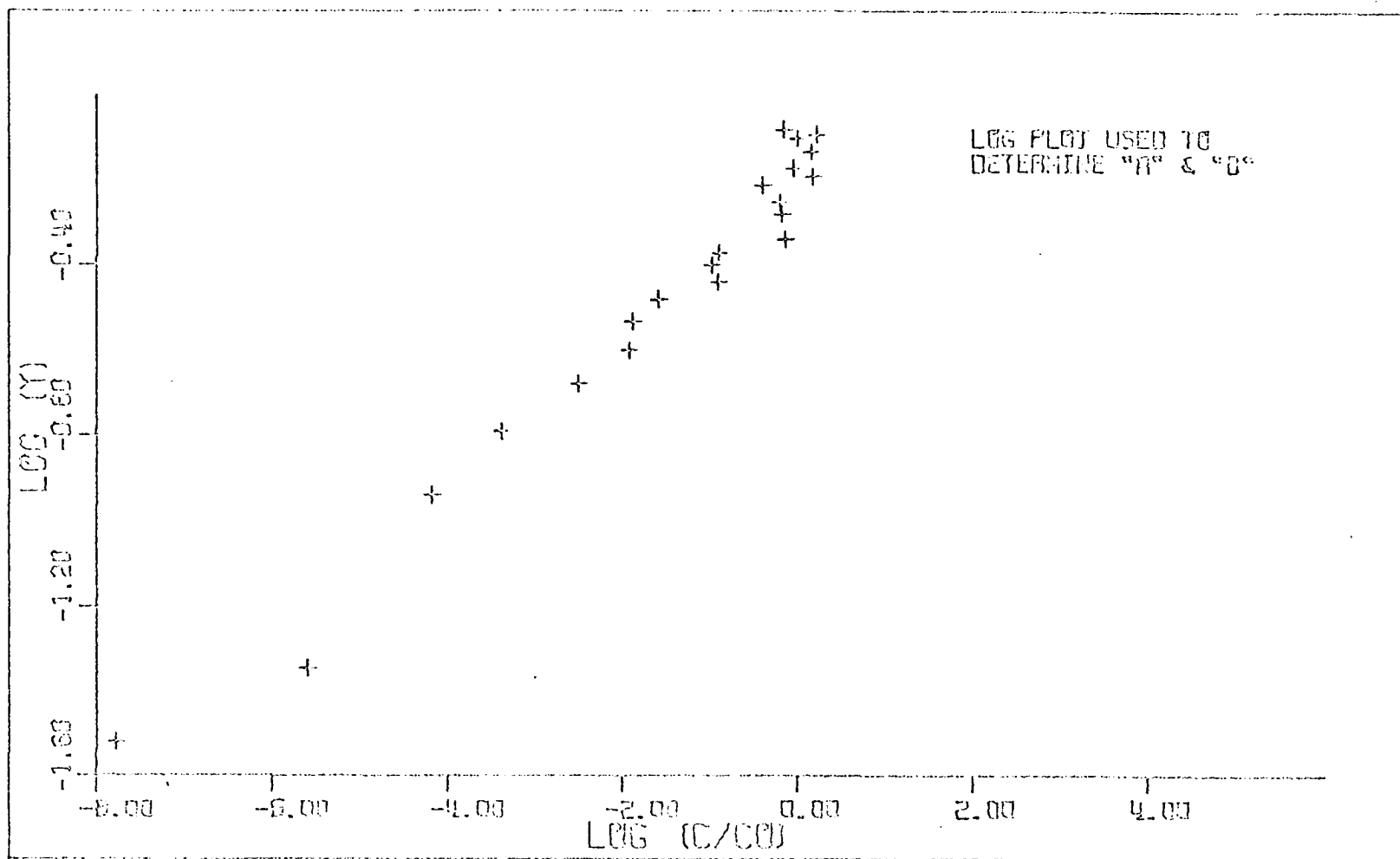


Figure 7. Logarithmic plot used to evaluate the constants a and b of LeBlanc's equation for soil column "D"

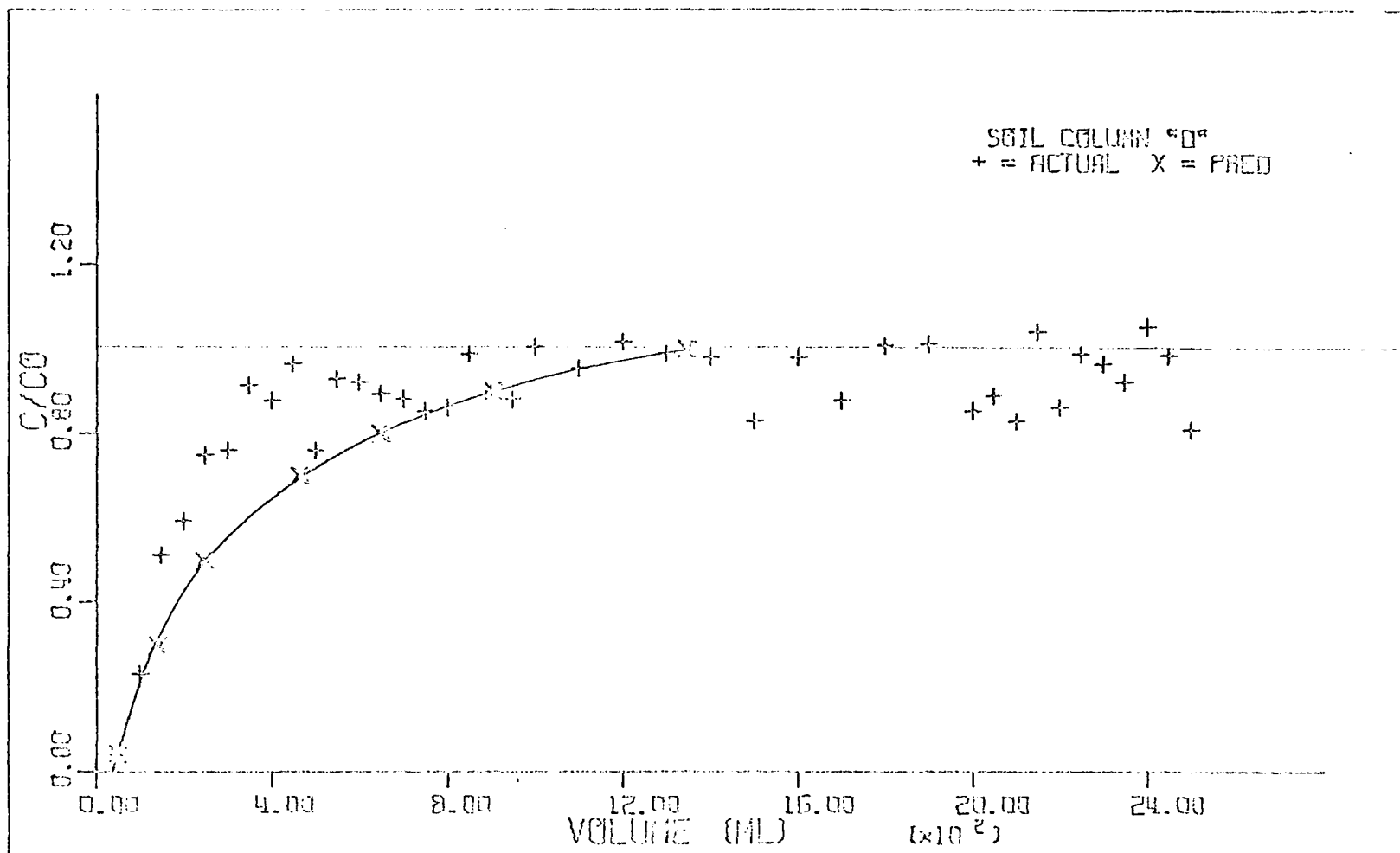


Figure 8. The "predicted" breakthrough curve of soil column "D" based on the values of the constants a and b of LeBlanc's equation determined using the breakthrough data of column "D"

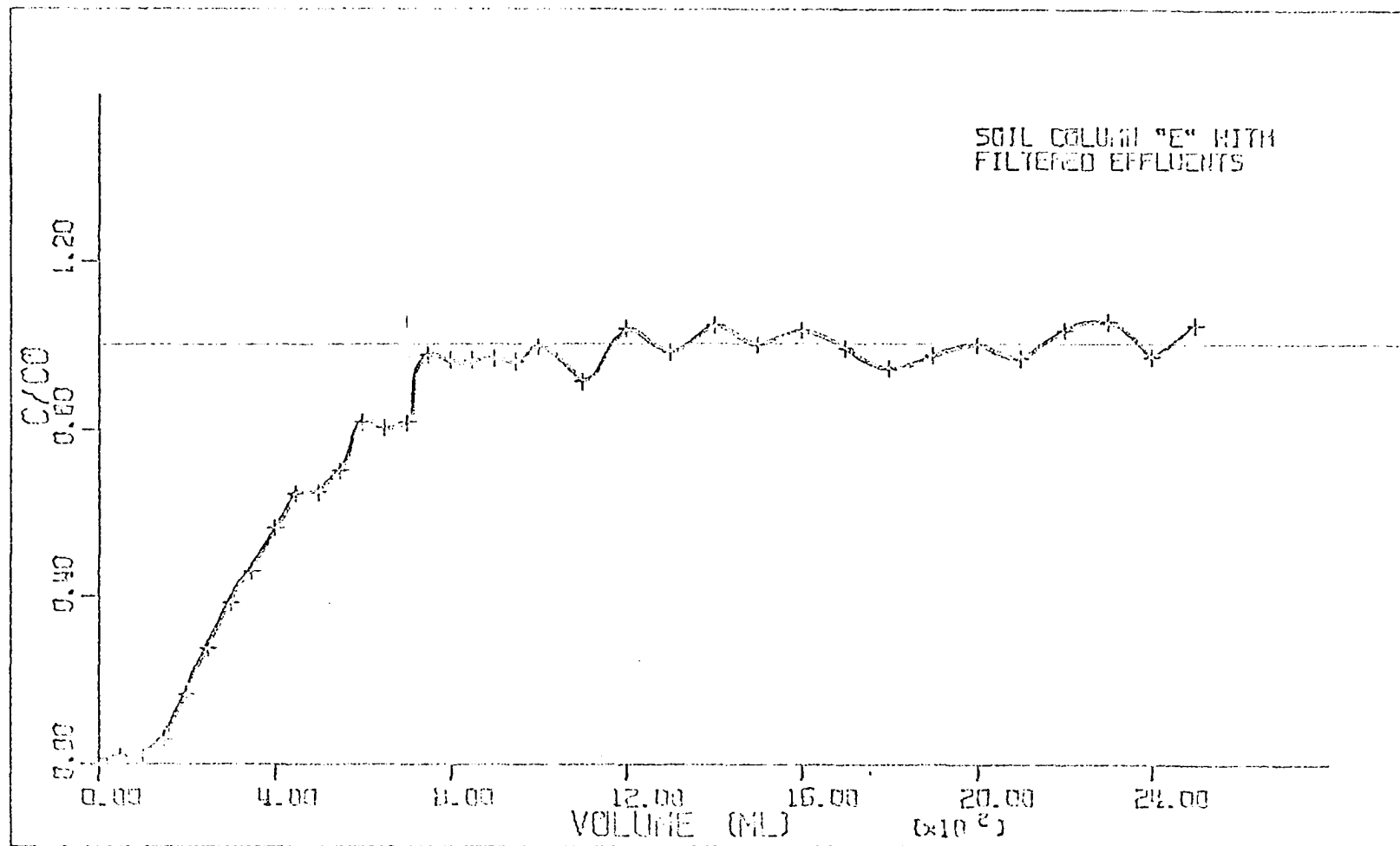


Figure 9. Breakthrough curve obtained for soil column "E", a repeat of column "D" with all effluent samples passed through 0.45 micron Millipore filters

Conclusions Concerning the Soil-Strontium System

Figure 8 shows that the breakthrough curves obtained by passing ^{89}Sr through the soil columns used were not the smooth "S-shaped" curves expected. It was thought that at least three different factors were responsible for the gross irregularities observed. These included the loss of clay particles, statistical counting errors, and the sample analysis technique. Approximately one-half inch of glass wool was used to support the soil within the glass column. While this was enough glass wool to prevent the erosion of the larger soil particles from the column, it may not have been enough to prevent the loss of some of the clay particles present. Clay particles represent the active fraction of the soil. They are responsible for the ion exchange properties contributed to the entire soil mass. Therefore, the periodic loss of clay particles may have resulted in widely varying strontium concentrations between consecutive effluent samples. In an effort to determine whether clay particles were actually being allowed to periodically pass from the soil column, the soil column test shown in Figure 6 was repeated, and each effluent sample was filtered through a 0.45 micron Millipore filter. Since clay particles may be as large as 2.0 microns, it was felt that the 0.45 micron filter paper would remove a large percentage of any clay particles that might have been present in the effluent. The resulting breakthrough curve, given in Figure 9, was less er-

ratio than the unfiltered breakthrough curve shown in Figure 6. However, the breakthrough curve of Figure 9 still shows some indication of variability between consecutive samples beyond that expected from simple breakthrough differences.

Statistical counting errors, inherent in radiochemical analyses, may also have contributed to the variability of the breakthrough curves. These counting errors should have been applied to both the control samples and the effluent samples taken. Fractional breakthrough values would then have been reported with a plus-or-minus error factor based on the propagated counting errors computed for a given confidence interval.

Another possible source of the variability observed in the breakthrough curves existed in the manner in which the control and effluent samples were taken and analysed. A 50 ml graduated cylinder was used to measure the samples collected. The use of a 50 ml pipette may have greatly reduced the possibility of sample volume differences. The analytical technique of evaporating the samples to dryness may have also contributed to an error term which should have been propagated to the final breakthrough data points.

Conclusions Concerning LeBlanc's Equation

When an attempt was made to reproduce a breakthrough curve based on the a and b values determined for LeBlanc's equation, it was observed that the prediction equation fit the

actual curve only over a limited region covering the lower C/C_0 values. Figure 8 shows the results of such an attempt. The C/C_0 values from approximately 0.40 to 1.00 deviated greatly from their predicted values. It was observed from the logarithmic plot of Figure 7 that these higher C/C_0 values tended to curve upward away from the least squares straight line which was fitted to the entire data set. The non-linearity observed for the data of Figure 7 suggested that LeBlanc's relationship was not valid for the higher values of C/C_0 . Whether this lack of agreement between the actual and the predicted results was due to a discrepancy in the hypothesis postulated by LeBlanc, or whether it was due to the existence of other factors, such as ionic diffusion into the interstitial pore spaces of the soil particles, was not known. Another possible source of error was the depth of the soil within the glass column. The 10 grams of soil used for each column resulted in a depth of approximately one inch. It was possible that such a small depth contributed to the short circuiting of strontium ions through the soil column. If such was the case, the exchange sites present on the outer surfaces of the soil particles would have been exhausted fairly rapidly. This would have resulted in a sharply rising breakthrough curve to a breakthrough value of about 50%. Once the direct short circuiting effects had been stabilized and the surface exchange sites exhausted, the slower process of ionic diffusion could have become the dominating phenomena. Though diffusion would

have been present throughout the entire column run, its magnitude could have been masked by the more pronounced effects of short circuiting and surface exchange during the early stages of a column run. Later work, using ion exchange resin in place of soil, appeared to confirm the assumption that diffusion is an important phenomenon to be considered in attempting to derive a relationship which will predict the movement of cations through soil.

Strontium Recovery from Soil

It was decided that the field testing of any breakthrough prediction equations found to be satisfactory using laboratory model soil columns would be made easier if the strontium adsorbed by the soil could be accurately removed. The Butler et al. (4) method for the removal of strontium from the soil using the liquid ion exchanger TIOA was tried. This method was chosen because of its relative simplicity compared with other extraction techniques suggested. Extractions made on three 50 gram soil samples indicated a natural activity of 285 pCi for the 50 gram samples.

An influent solution containing ^{89}Sr was measured to determine its activity per unit volume of solution. Fifty gram soil samples were placed in 600 ml beakers to which 150 ml of the strontium solution were added. The soil-strontium suspension was stirred for 60 minutes. The suspension was then filtered through #42 Whatman and 0.45 micron Millipore filters.

Fifty milliliter aliquots of the filtrate were then evaporated to dryness and their activities determined. By difference, the activity of the ^{89}Sr adsorbed by the 50 gram soil samples was calculated. The soil collected on the Whatman and Millipore filters was then analysed for strontium using the Butler solvent extraction method. Extraction efficiencies between 50% and 60% were observed.

An attempt was made to try a simplified approach for removing strontium from the soil samples. A soil sample on which ^{89}Sr had been deposited was placed in a 600 ml beaker. Approximately 100 ml of 6N HCl were added to the beaker, and the solution was stirred vigorously for 30 minutes. The suspension was then filtered through a #42 Whatman filter paper and a 0.45 micron Millipore filter. Fifty milliliter aliquots were then taken from the filtrate and evaporated to dryness for analysis. The evaporation was done slowly, using a hot plate, to avoid rapid boiling of the highly acidic samples. This simplified extraction technique resulted in the removal of between 93% and 100% of the ^{89}Sr which had been deposited on the soil. It was therefore concluded that in the interest of both time and accuracy, a simple wash of strontium saturated soil samples with a concentrated solution of HCl would result in an efficient removal of any strontium present.

Strontium Movement Through Soil Columns

With a technique perfected for removing strontium from soil using 6N HCl, an attempt was made to follow the movement of the radiostrontium through a soil column by removing soil samples at various depths throughout the column and extracting any ^{89}Sr which was present on the samples. This method of following the movement of strontium through soil offered an opportunity to test in the laboratory the procedure proposed for field studies in which small diameter seepage pits would be used. A glass column 75 cm long and 7.5 cm in diameter was used. After a predetermined volume of strontium solution tagged with ^{89}Sr was passed through the large soil column, soil samples of approximately 50 grams were taken at 5 cm intervals. Each soil sample was then extracted with the 6N HCl solution. After filtering the soil suspension through Whatman and Millipore filters, the filtrate from each sample was analysed for ^{89}Sr concentrations.

Two soil columns were tested in which soil samples were removed and analysed for ^{89}Sr . The same strontium concentration was used in the influent solutions of both soil columns. For the first extraction column, 250 ml of the ^{89}Sr solution were used. For the second test, 1250 ml were put through the soil column. The flow rate for each of the extraction column tests was approximately 13 ml/min. The results of the two strontium extraction tests are shown in Figure 10. Since the

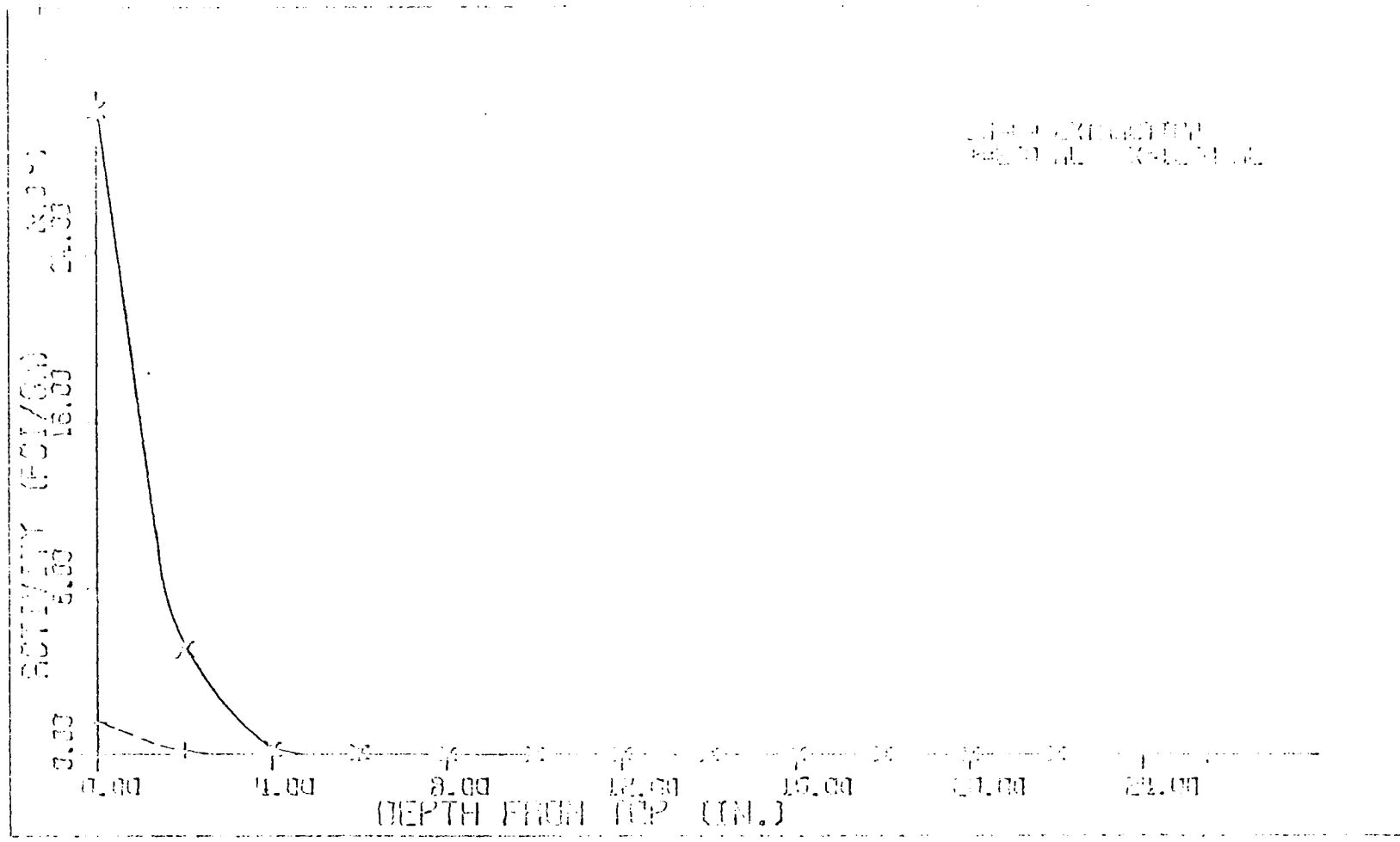


Figure 10. Results of strontium extraction from soil columns through which 250 ml and 1250 ml of influent solution had been passed at a flow rate of 13 ml/min

use of LeBlanc's equation had not been found to be satisfactory, no attempt was made to predict the location of the strontium front within either of the two soil columns.

The actual operation of a seepage pit results in the three dimensional dispersion of the waste solution into the soil environment. The use of soil columns, in which flow is essentially in one direction, results in a simplified model of actual field conditions. It was therefore decided to attempt to construct a more realistic model by using a large soil tank in which the synthetic waste solution would be allowed to move horizontally as well as vertically away from a modeled seepage pit.

The soil tank measured 60 inches across, 40 inches high, and 8 inches deep. The tank was constructed of aluminum on all sides except the front which was made of glass. The seepage pit consisted of a trench five inches wide located in the center of the tank. The pit had a gravel bottom and Plexiglass sides. Seventeen effluent holes had been drilled along the bottom of the tank for drainage purposes. Flexible tubing was used to connect all of the drainage outlets to a common drainage tube.

The soil used in the tank was taken from the same soil storage container used for the previous soil column experiments. After the soil was loaded into the tank, water was added from the top until the soil appeared to be saturated. The rate at which the influent solution was dripped into the

lagoon was regulated so as to maintain a constant liquid depth within the lagoon.

Since the two directional flow test was meant to be a qualitative study of the feasibility of using such models, the influent strontium concentration was not controlled. The flow rate was regulated only to maintain a constant lagoon depth. A strontium solution, similar in concentration to the solutions used for the previous soil column experiments, was prepared using strontium nitrate tagged with ^{89}Sr . The ^{89}Sr activity of the influent solution was found to be about 142,000 counts per minute for 50 ml samples. After 3200 ml of the synthetic waste had been allowed to pass into the soil from the seepage pit the flow was stopped. Thirty soil samples were removed from various locations throughout the tank. Any strontium present on the soil samples was removed using the simplified extraction technique previously described.

The two directional movement of the strontium waste through the soil tank resulted in a deposition of approximately 1300 pCi per gram of soil within a radius of about one inch from the bottom of the modeled seepage pit. The activity at a radius of about three inches from the pit was found to be about 300 pCi per gram of soil. Beyond a distance of about five inches from the pit no activity was observed on the soil samples above the six pCi/gram background radiation level which was present in the soil.

RESIN-CALCIUM MODEL OF THE
SOIL-STRONTIUM SYSTEM

Reasons for Using Resin and Calcium

Several handicaps were noted in determining column effluent concentrations radiochemically. A lag time of about one hour existed from the time a sample was taken until its activity could be determined. It was desirable to take effluent samples more frequently during the time in which the breakthrough curve was developing. Such a long lag time resulted in a greater influent volume being used than was actually required in order to avoid missing the more critical regions of the breakthrough curve.

There also appeared to be some discrepancies in determining the influent concentrations. Control samples were taken directly from the reservoir supplying the synthetic waste solution. When several duplicate control samples were taken there appeared to be a control range rather than a control value. In addition to the nonuniformity of the supply reservoir there also existed a statistical counting error for each sample counted.

Due to the erratic nature of the data collected using soil, it was decided to simulate soil with a cation exchange resin. The resin is similar in structure to soil, having a particle diameter of about one millimeter. The resin has an ion exchange capacity about 100 times greater than soil. As

an extremely uniform material it was felt that the ion exchange resin would represent an idealized soil system.

The ion exchange resin selected was Dowex 50W-X8, with a cation exchange capacity of 5.0 meq-gram on a dry weight basis or 1.9 meq-ml on a wet volume basis. Approximately 0.9% of the resin was retained on a U. S. No. 35 Sieve and 1.2% passed a U. S. No. 70 sieve.

Since the system was being altered by the replacement of soil with ion exchange resin, it was also decided to further idealize the system by substituting stable calcium for radioactive strontium. The ionic strength of the influent solution was tightly controlled by carefully weighing required amounts of oven dried calcium carbonate powder. The calcium concentration could easily be determined using a standard water hardness test. The calcium analysis procedure employed was one obtained from the Hach Chemical Company of Ames, Iowa.

The analytical procedure used was as follows:

1. Pipette a known volume of sample into a 250 ml Erlenmeyer flask.
2. Add approximately 1 ml of Type II Strong Buffer Solution. Swirl to mix.
3. Add 0.5 gram of ManVer Indicator Powder using a 0.5 gram measuring spoon.
4. Titrate with Standard HexaVer Solution. At the end point the solution changes from wine-red to pure blue.
5. One milliliter of titrant indicates the presence of one milligram of hardness as CaCO_3 .

The time required to analyse one sample was about 60 seconds.

This permitted the taking of a minimum number of samples while at the same time allowing many samples to be taken during the critical period when the breakthrough curve was being formed.

The irregularities observed in many of the strontium breakthrough curves using soil as the exchange medium suggested that more than one mechanism was responsible for the transport of the strontium through the column. If the ion exchange were the only factor to be considered, the breakthrough curves should have been smoother and nearly symmetric about the 50% breakthrough point. However, the breakthrough curves showed a tendency to oscillate beginning at about the 60% breakthrough point and continuing for the rest of the run. Furthermore, at about the 70% to 80% breakthrough point the breakthrough curves became almost horizontal. It was possible that the nearly vertical portion of the curve reflected an initial short circuiting through the column, and the nearly horizontal plateau actually represented the period in which the breakthrough column was at its greatest efficiency.

The plateau also suggested the existence of diffusion as a major contributor to the breakthrough process. While cations moving through the column could easily exchange onto the sites located on the surface of the soil particles, many sites were available in harder to reach passages within the soil structure. Montmorillonite clay contains spaces between the layers of its crystalline structure into which cations may migrate and become attached through the process of isomorphous

substitution. Diffusion would be a slow process. Therefore, it was conceivable that the ion exchange sites on the outer surface of the soil particles could rapidly be depleted, thereby giving the sharp breakthrough curve observed to about the 70% point. While interstitial diffusion was also taking place during this initial phase, it was largely subordinated by the surface exchange mechanism. Once the surface sites were exhausted, however, the diffusion process predominated, and the breakthrough curve very slowly approached the 100% level.

It was felt that the system could be idealized by substituting a cation exchange resin for the soil particles and stable calcium for the radiostrontium constituent. This would permit more accurate observations of the individual transport mechanisms affecting the movement of cations through a porous medium. Knowledge gained from such a substitution could then be related to the soil-strontium system.

Modifications to LeBlanc's Equation

When the constants a and b of LeBlanc's equation were evaluated based on a complete soil column test from zero to 100 percent breakthrough, it was found that above 70 percent and below 30 percent of breakthrough the predicted curve deviated considerably from the actual breakthrough curve. In most cases LeBlanc's breakthrough curves were not shown beyond the 70 percent point. Therefore, before any laboratory work was

initiated using the resin-calcium system LeBlanc's breakthrough prediction equation was re-examined.

As an alternative to LeBlanc's concept that the fractional area above a breakthrough curve should be a constant for a given breakthrough fraction, a new approach was postulated which stated that the fractional area to the right of a breakthrough curve should be a constant for a given breakthrough fraction. This constant, which was assumed to be a function of the breakthrough fraction being investigated, was also taken to be $a(C/C_0)^b$. The new approach was thus a continuation of LeBlanc's hypothesis and incorporated the parameters established by LeBlanc. For the sample breakthrough curve shown in Figure 11 the constants a and b were to be evaluated for some breakthrough fraction C/C_0 which was observed to occur at a throughput volume of V. The total throughput volume required to reach 100% breakthrough was designated as V_T . The six areas resulting from passing a vertical and a horizontal line through the point P on the curve corresponding to the volume V were numbered A_1 through A_6 .

LeBlanc's analysis would have begun by determining the Y variable for point P:

$$Y = \frac{A_1 + A_4}{A_1 + A_4 + A_5} \quad [8]$$

This value for Y would then have been equated to the general function

$$Y = a(C/C_0)^b \quad [9]$$

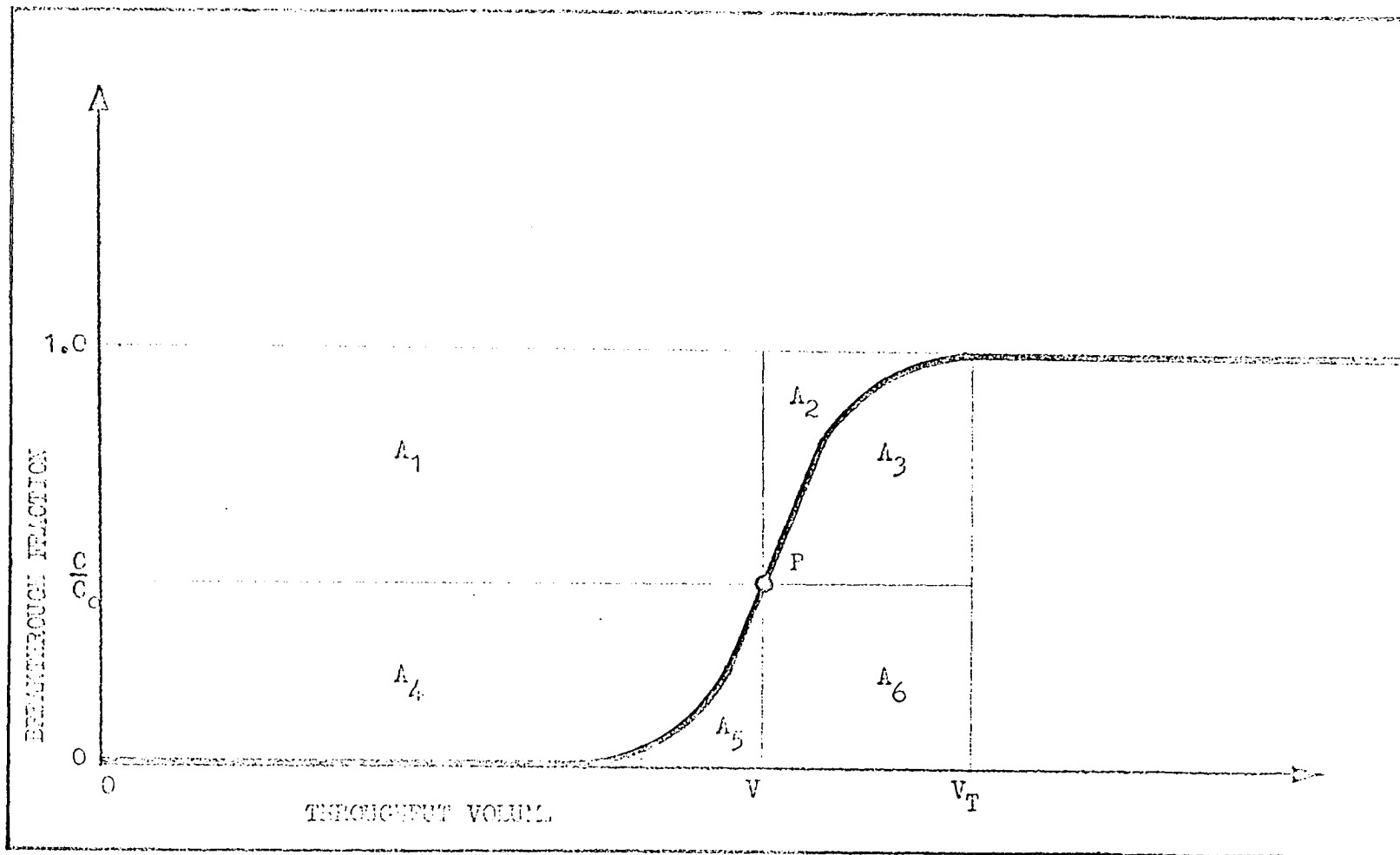


Figure 11. Typical breakthrough curve showing the areas used in the modification of LeBlanc's equation

The modified approach would require the following analysis:

$$Y' = \frac{A_4}{A_4 + A_5 + A_6} \quad [10]$$

$$Y' = a(C/C_0)^b \quad [11]$$

It can be seen from Figure 11 that

$$A_4 + A_5 + A_6 = V_T \left(\frac{C}{C_0} \right) \quad [12]$$

$$A_1 + A_4 + A_5 = 1(V) = V \quad [13]$$

$$A_1 = V \left(1 - \frac{C}{C_0} \right) \quad [14]$$

Combining [10], [11], and [12]:

$$\frac{A_4}{V_T \left(\frac{C}{C_0} \right)} = a \left(\frac{C}{C_0} \right)^b \quad [15]$$

Substituting [13] and [14] into [8]:

$$Y = \frac{V \left(1 - \frac{C}{C_0} \right) + A_4}{V} \quad [16]$$

In terms of A_4 [16] becomes

$$A_4 = V \left(Y - 1 + \frac{C}{C_0} \right) \quad [17]$$

Substituting [17] into [15] and combining C/C_0 terms as much as possible:

$$Y - 1 + \frac{C}{C_0} = \frac{a}{V/V_T} \left(\frac{C}{C_0} \right)^{b+1} \quad [18]$$

A Langmuir isotherm was obtained by using the data collected from several soil columns. In the resin-calcium system

X represented the amount of calcium adsorbed on M grams of resin. The straight line portion of Langmuir's curve may be represented by

$$\frac{C_o}{X/M} = A + BC_o \quad [19]$$

where A is the value for $\frac{C_o}{X/M}$ if the straight line were extended to $C_o = 0$, and B is the slope of the straight line. At complete breakthrough [18] reduces to

$$Y = a. \quad [20]$$

Thus, the maximum amount of calcium that can be adsorbed on the resin would be

$$X = aC_oV_T. \quad [21]$$

Substituting [21] into [19] and solving for the constant a:

$$a = \frac{M}{V_T(A + BC_o)}. \quad [22]$$

Substituting [22] into [18] yields

$$V(Y - 1 + \frac{C}{C_o}) = \frac{M}{A + BC_o} (\frac{C}{C_o})^{b+1} \quad [23]$$

in which the volume required for total breakthrough V_T is not required. This is desirable since the upper shoulder of the breakthrough curve approaches almost asymptotically to the 100% breakthrough line. It is very difficult to determine experimentally the exact volume at which the breakthrough curve reaches the 100% breakthrough line.

The coefficient of the right hand side of [23] is a constant for a given column being loaded with a solution of a

given concentration. The values which make up this coefficient were collected into a single constant called α . The $b + 1$ exponent in the right hand side of [23] was combined into one exponent called β . The incorporation of α and β resulted in the alteration of [23] to the form:

$$V\left(Y - 1 + \frac{C}{C_0}\right) = \alpha\left(\frac{C}{C_0}\right)^\beta \quad [24]$$

where

$$\alpha = \frac{M}{A + BC_0} \cdot \quad [25]$$

The β of [24] must be experimentally determined but should be a constant. The α term can be calculated by [25].

Once β is determined, [24] can be solved by a step-wise iterative process to determine the predicted value of V for an incremented value of C/C_0 . In order to simplify such a procedure, a computer program was written which permitted the rapid prediction of the breakthrough curve desired.

Modifications to the Experimental Apparatus

With the replacement of the soil-strontium system with a resin-calcium system, the apparatus itself was also examined for possible improvements. The flow rate through the previous soil columns was dependent on the hydraulic head available between the influent solution reservoir and the column effluent tube. The flow rate could be measured, but no attempt was made to control it or regulate it at a predetermined value. It

was therefore decided to install a flow rate meter on the influent line to the column together with a valve sensitive enough to act as a fine control adjustment for the flow rate meter.* The calibration curve for the flow rate meter used is shown in Figure 12. With such a curve, any flow rate within the range of the calibrated bead could easily be obtained. Figure 13 shows a schematic diagram of the apparatus used for the resin-calcium experiments. The glass column used to hold the ion exchange resin was the same 2.20 cm inside diameter column used for the soil column breakthrough tests.

Evaluation of α and β

Eight resin columns were tested in order to determine the validity of calculating α by [25] and to determine the value of the exponent β . In order to use [25] the constants A and B had to be evaluated. This determination was begun by graphically determining the fractional area above the entire breakthrough curve. This fraction, referred to as F, represented that part of the total amount of calcium put through the resin column that was adsorbed by the resin. Referring to Figure 12 this ratio may be described as

$$F = \frac{A_1 + A_2 + A_4}{A_1 + A_2 + A_3 + A_4 + A_5 + A_6} \cdot \quad [26]$$

*A Brooks Rotameter Company flow rate meter, Model R-2-15-C, was selected.

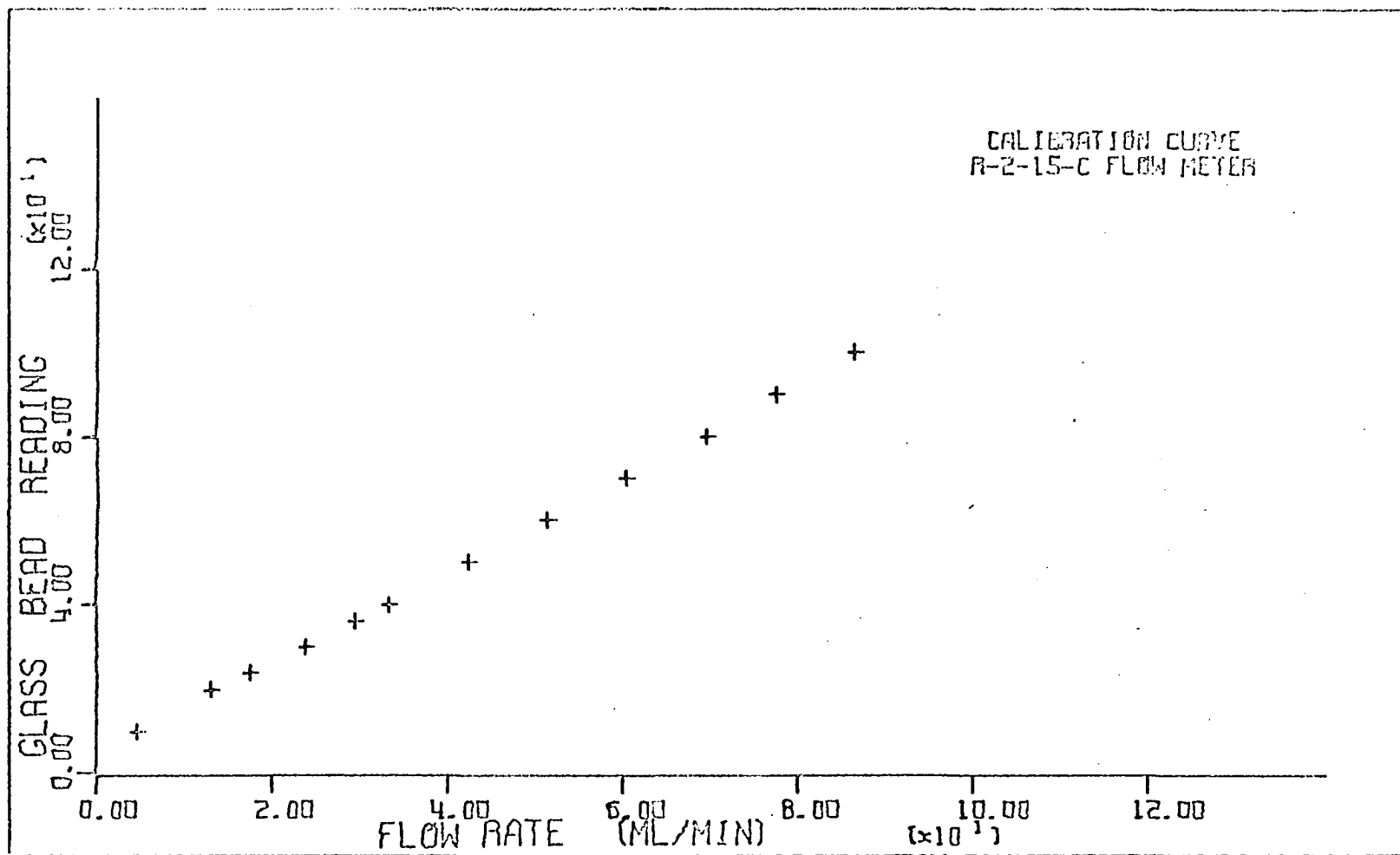


Figure 12. Calibration curve obtained based on the glass bead in a Brooks Rotometer Company, Model R-2-15-C, flow meter

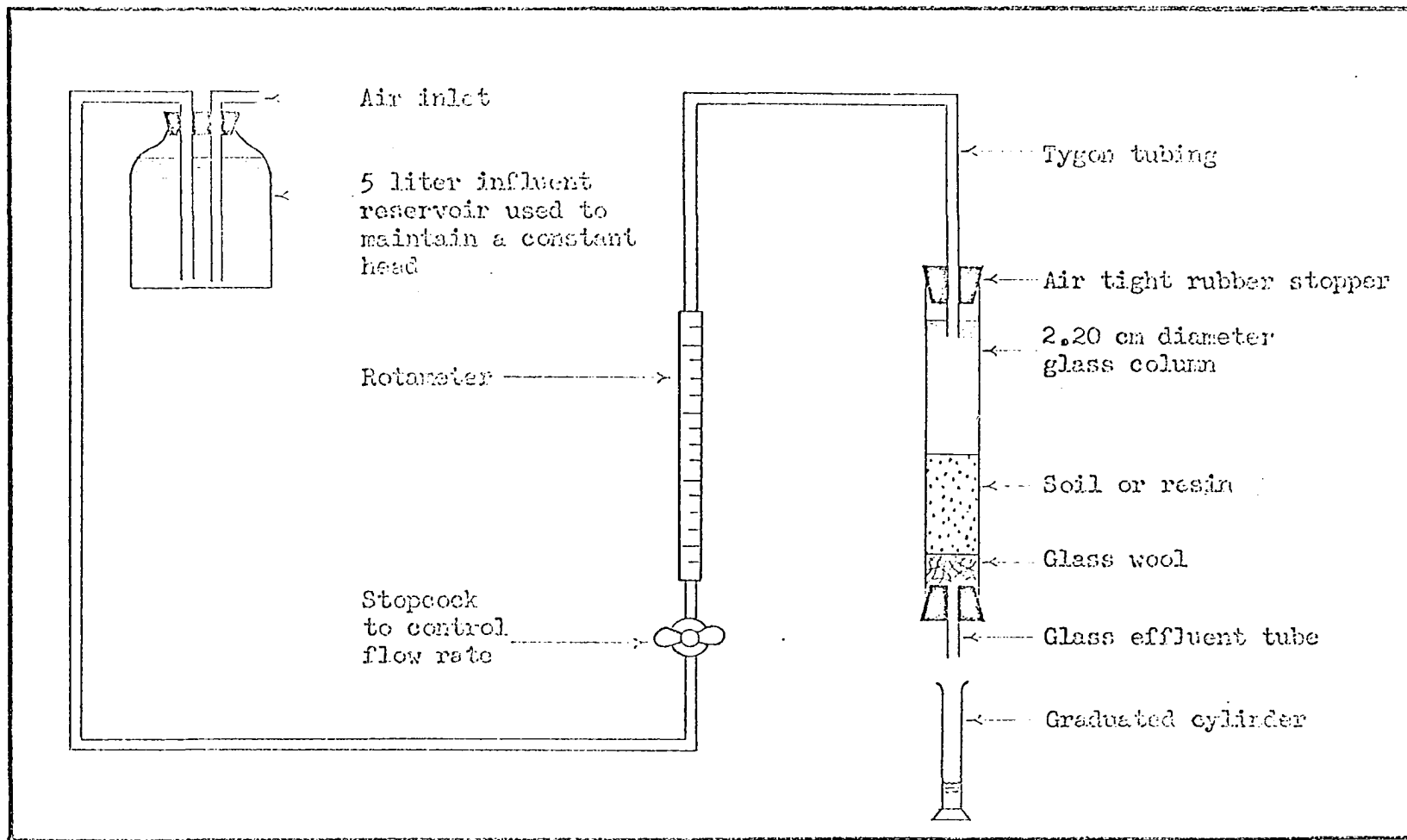


Figure 13. Improved apparatus used for breakthrough column experiments

The total amount of calcium deposited during the resin column test was then calculated by

$$X = FC_o V_T . \quad [27]$$

The influent solution was tested to determine the exact calcium concentration. The procedure used was the same HexaVer titration method employed in the analysis of the calcium breakthrough curves.

At the time these experiments were conducted the major parameters which were thought to govern the movement of the cations through the resin were the influent concentration, the flow rate, and the resin bed depth. Each resin column tested was coded according to the values used for these parameters. Therefore, a column test designated 250-2-4" indicated an influent concentration of 250 ppm calcium as CaCO_3 , a flow rate of 2 GPM/ft², and a resin bed depth of 4 inches.

After the 100% breakthrough value was reached, the resin was washed with 1N HCl until no more calcium was eluted. The column was then flushed with distilled water and the resin transferred to a weighing bottle. The resin was then dried at 110 °C for 24 hours and weighed. This provided the column bed weight M required for the Langmuir isotherm.

With C_o , X, and M measured for a given resin column test, one point on a Langmuir isotherm could be plotted. The first three columns that were run differed only in the influent concentrations used. The three resulting points were used to

form the Langmuir isotherm shown in Figure 14. The last five resin columns were run at the same influent concentration as the first column. Their isotherm points, not shown in Figure 14, were clustered around the point obtained for the first column run.

The isotherm obtained resulted in the following values for the constants desired:

$$A = 0.0$$

$$B = 0.197 .$$

It was then possible to simplify [25] to

$$\alpha = \frac{M}{0.197 C_0} \quad [28]$$

The cation exchange capacity of the resin used was given as 5.0 meq/gram. This exchange capacity would be designated as X/M following the notation used. The inverse of the exchange capacity would therefore be M/X = 0.200 grams/meq. The experimentally determined value of A = 0.0 results in the constant B of [19] having a theoretical value of 0.200 grams/meq, close to the determined value of B = 0.197 grams/meq. Since the exchange capacity of the ion exchange resin remained constant over the C₀ values used, the use of a Langmuir isotherm was not required.

The constants α and β could be determined numerically for each resin column run by taking the logarithm of each side of [24]:

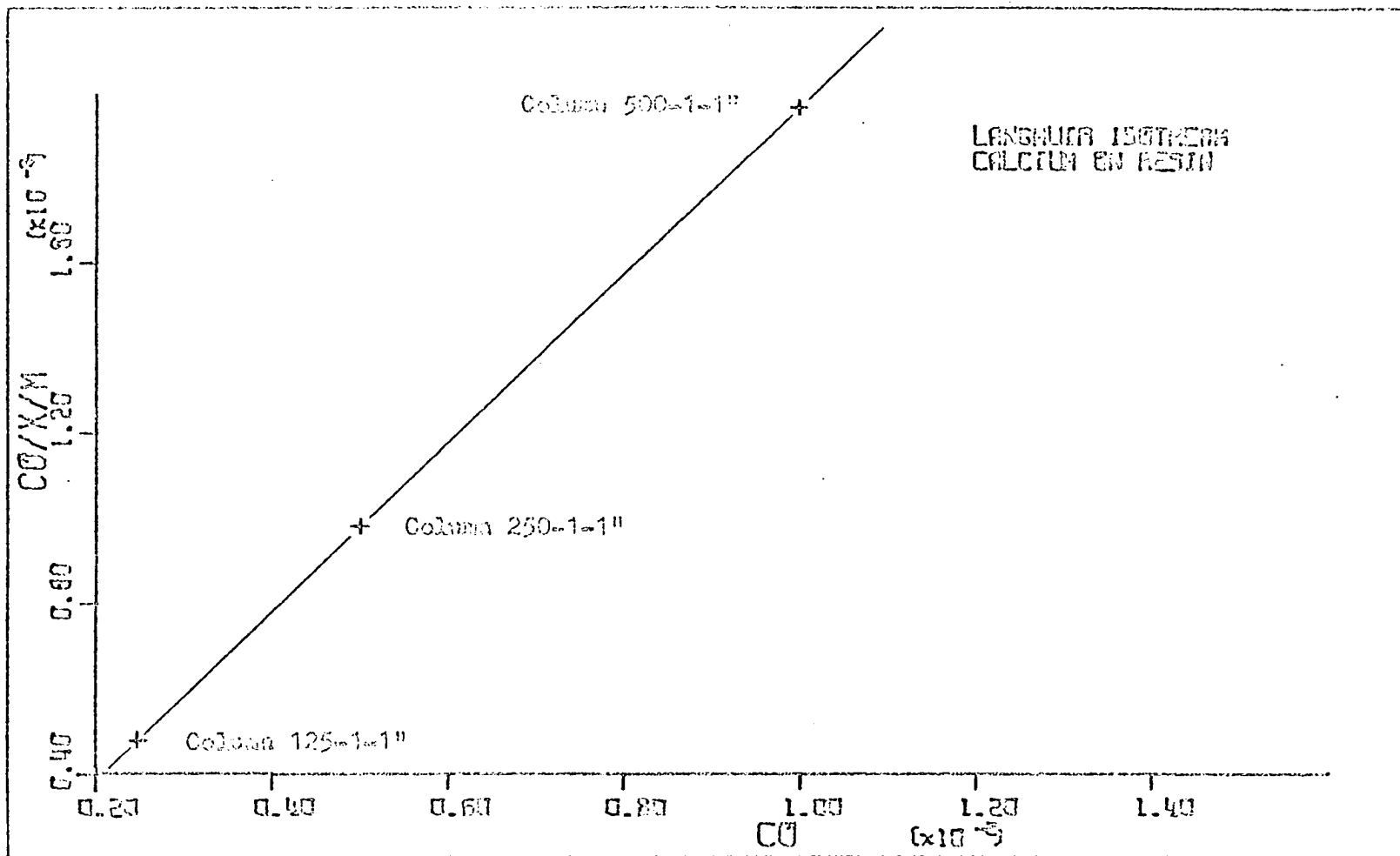


Figure 14. Langmuir isotherm obtained on a column basis by passing calcium solutions through Dowex 50W-X8 cation exchange resin

$$\log V(Y - 1 + \frac{C}{C_0}) = \log \alpha + \beta \log \frac{C}{C_0} . \quad [29]$$

A plot of the left hand side of [29] versus $\log (C/C_0)$ should yield a straight line with a slope of β and an ordinate intercept of $\log \alpha$.

When [29] was represented graphically the result was not a straight line. Attention was then focused on the breakthrough curves obtained for the initial eight conditions. Figure 15 shows a typical such curve. Figure 15 shows that the curve does not begin at $C/C_0 = 0.0$, but rather at an initial breakthrough value of about 6%. It was believed that a critical combination of high flow rate and low resin bed depth might result in short circuiting, perhaps mostly down inside walls of the column. If this were true, [29] would be valid only if this short circuiting effect were removed from the data points. The method chosen to offset this effect was one of normalizing the breakthrough curves against an assumed short circuiting plateau. Thus, if P represented the C/C_0 value of the plateau for a given breakthrough curve, then the normalized value of C/C_0 , represented as C'/C_0 , was calculated by

$$C'/C_0 = \frac{C/C_0 - P}{1 - P} . \quad [30]$$

A computer program was written which would normalize the breakthrough data collected, solve [29] for each normalized data point, fit a least squares straight line through the re-

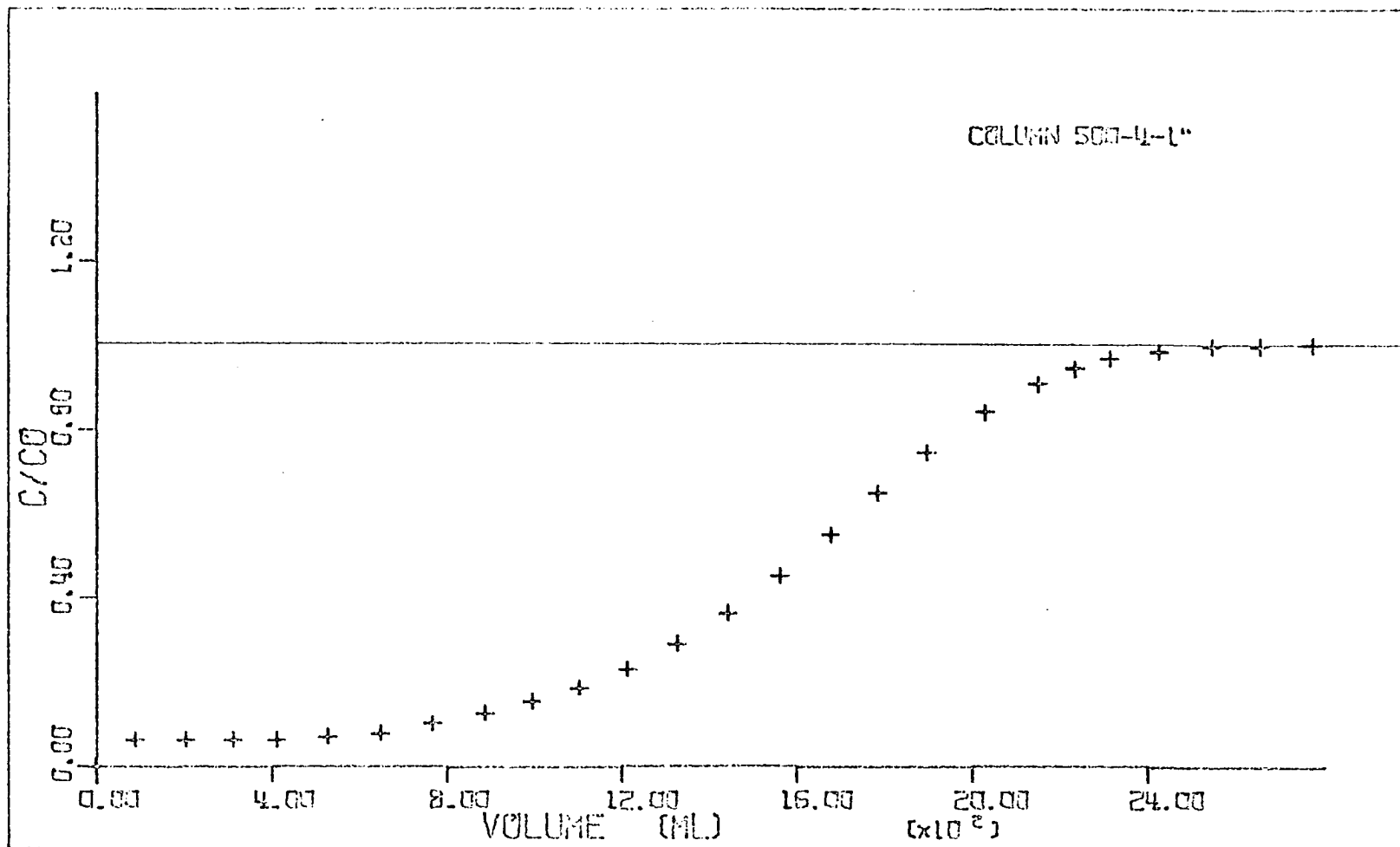


Figure 15. Typical calcium breakthrough curve using an ion exchange resin in a 2.2 cm diameter glass column

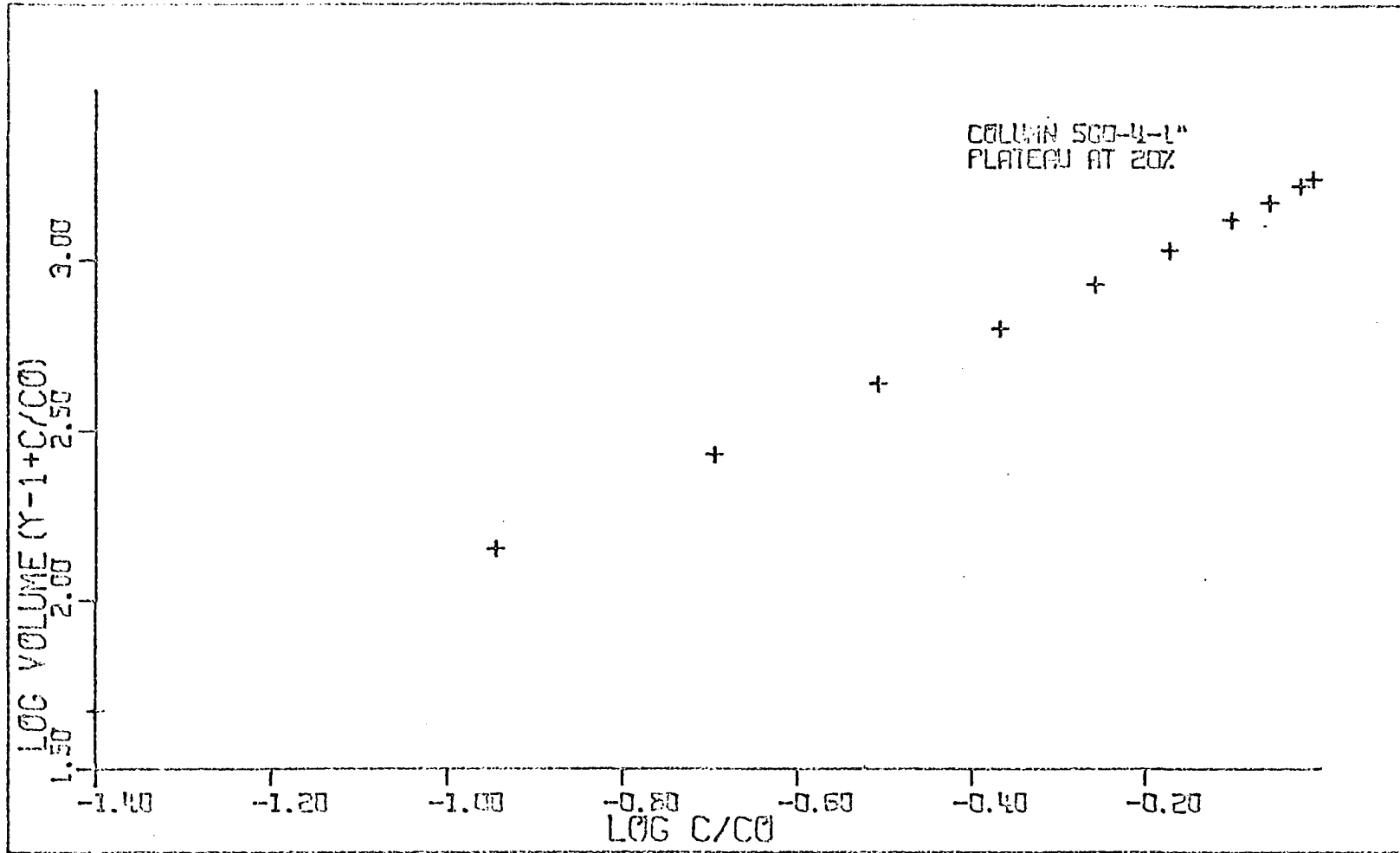


Figure 16. Logarithmic plot used to evaluate the constants α and β for ion exchange column 500-4-1" after breakthrough fractions were normalized to the 20% breakthrough level

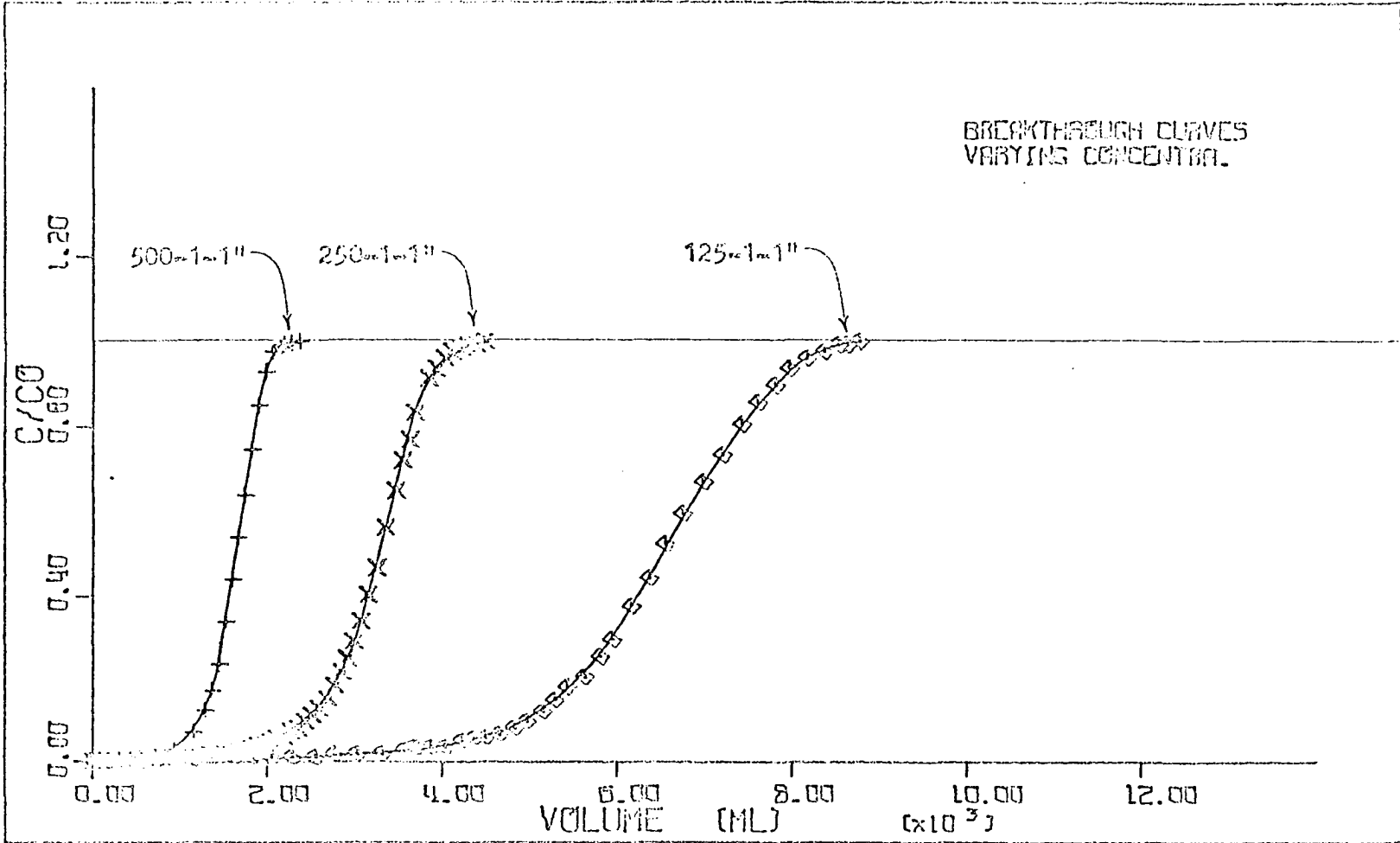


Figure 17. Calcium breakthrough curves using 2.20 cm diameter resin columns -- flow rate and bed depth held constant, influent concentrations varied

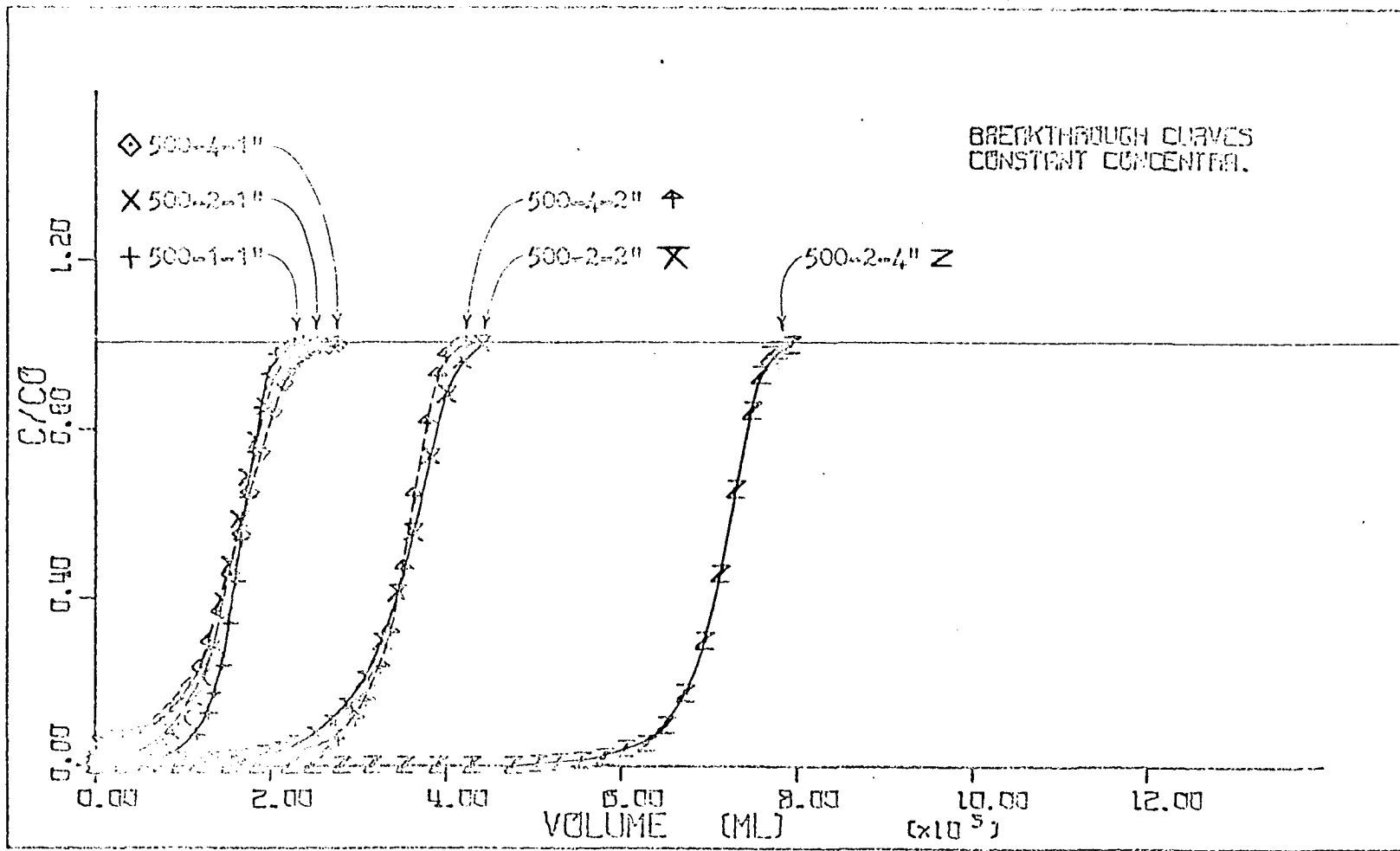


Figure 18. Calcium breakthrough curves using 2.20 cm diameter resin columns -- constant influent concentrations, variable flow rates and bed depths

sulting points, determine the values of the constants α and β , and graph the normalized breakthrough data points used in evaluating α and β . Figure 16 shows the logarithmic plot for the breakthrough curve of Figure 15.

Table 1 gives a summary of the eight initial calcium breakthrough tests. Figure 17 contains the breakthrough curves observed for the first three runs in which the influent concentration was varied but the flow rates and resin bed depths were held constant. Figure 18 contains the breakthrough curves obtained when the influent concentration was held constant at 500 ppm of calcium as CaCO_3 , but flow rates were varied. Values of α for each column test were first calculated from [28]. This value was then compared with the graphical determination done with the aid of the computer program. Table 1 also shows the plateau value used for each column evaluation.

Table 1 shows that the value for β is very nearly a constant. The average of β for the eight tests made was 1.13. With this average value of β , an entire breakthrough curve could be predicted for a given influent concentration, flow rate, and resin bed depth.

Breakthrough Prediction Using the Modified LeBlanc Equation

In order to test the validity of using a constant value of β and a computed value of α in predicting the relative location and shape of a breakthrough curve, the following ini-

Table 1. Values obtained for α and β for the eight initial breakthrough curves developed using ion exchange resin and calcium

Run	Influent Conc. [ppm]	Flow Rate [GPM/ft ²]	Resin Depth [in]	Plateau Percent	β	α by [28]	α actual
1	500	1	1	2	1.14	1651	1606
2	250	1	1	2	1.14	3280	3136
3	125	1	1	4	1.11	6670	6346
4	500	2	1	10	1.14	1652	1560
5	500	4	1	20	1.14	1738	1692
6	500	2	2	2	1.06	3510	3325
7	500	4	2	4	1.11	3490	3442
8	500	2	4	0	1.07	7090	7090

tial conditions were chosen for a test column run:

$$C_o = 500 \text{ ppm Ca}^{++} \text{ as CaCO}_3$$

$$\text{flow rate} = 4 \text{ GPM/ft}^2$$

$$\text{bed depth} = 4 \text{ inches}$$

A comparison of the actual and predicted breakthrough curves is shown in Figure 19. It can be seen that [24] together with [25] predicts a parabolic breakthrough curve. Although the predicted curve closely forecasts the actual curve until about the 95% breakthrough point, the predicted curve does not yield an upper shoulder to form an "S-shaped" curve.

Conclusions Concerning the Modified LeBlanc Equation

Had the actual breakthrough curve of column 500-4-4", shown in Figure 19, been one in which the upper shoulder began to curve at a lower breakthrough fraction, the predicted curve

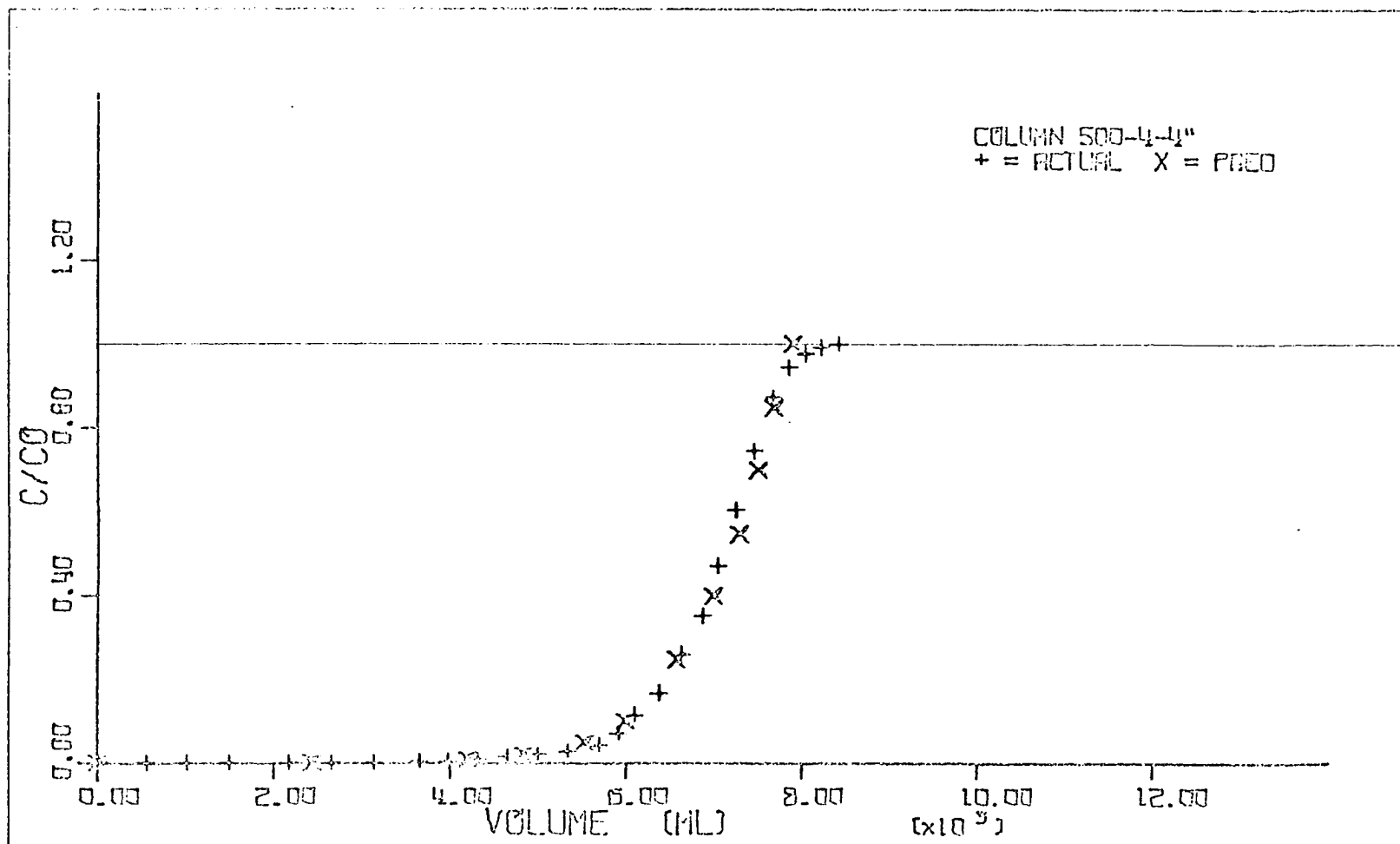


Figure 19. Actual calcium breakthrough curve using 2.20 cm diameter resin column operated at 500-4-4" compared to the predicted curve based on modifications made on LeBlanc's equation

would have been much more in error. It was therefore concluded that while [24] did describe the breakthrough phenomena better than its predecessor formulated by LeBlanc, the parabolic prediction equation was still not an accurate representation of the actual breakthrough curves.

Compounding the errors introduced by the geometric shape of [24] was the existence of the breakthrough plateaus observed. The small diameter column was used as a model of actual field conditions. While side wall short circuiting appeared to exist in the column model, its analog would not be expected under actual field conditions. It was therefore concluded that the flow rate to bed depth ratio was extremely important in modeling actual conditions. If this ratio were allowed to become too high, the efficiencies of the exchange columns were unrealistically lowered, and actual conditions were no longer being accurately modeled.

The curves shown in Figure 18 suggest that the relative location of a breakthrough curve appears to be governed by the resin bed depth which is simply a measure of the amount of resin present. The relative shapes of columns run at the same influent concentration and bed depth can be altered by varying the flow rate. However, excessively fast flow rates for a relatively small bed depth will result in a short circuiting plateau which increases in intensity as the flow rate is increased.

Adaptation of Hinshelwood's Equation

Due to the difficulties involved in attempting to fit "S-shaped" data with a parabolic equation, it was decided to explore a completely different approach from the modified form of LeBlanc's equation. Hinshelwood et al. (9) derived an equation for the adsorption of gases onto granular particles which would describe the "breakdown" of the gas column. This predicted the time required for the first appearance of the adsorbate in the gas effluent stream and was given as

$$t = \frac{1}{KC_0} [\ln(e^{KN_0\lambda/L} - 1) - \ln(C_0/C - 1)] \quad [31]$$

where

t = breakdown time of the column [sec]

N_0 = number of active centers per unit volume

L = linear flow rate [cm/sec]

λ = column length [cm]

K = a constant

and C and C_0 are as previously described. Kipling (11) later modified [31] to describe the adsorption of solutions by porous solids. He observed that for liquid-solid interactions the $e^{KN_0\lambda/L}$ term was usually much greater than unity. It was thus possible to simplify [31] to

$$t = \frac{1}{KC_0} \left[\frac{KN_0\lambda}{L} - \ln(C_0/C - 1) \right] . \quad [32]$$

The term $\ln(C_0/C - 1)$ in [32] has a value of zero when

$C/C_0 = 0.50$. This term results in [32] assuming a symmetric "S-shape" about the 50% breakthrough fraction. The symmetry is broken only when the throughput volume is decreased to zero. Since no negative volumes can exist, [32] is actually bounded on the left by $V = 0.0$. Kipling observed that if the constant K were multiplied by $L^{0.5}$, where L was assumed to be the linear flow velocity through the column, then [32] could be more accurately applied to a liquid-solid system. This was justified by Kipling because the rates of diffusion are lower in the liquid phase than in the gaseous phase. Thus, [32] was modified to the form:

$$t = \frac{1}{KC_0 L^{0.5}} \left[\frac{KN_0 \lambda L^{0.5}}{L} - \ln(C_0/C - 1) \right] . \quad [33]$$

The volumetric flow rate Q , in units of volume per unit time, is related to the linear flow rate L by the expression:

$$L = \frac{Q}{A} . \quad [34]$$

Substituting [34] into [33] and combining terms:

$$t = \frac{N_0 \lambda A}{C_0 Q} - \frac{(A/Q)^{0.5}}{KC_0} \ln(C_0/C - 1) . \quad [35]$$

The volume V which has passed through the column at time t may be calculated by

$$V = Qt . \quad [36]$$

Thus, by multiplying [35] by Q and equating the product to [36]:

$$V = \frac{N_o \lambda A}{C_o} - \frac{\sqrt{QA}}{KC_o} \ln(C_o/C - 1) . \quad [37]$$

Once the constant K has been determined, [37] should predict the volume V of influent solution moving at flow rate Q required to produce an effluent breakthrough fraction of C/C_o beneath a column of length λ and surface area A whose volumetric exchange capacity is N_o . The constant K can easily be evaluated for a particular resin column breakthrough curve by plotting V versus $\frac{\sqrt{QA}}{C_o} \ln(C_o/C - 1)$. The slope of the resulting straight line will be the negative of $1/K$.

Such an evaluation was made using a six inch deep resin column loaded with an influent solution containing 500 ppm of calcium as CaCO_3 . The flow rate was 2 GPM/ft². Figure 20 shows the breakthrough curve obtained. The graph used to evaluate the constant K is shown in Figure 21. A straight line could be fitted to all the data points except those corresponding to the initial breakthrough values. The value of K for the breakthrough curve obtained was found to be 5.46 with units of $\text{cm}^{5.5}/\text{meq-min}^{0.5}$.

The evaluation curve of Figure 21 also afforded a check on the volumetric exchange capacity of the ion exchange resin used. The chemical analysis of the resin listed this exchange capacity as 1.9 meq/ml. At $C/C_o = 0.50$ the breakthrough volume may be equated to

$$V = \frac{N_o \lambda A}{C_o} . \quad [38]$$

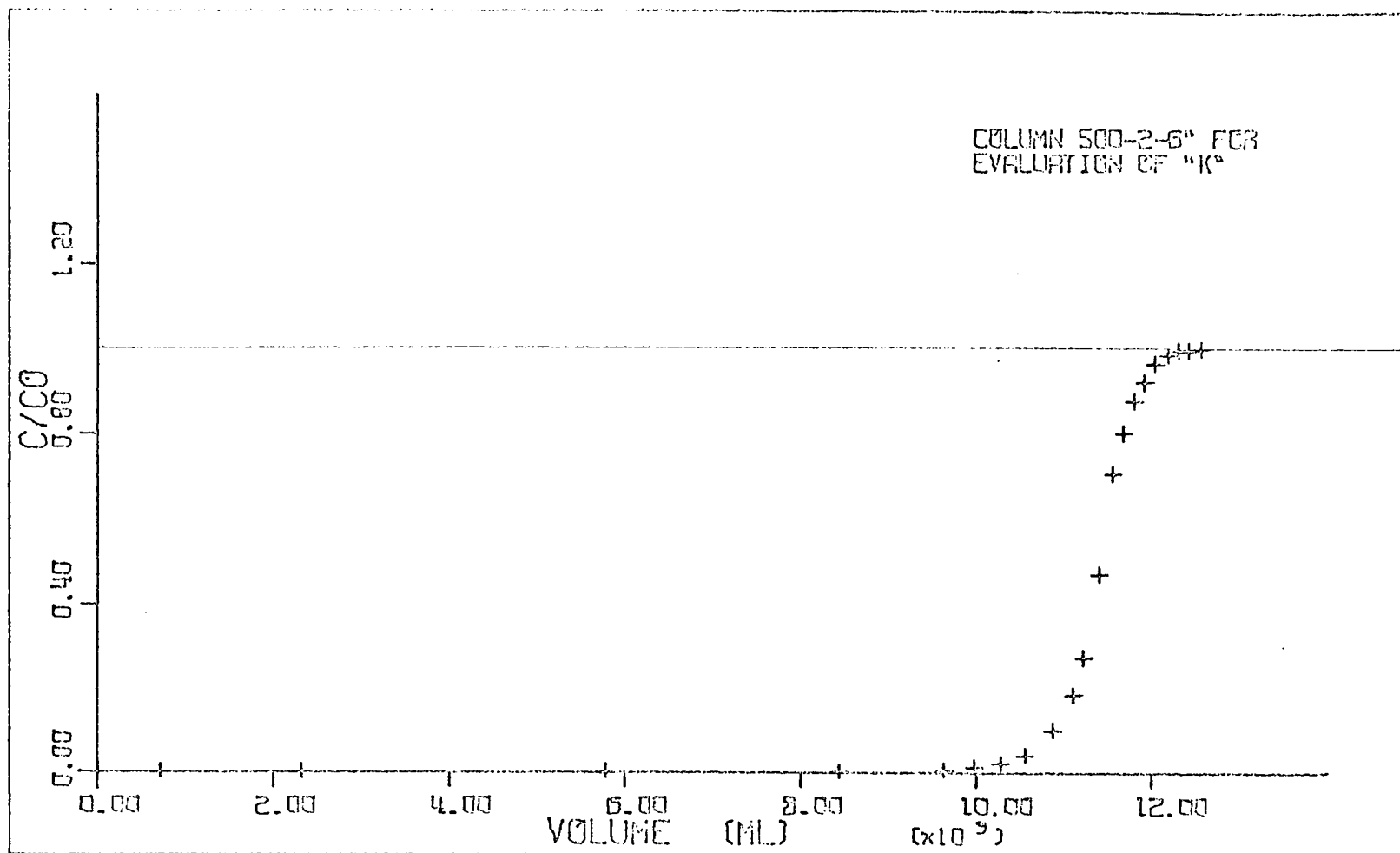


Figure 20. Calcium breakthrough curve for run 500-2-6" -- used to evaluate the constant K in Hinshelwood's equation

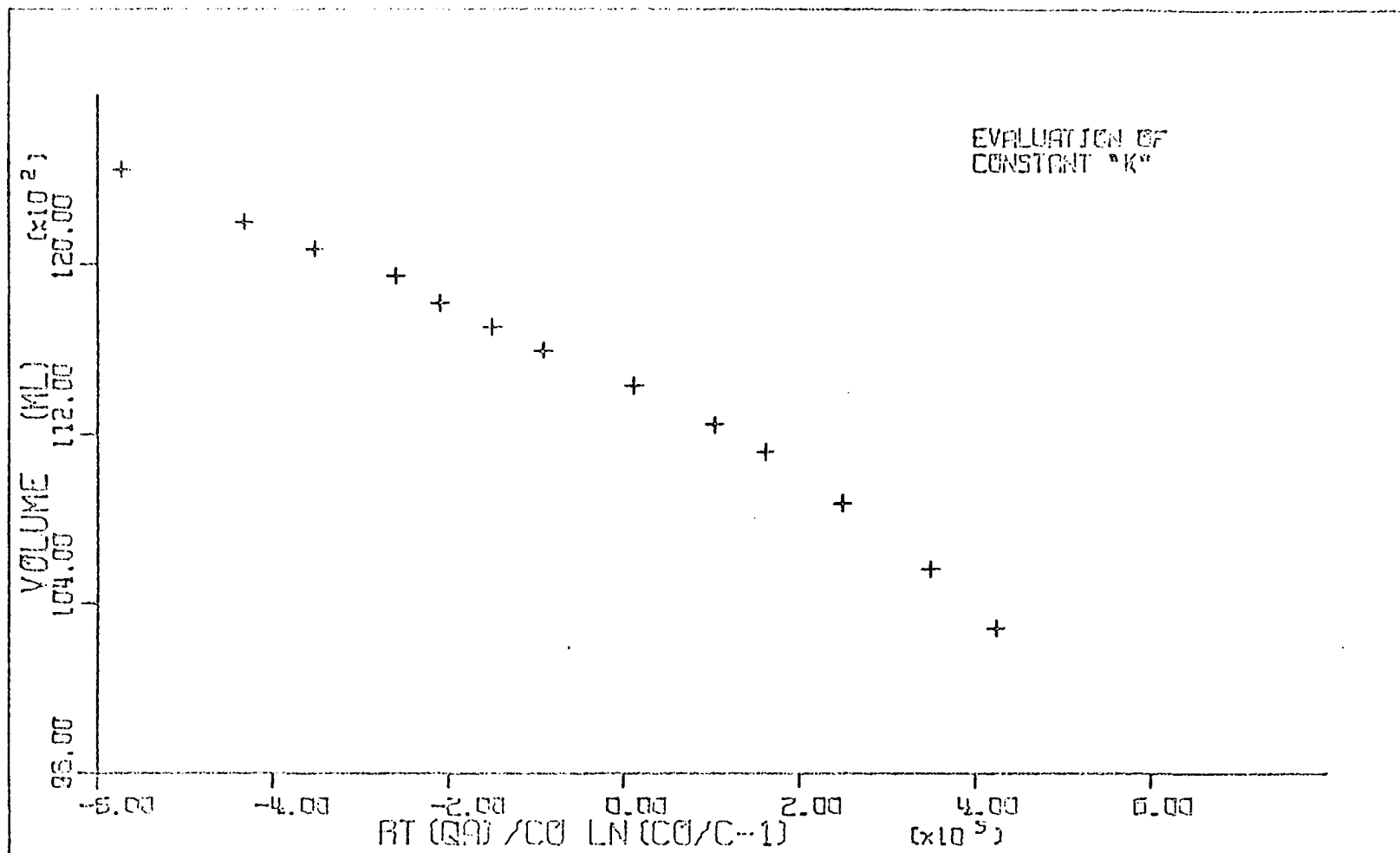


Figure 21. Curve used to evaluate the constant K in Hinshelwood's equation
 -- values obtained from breakthrough column 500-2-6"

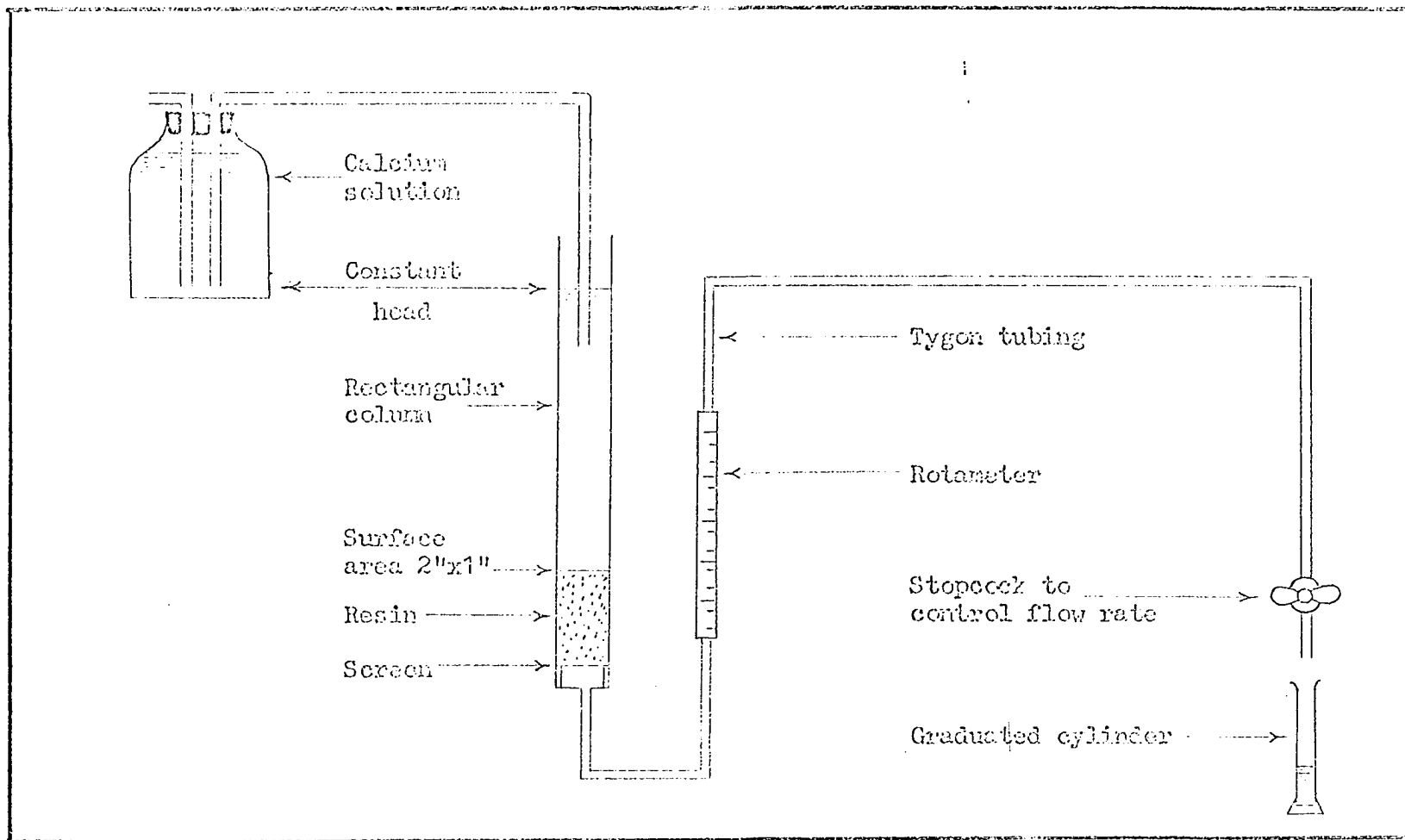


Figure 22. Apparatus used to verify Hinshelwood's equation

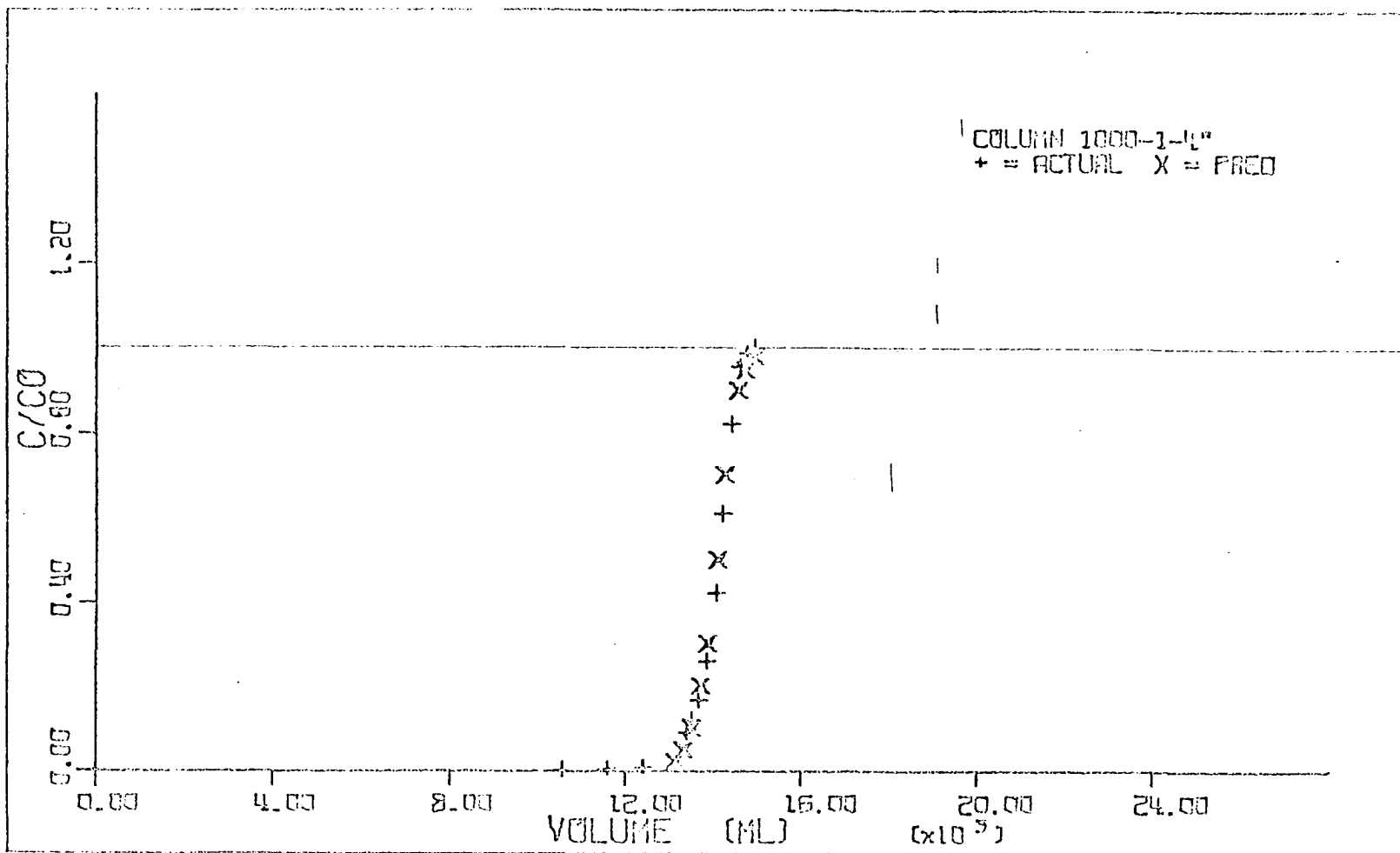


Figure 23. Actual calcium breakthrough curve using 2" x 1" rectangular resin column operated at 1000-1-4" compared to the predicted curve based on Hinshelwood's equation

Solving [38] for N_0 confirmed the assay value of 1.9 meq/ml for the volumetric exchange capacity of the ion exchange resin.

Prediction Using Modified Hinshelwood Equation

With the constant of [37] determined and the resin exchange capacity verified, the equation could then be used to predict the breakthrough curve expected from a column test with any combination of the variables used in [37]. In order to rigorously test [37], it was desirable to change the pertinent variables as much as possible from the values used to determine the constant K. Thus, the 2.20 cm diameter column was replaced with a rectangular column with surface dimensions of 2" x 1". The influent concentration was increased from 500 ppm to 1000 ppm calcium as CaCO_3 , the depth was lowered from 6 inches to 4 inches, and the loading rate was lowered from 2 GPM/ft² to 1 GPM/ft². The experimental apparatus is shown schematically in Figure 22. A predicted curve was first computed using [37] with the following values:

$$\begin{aligned} N_0 &= 1.9 \text{ meq/ml} \\ \lambda &= 11.5 \text{ cm} \\ A &= 12.9 \text{ cm}^2 \\ C_0 &= 0.01985 \text{ meq/ml} \\ Q &= 52.5 \text{ ml/min} \\ K &= 5.46 \text{ cm}^{5.5} / \text{meq-min}^{0.5} . \end{aligned}$$

The actual breakthrough curve obtained together with the breakthrough curve predicted are shown in Figure 23.

Conclusions Concerning Modified Hinshelwood Equation

Hinshelwood's equation thus appears to give a reliable indication of the location and shape of a calcium breakthrough curve using an ion exchange resin. While the equation does generate an "S-shaped" prediction curve, it should be noted that the curve is nearly symmetric about the 50% breakthrough point. This was true for the ion exchange resin used. However, for some of the soil columns tested an almost flat plateau developed around the 70% breakthrough values. It was assumed that the uniformity of the ion exchange resin as well as its good stability contributed to a more symmetric breakthrough curve. The column depths and flow rates used for the resin column tests may also have added to the nearly symmetrical shape of the breakthrough curves obtained.

Calcium Extraction

The desirability of being able to follow the progress of strontium through soil by extracting the adsorbed strontium has been discussed previously. Therefore, when using the resin-calcium model of the soil-strontium system, it became desirable to be able to follow the movement of the calcium through the ion exchange resin utilizing an extraction technique.

The process of extracting calcium from resin was faster and simpler than the process of removing strontium from soil. Approximately 1.5 ml of resin were used for each extraction

sample. One-eighth inch inside diameter glass tubing was partially stoppered at one end with about one inch of glass wool. The 1.5 ml resin sample was then poured on top of the glass wool. Ten such extraction columns were made and connected together with Tygon tubing so that any or all of the extraction columns could be used simultaneously. The extraction columns were connected by a common influent line to a reservoir containing 1N HCl. Figure 24 shows a schematic diagram of the extraction apparatus.

By making several test extractions it was determined that all of the calcium present on a 1.5 ml sample could be eluted with about 400 ml of 1N HCl. Figure 25 shows a typical desorption curve. Therefore, a 500 ml volumetric flask was placed under each of the ten extraction tubes. A 25 ml aliquot was taken from the 500 ml of eluent collected and analysed for calcium.

The 1 N HCl used for the calcium elution was too acidic for the Type II buffer solution used in the water hardness test obtained from Hach Chemical Company. The buffer solution could not raise the pH to the required value of 10 for the hardness titration. It thus became necessary to first titrate the 25 ml aliquots with a concentrated solution of sodium hydroxide. A pH-meter was used to determine when enough NaOH had been added to neutralize the 1N HCl. The required amount of Type II buffer was then added to bring the pH up to 10.

As a control test 25 ml samples of pure 1N HCl were neu-

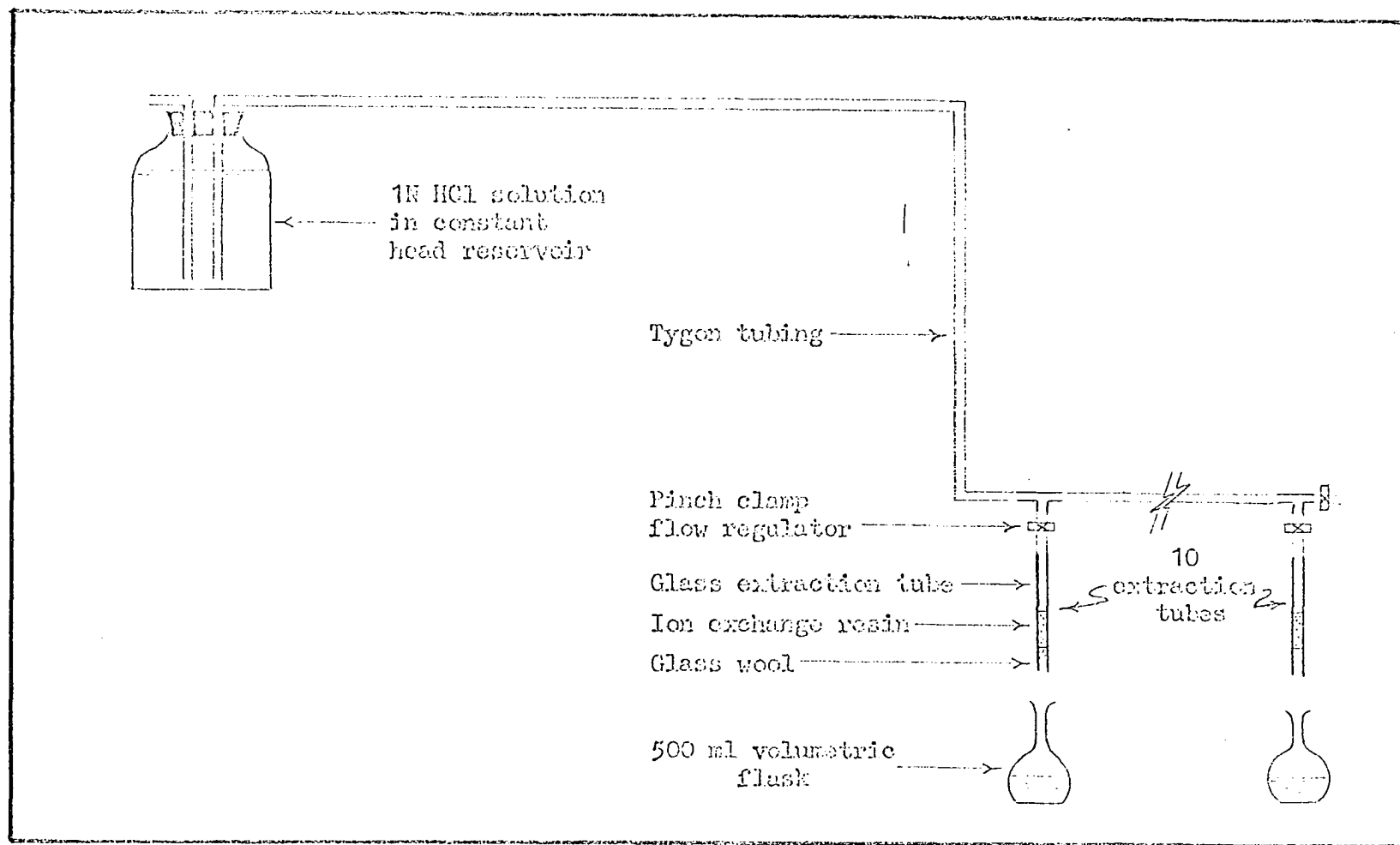


Figure 24. Apparatus used for calcium extraction from ion exchange resin

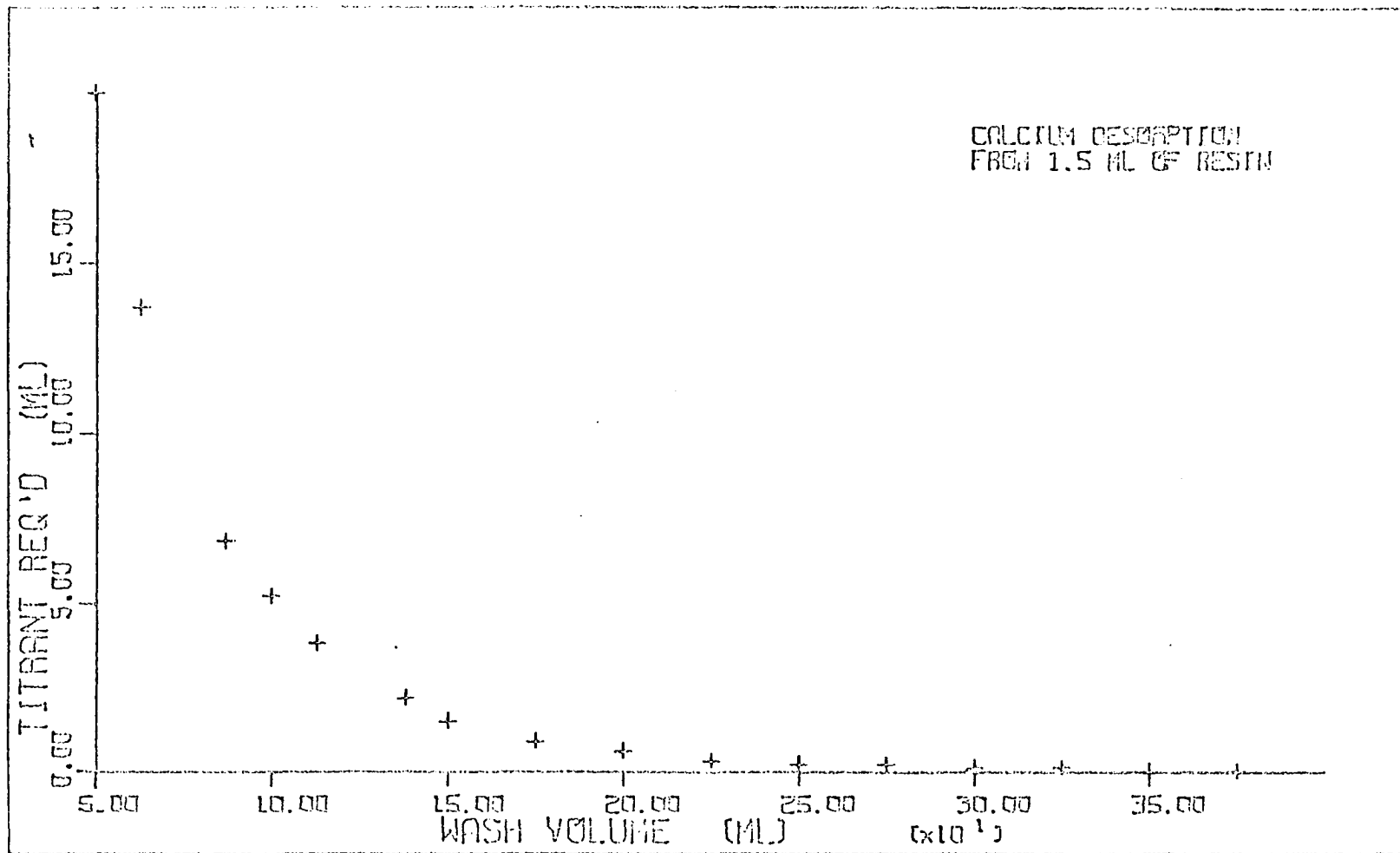


Figure 25. Calcium desorption curve obtained from eluting 1.5 ml Dowex 50W-X8 cation exchange resin with 1N HCl after saturating the resin with 500 ppm calcium as CaCO_3

tralized with the NaOH solution and buffered to a pH of 10. The controls were then tested for hardness by the Hach method. It was observed that these controls had a hardness of 0.20 mg as CaCO_3 per sample. Since sodium cations were the only ions present which might have interfered with the ManVer indicator, even though theoretically they should have had no effect on the indicator, it was assumed that the very large amounts of sodium added caused an interference hardness of 0.20 mg as CaCO_3 per sample. In all NaOH neutralizations of 25 ml samples containing 1N HCl, this interference hardness value was subtracted from the amount of HexaVer titrant required.

Calcium Front Through Resin

The 2" x 1" rectangular column used as part of the apparatus shown in Figure 22 was designed with a removable front plate for easy access to the exchange material being used. The column was used for a predetermined time period which was short enough so that no calcium appeared at the bottom of the column. At the completion of such a test, the column was drained, the front face of the column was removed, and resin samples were obtained from various locations within the column. From each of these resin samples, 1.5 ml extraction samples were taken, and any calcium present was removed using the extraction apparatus previously described.

The above approach was used several times with the rectan-

gular column with the removable front cover. Solving [37] for the bed depth λ resulted in

$$\lambda = \frac{VC_0}{AN_0} + \frac{\sqrt{Q/A}}{KN_0} \ln(C_0/C - 1) . \quad [39]$$

The quantity λ was interpreted as the depth at which a given breakthrough fraction C/C_0 should be located after the column was exposed to V milliliters of influent solution. It was further reasoned that if the calcium concentration in solution at depth λ were a certain fraction of the calcium concentration of the influent solution, then the ion exchange resin at that depth should be saturated with calcium to the same degree. Thus, if the liquid phase at a given depth contained 30% of the calcium concentration which would eventually be observed at that depth, then the resin at the same location would also contain 30% of the calcium concentration which it would eventually be expected to adsorb. The N_0 value assumed for the resin was the 5.0 meq/gram indicated in the chemical analysis listing on the bottles of resin purchased.

A typical extraction column was run with the following values for the pertinent parameters:

$$\begin{aligned} V &= 15,090 \text{ ml} \\ C_0 &= 3.03 \times 10^{-2} \text{ meq/ml} \\ Q &= 105 \text{ ml/min} \\ N_0 &= 1.9 \text{ meq/ml} \\ A &= 12.90 \text{ cm}^2 \end{aligned}$$

$$K = 5.46 \text{ cm}^{5.5}/\text{meq-min}^{0.5}$$

$$\text{column depth} = 39.8 \text{ cm}$$

It was then possible to solve [39] to predict the depths at which certain resin saturation percentages would be expected. Resin samples were taken at thirteen depths at the conclusion of the test and analysed for their calcium content by the extraction procedure described. Figure 26 shows a comparison between the predicted and observed resin saturation percentages.

It can be seen from Figure 26 that the use of [39] resulted in a close prediction of the location of the calcium saturation front which was moving through the large resin column. The band width of the saturation front, or the distance along the column from 100% resin saturation to 0% resin saturation, was governed by the $\frac{\sqrt{QA}}{KN_0}$ coefficient in [39]. In order to obtain a larger and more discernible band width for the column used, only the flow rate Q could be used to increase the controlling coefficient. The 105 ml/min value of Q , used to produce the curve of Figure 26, represented a surface loading rate of 1 GPM/ft². This resulted in a band width of only about 2 cm. If the flow rate were increased 25 times, this band width should be spread over a distance only 5 times greater or 10 cm. While this would have allowed more resin samples to be taken within the band width, such a high flow rate would have been extremely greater than any flow rate expected under actual field conditions.

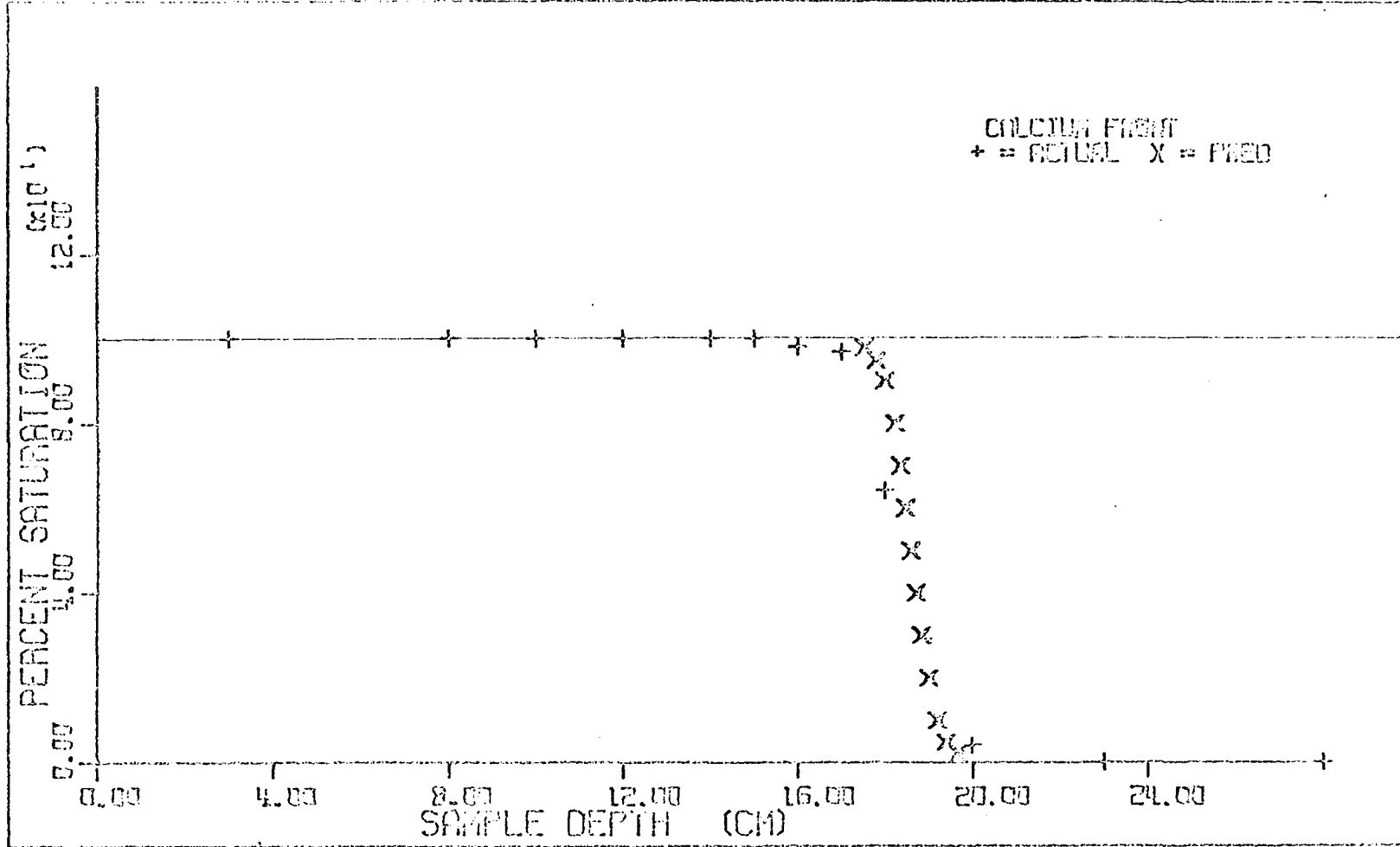


Figure 26. Location of actual calcium front using 2" x 1" rectangular resin column operated at 1500-1-16" compared to the predicted location based on Hinshelwood's equation

The saturation band width could also be enlarged by using an exchange material with a smaller volumetric exchange capacity N_0 . Soil has a cation exchange capacity from 50 to 100 times less than the ion exchange resin used. Therefore, a very large saturation band width would be expected in a similarly constructed soil column.

Two Directional Flow Models

The use of soil and resin columns greatly simplified the hydraulic considerations which contribute to the movement of ions through porous media. However, such columns were only models of the more complex conditions which would be observed under a radioactive waste disposal pit. Many physical parameters observed in the columns will differ from their counterparts beneath an actual waste pit. One such parameter is the number of directions which may be taken by the waste. In column studies only vertical movement existed. Under actual conditions movement may be in any horizontal direction away from the waste pit as well as in the vertical direction downward. Thus, a somewhat more complicated stage in the investigation of radioactive waste movement through soil would be the examination of dispersion systems in which flow would move in two directions.

If a liquid is moving through a saturated porous medium, then the amount of liquid entering any differential element during a given time is exactly equal to the amount of liquid

leaving the element. This is simply a conservation of mass. Figure 27 shows such a differential element located in a Cartesian coordinate system. The element has dimensions of ΔX , ΔY , and ΔZ . Considering only the flow in the X-direction, the rate at which liquid is entering the element is given as

$$Q_x = A_x V_x \quad [40]$$

where

$$Q = \text{flow rate} \quad [\text{cm}^3/\text{sec}]$$

$$A = \text{area} \quad [\text{cm}^2]$$

$$V = \text{linear velocity} \quad [\text{cm}/\text{sec}]$$

and the subscripts denote the direction in which the parameters are being observed. From Figure 27 it can be seen that [40] may be written as

$$Q_x = (\Delta Y \Delta Z) V_x \quad [41]$$

The change in velocity of the liquid as it passes through the differential element may be represented by

$$\Delta V_x = \frac{\delta V_x}{\delta X} \Delta X \quad [42]$$

The exit velocity of the liquid is equal to the entrance velocity plus the change in velocity. The net accumulated flow into the element in the X-direction could thus be represented by

$$\begin{aligned} Q_{x\text{-net in}} &= Q_{x\text{-in}} - Q_{x\text{-out}} \\ &= (\Delta Y \Delta Z) V_x - (\Delta Y \Delta Z) \left(V_x + \frac{\delta V_x}{\delta X} \Delta X \right) \\ &= -\frac{\delta V_x}{\delta X} \Delta X \Delta Y \Delta Z \quad [43] \end{aligned}$$

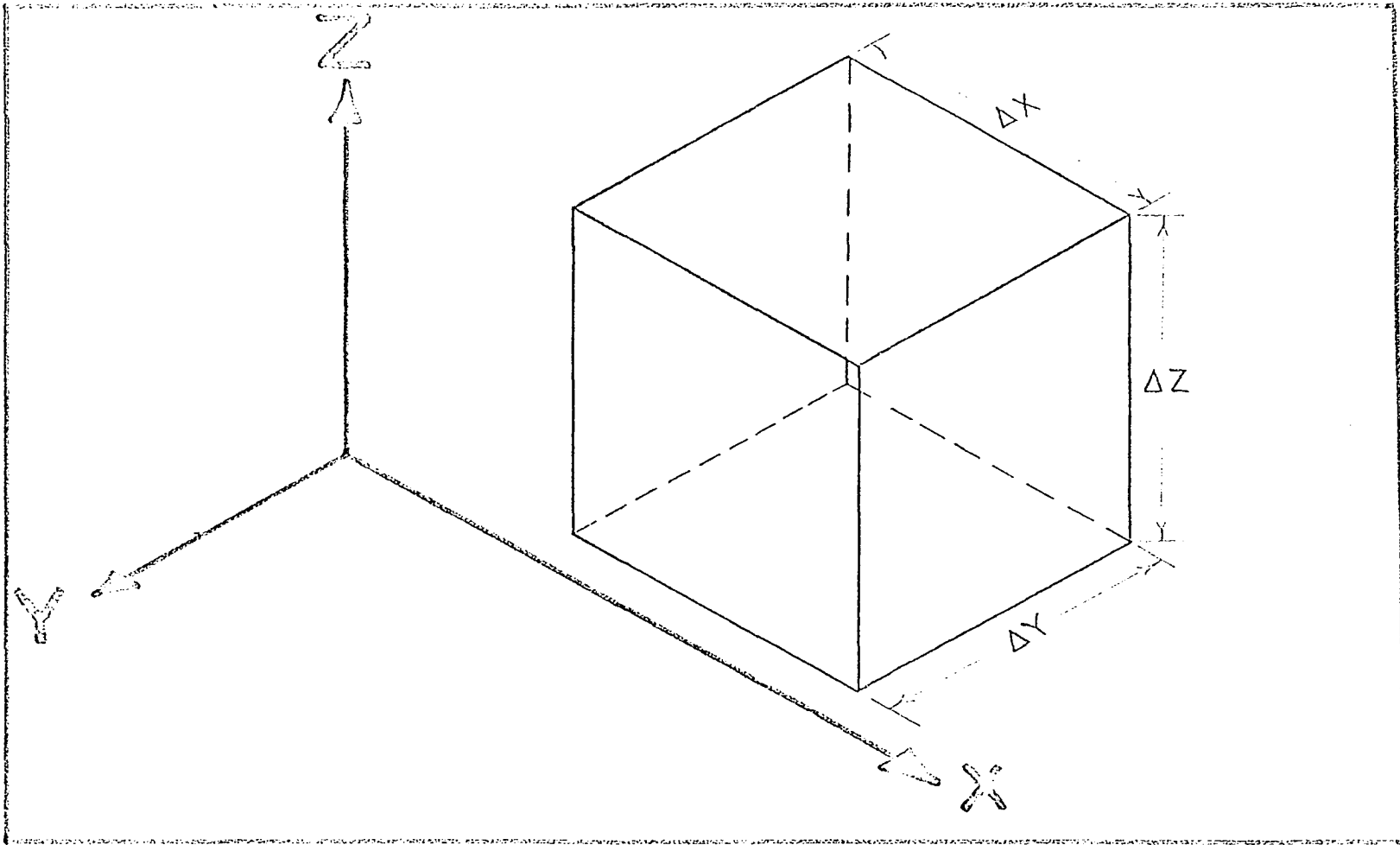


Figure 27. Differential element of a porous material subjected to saturated flow

Using a similar argument it can be shown that the net flow into the differential element in the Y-direction and the Z-direction may be represented as

$$Q_{y\text{-net in}} = - \frac{\delta V}{\delta Y} \Delta X \Delta Y \Delta Z \quad [44]$$

$$Q_{z\text{-net in}} = - \frac{\delta V}{\delta Z} \Delta X \Delta Y \Delta Z \quad [45]$$

The total amount of liquid entering the element is the sum of [43], [44], and [45]:

$$Q_{\text{net in}} = - \left(\frac{\delta V}{\delta X} + \frac{\delta V}{\delta Y} + \frac{\delta V}{\delta Z} \right) \Delta X \Delta Y \Delta Z \quad [46]$$

The total amount of liquid entering the element may also be represented by

$$Q_{\text{net in}} = \frac{\delta \theta_v}{\delta t} \Delta X \Delta Y \Delta Z \quad [47]$$

where θ_v represents the volumetric water content of the porous material. Equating [46] and [47]:

$$\frac{\delta \theta_v}{\delta t} = - \left(\frac{\delta V}{\delta X} + \frac{\delta V}{\delta Y} + \frac{\delta V}{\delta Z} \right) \quad [48]$$

The relationship shown in [48] is an expression of the conservation of mass within the differential element.

Under saturated flow conditions, Darcy's law is assumed to be valid. Expressed in the differential form and considering movement in the X-direction only, Darcy's law may be written as

$$V_x = - K \frac{\delta h}{\delta X} \quad [49]$$

where K represents the saturated hydraulic conductivity of the

porous medium which is assumed to be constant in all directions. The term $\delta h/\delta X$ represents the change in the hydraulic potential of the liquid over the distance ΔX . Substituting [49] and its similar representations for the velocities in the Y-direction and the Z-direction into [48]:

$$\frac{\delta \theta_v}{\delta t} = K \left(\frac{\delta^2 h}{\delta X^2} + \frac{\delta^2 h}{\delta Y^2} + \frac{\delta^2 h}{\delta Z^2} \right) . \quad [50]$$

If the porous material is saturated and at steady state conditions, then the change in the differential element's volumetric water content with time is equal to zero. Therefore, [50] becomes

$$\frac{\delta^2 h}{\delta X^2} + \frac{\delta^2 h}{\delta Y^2} + \frac{\delta^2 h}{\delta Z^2} = 0 \quad [51]$$

which is known as LaPlace's equation. If it is assumed that flow moves only in two directions then [51] reduces to

$$\frac{\delta^2 h}{\delta X^2} + \frac{\delta^2 h}{\delta Y^2} = 0 . \quad [52]$$

Kirkham and Powers (13) give a general solution to [52] as

$$h = A \pm BX \pm CY \pm \frac{\sinh \frac{X}{E_n} \text{ or } \alpha_n \sin \frac{Y}{c} \text{ or } (b \pm \text{ or }) \text{ or } (c \pm \text{ or })}{\cosh \frac{X}{E_n} \text{ or } \alpha_n \cos \frac{Y}{c} \text{ or } (b \pm \text{ or }) \text{ or } (c \pm \text{ or })} \quad [53]$$

where A, B, C, E_n , α_n , b, and c are constants. These constants can be evaluated based on the boundary conditions imposed on a particular two directional flow problem. After the constants have been evaluated, [53] should accurately describe the hydraulic potential lines which, for a homogeneous, isotropic,

porous medium, will be perpendicular to the flow lines throughout the medium.

The stream function ψ represents the lines of flow through the porous material. The stream function may be normalized to represent fractional values of influent flow into the system. Thus, the difference between the values of two adjacent stream functions will equal the percentage of the total flow which passes between those particular stream lines. The stream functions may be calculated from the potential function by the use of the Cauchy-Riemann equations:

$$K \frac{\delta h}{\delta x} = \frac{\delta \psi}{\delta y} \quad [54]$$

$$K \frac{\delta h}{\delta y} = - \frac{\delta \psi}{\delta x} . \quad [55]$$

Boundary Value Solutions

Evaluation of the constants used in [53] required the determination of the boundary conditions which surround the saturated flow problem being investigated. Once the boundary conditions have been chosen any one of several mathematical techniques may be used to evaluate the constants so that each of the boundary conditions is satisfied.

Since the problem under consideration was the movement of radioactive waste beneath a waste seepage pit, boundary conditions were chosen which would closely approximate the actual conditions under such a pit. The solution of [53] for certain

boundary conditions can become a complex if not impossible task. Therefore, it was decided for the initial experiments to incorporate a set of boundary conditions for which a solution had already been obtained and which also reasonably described the conditions being modeled. Kirkham's (12) solution to a particular drainage ditch problem appeared to satisfy the above criteria. Figure 28 shows the boundary conditions of Kirkham's model. Drainage ditches existed on either side of a ponded water supply, and each contained a different level of drainage water. The water supply was bounded by ditch banks of infinite width. The soil immediately beneath the ditch banks was assumed to be impervious to soil water movement.

In order to give the seepage pit's side walls finite dimensions, a constant of integration was evaluated by assuming that $\psi = 0$ at $x = w$ and $y = d$ where w was the width of the side wall and d was the depth of the resin. The third boundary condition listed in Figure 28 shows that the hydraulic head is equal to $d + t$ across the entire surface of the resin. However, under the side wall of the seepage pit this is not true. The 0% flow line which runs from the left hand corner of the seepage pit to the drainage ditch actually describes an upper flow region boundary, shown as the curved line AB in Figure 28, across which no water flows. For small values of w compared to the total width $2s$, the position of AB does not greatly change the flow region. However, if w is large com-

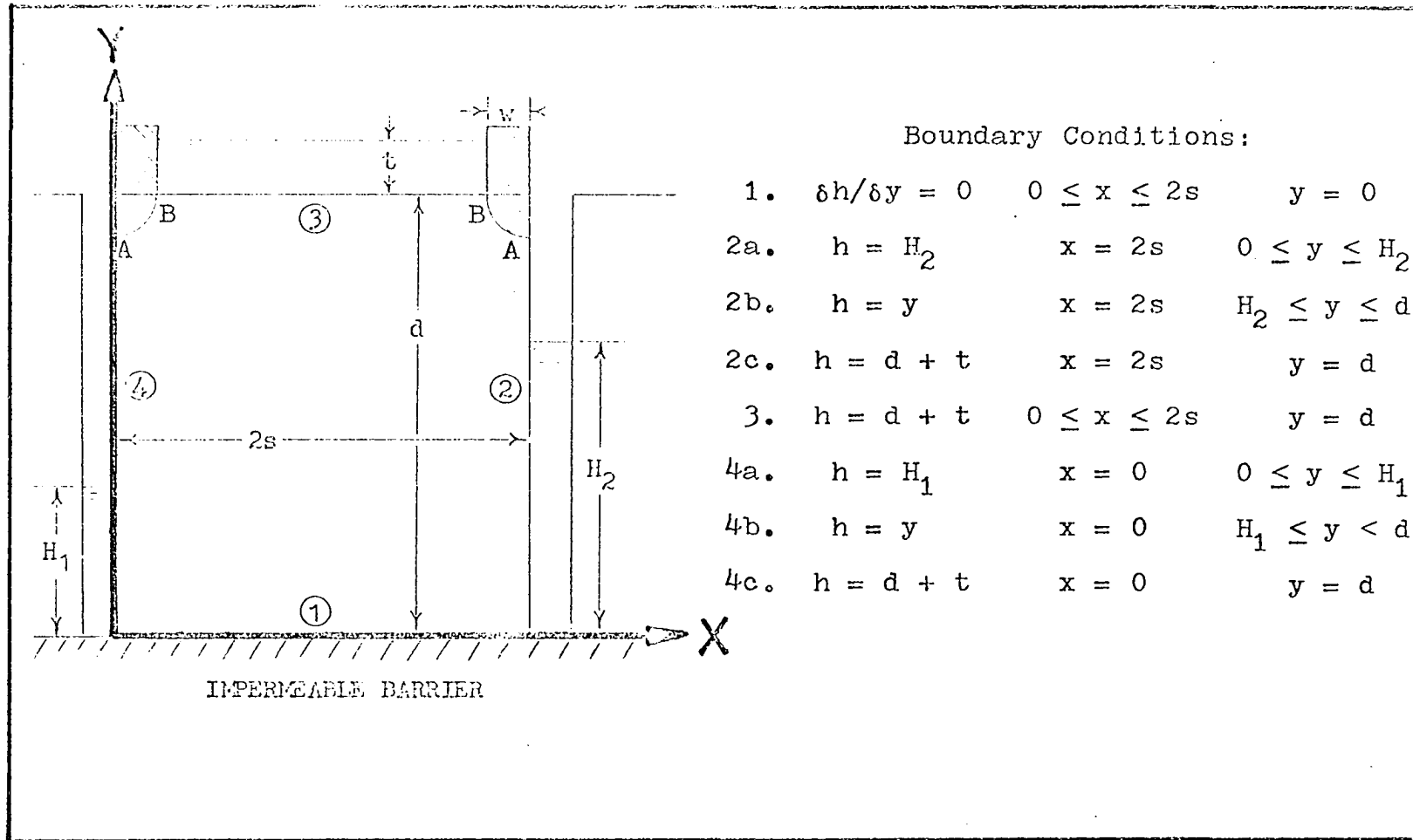


Figure 28. Two directional flow model and boundary conditions used in loading ion exchange resin with a calcium solution

pared to $2s$, then Kirkham's mathematical model would not be expected to be applicable. The upper limit to flow under the side walls of the seepage pit is actually a non-linear boundary condition which does not lend itself to a Fourier series solution. Dagan (6) suggests the use of matched asymptotic expansions to represent such non-linear boundary conditions.

Since a solution was available to the two directional flow problem with the boundary conditions shown in Figure 28, an attempt was made to apply that solution to the two directional flow tank. Kirkham's solution for the potential function was:

$$h = d + t + \sum_{\text{ODD}}^{\infty} A_m \frac{\sinh \frac{m\pi x}{2d}}{\sinh \frac{m\pi 2s}{2d}} \cos \frac{m\pi y}{2d} + \sum_{\text{ODD}}^{\infty} B_m \frac{\sinh \frac{m\pi (2s - x)}{2d}}{\sinh \frac{m\pi 2s}{2d}} \cos \frac{m\pi y}{2d} \quad [56]$$

where

$$A_m = -\frac{4t}{m\pi} \sin \frac{m\pi}{2} - \frac{8d}{m^2 \pi} \cos \frac{m\pi H_1}{2d} \quad m = 1, 3, \dots \quad [57]$$

$$B_m = -\frac{4t}{m\pi} \sin \frac{m\pi}{2} - \frac{8d}{m^2 \pi} \cos \frac{m\pi H_2}{2d} \quad m = 1, 3, \dots \quad [58]$$

The dimensions d , t , s , H_1 , H_2 , x , and y are shown in Figure 28. Applying [54] and [55] to [56], Kirkham obtained the stream function relationship:

$$\frac{\psi}{K} = \alpha + \sum_{\text{ODD}}^{\infty} A_m \frac{\cosh \frac{m\pi x}{2d}}{\sinh \frac{m\pi 2s}{2d}} \sin \frac{m\pi y}{2d} - \sum_{\text{ODD}}^{\infty} B_m \frac{\cosh \frac{m\pi(2s-x)}{2d}}{\sinh \frac{m\pi 2s}{2d}} \sin \frac{m\pi y}{2d} \quad [59]$$

where A_m and B_m were given by [57] and [58], respectively, and K was the saturated hydraulic conductivity of the soil. The constant α in [59] is evaluated by assuming that no flow enters the soil from the pond under the ditch banks. Thus, $\psi = 0$ at $x = w$ and $y = d$, and [59] was solved for α :

$$\alpha = - \sum_{\text{ODD}}^{\infty} A_m \frac{\cosh \frac{m\pi d}{2d}}{\sinh \frac{m\pi 2s}{2d}} \sin \frac{m\pi d}{2d} - \sum_{\text{ODD}}^{\infty} B_m \frac{\cosh \frac{m\pi(2s-w)}{2d}}{\sinh \frac{m\pi 2s}{2d}} \sin \frac{m\pi d}{2d} . \quad [60]$$

In working with stream functions it is usually more convenient to define them as percentages of the total flow. Therefore, any stream function $\psi(x,y)$ calculated was normalized against the total flow and multiplied by 100 to obtain the percentage stream function $\psi^o(x,y)$. Referring to Figure 28:

$$\psi^o(x,y) = \frac{100 \psi(x,y)}{\psi(2s-w,d) - \psi(w,d)} . \quad [61]$$

In order to draw the predicted stream lines for the two directional flow model shown in Figure 28, it was necessary to solve [61] for many points throughout the model. Since the

solution of [61] for any point also required the solution of [57], [58], [59], and [60], a computer program was used to expedite the analysis. The series solutions required in [57], [58], [59], and [60] were programmed as iterative steps which continues until successive solutions agreed to within two places to the right decimal. This resulted in each series being resolved to within four to six significant figures.

Using this computer program, flow lines were drawn through the soil profile shown in Figure 28 for varying values of the pertinent constants. The volume flowing between any two adjacent flow lines represented a known percentage of the total flow. Therefore, each adjacent pair of flow lines represented the side of a curved, one directional flow column whose cross sectional area varied with depth. A successful analysis of the breakthrough curves obtained from the soil and resin columns could be combined with the mathematical representation of a two directional flow model. By assuming that the two directional flow model contained many linear columns, a breakthrough analysis for the two directional flow system could be obtained.

Hydraulic Testing of the Two Directional Flow Model

Once suitable boundary conditions were chosen which would adequately simulate the actual field conditions expected, it then became necessary to construct a physical model which would reproduce those boundary conditions. Experience gained

from the construction of the Plexiglas column with a removable front plate, shown as part of the apparatus of Figure 19, was applied to a model in which flow could move in two directions. Dimensions of 18" x 18" x 1" were chosen. Three-eighths inch Plexiglas was used for the removable front plate. This thickness enabled a water tight seal to be made between the front plate and the sides and bottom with only stopcock grease as a sealant. Bolts with wing nuts were placed at three inch intervals around the sides and bottom of the model to secure the front plate. A well was formed down one side of the model with two one-inch strips of one-eighth inch thick Plexiglas. This provided support for the one inch wide piece of 200 mesh stainless steel wire which was used to keep the ion exchange resin from entering the well. At the base of the well a three-quarter inch diameter hole was drilled. This hole was fitted with a number "0" rubber stopper through which a one-eighth inch hole had been drilled. A two foot length of glass tubing was then inserted into the rubber stopper. The glass rod could be extended up through the well to any height desired. This arrangement provided a constant head overflow weir by which the depth of the drainage ditch, represented by the well, could be preset.

When the front plate was sealed in place and the wire and rubber stopper inserted, the tank was then partially filled with water. The ion exchange resin was then slowly poured into the model thereby allowing all air to be driven out which

might otherwise have been trapped. Such a loading procedure could be used with resin and not with soil due to the uniform particle size of the former. If soil were loaded in such a manner, it would grade itself upon settling. This would result in unrealistic flow conditions.

Once the resin was loaded into the two directional flow model to the desired depth, the seepage pit was then modeled at the surface of the resin on the opposite side of the tank from the drainage ditch. This was done by inserting a 1" by 3/8" piece of Plexiglas whose sides had been coated with stopcock grease. This wall could be placed at any desired distance from the side of the model and extended into the resin to a depth of about one inch. A strip of 200 mesh stainless steel wire was used for the floor of the seepage pit. Without this floor the resin tended to flow into the modeled pit.

The two directional flow model was designed to represent one half of Kirkham's model shown in Figure 28. With the drainage ditch depths H_1 and H_2 of Figure 28 assumed for simplicity to be equal, the drainage problem became symmetric about a line drawn through the center of the seepage pit.

Before making an actual run with the two directional flow model using a calcium influent solution, it was desired to test the model hydraulically. This was done to verify that the flow lines which could be predicted using the computer program would accurately represent the actual flow lines observed within the model. The modeled seepage pit had a width of two

inches and a depth of one inch. The bottom of the pit was eleven inches from the bottom of the tank. The drainage ditch effluent elevation was set at six inches from the bottom of the tank. As distilled water was removed from the tank over the constant elevation weir in the drainage ditch, fresh distilled water was drawn into the seepage pit so that the water depth in the pit remained at a constant one inch.

Prior to beginning water movement through the model the ion exchange resin was saturated with distilled water to the surface of the resin. After flow was begun the resin near the surface was observed to be drying. This was the region through which no flow was occurring. The water in this region drained into the dynamic region below. When no more vertical draining was observed, the two directional flow model was assumed to be in hydraulic equilibrium, and the flow lines were then located.

Mapping of the flow lines was done by dropping dye pellets onto the bottom of the seepage pit near the front plate of the Plexiglas model. As the pellets dissolved, their paths through the resin were easily observed, and the centerlines of the paths were reproduced on the front face of the model using a grease pencil. Potassium permanganate crystals were first used in the dye study. They were large purple crystals which dissolved slowly. However, once a potassium permanganate crystal was spent, the outline of its path could still be seen. The effect of this staining on the exchange capacity of the resin was not known. The residual outline also partially

masked subsequent dye traces. Indigo carmine dye was then tried. The crystals were smaller than the potassium permanganate crystals and did not last as long. However, the indigo carmine did give brilliant blue traces which completely disappeared once the crystals had dissolved.

The flow line traced with a dye crystal in the left hand corner of the seepage pit was arbitrarily called the 0% flow line. Since the drainage ditch was to the left of the seepage pit, this flow line was the closest flow line to the surface of the resin. Therefore, the dye crystal placed in the right hand corner of the seepage pit resulted in the 100% flow line. It was assumed that all of the flow lines would travel an equal distance from the seepage pit to the drainage ditch to the left of the seepage pit. The assumption, though not completely valid, resulted in the dye traces representing flow values based on the fractional distance of the dye crystals from the left hand side of the seepage pit. Thus, a dye crystal placed one half inch from the left side of the two inch wide pit traced the 25% flow line. The flow lines observed are shown in Figure 29, and the predicted flow lines are shown in Figure 30.

The predicted flow lines were not in agreement with the observed flow lines. The flow medium became almost completely filled with the impermeable area beneath the seepage pit walls. For the relatively large value of w used in the tank model compared to the total model width $2s$, the third boundary

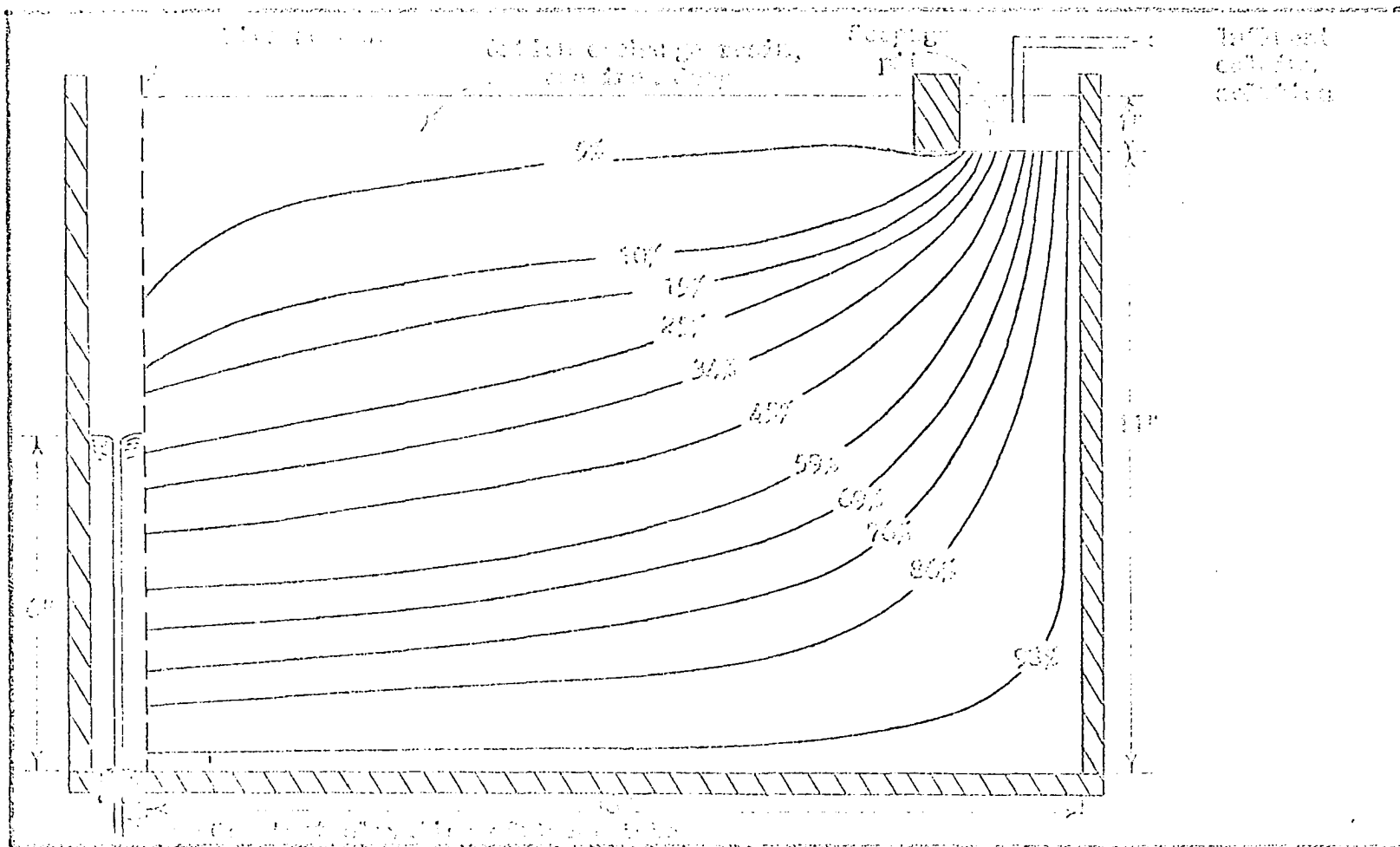


Figure 29. Flow lines observed in the two directional flow model using indigo carmine dye crystals

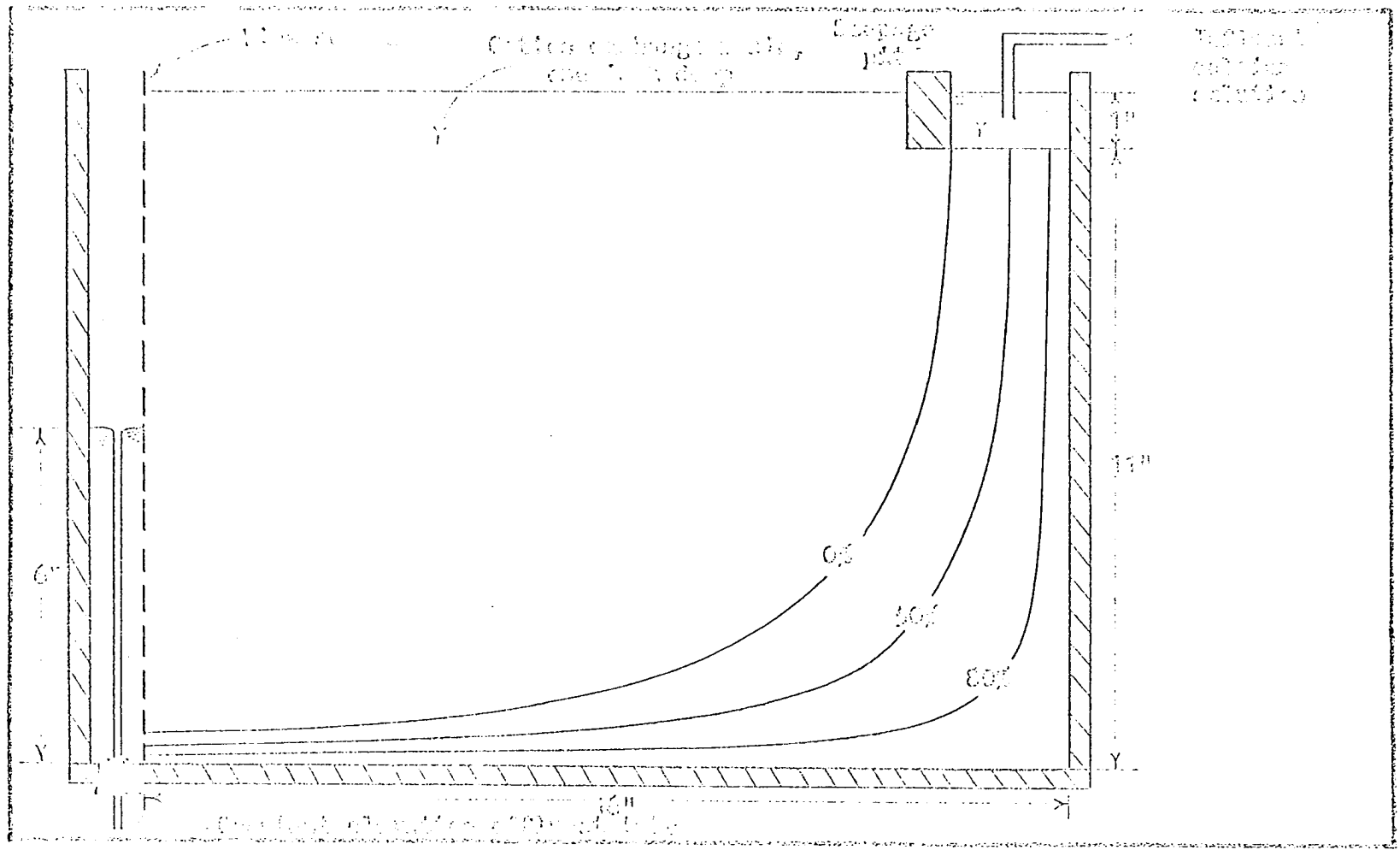


Figure 30. Predicted flow lines for the two dimensional model based on the computer solution of Laplace's equation for the given boundary conditions

condition given in Figure 28 was excessively violated. Therefore, the mathematical model indicated in Figure 28 could not be used.

For complex boundary conditions, such as would be encountered under actual field conditions, solutions to Laplace's equation in two dimensions may be difficult if not impossible. Another method of modeling the hydraulic behavior of a two directional flow system consists of the building of an electric analog to the hydraulic system. Darcy's law, assumed to be valid under saturated conditions, may be written in the form:

$$Q = KA \frac{H_1 - H_2}{L} \quad [62]$$

in which

Q = flow rate per unit time [cm^3/hour]

K = saturated hydraulic conductivity [cm/hour]

A = cross sectional area over which flow is taking place [cm^2]

H 's = hydraulic heads at two points within the soil mass measured from a common reference level [cm]

L = distance between the above points [cm]

Darcy's law corresponds directly to Ohm's law:

$$I = \sigma A \frac{V_1 - V_2}{L} \quad [63]$$

where the saturated hydraulic conductivity K is analogous to the specific electrical conductivity σ . Thus, the flow of water through a porous medium may be modeled by the flow of electrons through a conducting medium. If the soil profile

beneath a waste pit could be accurately mapped and reproduced by an electric analog, then the movement of water through that profile could easily be observed by monitoring the current flowing through the model. Obstructions in the soil profile such as strata of varying permeabilities could be accounted for in the electric model by varying the electrical resistance in the corresponding location within the model. A versatile electric analog is thus desirable in which boundary conditions and consistency variations could easily be constructed. The use of heavy papers coated with conducting substances are available commercially. The use of gelatins is also possible. This may provide an excellent material with which to construct models in which flow moves in three directions. A possible alternative to commercially produced materials is the use of large sheets of silver halide coated X-ray film. Strata conductivities might be successfully modeled by varying the X-ray intensity striking the film at the desired location.

Since flow lines through the tank model had already been determined, it was decided to use the observed flow lines together with the breakthrough prediction relationship shown in [39] to predict the movement of the calcium front through the two directional flow model constructed. While this approach did not offer the versatility of combining a breakthrough equation with a two dimensional solution to LaPlace's equation, it did allow a breakthrough prediction to be made for a condition in which flow was moving in two directions. Furthermore,

had the porous medium consisted of stratified layers of different resins, each with its own saturated hydraulic conductivity such a technique employing visual observations of flow patterns would prove to be better adaptable to the actual conditions than the use of a computerized solution to LaPlace's saturated flow equation. Also, the visual approach is not limited to boundary conditions for which mathematical solutions are possible.

In applying [39] to the ion exchange resin columns, the right hand term was seen to be very small compared with the other terms. It is thus possible to simplify [39] to

$$\lambda = \frac{VC_o}{AN_o} \cdot \quad [64]$$

For a linear column λ represents the column length and A represents the cross sectional area of the column. The volume of the column would thus be λA . Therefore, [64] may be rewritten as

$$\text{Column Volume} = \frac{VC_o}{N_o} \cdot \quad [65]$$

For the two directional flow system shown in Figure 29 any two adjacent flow lines are assumed to describe a non-linear column whose cross sectional area varies linearly with the length of the column. The volume entering such a column is equal to the total volume flowing through the seepage pit multiplied by f which is the difference between the fractional values of the flow lines used to describe the column. If the curved col-

umns of Figure 29 are assumed to be trapezoids with end dimensions of a and b inches, then [65] becomes:

$$0.5(a + b)(\lambda)(2.54 \text{ cm}) = \frac{fVC_0}{N_0} \quad [66]$$

since the columns are each one inch in depth. The resin was loaded with 40 liters of a calcium solution containing 3×10^{-2} meq/ml. Therefore, [66] simplifies to

$$\lambda = \frac{198.5 f}{a + b} \quad [67]$$

where λ is measured in centimeters.

Using [67], the location of the calcium front in each of the non-linear columns of Figure 29 was predicted. After the 40 liters of the calcium solution were passed through the resin, the tank was drained and the front face removed. Twenty resin samples from various locations were taken and purged of calcium using the extraction apparatus shown in Figure 24. After extraction, each resin sample was weighed and the amount of calcium present on the sample in units of meq/gm was computed. This amount of calcium per unit weight of resin was then compared to the manufacturer's indicated exchange capacity of the resin of 5.0 meq/gm to obtain the percent of saturation of each resin sample. In Figure 31 the straight lines between adjacent flow lines represent the predicted location of the calcium front based on [67]. The circles indicate the location of a particular resin sample, and the numerical value within a circle gives the percent of sat-

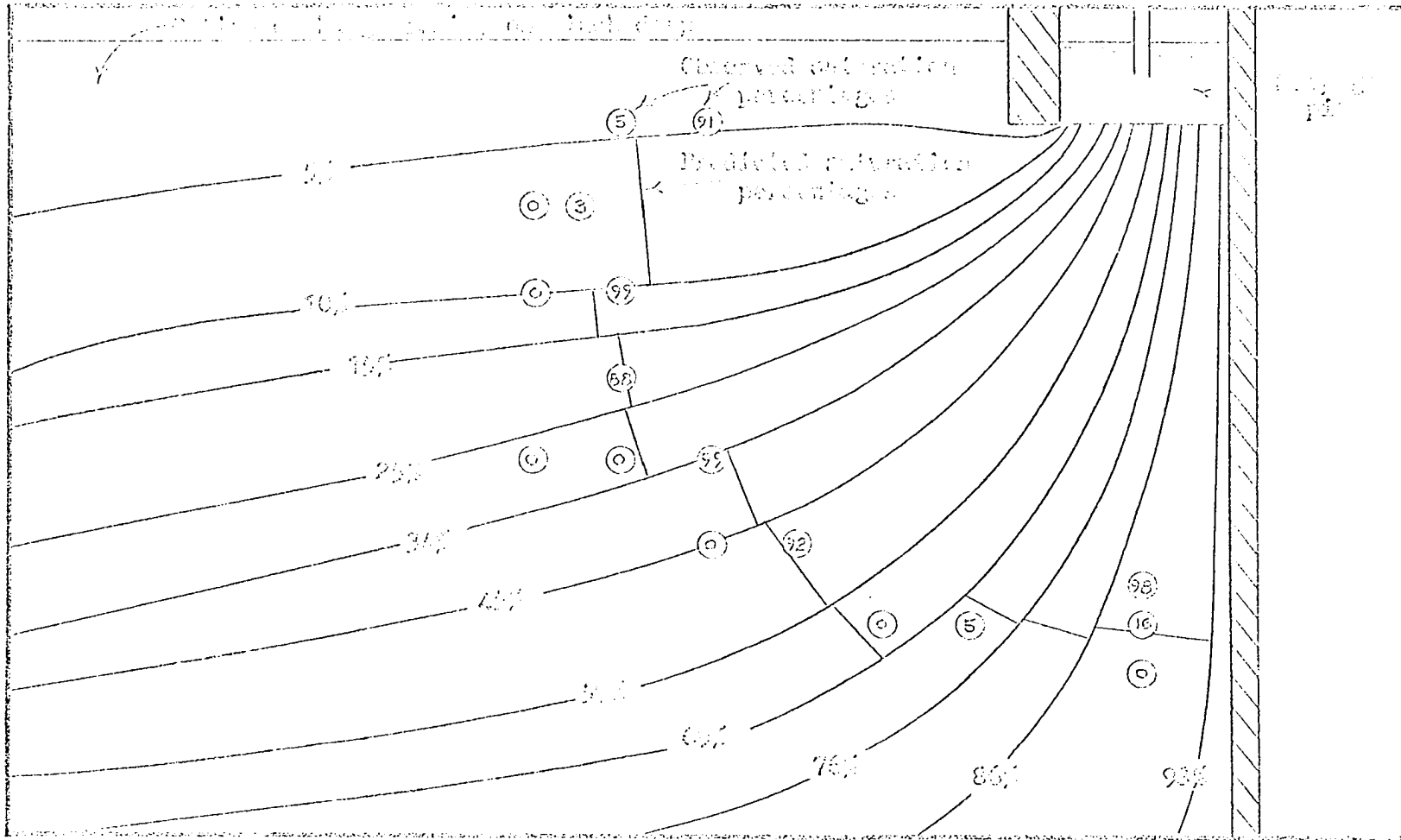


Figure 31. Predicted location of the calcium front in the two dimensional model compared to the percent saturation of resin samples taken from the model.

uration of that sample. Good agreement was observed between the predicted location and the actual location of the calcium front in the two directional flow model using the ion exchange resin.

REVISED SOIL COLUMN EXPERIMENTS

Reasons for Returning to Soil

The use of a calcium exchange resin to simulate an idealized soil proved to be a helpful substitute. It provided the means for investigating the effects of various ion transport mechanisms while other parameters were held constant. Likewise, the substitution of calcium for the radiostrontium used in obtaining earlier breakthrough curves further permitted a close examination of the relevant transport mechanisms. Since the breakthrough curves obtained with the use of calcium and resin could be reproduced if the pertinent variables were held constant, more validity could be placed in the resin-calcium results than in the previous work with the soil-strontium system.

The resin-calcium work resulted in improvements in the general technique of obtaining breakthrough curves and in the correlation of the breakthrough data. Breakthrough curves could be predicted in advance with a reasonable degree of accuracy as demonstrated by the results of column 1000-1-4" shown in Figure 23. Despite the many advantages of working with the idealized resin-calcium system, it was felt that if the knowledge gained from such work could not be related to a more realistic soil system, then such idealized results were virtually meaningless. It was therefore decided to return to using soil as the adsorption medium. The continued use of

calcium or the use of stable strontium seemed to be advisable due to the difficulty and time required for effluent analyses using radiostrontium as the influent tagging agent.

Physical Properties of the Soil Used

An investigation of the physical properties of the soil to be used was made. While only one type of soil was used for this study, future work could conceivably involve the use of various soil types. A physical description of the soil used in obtaining the breakthrough curves presented in this paper may be useful in correlating this work with future investigations. All soil analysis samples were taken from the common soil storage container.

A sample of the air dried soil was placed in a container of known volume. After the soil and container were dried in an oven at 110 °C for 24 hours, the weight of the soil was found to be 64.3893 grams. This resulted in a bulk density of 1.269 grams/cm³. Two 15 gram air dried soil samples were then used to determine the particle density of the soil. This was done following the standard pycnometer method. The particle density for both samples was found to be 2.605 grams/cm³.

The flow of liquids through a porous medium is governed in part not only by the total porosity of the medium but also by its pore size distribution. In an effort to determine the pore size distribution of the soil being used, a moisture tension curve was first constructed. This was done using a Tempe

cell apparatus for soil moisture contents greater than about 18%. A pressure cooker apparatus was used to produce the greater pressures required to remove water from the soil with a moisture content in the range of 13% to 18%, and a pressure plate was used for soil moisture contents as low as 8%. This resulted in a soil suction range of from zero to about 13.8 bars. The distribution of pore sizes is summarized in Table 2.

An important parameter in describing the physical condition of a soil is the ease with which the soil will conduct water. Since the soil used for the column studies was used under saturated conditions, the conductivity factor became the saturated hydraulic conductivity. It was convenient to set up a soil column with cross sectional area A and length L , begin the flow of the influent solution through the column with a flow rate of Q , measure the hydraulic head difference between the inlet and outlet levels, and calculate the saturated hydraulic conductivity K using [62]. This was done using two nearly identical soil columns each with a diameter of 7.60 cm and containing approximately 7.1 cm of soil. Tap water was used to determine K for the first column, and distilled water was used for the second column. At the beginning of the analysis the column in which tap water was used showed a K value of 8.46 cm/hour, while the column using distilled water resulted in a K value of 6.58 cm/hour. Flow through the columns was allowed to continue for about 150 hours with the same influent and effluent hydraulic heads maintained. Values of K were de-

Table 2. Pore size distribution of soil used in obtaining breakthrough curves

Pore Size Range [microns]	Percent of Pores in This Range
1 - 4	1.5
4 - 10	3.4
10 - 15	3.5
15 - 25	4.8
25 - 50	7.2
50 - 150	17.6

terminated at regular intervals by measuring the flow rate Q through the columns. During the first two hours the values for K were fairly constant. However, after about 70 hours of flow the conductivity of the column using tap water was observed to have increased to a maximum value of about 11.3 cm/hour. The conductivity of this column then steadily decreased and began to level off at a value of about 6.8 cm/hour after 150 hours of flow.

The column using distilled water behaved in a much different manner. After about four hours of flow the values of K began to decrease slowly but steadily, stabilizing at a value of about 4.7 cm/hour. The ions present in the tap water were assumed to have had a definite effect on the hydraulic conductivity of the soil by chemically reacting with the ions present in the soil. The results of this test emphasized the need for having a rate measuring and a rate controlling device on any soil column if the flow rate through that column is to be held

constant.

Soil Column Technique

Previous soil column experiments were carried out in glass columns with an inside diameter of 2.20 cm. The columns contained approximately one inch of soil. In an effort to eliminate the problems associated with using such small amounts of soil, such as short circuiting effects between the soil and the side walls of the glass column, larger volumes of soil were used for future columns. A larger glass column was obtained which had a inside diameter of 6.0 cm. Though the depth of the soil was varied as required, it was never less than about three inches. This resulted in an increase in the soil mass used from about 50 grams with the 2.20 cm diameter columns to about 300 grams with 6.0 cm diameter columns. Soil masses as high as about 800 grams were eventually used with the larger diameter columns.

Another improvement in the soil column technique was in the process of saturating the soil before a test was begun. Previous soil columns were presaturated by allowing distilled water to filter through the column downward from the surface of the soil. Only enough water was used so that the water surface was slightly above the soil surface, and the entire wetting process was completed in a few minutes. With the large soil columns the presaturation process was done from the bottom of the column over a period of about 24 hours. A constant head

was leaving the column than was entering. The results of this first run are shown in Figure 32.

Calcium carbonate has a relatively low solubility in water. Perelman (25) gives the solubility of CaCO_3 in distilled water at 20 °C and one atmosphere pressure as 0.016 grams/liter. As the pH of the solution decreases, the solubility of CaCO_3 in the solution increases. Therefore, in obtaining a calcium influent solution it was necessary to lower the pH with the addition of hydrochloric acid. The pH of the influent solution used to obtain the breakthrough curve shown in Figure 32 was found to be 3.5. The resulting breakthrough curve indicated that the low pH influent solution permitted large amounts of naturally occurring calcium to become dissolved in the influent solution. The influent solution was thus acting as an elution solution in which the peak effluent concentration was reached after about 1.5 liters had been put through the column. Beyond this volume, the amount of natural calcium entering into solution was observed to decrease and the breakthrough curve, which had become a desorption curve, began to reflect this decrease in cation removal. While the effluent samples were not analysed in a manner which would differentiate between the hardness cations of magnesium, calcium, and strontium, it was assumed that natural calcium was the major constituent in the effluent samples. Bear (1) has reported the chemical contents of a number of soils and has found That a Marshall silt loam taken in Missouri contained

Mariotte bottle was used with the hydraulic head at the same level as the surface of the soil. The relatively small head differential that resulted provided a small but steady driving force for the saturation of the soil sample. In this way the entrapment of air within a soil sample was minimized.

The use of calcium in the influent solution resulted in rapid and accurate analyses of the effluent samples which were collected from the ion exchange resin columns. It was decided to use the same procedure when using the large soil columns.

Interference of Natural Ions

The problem of interference between the calcium used in the influent solution and the natural divalent cations found in the soil samples became apparent during the first soil-calcium breakthrough test. The effluent analysis technique was the Hach Chemical Company water hardness test as previously described. This test was sensitive to all of the divalent hardness cations, and could not distinguish between the calcium ions entering the column in the influent solution and those divalent cations diffusing from the soil matrix into the influent solution. When a soil column was constructed in the 6.0 cm diameter glass column to a depth of 11.9 cm and an influent solution containing 201 ppm of calcium as CaCO_3 was passed through the column at a flow rate of 0.25 GPM/ft^2 , a breakthrough curve resulted which indicated that more calcium

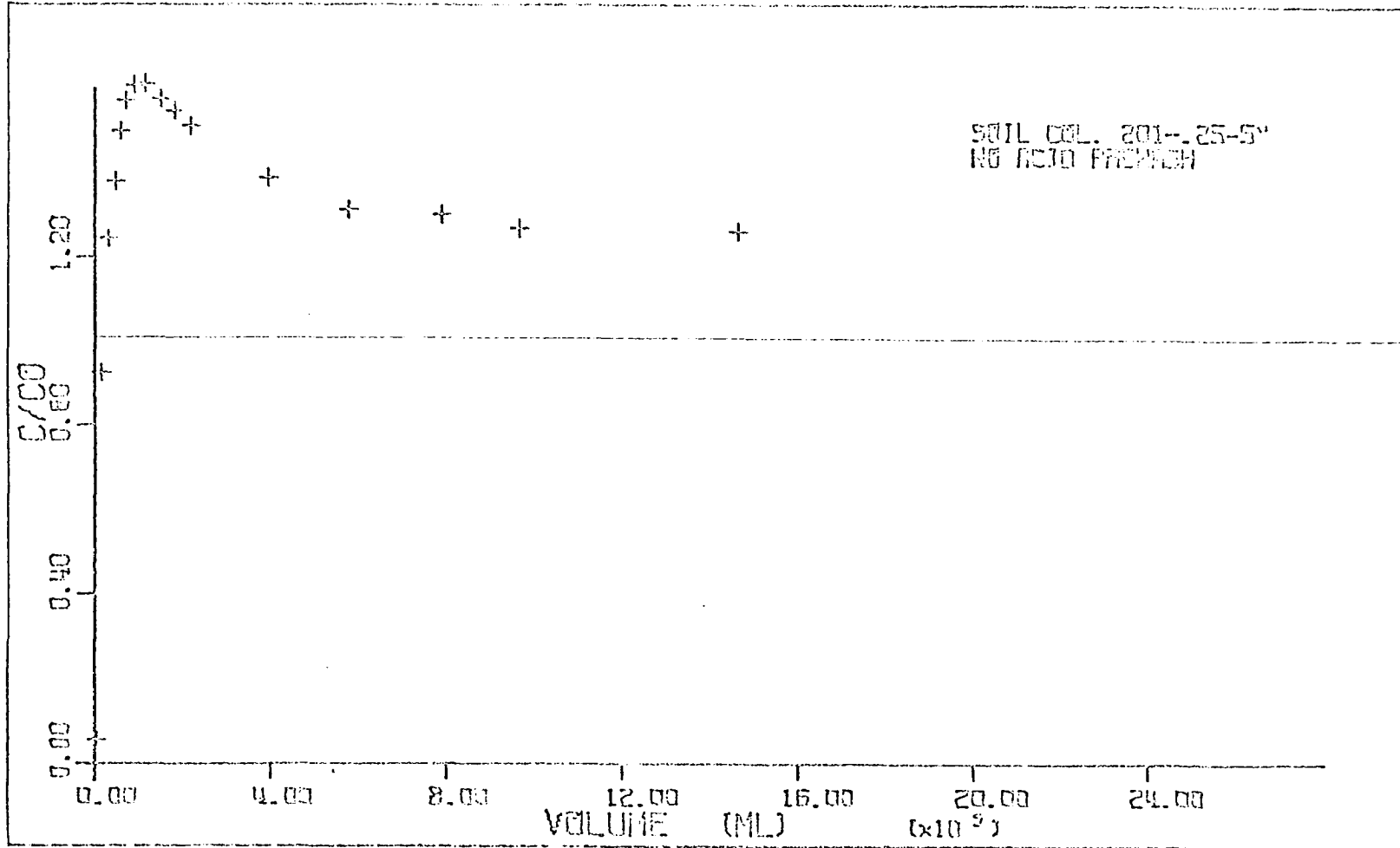


Figure 32. Calcium breakthrough curve obtained using the 6.0 cm diameter glass column operated at 201-.25-5" without prewashing the soil with HCl

about 1.1% CaO and 0.28% MgO. Also, due to their relative insolubilities, calcium carbonate crystals tend to form within the soil matrix.

In order to study the movement of calcium through soil, it was decided to first remove any calcium present in the natural soil either in the form of solid calcium carbonate or as the calcium ion exchanged on the clay fraction of the soil. Washing the soil with a strong solution of HCl seemed to be the simplest method of purging the soil of natural calcium. When a solution of HCl at a pH of 1.0 was used, large amounts of organic matter were also removed from the soil. Since it was desirable to work with a soil sample which approached natural soil as close as possible, a weaker acid solution was used. It was found that at a pH of 2.0 organic matter was not being removed to a noticeable extent. However, it was believed that at least some organic matter was being removed, as the effluent samples could not be titrated in the regular manner due to a color interference near the end point. This meant that it was impossible to determine when natural calcium was no longer being removed from the soil and appearing in the effluent samples. Therefore, the soil columns were washed with a predetermined amount of a HCl solution at a pH of 2.0 and then washed with a solution of HCl at the same pH as the influent calcium solution which varied from 3.0 to 4.0. Samples from the second acid wash could then be titrated in the usual manner for the purpose of detecting the presence of natural cal-

cium in the wash solution. When no natural calcium could be detected in the effluent samples, the column was considered ready for the calcium influent solution.

Results of Soil-Calcium Tests

Five soil columns were tested using the acid prewash method previously described. When a complete breakthrough curve had been obtained for the last column, the soil was purged of the deposited calcium using the HCl wash technique. With the influent concentration and flow rate held constant, a second breakthrough curve was obtained for the same soil sample. This sixth test was done to determine the reproducibility of the method used. A composite of the first five column tests is shown in Figure 33. Figure 34 shows the results of the last two breakthrough curves.

The breakthrough curves obtained using stable calcium on large soil columns showed a significant improvement over the earlier breakthrough curves obtained using soil and a strontium solution tagged with ^{89}Sr as shown in Figure 6. The good degree of reproducibility, as indicated in Figure 34, demonstrated the improved control possible using stable calcium influent solutions on large mass soil columns.

The breakthrough curves shown in Figure 33 do not possess the symmetry exhibited by the breakthrough curves obtained using the ion exchange resin shown in Figure 17 and Figure 18. Therefore, the use of [37],

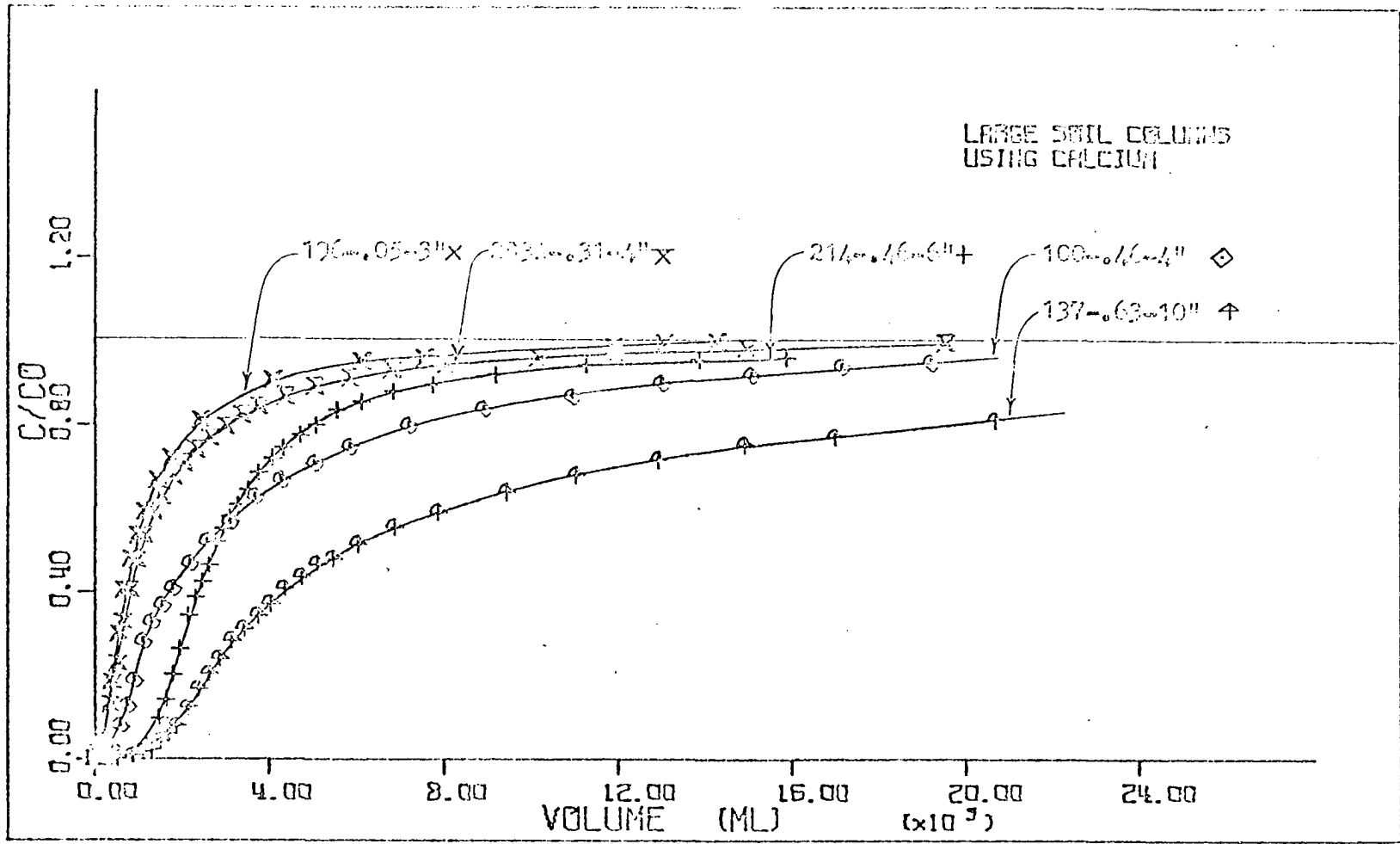


Figure 33. Calcium breakthrough curves obtained using a 6.0 cm diameter soil column after first washing the soil with a solution of HCl at a pH of 2.0

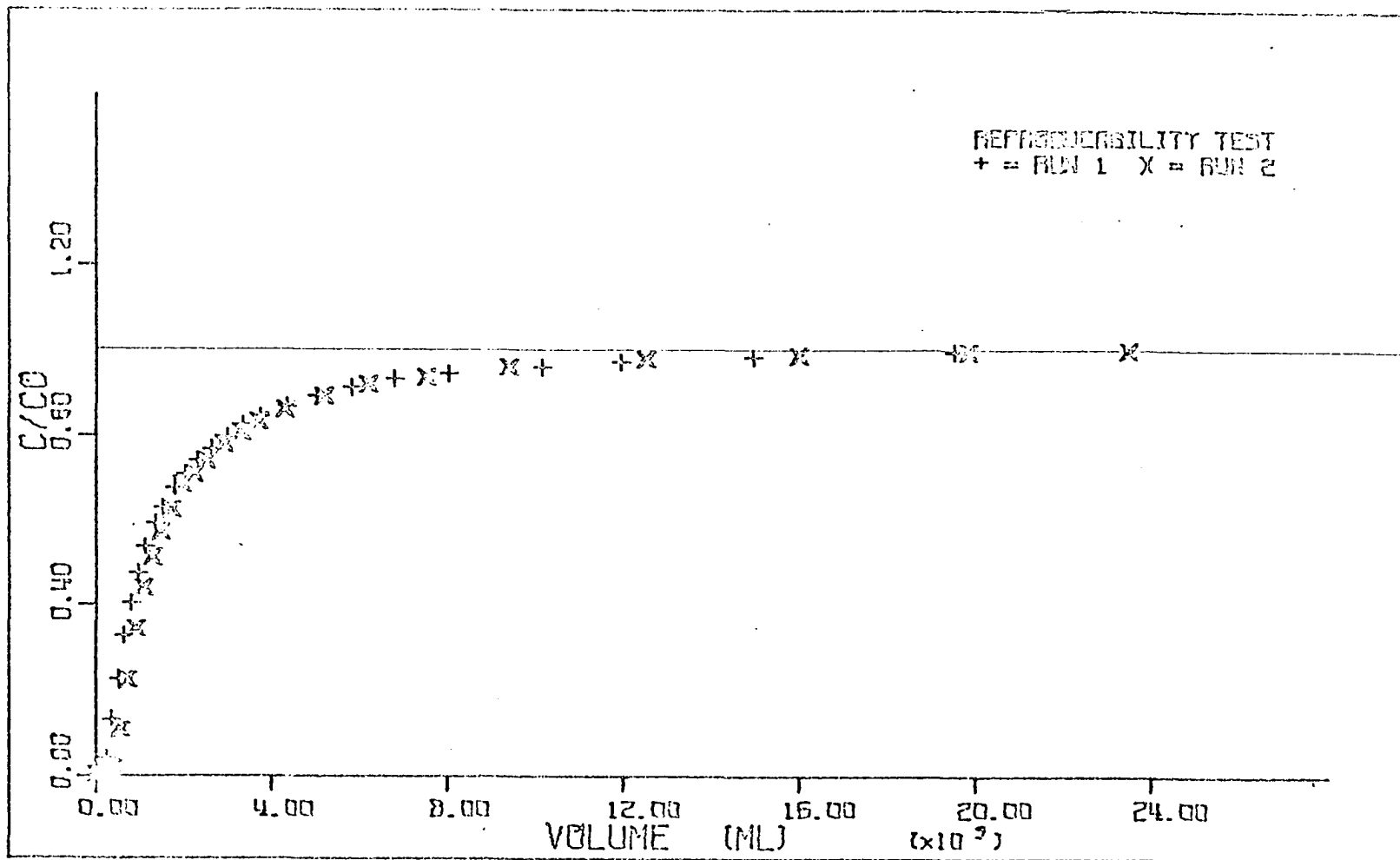


Figure 34. Calcium breakthrough curves obtained using the same 6.0 cm diameter soil column run under the same 283-.31-4" conditions

$$V = \frac{N_o \lambda A}{C_o} - \frac{\sqrt{QA}}{kC_o} \ln(C_o/C - 1) \quad [37]$$

which accurately predicted the location and shape of breakthrough curves obtained using the ion exchange resin, could not be used for the similarly run soil columns. An empirical approach was tried in order to obtain an equation for each of the soil-calcium breakthrough curves. Though the curves appear to be exponential, this type of relationship did not seem to describe the data collected. Another empirical function was tried in which the volume V at which a particular breakthrough fraction C/C_o was observed was assumed to be

$$C/C_o = 1 - \frac{R}{V^n + S} \quad [68]$$

where R , S , and n represented empirical constants. Multiplying both sides of [68] by $V^n + S$:

$$(1 - C/C_o)V^n = R - (1 - C/C_o)S. \quad [69]$$

If the relationship were valid, then a plot of the left hand side of [69] versus $(1 - C/C_o)$ should result in a straight line with a negative slope of S and an ordinate intercept of R . By trying various values of the exponent n , it was observed that there existed a particular value of n for each breakthrough curve which would render [68] valid. This also resulted in distinct values for the constants R and S for each breakthrough curve. Such an evaluation of [68] permitted an equation to be written for each breakthrough curve based on the

data collected for that curve. This represented a significant improvement over similar efforts using LeBlanc's approach as shown in Figure 8. A typical breakthrough "prediction" based on the R, S, and n values obtained for column 137-.6-10" is shown in Figure 35.

Since the constants R, S, and n varied among the six soil columns which were tested, a relationship was sought which would relate the constants to some measurable parameter. The values for the constants and the experimental variables for each of the six soil columns tested are shown in Table 3. No such relationship could be found for the constant n. However, some degree of consistency was observed among the various values for the constants R and S. A trend was observed to develop if the values obtained for R were plotted against the product of the flow rate Q times the soil mass M for each of the columns. This trend can be seen in Figure 36. When a straight line was fitted to the data points of Figure 36 the relationship

$$R = \frac{QM}{6} \quad [70]$$

was derived. Figure 37 shows a similar effort at correlating the constant S with the quotient of the soil mass M divided by the influent concentration C_0 . The linear relationship derived was found to be

$$S = \frac{M}{50 C_0} \cdot \quad [71]$$

While the results of the graphs shown in Figure 36 and in

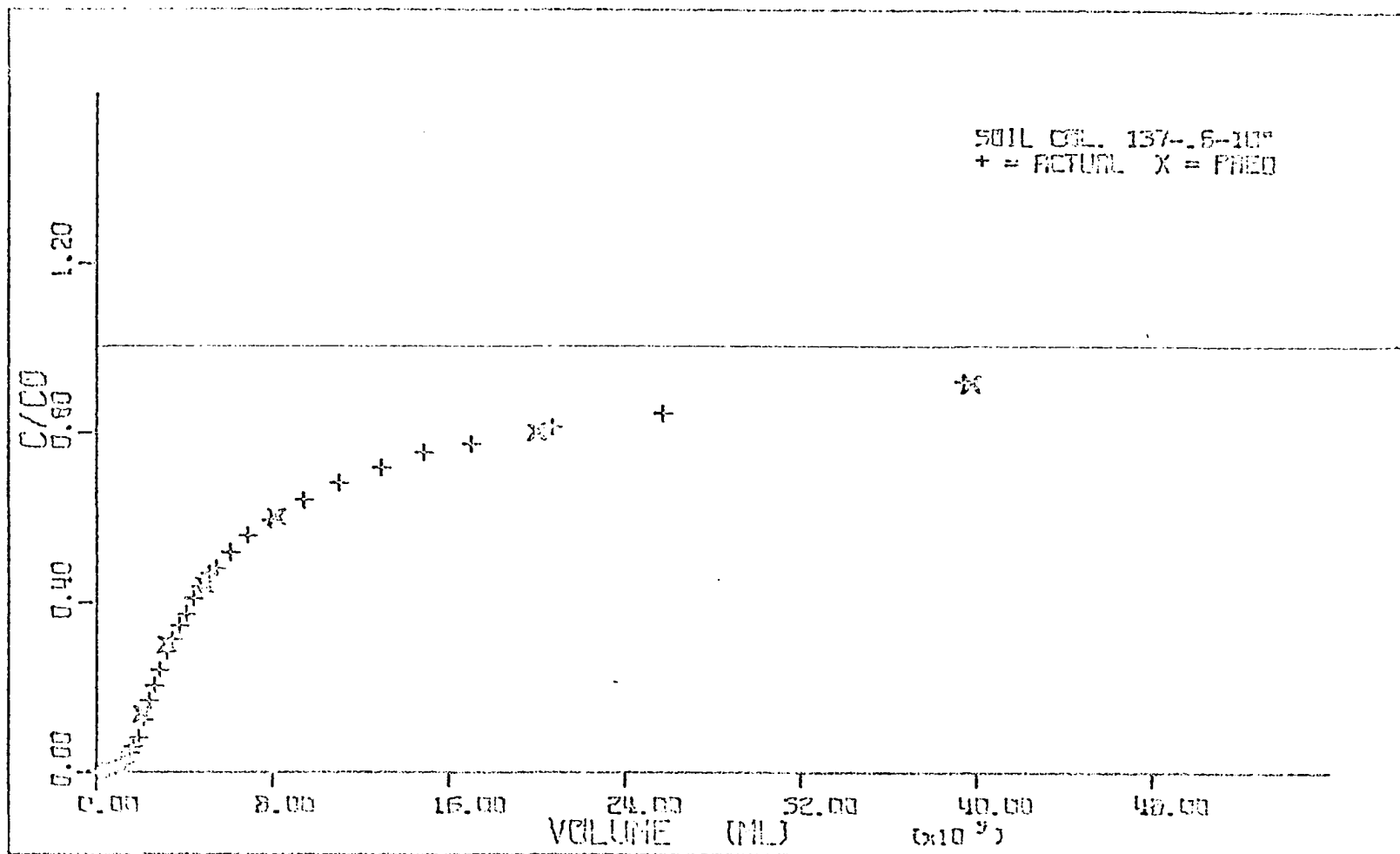


Figure 35. The "predicted" breakthrough curve of soil column 137-.6-10" based on the values of the constants R, S, and n determined using the breakthrough data of column 137-.6-10"

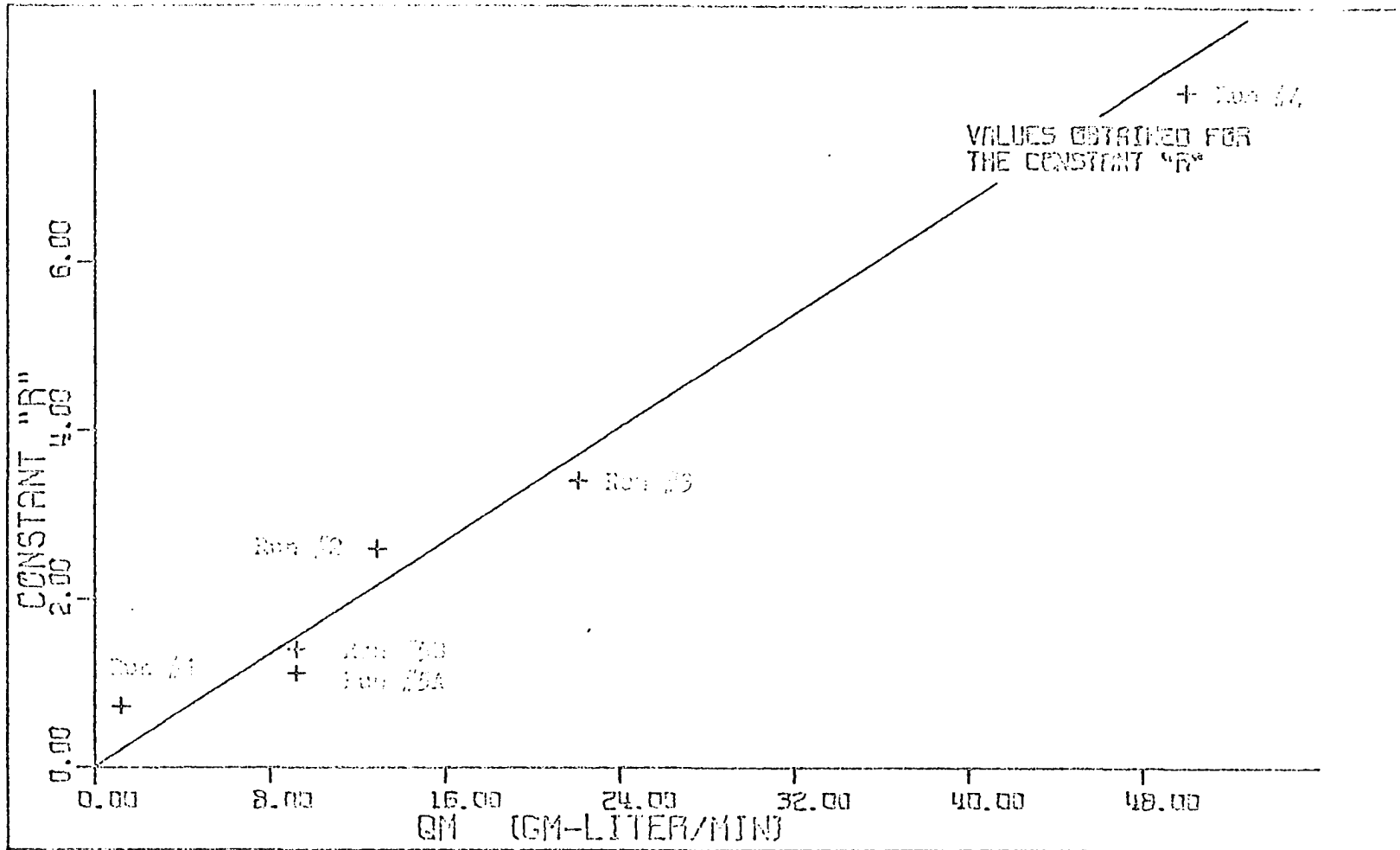


Figure 36. An attempt to correlate the values obtained for the constant R with the product of the flow rate Q and the soil mass M for each of the soil-calcium breakthrough curves

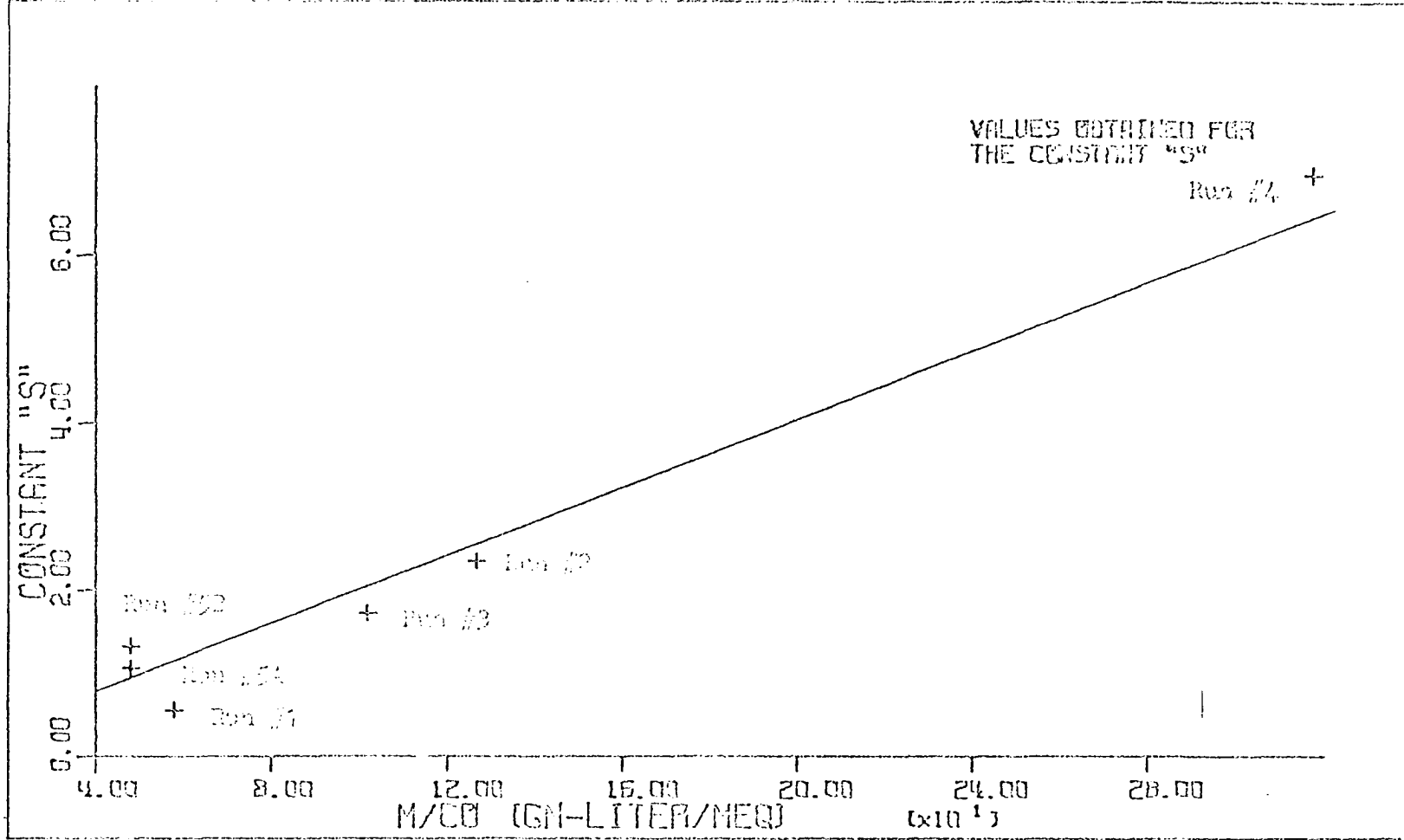


Figure 37. An attempt to correlate the values obtained for the constant S with the quotient of the soil mass M divided by the influent concentration C_0 .

Table 3. Calculated values for the constants R, S, and n obtained from the soil-calcium breakthrough curves

Run	Influent Conc. [meq/l]	Soil Mass [gm]	Flow Rate [l/min]	Influent pH	R	S	n
#1	3.92	227	0.0050	3.0	0.77	0.56	1.4
#2	2.00	251	0.0516	3.9	2.62	2.36	1.2
#3	4.28	437	0.0507	3.5	3.40	1.73	1.7
#4	2.47	786	0.0639	4.0	8.00	6.96	1.2
#5A	5.67	273	0.0339	3.4	1.12	1.09	1.4
#5B	5.67	273	0.0339	3.4	1.40	1.33	1.5

Figure 37 do show a trend in their various relationships, they do not result in completely linear functions. Since no similar relationship could be found for the constant n, [68] could not be solved for the general case.

Table 3 includes the pH which resulted when CaCO_3 was dissolved with the aid of HCl to form the influent solutions for each test. It was the intent of this study to avoid working with influent solutions containing more than one ionic species due to their competitive nature. However, the hydrogen ion concentration in the influent solution represented a significant quantity of an ionic species which was capable of competing with the calcium ions for exchange sites. The magnitude of this competition can be illustrated by converting the pH values into hydrogen ion concentrations in units compatible with the units used to describe the influent calcium concentrations. Such a tabulation is given in Table 4 together with the calcium to hydrogen ratio and normalized cal-

Table 4. Comparison of calcium and hydrogen concentrations for the first five soil-calcium tests

Run	Influent Calcium Conc. [meq/l]	Influent Hydrogen Conc. [meq/l]	Calcium to Hydrogen Ratio	Calcium Exchange Capacity [meq/gm]
#1	3.92	1.000	3.92	0.0380
#2	2.00	0.126	15.88	0.0390
#3	4.28	0.316	13.56	0.0404
#4	2.47	0.100	24.70	0.0486
#5A	5.67	0.400	14.18	0.0491

cium exchange capacities for each of the first five tests.

While the relative amounts of calcium and hydrogen ions present in the influent solutions varied over a considerable range, there appeared to be no relationship between the calcium to hydrogen ratio and the exchange capacity of the soil samples for calcium.

In an effort to determine if there was any significant competition between the calcium and the hydrogen ions for the exchange sites in the soil, a series of soil-calcium tests were made in which only the influent pH was varied. For each test 300 grams of air dried soil were used. This resulted in a column depth of 10.0 cm. The flow rate was held at a constant value of 69.8 ml/min for each of the tests. In order to insure that each soil column was a nearly exact copy of every other soil column, all of the columns were prewashed with 80 liters of HCl solution at a pH of 2.0. The columns were then washed with two liters of a solution of HCl at the same pH as

the influent calcium solution to be used. The column runs were terminated at a breakthrough fraction of about 85%, and a calcium exchange capacity for each column was determined using that terminal breakthrough value. Three soil columns were run in this manner, each with a different pH. A fourth soil column was run under the exact same conditions as the third column in order to test for reproducibility. Figure 38 shows the breakthrough curves obtained for the three different pH solutions, and Figure 39 shows the degree to which a breakthrough curve run under these controlled conditions could be reproduced.

Figure 39 reflects a better degree of reproducibility than was observed during the earlier soil column tests shown in Figure 34. This may be due to the varying amounts of acid solutions used to purge the columns of calcium in the tests of Figure 34. Since columns #5A and #5B represented the same soil sample, the initial acid wash was the same for both columns. However, at the conclusion of run #5A the column was again purged with approximately 60 liters of a solution of HCl at a pH of 2.0. This additional volume of acid may have contributed to the slight variance between runs #5A and #5B. The breakthrough curves shown in Figure 39 were obtained after each soil sample was washed with the same volume of HCl solution.

A tabulation of the results obtained when only the pH of the influent solution was varied is given in Table 5. It can be seen from Table 5 that the calcium/hydrogen ratio had a de-

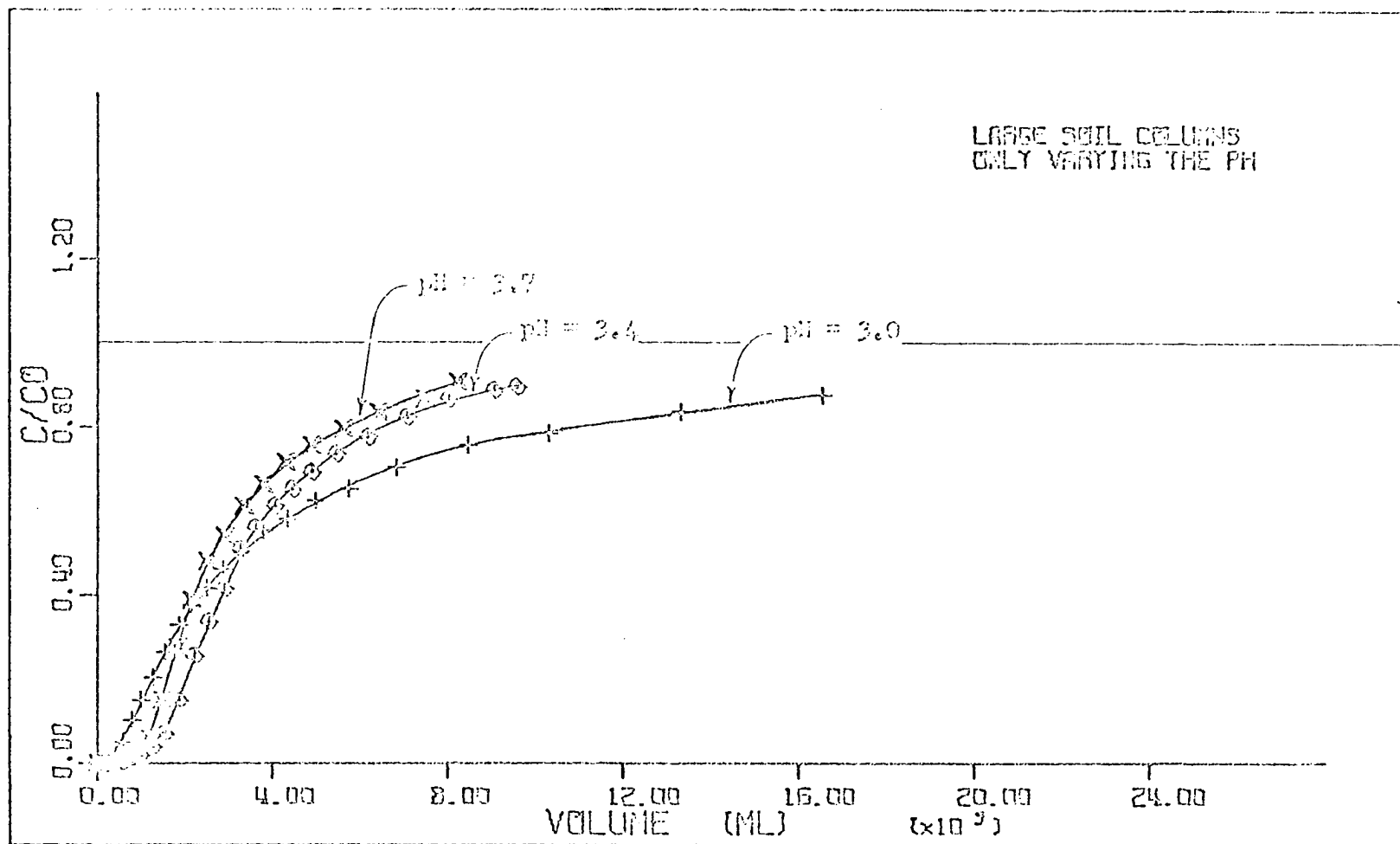


Figure 38. Calcium breakthrough curves obtained using a 6.0 cm diameter soil column each operated at 98-.63-4" with only influent pH allowed to vary

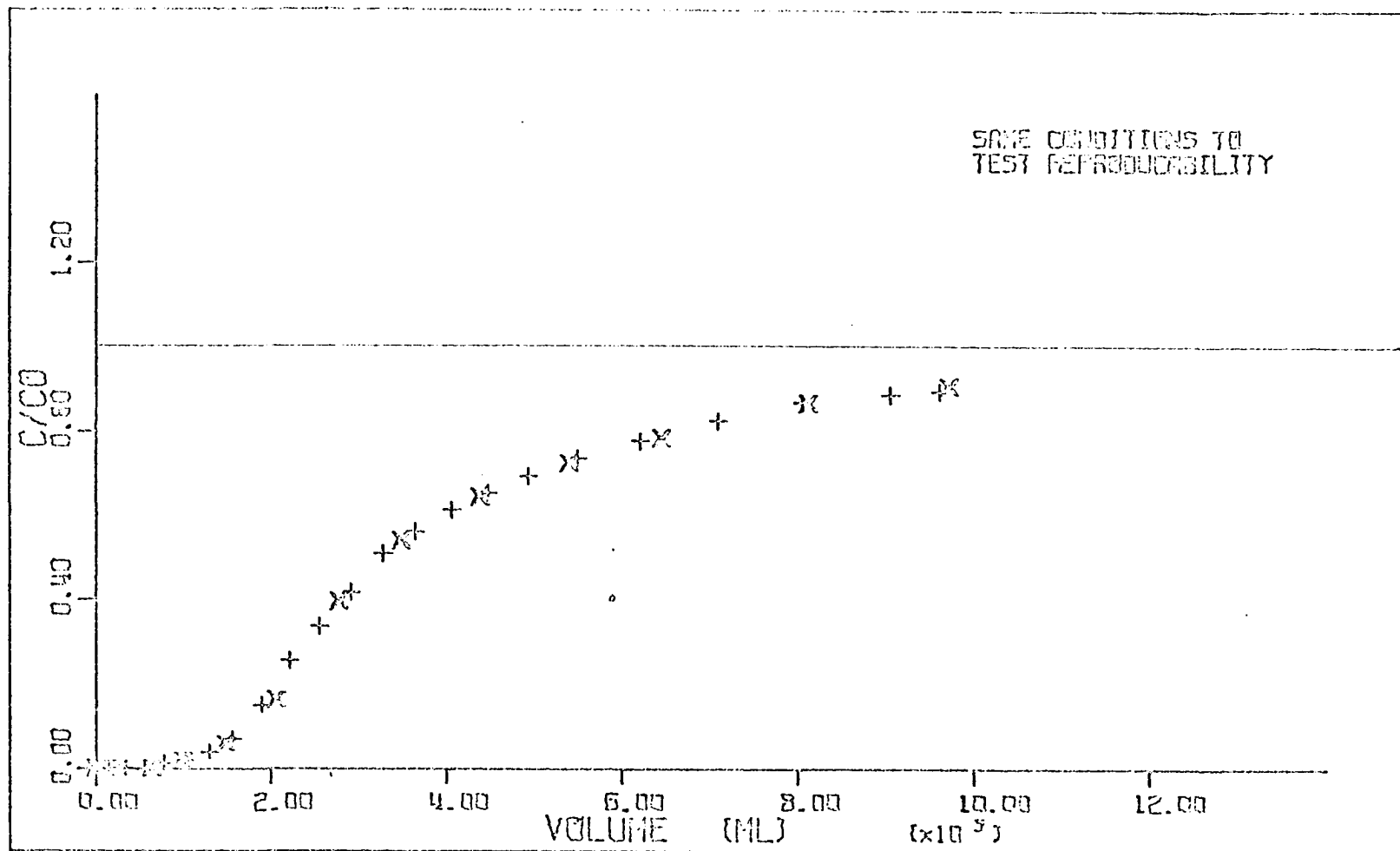


Figure 39. Calcium breakthrough curves obtained using a 6.0 cm diameter soil column run under the exact same conditions of 98-.63-4"

finite effect on the calcium exchange capacities of the identical soil samples. As the ratio was increased there was a corresponding, although not a linear, increase in the exchange capacity of the soil. Figure 38 also emphasized the effect of the pH of the influent solution on the location and shape of the resulting breakthrough curve.

Use of Stable Strontium

The competitive effect of hydrogen ions in solution with calcium apparently played a significant role in controlling the resulting calcium breakthrough curves. However, the hydrogen ions were required in the influent solution in order to increase the solubility of the CaCO_3 . In an effort to eliminate the problem of hydrogen competition it was decided to use stable strontium as the influent cation. Stable strontium in the form of $\text{Sr}(\text{NO}_3)_2$ is highly soluble in distilled water at a neutral pH. The use of stable strontium resulted in benefits other than the reduction of hydrogen ion competition. Since strontium is practically nonexistent in soil, the problem of natural strontium appearing in the effluent samples was eliminated. When the need was removed for prewashing the soil sample with a strong solution of acid, the soil could be used in a condition closer to its natural state. Organic matter within the sample was not disturbed, and the natural exchange capacity of the soil was also left undisturbed. Finally, it

Table 5. Comparison of calcium and hydrogen concentrations for soil-calcium tests in which only the pH of the influent solution was varied

Run	Influent Calcium Conc. [meq/l]	Influent pH	Influent Hydrogen Conc. [meq/l]	Calcium to Hydrogen Ratio	Calcium Exchange Capacity [meq/gm] ^a
#7	1.96	3.0	1.00	1.96	0.0226
#8A	1.96	3.4	0.40	4.90	0.0264
#8B	1.96	3.4	0.40	4.90	0.0264
#6	1.96	3.7	0.20	9.80	0.0338

^aBased on breakthrough fractions of 85%.

had been assumed that calcium could be used to simulate strontium due to the similarities in their chemical behavior. Any differences, however slight, could be eliminated by returning to the use of strontium.

When distilled water was passed through a soil column, some hardness cations were detected in the effluent samples. This was probably due to the fact that it is possible to dissolve at least some calcium in water at a neutral pH. Small amounts of loosely held calcium may have disassociated from the soil matrix and diffused into the distilled water wash solution. It was found that for a soil depth of about four inches in the 6.0 cm diameter glass column, a prewash consisting of about six liters of distilled water was enough to remove any detectable amount of hardness cations from the soil.

Strontium nitrate was dissolved in distilled water to give a concentration of 649 mg $\text{Sr}(\text{NO}_3)_2$ per liter. The pH of

the solution was found to be 6.0 which was the same pH as the distilled water used to dissolve the strontium. The stable strontium breakthrough curve shown in Figure 40 was obtained when the column was operated at a flow rate of 42.0 ml/min. As with the breakthrough tests using calcium on soil, the stable strontium curve represented a significant improvement over the earlier breakthrough curves in which radiostrontium was used.

The exchange capacity of the soil was noticeably altered when the soil was not prewashed with a strong HCl solution. When this was done to purge the soil of natural hardness cations the exchange capacity was found to average about 0.04 meq/gram. The breakthrough curves obtained without prewashing the soil, shown in Figure 40, resulted in an exchange capacity of 0.0055 meq/gram of soil.

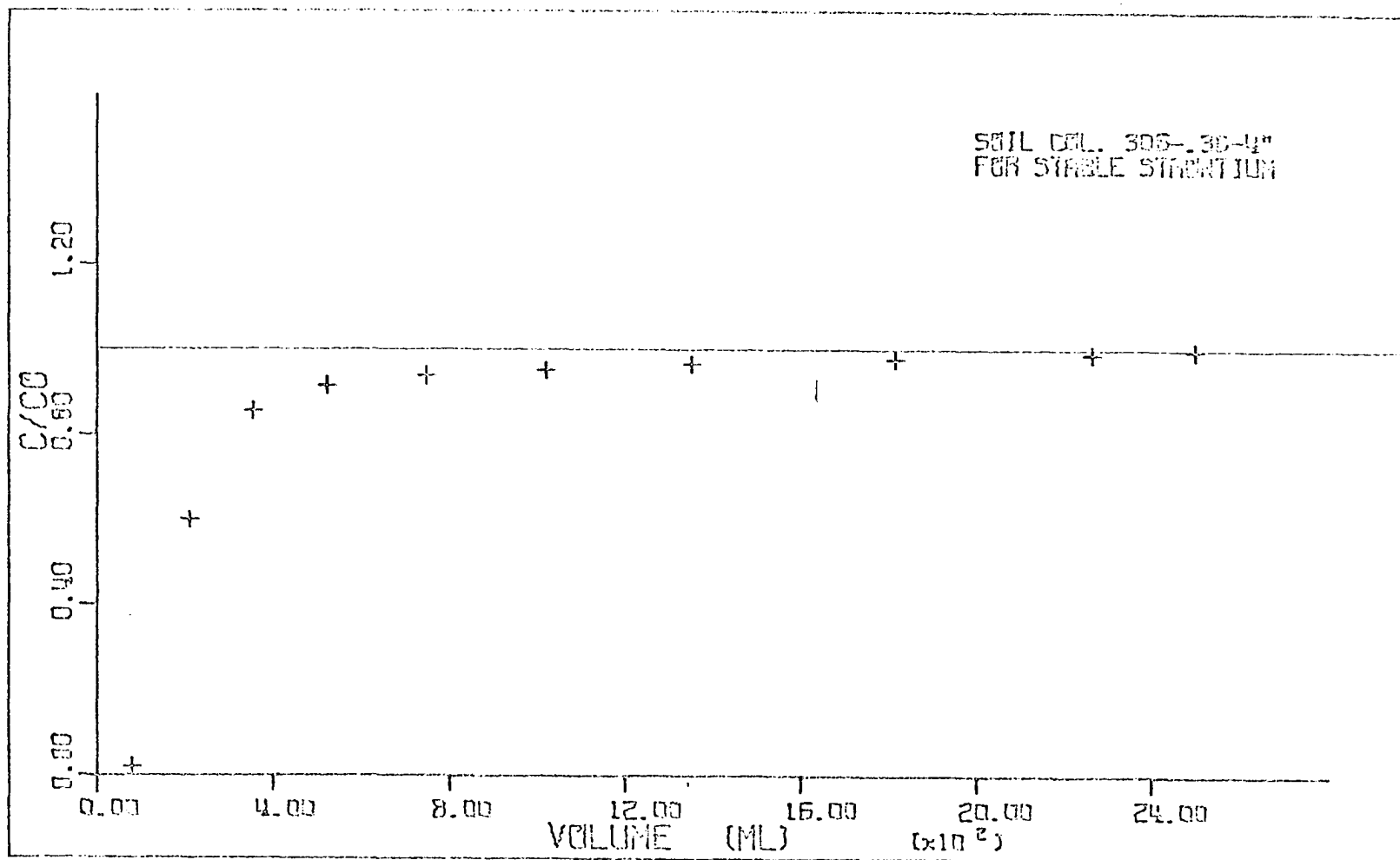


Figure 40. Breakthrough curve obtained using a 6.0 cm diameter soil column operated at 306-.38-4" using stable strontium

DISCUSSION

At the beginning of this study two important assumptions were made. The first was that the soil beneath a waste seepage pit was homogeneous and isotropic. The second assumption was that the soil was saturated prior to the filling of the waste pit. If these two assumptions were true, then a soil sample taken at any location beneath a waste pit would have physical and chemical properties identical to those of a soil sample taken at any other location beneath the same pit. This would permit a soil sample taken anywhere beneath the pit to be brought into the laboratory, confined in a soil column, and subjected to ionic loading similar to that expected to result from the use of the waste pit. Results thus obtained could be extrapolated from the laboratory study to accurately predict the operational effects of the waste pit.

Although the above assumptions are not true, they have permitted a systematic investigation of the various parameters which were believed to be responsible for the phenomena of ionic movement through soil. The assumption of a homogeneous isotropic soil resulted in a cation exchange resin being substituted for the soil material. Since the resin possessed these characteristics, its use permitted a careful study of the relevant parameters. All parameters except one could be held constant, and the effects of varying that parameter could be investigated. In addition, the resin possessed a physical

integrity lacking in soil. The same resin sample could be used, cleaned, and reused with little structural damage. Since soil may degrade after being subjected to prolonged flow, an uncertainty arose in attempting to reuse a particular soil sample.

The hydraulic characteristics of the soil must be understood before the chemical interaction between the contaminating ions and the soil can be extrapolated from laboratory studies to accurate field predictions. Once the velocity and direction of water moving through the soil can be predicted at any given time, the exchange capacity of the soil for the ionic species being observed may be used to predict their movement through the soil. The second basic assumption made, that the soil beneath the waste pit was saturated, limited the value of the results obtained through the use of saturated laboratory columns. However, the assumption did permit a good degree of reproducibility which would not have been possible had the water content of the soil columns not been controlled.

When assumptions are made which permit better experimental design but which, at the same time, result in a deviation from reality, the problem arises of relating laboratory results back to the actual conditions. The use of [37], which very accurately predicted the location and shape of a breakthrough curve obtained using the ion exchange resin, did not appear to accurately represent a breakthrough curve obtained using soil. For simplification, some of the soil samples were

purged of natural calcium. While the breakthrough curves obtained from such soil samples reflected a total adsorption capacity of the soil, the use of non-purged samples would have better represented the true adsorption capacity of the soil found beneath a waste seepage pit.

From a purely empirical approach, [68] seemed to offer some interesting possibilities. Through its governing constants R , S , and n , it permitted an equation to be written on the breakthrough data obtained for a given column run which would accurately reproduce that same breakthrough curve. Unfortunately, a function which would relate a particular constant for all of the soil column runs made could not be found. This was perhaps due to the fact that the pH of the influent solutions was not held constant. When the influent calcium concentration, soil mass, and flow rate were held constant and the pH of the influent solution was allowed to vary, a definite effect on the location and shape of the breakthrough curves was noted.

In attempting to move from one directional flow columns to two directional flow systems, certain hydraulic problems were encountered. Darcy's law was combined with the law of conservation of mass to yield LaPlace's equation which was used to describe the movement of water through a saturated porous medium. The solution of LaPlace's equation for a particular two dimensional saturated flow problem depends on the boundary conditions established for that problem. Solutions have been

obtained for simplified drainage problems with linear boundary conditions with the assumption that the porous medium is homogeneous and isotropic. However, the application of a solution to Laplace's equation to a two directional flow model was hampered by the boundary conditions chosen for the model. Some hydraulic modeling was attempted using potassium permanganate and indigo carmine dye crystals. While the results were found to be completely satisfactory, the labor required to construct the two dimensional tank and carry out the dye traces was excessive compared to the use of electric analog models.

The approach taken in attempting to arrive at an accurate equation which would predict the movement of radiostrontium through soil involved the use of laboratory models to simulate actual field conditions. While much was learned by such an approach concerning the mechanisms which govern the movement of divalent cations through soil, the final objective of developing waste seepage pit design criteria was not attained. Predictions were made and their results tested for laboratory soil columns. These columns, while containing soil, actually represented a very idealized soil in which worm holes, root holes, gradations, stratifications, obstructions, etc., were not variables with which to contend. Therefore, the formulation of a finalized design plan could not be made at this time. It was felt, however, that a pilot study could be made with some degree of success based on the information obtained. Such a study might consist of constructing a small diameter

waste pit in the field. The pit could be filled with a synthetic waste solution containing strontium ions in the form of strontium nitrate. After a predetermined volume of the synthetic waste solution had been allowed to filter into the soil beneath the pit, the dumping operation could be halted and the location of the contamination front determined by removing soil samples at various locations beneath the pit.

Before conducting such a field test, it would be advantageous to estimate the location of the contamination front based on the information obtained from the laboratory studies. One of the first parameters to be considered is the infiltration rate of the waste solution into the ground. This represents possibly the largest source of error in attempting to extrapolate laboratory data to the field. Infiltration rates may vary not only among various geographical locations but also from place to place within a given field. Thus, it would probably be necessary to conduct infiltration rate studies at virtually the same location at which the pilot operation would be located. Ligon and Johnson (16) have studied infiltration capacities of soils similar to the soil type found at the ALRR site. Their results show that infiltration rates on that type of soil varied between 0.03 ft/day and 2.0 ft/day. This represents a range large enough to offset any valid information gained from laboratory studies. However, in an attempt to make at least a rough estimate as to the location of the contamination front beneath a model waste pit, an average infil-

tration rate of 1.0 ft/day will be used.

In addition to the undisturbed infiltration rate which would be observed at the test site, consideration would also have to be given to the manner in which the test pit was constructed. If the top layer of the pit floor were scarified and compacted during construction, the infiltration rate might be reduced by as much as several orders of magnitude. Compaction could easily result from walking on the pit floor. The presence of a porous mat on the pit floor could also affect the performance of the test pit.

An increase in the depth of the waste pit would provide added head with which to increase the infiltration rate. However, in attempting to estimate the location of a contamination front, it will be assumed that the waste depth is not great enough to cause an appreciable increase in the rate on infiltration. For a waste depth on the order of a foot, this is probably not a bad assumption.

In order to attempt a test pit design, it will be assumed that the pit will be three feet in diameter. This gives a pit floor area of $6,570 \text{ cm}^2$. If 5,000 liters of a waste which contain 30 meq/liter of stable strontium were allowed to filter from the test pit into a presaturated soil at a natural infiltration rate of 1 ft/day, it is desired to predict the depth at which the contamination front will be found.

Assuming a bulk density of 1.269 grams/cm^3 as was determined by laboratory analysis, the soil mass M as a function of

the depth L in centimeters may be calculated as:

$$M = (1.269 \text{ gms/cm}^3)(6,570 \text{ cm}^2)(L \text{ cm}) = 8320 L \text{ grams .}$$

From Table 3 an average value of n of 1.3 is assumed. Solutions to [70] and [71] may then be substituted into [68]. For the example cited:

$$R = 193 \text{ L gm-liter/min}$$

$$S = 5.5 \text{ L gm-liter/meq}$$

The value chosen for C/C_0 will depend upon the concentration in the influent waste solution and the concentration considered tolerable at the depth L. It will be assumed that a concentration at depth L equal to 5% of C_0 will be considered to be the maximum allowable concentration. Thus, $C/C_0 = 0.05$. Therefore, [68] becomes:

$$0.05 = 1 - \frac{193 \text{ L}}{5000^{1.3} + 5.5 \text{ L}}$$

or $L = 325 \text{ cm}$. This is about eleven feet, which is the approximate average depth of the water table at the ALRR site.

The time required for the concentration at $L = 325 \text{ cm}$ to equal 5% of C_0 is about 25 days. This represents a large time investment for one experiment. Therefore, it might be advisable to operate two or more field model pits simultaneously. During the time in which the pit models are in operation, care should be taken to protect the site from outside influences such as rain.

The location of the contamination front may be determined

by removing soil samples from beneath a seepage pit for laboratory analysis. The analysis may involve extracting the ions adsorbed on the soil and determining the amount of stable strontium in the filtrate by a chemical procedure or by flame spectrometry.

CONCLUSIONS

An attempt was made to develop a rapid and reliable method for predicting the rate of movement of strontium through soil. The approach adopted was one in which laboratory models were used to simulate some of the conditions expected to exist in the soil located beneath a radioactive waste seepage pit. This investigation yielded the following conclusions:

1. The empirical approach initiated by LeBlanc and modified to the form of [24] may be used to predict the movement of strontium through a soil column. However, LeBlanc's equation was shown to be valid only between the 30% and 70% breakthrough fractions. Solutions to LeBlanc's equation and to [24] were complicated, involving the determination of areas beneath the observed breakthrough curves. Computer solutions were convenient in analysing the laboratory soil column data, but the need for a computer by a seepage pit designer wishing to use the prediction equations was a disadvantage for the use of the equations.
2. Care must be taken to insure that the laboratory apparatus will give reproducible results. A rotameter was installed in the column influent line so that a predetermined flow rate could be chosen. The rotameter also provided a visual check on the preset flow rate, insuring a constant flow rate throughout a soil column test. The slow wetting of the soil contained

in the columns from the bottom was done in an effort to produce a soil which closely approached 100% saturation. Rapid wetting of the soil from the top of the column may result in entrapment of air within the soil matrix. This will clog pore spaces and affect the flow of solutions through the soil.

3. A cation exchange resin may be used to simulate soil.

This provided a means of studying individual parameters which were thought to influence the movement of strontium through soil. The parameters investigated were flow rate, column bed depth, and the concentration of the influent solution. A possible disadvantage of the resin is that it results in a soil model which is too idealistic. Due to its uniform particle size and absence of large interstitial spaces, the resin was assumed to adsorb cations by the mechanism of ion exchange. However, the adsorption rate using soil was apparently governed by the rate at which the cations in solution diffused to the exchange sites within the soil particles. The difference in diffusion rates for resin and soil was characterized by differences in the shapes of the breakthrough curves obtained using the two materials. The symmetric "S-shaped" breakthrough curves obtained when the resin was used indicated that little diffusion was taking place. The breakthrough curves obtained using soil columns tended to rise very rapidly to about the 80% breakthrough value. This rise was followed by a leveling of the curve and a slow rise to the 100% breakthrough fraction. It was assumed that the cations in solution were exchanging onto

the sites located at the outer surface of the soil particles during the rapid rise phase of the breakthrough curve. When these surface sites were exhausted the relatively slow process of diffusion governed for the remainder of the soil column run.

4. The use of stable calcium in place of radioactive strontium results in faster and more accurate analyses of the concentrations present in the influent and effluent solutions.

5. A laboratory model in which flow moves in two directions may be a useful interim step between soil columns and field testing of information obtained from the columns. Some work was done using a modeled seepage pit contained in a glass tank. Mathematical models of two directional flow can be complicated to derive and can be further complicated by the presence of strata of varying types of soil beneath the seepage pit. Dye traces of the flow lines are time consuming. An electric analog appears to be a good alternative to a dye trace of the soil being investigated.

6. Field testing of knowledge gained from the use of laboratory models might be done by removing soil samples beneath a test seepage pit and extracting the contaminating ion. Several extraction techniques were tried and a simplified approach was adopted.

7. The pH of the influent solution is an important parameter which must be considered. The competition between hydrogen ions and other cations in solution for exchange sites may affect the exchange behavior of the species being studied.

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