

ION EXCHANGE IN EXFOLIATED VERMICULITE

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ABSTRACT

This work is intended to give an insight into the use of exfoliated vermiculite as an ion exchange medium for the removal of certain transition metal ions from low concentration waste waters. Two different size grades of exfoliated vermiculite were employed; as supplied by a commercial source.

Both batch and column processes have been investigated and centrifuge operation discussed. A simple model has been found to fit the column data reasonably accurately provided the flow rate was low. Diffusion coefficients have been estimated, from the model, to be of the order  $10^{-9} \text{ cm}^2.\text{sec}^{-1}$ .

The times taken to breakthrough were in the order  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$ . It was found that the smaller grade vermiculite increased the breakthrough time considerably over that of the larger grade.

Total cation exchange capacities of nickel and zinc were of the order  $1 \text{ meq.g.}^{-1}$ , whilst those of copper and chromium were of the order  $2 \text{ meq.g.}^{-1}$ . These values are of the same order as those found in the literature.

#### ACKNOWLEDGEMENTS

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## 1. INTRODUCTION

Public opinion is very concerned with the problems of water pollution, and pressure has often been brought to treat such effluent. Often this waste is inorganic, such as in the metal plating industry, and is in fact toxic because of the heavy metals present, eg. chromium, nickel, copper, zinc and cadmium which interfere with life in the rivers in which such waste is discharged. Hence there is an obvious need for treatment, but the cost is often prohibitive.

A possible course here was that of ion exchange so that a less noxious ion, for example magnesium, passes into solution, but this is still an expensive process as the ion exchange resin and the contacting equipment are costly. It was therefore considered worthwhile investigating whether an alternative cheap, readily available natural material, eg. a soil, could be used. The soil would probably be used once, no regeneration, and then utilized in some other way, or possibly if it was thought necessary, the metal could be recovered.

Exfoliated vermiculite was found to have a fairly high cation exchange capacity for such metal ions (Mohn 1973), and so it was decided to investigate its use by cheap, simple methods of contact, eg. batch or fixed bed operation. Concentrations in the range 25-200 ppm (by weight) were considered suitable for this study (Mohn 1973).

Once saturated the exfoliated vermiculite could be dried and used in the building industry in the usual way, eg. insulation, light weight cement, etc. Alternatively a way of recovering the metal could be developed and hence the vermiculite regenerated.

Vermiculite is an aluminium-iron magnesium silicate, resembling mica in appearance. Hydrated magnesium ions are contained in sites in the regions between the silicate layers, and these ions are free to move and are available for exchange. The detailed structure of vermiculite and the process of exfoliation, together with the exchange

properties are explained in detail in chapter 2.

Chapter 3 deals with the methods available for operating the process - namely batch, fixed bed and centrifuge. The first two were chosen because they represent the cheapest and simplest methods of operation; the latter was included as it was thought this process deserves further investigation at a later date, as it has several advantages over the other two techniques, although it is more expensive especially for the process control. Laboratory and industrial scale apparatus are also discussed.

The theory of ion exchange is discussed in Chapter 4. Ion exchange equilibria, ion exchange kinetics, rate determining mechanisms and simple mathematical models are all included. The models considered are the Proportionate-Pattern case (unfavourable equilibrium) and the Constant-Pattern case (favourable equilibrium). Both particle diffusion controlled and film diffusion controlled, together with combined resistance control, are outlined.

The experimental details and results are given in Chapter 5 and the discussion and conclusions are presented in Chapter 6. Suggestions for further work are outlined in Chapter 7.

## 2. ION EXCHANGE AND VERMICULITE

### 2.1 THE MECHANISM OF ION EXCHANGE

There are solids in which cavities are filled with positive and negative ions that make up a salt. In the dry state, the ions retain their average position in the framework, but when immersed in a polar liquid, water for example, one or both ions are free to move. It is often found that one ion is free to move through the solid whilst the other is held firmly to the framework. The mobile ion can move into the surrounding liquid if the solid as a whole remains electrically neutral, that is if ions of equivalent charge pass from the liquid into the solid. The same requirement of electrical neutrality excludes from the solid, ions of the same polarity as those held firmly by the framework, see below. The net result of the process is to exchange mobile ions in the solid for ions of the same polarity in the liquid. The process is termed ion exchange and can be used for replacing those in solution by others with more suitable properties, or to recover ions from solution.

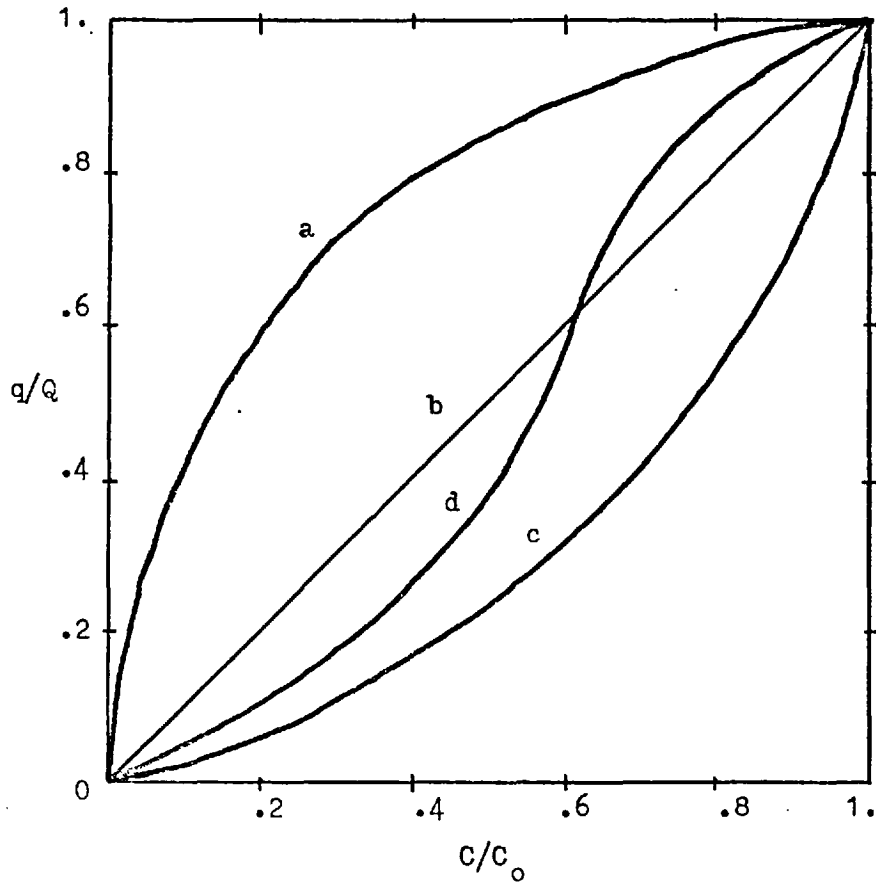
The tendency for ion exchange reactions to reverse vary greatly. If at equilibrium the exchange is predominantly in the forward direction the reaction is considered to be favourable, and if predominantly in the reverse direction it is said to be unfavourable. Where the forward and backward reaction have the same tendency the process is linear. If the reaction is characterised by being partially favourable and partially unfavourable it is said to be sigmoidal.

Figure 1 illustrates the various types of equilibrium curve. Here the lines are for constant total normality, ie. isonormals, and represent the path followed in a simple exchange reaction.

Equilibrium could be qualitatively described in terms of the

affinity of the exchanger for one ion relative to that for another. For dilute solutions the relative affinities usually follow a pattern. That is, affinity is in order of valence, divalent being more strongly held than monovalent, and among ions of the same valence, affinity has been found to increase with decreasing hydrated ionic radius (Nachod/Schubert, 1956). Within a given <sup>vertical</sup> group the hydrated radius decreases, so affinity increases, with atomic weight.

Attainment of ion exchange equilibrium is complicated by the existence of electrostatic as well as concentration differences. If, for example, a cationic resin is immersed in a dilute solution of electrolyte, the cations in the resin, which are the counter-ions in this case, will tend to diffuse out of the resin. From the solution, both the original counter-ions and co-ions will tend to diffuse into the resin. But the condition of electro neutrality has to be maintained. The net positive charge is constant if, for every <sup>at</sup> solution counter-ion diffusing into the resin, a resin counter-ion diffuses out into solution. Since the negative charges on the resin are fixed, no such exchange of anions can occur. Movement of small numbers of anions down the anion concentration gradient will generate an electrostatic potential between resin and solution which effectively excludes the anions. This is known as the Donnan potential.



THE DIFFERENT TYPES OF ION EXCHANGE EQUILIBRIA:

- a) favourable
- b) linear
- c) unfavourable
- d) sigmoidal

FIGURE 1

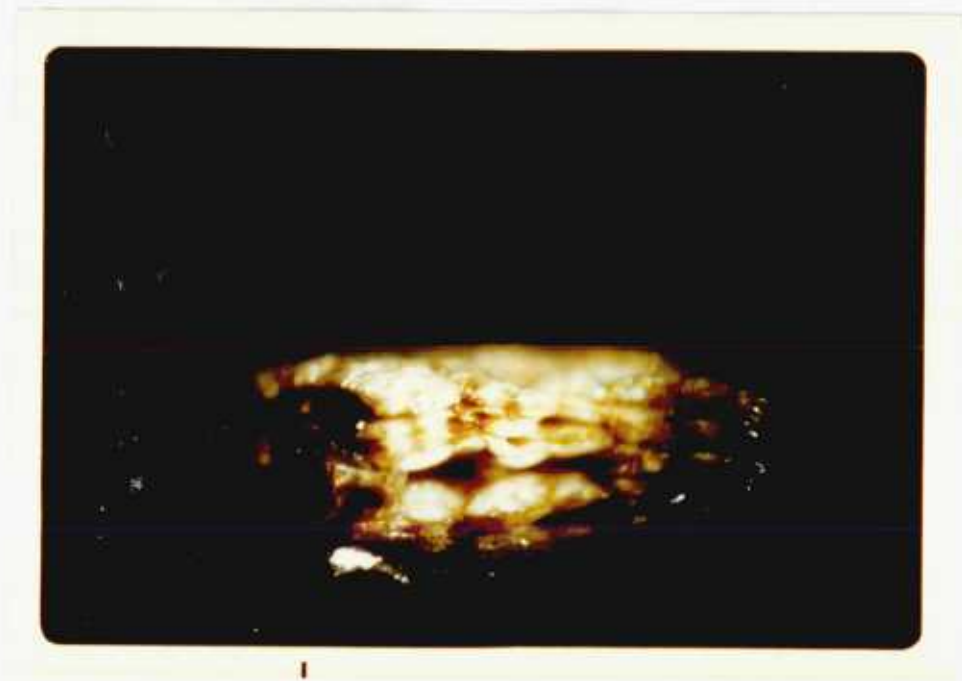
## 2.2 THE STRUCTURE OF VERMICULITE

Vermiculite is the geological name given to a group of hydrated laminar minerals which are aluminium-iron-magnesium silicates resembling mica in appearance. The unit cell of vermiculite has the approximate composition  $(\text{MgFe})_3(\text{AlSi})_4\text{O}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$ . Work has shown that vermiculite is neutral layers of  $(\text{MgFe})_3(\text{AlSi})_4\text{O}_{10}(\text{OH})_2$  alternating with layers of water. On heating slowly water is driven off and the solid layers exfoliate (unfold), see photograph 1, into curled filaments resembling worms. When carried out at  $750^\circ\text{C}$  the water is driven off and the neutral layers take the talc structure (Black, 1960). Basically the aluminosilicate structure of the clay is composed of alternating, parallel, two dimensional layers formed from silicate tetrahedra and aluminate octahedra, see figure 2. This silicate layer is approximately  $10 \text{ \AA}$  thick (Walker, 1969).

Vermiculite is formed in the clay fractions of certain soils by the leaching action of supergene solutions by the replacement of the interlayer  $\text{K}^+$  of biotite or phlogopite with exchangeable  $\text{Mg}^{2+}$ , exchangeable  $\text{Ca}^{2+}$  (to a much lesser extent than  $\text{Mg}^{2+}$ , see below \*) and a double water layer (Mohn, 1973); it therefore should be regarded as a clay mineral. Its characteristic properties such as, high cation exchange capacity (CEC), the ability to form complexes with organic substances and a variable interlamellar spacing depending on the exchangeable cation present and the humidity of the sample bear a striking resemblance to those of montmorillonite. The

\*  $\text{Mg}^{2+}$  is preferred over  $\text{Ca}^{2+}$  as (Peterson/Rhoades/Area/Coleman, 1965)

- i)  $\text{Mg-H}_2\text{O}$  structure is very stable, primarily because of high charge on silicate lattice
- ii) does not readily accommodate  $\text{Ca}^{2+}$  ion - disruption and expansion of the structure
- iii) looser  $\text{Ca-H}_2\text{O}$  interlayer should more freely admit  $\text{Mg}^{2+}$ .



PHOTOGRAPH 1. EXFOLIATED VERMICULITE  
Approximately 10 times magnification.  
- note, much smaller particles were  
used in the experiments.



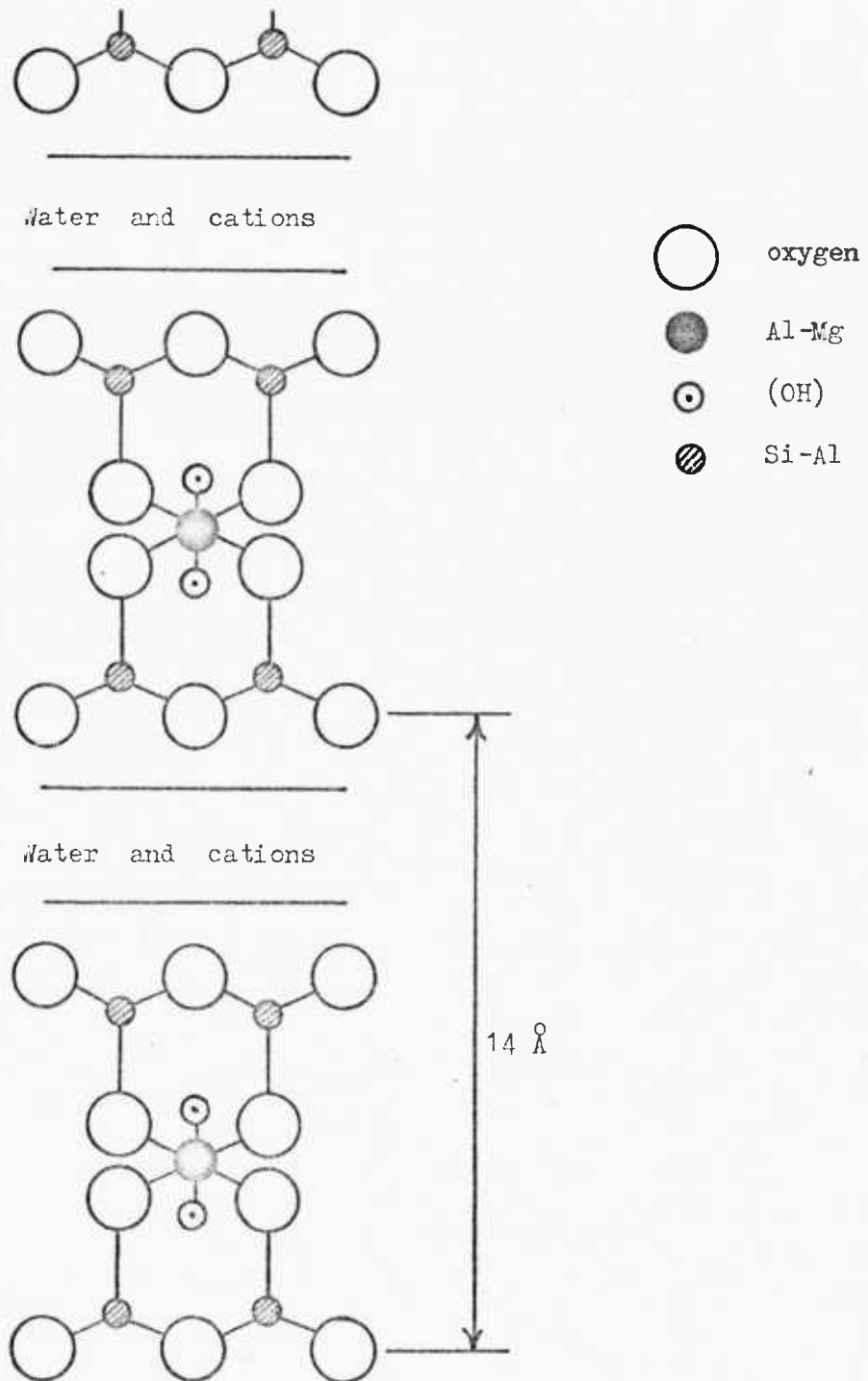


FIGURE 2  
THE STRUCTURE OF VERMICULITE

structures are also similar, and, as far as is known, consist of complex silicate layers interleaved with layers of water molecules carrying exchangeable cations (Mathieson/Walker; 1954).

It has been shown that the interlamellar  $Mg^{2+}$  ions are located in a plane midway between silicate layers. These ions are hydrated and consist of two sheets of distorted hexagonally linked water molecule sites with cations occupying definite positions in the midway plane. Chemical data require only  $\frac{1}{3}$  of the cation sites, and  $\frac{2}{3}$  of the water sites to be occupied, but random filling is not a requirement of such data and a well ordered structure seems probable. The cavities not occupied are believed to form a weak spot for entry into the structure (Barshad; 1954). In the interlamellar region, the water molecules within the sheet are linked by weak hydrogen bonds and the individual water sheets are held together by the cations. The hydrogen bonds binding the water molecules to the oxygen atoms of the silicate surfaces are probably stabilised to some extent by electrostatic forces acting through the water molecules. The location of the water molecules sites is determined by the surface of the silicate layers.

The interlayer cations and water molecules are mobile at ordinary temperatures, but migrate between specific sites. The cation sites are regularly spaced  $5.3 \text{ \AA}$  apart, but with divalent ions only about  $\frac{1}{3}$  of available sites are occupied and the mean distance between cations is about  $9 \text{ \AA}$ . Reaction spreads in a highly regular fashion from the edge towards the interior and the experiments indicate diffusion control (Walker; 1969).

Replacement of interlayer Mg by Sr involves a change from  $14.4 \text{ \AA}$  to  $15 \text{ \AA}$ , the increase being due to the different size of the Sr ion. In fact there is a contracted state for  $K^+$ ,  $NH_4^+$ ,  $Cs^+$  or  $Rb^+$ , and an expanded state for  $Ba^{2+}$ ,  $Na^+$ ,  $Li^+$ ,  $H^+$ ,  $Ag^+$  (Barshad; 1954).

TABLE 1 CHEMICAL ANALYSIS

	A	B	C	D
SiO <sub>2</sub>	39.37	37.7	36.7	37-42
TiO <sub>2</sub>	1.25			
Al <sub>2</sub> O <sub>3</sub>	12.08	13.9	13.2	10-13
Fe <sub>2</sub> O <sub>3</sub>	5.45	5.5	4.7	5-17
FeO	1.17	0.5	0.6	1-3
MnO	0.3			
MgO	23.37	27.6	23.6	14-23
CaO	1.46	3.1	0.2	
Na <sub>2</sub> O	0.8			
K <sub>2</sub> O	2.46	0.1	0.4	
H <sub>2</sub> O +105°C	5.18			
H <sub>2</sub> O -105°C	6.02			
H <sub>2</sub> O		12.0	20.1	8-20
CO <sub>2</sub>	0.6			
P <sub>2</sub> O <sub>5</sub>	0.15			
Li <sub>2</sub> O	0.03			
BaO	0.03			
Cl	0.02			
SO <sub>3</sub>	0.02			
S	0.18			

A. Vermiculite - *Mandouval*

B. Budnikov/Savelyev/Petrovykh; 1967

C. Peay/Hild; 1961

D. Epel'baum/Robnov; 1972

So if contracted, replacement is by ions that cause expansion, but if already expanded, they <sup>a</sup>may be replaced by either. Lithium and silver (and Na under certain conditions) cause expansion to the point of disintegration.

In fact large monovalent ions become fixed and reduce the Cation Exchange Capacity appreciably, as seen in Table 2 below.

TABLE 2 (Sawhney; 1969)

MINERAL vermiculite	SATURATING CATION			% DECREASE IN CEC ON SATURATION WITH	
	Na or Ca	K	Cs	K	Cs
Libby	140	102	36	27.1	74.1
Transvaal	127	118	35	7.1	72.5
Llano	146	139	52	4.4	63.8

The ammonium ion has a marked affect on the release and fixation of potassium ions, for example, by vermiculite, presumably due to the similarity of the two ions, with respect to size and chemical reactivity. Apparently, the presence of the ammonium ion causes the vermiculite to contract so that  $K^+$  ion is prevented from either entering or leaving the structure. Other ammonium compounds were tried to see what affect they had and it was found that n-butyl-amine hydrochloride had little effect, but 2,4 diaminophenol dihydrochloride and aniline hydrochloride greatly reduced adsorption. In these latter cases, however, the lattice size was little changed and so it must be assumed that the surface of the vermiculite becomes clogged with ions  $K^+$  cannot replace, (Kortland; 1961).

Walker (1949) describes the affect obtained when vermiculite is heated to  $110^{\circ}\text{C}$ . The talc like layers  $9.26 \text{ \AA}$  (Gruner; 1934) high, alternate with water layers  $4.95 \text{ \AA}$  high. Previous work had shown that apparently half the water was driven off but no noticeable change in distance of the structure had been noted. Experiments showed, however, that heating to  $110^{\circ}\text{C}$  in a sealed atmosphere to stop the

rehydration, gives a basal reflection of  $11.8 \text{ \AA}$  instead of  $14.2 \text{ \AA}$ , giving a water layer thickness of  $2.54 \text{ \AA}$ ; approximately half the original value. It is apparent, therefore, that removal of half the water is accompanied by the replacement of an original double layer by a single water-layer. The rapid rehydration is believed to be connected with the high cation exchange capacity.

Searle and Grimshaw (1959) note that heating to moderately high temperatures causes the collapse to  $9.26 \text{ \AA}$ , but rapid heating causes exfoliation, a process that can increase the volume up to 100 fold, presumably due to <sup>t</sup>he explosive release of water pushing the silicate layers apart.

TABLE 3 Sizes and densities of the standard grades of exfoliated vermiculite are as follows (as supplied by Mandoval Ltd.).

GRADE	SIZE	lb.ft. <sup>-3</sup>	DENSITY kg.m. <sup>-3</sup>
Fine	2 mm down	5½-7	88-112
Superfine	1 mm down	6½-9	104-144
Micron	0.5 mm down	6½-10	104-160

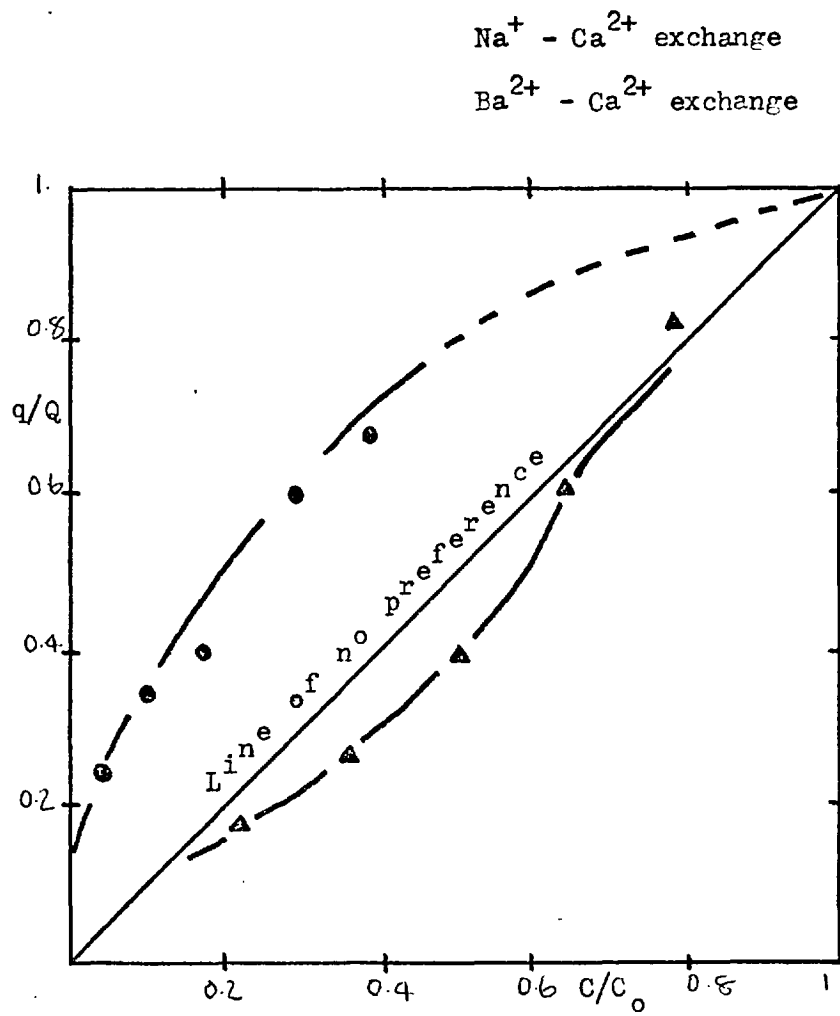
### 2.3 ION EXCHANGE IN VERMICULITE

The basic principles for ion exchange on vermiculite have been discussed in the preceding section, together with many other features of the exchange, and they will not be discussed further here.

Wild and Keay (1964) have shown that the cation exchange capacity of vermiculite depends on the nature of the exchanging ions, the charge of the crystal lattice and the <sup>e</sup>change from expanded to contracted interlayer spacing. The order of affinity of ions decreases as the unhydrated ionic radius increases and vermiculite has a preference for divalent ions over monovalent ions, and trivalent over divalent ions. They studied the exchange of Na, Mg, Ca, Sr and Ba ions with vermiculite and found that vermiculite shows a greater affinity for the divalent ions than for Na<sup>+</sup>. Some of the results are shown in figure 3.

The preference of vermiculite for higher valent ions appears to be due to the greater entropy of the multivalent ion-vermiculite system.

Bower and Troug (1940) found that a number of cations which form weak bases were sorbed in excess of the cations which form strong bases. Demunbrun and Jackson (1956) also noted this phenomena with copper and zinc, both of which form weak bases, and explain the difference by saying that they react with the structural hydroxides of the several layer silicate clays, as evidenced by a decrease in hydroxyl absorption peaks. It is possible that this special reaction is responsible, in part at least, for the additional increment in exchange capacity found with such materials.



ION EXCHANGE ON VERMICULITE AT 25°C

FIGURE 3

TABLE 4. CATION EXCHANGE CAPACITIES OF UNTREATED VERMICULITE

CEC meq/100g.	EXCHANGED CATION	REFERENCE
160	Not stated	Amphlett (1964)
90-100	Not stated	Vermiculite (1972)
120-160	Not stated	Barshad (1948)
133	Mg <sup>2+</sup>	Keay & Wild (1964)
124	Ca <sup>2+</sup>	Keay & Wild (1964)
120	Sr <sup>2+</sup>	Keay & Wild (1964)
124	Ba <sup>2+</sup>	Keay & Wild (1964)
133	Na <sup>+</sup>	Keay & Wild (1964)
115-159	Not stated	Malcolm & Kennedy (1969)
100-170	Not stated	Weiss (1958)
159	K <sup>+</sup>	Alexiades & Jackson (1965)
120-160	Not stated	Keay & Wild (1961)
100-130	Not stated	Walker (1949)
EXCHANGE ON EXFOLIATED VERMICULITE:		
92	Zn <sup>2+</sup>	Mohn (1973)
190	Cu <sup>2+</sup>	Mohn (1973)
225	Cr <sup>3+</sup>	Mohn (1973)



### 3. METHODS OF OPERATION IN PRACTICE

#### 3.1 BATCH OPERATION

This is the simplest procedure for ion exchange. In this case the exchanger and electrolyte are charged into a suitable vessel and contacted until exchange equilibrium is obtained. The reaction may be represented by:



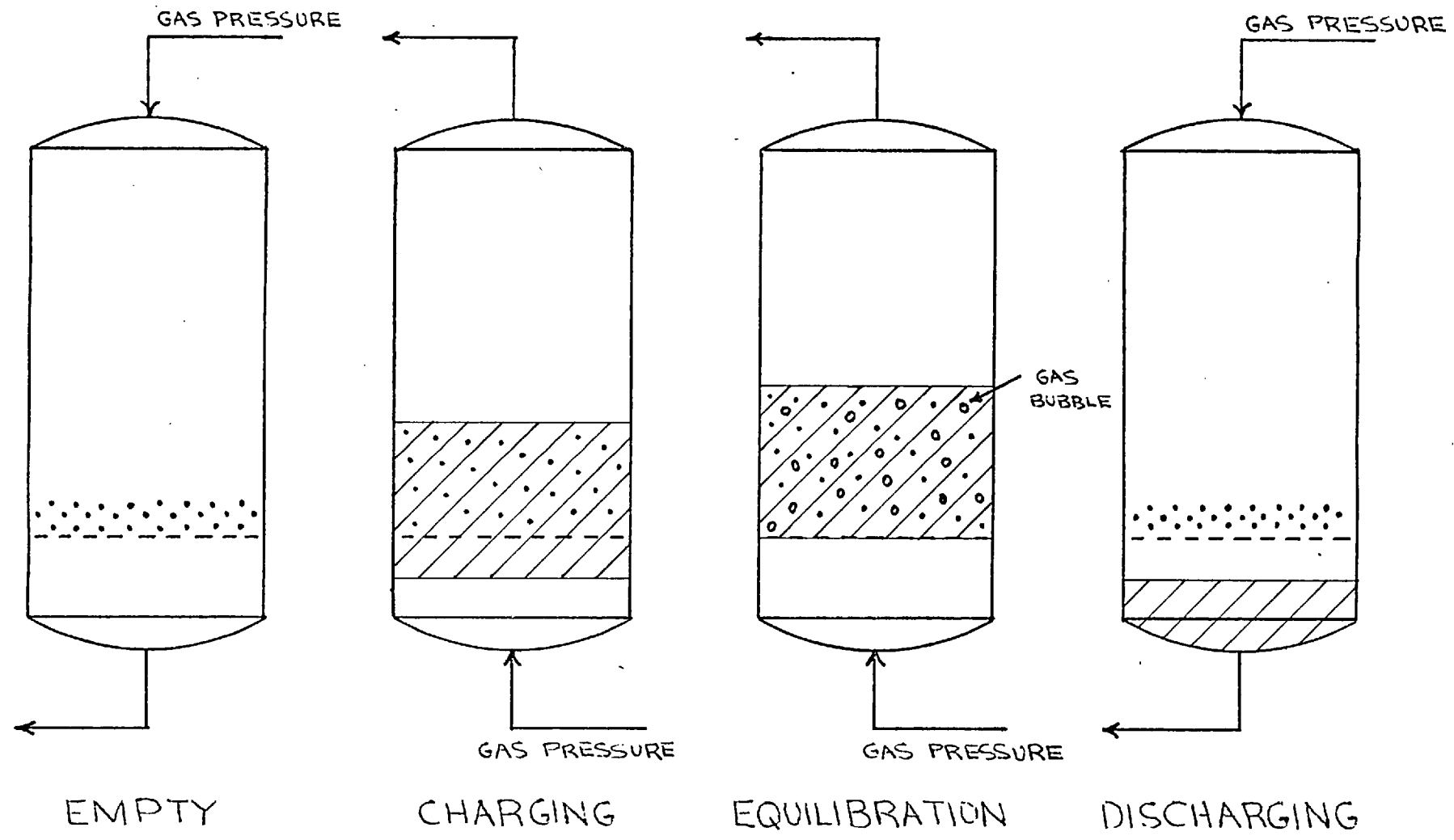
for the exchange of ions  $\text{C}_1$  and  $\text{C}_2$  of valence  $x$  and  $z$  respectively.

Obviously the degree to which the process occurs, in a finite time, is dependent on the equilibrium constant. In most cases batch-wise operation is limited to cases where the equilibrium is well to the right of the above reaction. Once equilibrium has, however, been attained it becomes necessary to filter out the exchanger, and if further separation is required, contacting with another portion of the exchanger. This process could therefore be carried out in a series of batch operations until the desired concentration is reached, but, as mentioned below, it is in this way that the column operation is usually adopted.

For industrial scale operation it should serve to describe two types of equipment. Firstly, it is customary to use a suitably modified stirred tank, as for example in figure 4. Here the exchange solution is injected through the base valve, and maintained fluidised by a continuous gas injection so that the equilibrium is achieved more quickly. Once the reaction is complete the tank is drained through the base valve. Regeneration can then be tackled in a similar way, using the regenerant instead of the exchange solution, or, the tank could be recharged with resin.

Secondly, the 'resin in pulp' (RIP) (Dorfner 1972) process

FIGURE 4



should be mentioned. It is the process used in the uranium recovery industry, and in operation the ion exchanger is charged into baskets which are moved up and down within the exchange solution.

### 3.2 CENTRIFUGE OPERATION

Cumberland and Broadbent (1969) reported on the application of the basket centrifuge when using vermiculite as an ion exchanger.

They noted the principle considerations for a fixed flow rate are:-

- i) the void space which determines how much contact there is between particles and solution,
- ii) the degree of turbulence around each particle, ie. determining the thickness of the surface film,
- iii) the particle size which is obviously related to the available area of contact.

The choice of the centrifuge as the operating unit meant that the relatively high centrifugal forces gave rise to a fairly high flow rate through the bed, together with bed compaction. So, to be successful, the increase in apparent rate of exchange must compensate for the shorter contact time resulting from the higher throughput. It was found that smaller particles were required.

The advantages were found to be:-

- a) a shorter contact time was possible in order to achieve a comparable decontamination efficiency, using a finer grade of vermiculite,
- b) should the bed become partially blinded by suspended solids in the effluent feed, the normal operating rate could be regained by ploughing off a thin layer of bed, thus removing the affected part,
- c) the removal of the exhausted bed is simple, clean and rapid.

The one major disadvantage they reported, is that more accurate control is required, so that the higher cost must be outweighed by the centrifuge's merits which are mainly noticeable when:-

- i) acceptable flow rates are unsuitable for column operation,

ii) a smaller quantity of the material is required due to the increased rate of exchange obtainable.

One further point to notice is that the much lower cost of vermiculite may well offset the difference in cost between using this technique and using a synthetic ion-exchanger in a column.

### 3.3 COLUMN OPERATION

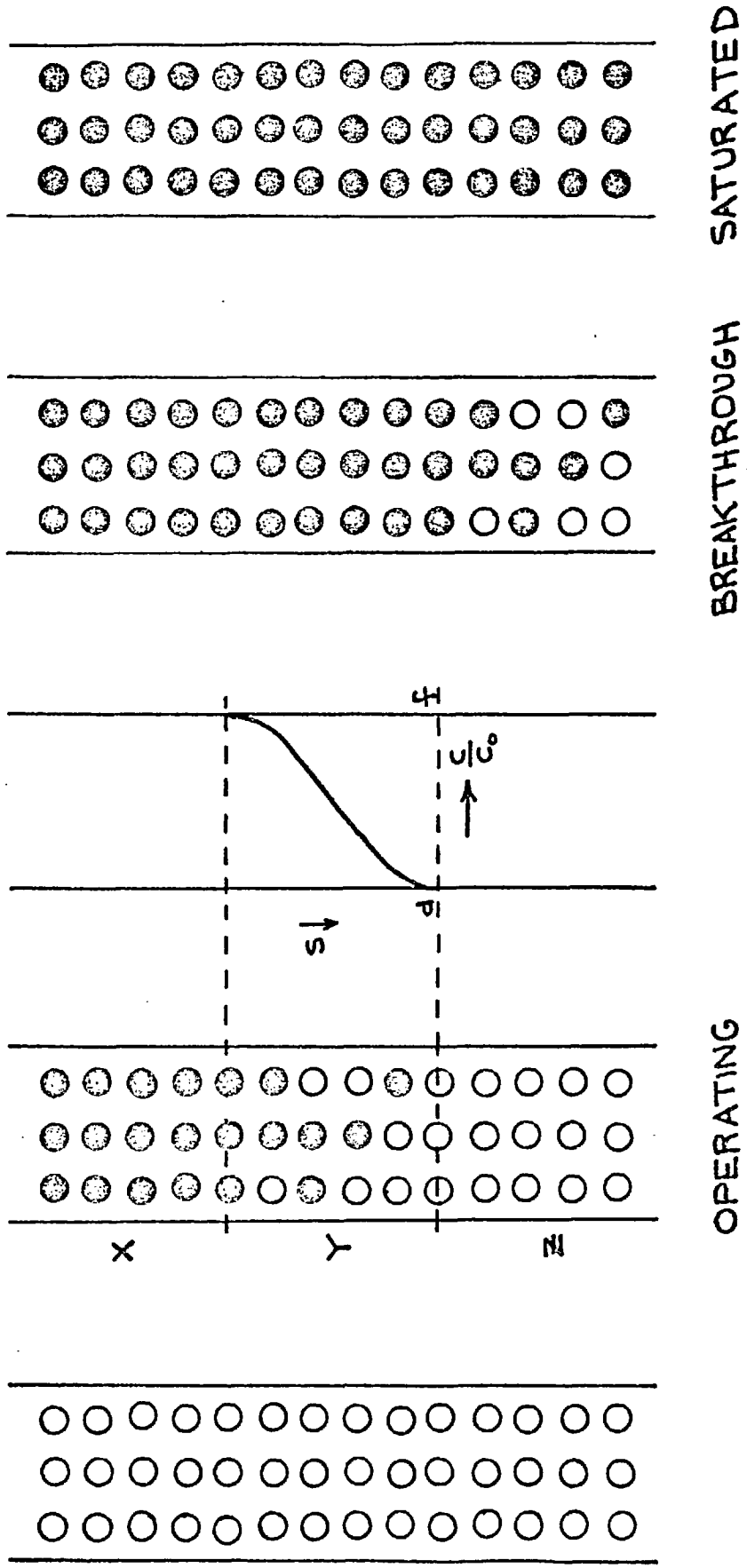
If the cation  $C_1^+$  of an electrolyte  $C_1^+Y^-$  is to be replaced by a cation  $C_2^+$  the process, in principle, could be carried out as a batch operation as described above. This, however, would require a large excess of ion exchanger or repeated equilibrations with portions of the ion exchanger. In a column this result is achieved as one operation, as on its way through the column the solution comes into contact with exchanger in the  $C_2^+$  form over and over again. Therefore all the  $C_1^+$  should be removed, provided the operating conditions are suitable.

Ordinarily the process consists of percolation, usually downflow, of a solution through a column packed with ion exchanger. The column is therefore packed with ion exchanger and rinsed through with distilled water, then it is ready for the solution to be passed.

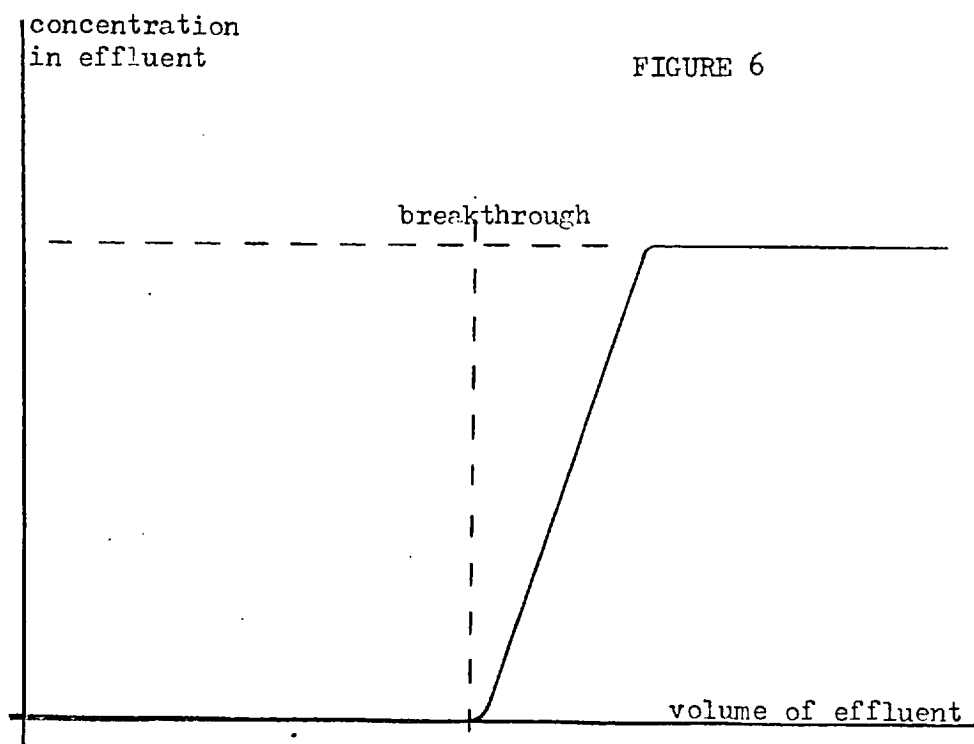
Now, before describing the process which occurs in the column, it is useful to make a few definitions. Firstly, the total number of exchanging groups in the column, usually expressed in milliequivalents (meq.'s), is called the TOTAL CAPACITY of the column. Whilst in operation, however, there is another expression used for the filter capacity, or BREAKTHROUGH CAPACITY, which is defined as the quantity of ions which can be taken up quantitatively by the column, operating under specific physical conditions, without any leakage of the ion  $C_1^+$  into the effluent stream. It is obvious that this value is lower than the total capacity and that it is dependent on a number of variables, eg. particle size, filtration rate, solution composition, etc. Finally the column would be required to operate at maximum efficiency and so the ratio of the break<sup>e</sup>through capacity to the total capacity is defined, and called the DEGREE OF UTILIZATION.

THE SORPTION STEP - Consider, as above, the exchange between a solution of  $C_1^+Y^-$  and an ion exchanger with exchangeable ion  $C_2^+$ . The principle is illustrated in figure 5.

FIGURE 5



The solution  $C_1^+Y^-$ , is introduced into the top of the column. Here the influent comes into contact with the top layer of ion exchanger and an equivalent amount of  $C_2^+$  ions are transferred into the solution. In ideal cases this could go to equilibrium, see below. Now, as the solution moves downward, the 'front' comes into contact with the  $C_2^+$  saturated ion exchanger. The uptake of  $C_1^+$  ions therefore continues; the reaction trying to achieve equilibrium in which the quantity of  $C_1^+$  ions in solution is less than the original. Simultaneously a new portion of  $C_1^+Y^-$  solution comes into contact with the top layer of the ion exchanger, which takes up a further amount of  $C_1^+$  ions. Therefore, after a certain amount of time, sufficient solution has been passed through the column to saturate the upper portion of the bed, 'x' in the figure, and so this part no longer fulfills a useful purpose, whereas the bottom is still in the  $C_2^+$  form.



NOTE: The area between the two curves, to the left of any abscissa value is proportional to the weight of ion taken up by the exchanger in the exhaustion up to that time.



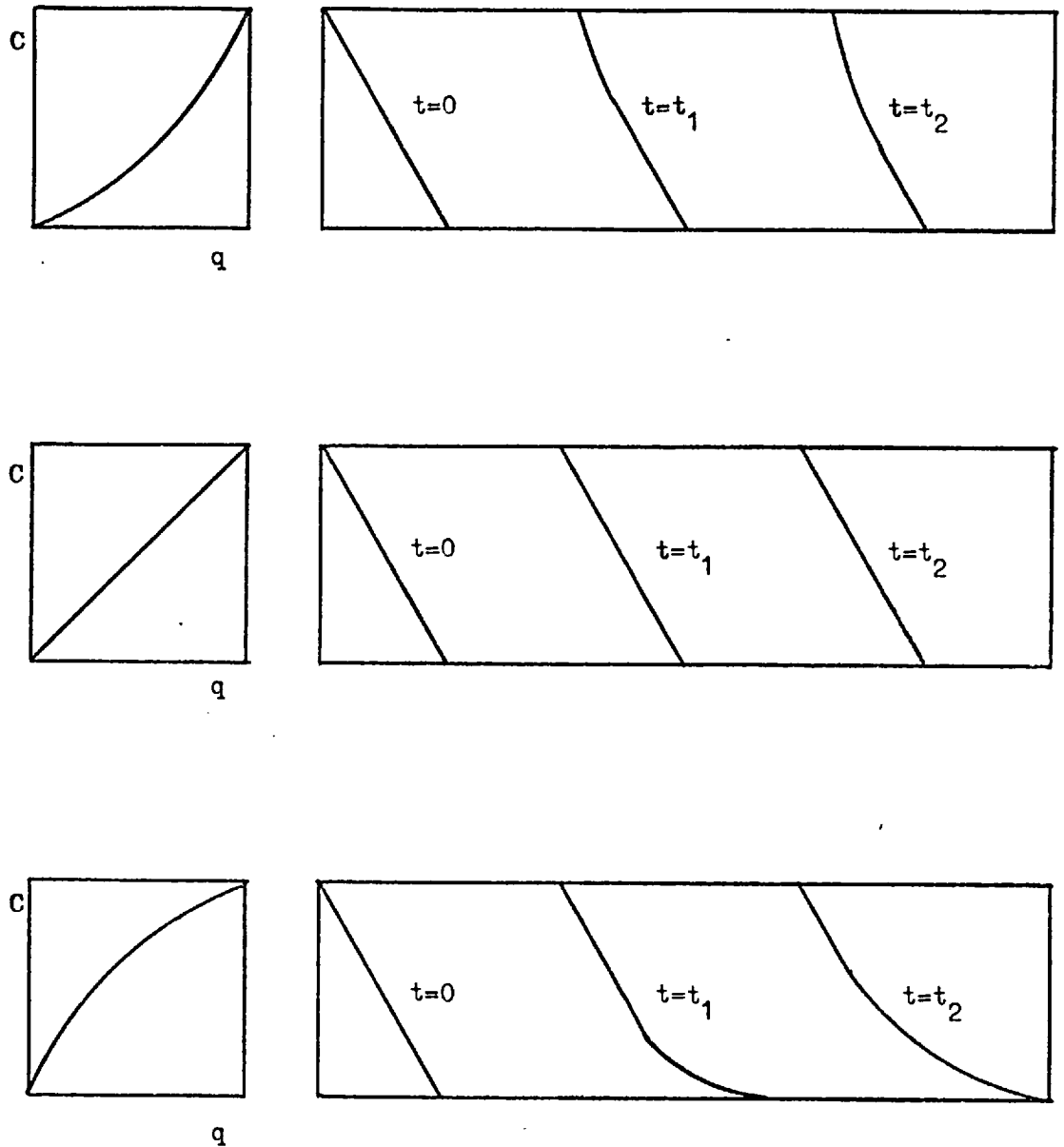
So at this point the concentration of  $C_1^+$  ions (C) in solution is, in the upper part of the column, the same as the influent ( $C_0$ ), whereas in the lower part 'z' it is equal to zero. In the intermediate zone both  $C_1^+$  and  $C_2^+$  are present in the resin and solution. Here the concentration varies with location - being a  $f(s)$  as indicated in the diagram. Obviously the effluent is free from  $C_1^+$  and contains an equivalent amount of  $C_2^+$  until such time as sufficient solution has been passed through the column so the boundary 'df' reaches the bottom of the resin bed. Breakthrough has then occurred. This is represented diagrammatically in figure 6 above.

**EQUILIBRIUM** - This is important as separation can only be accomplished when the exchanger exhibits different equilibrium affinities for the different components. See Coulson and Richardson (1971) for mathematical details.

Favourable equilibrium means that the ion  $C_1^+$  is preferred to the ion  $C_2^+$ , and so there is a sharp breakthrough boundary. It also means that the operation is self stabilising, ie. ions  $C_2^+$  behind the boundary are preferentially displaced by  $C_1^+$  and hence catch up with the boundary. Meanwhile any ions  $C_1^+$  ahead of the boundary are retained by the exchanger until the boundary passes, and therefore any perturbations are counteracted and the boundary is said to be **SELF-SHARPENING**. See figure 7.

If, on the otherhand, equilibrium is unfavourable the situation is reversed. Any  $C_2^+$  behind the boundary falls further behind, and any ions  $C_1^+$  in front accelerate away - hence boundary spread is enhanced and it is said to be **NON-SHARPENING**.

**DISTRIBUTION** - There are exchangeable ions in both the solid phase and the moving liquid phase, and the exchange depends on the distribution between these two phases. Therefore the distribution coefficient is introduced and defined by:



Effect of the shape of the isotherm on the development of a sorption wave through a bed with the initial distribution of sorbate shown at  $t=0$ .

FIGURE 7

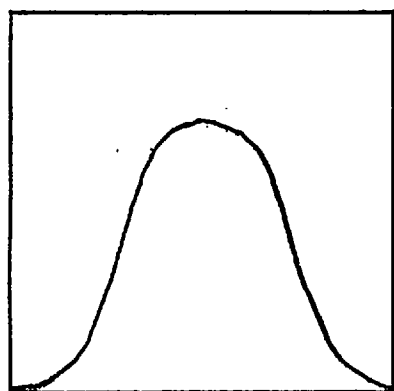
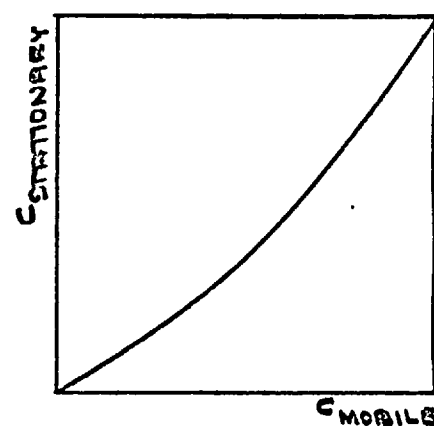
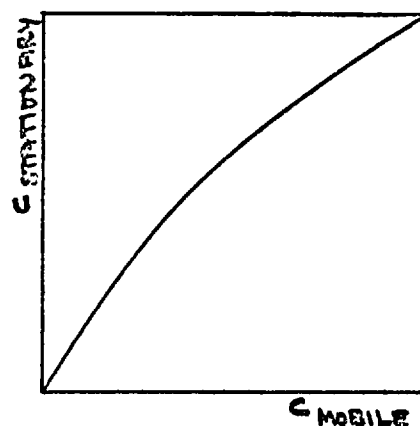
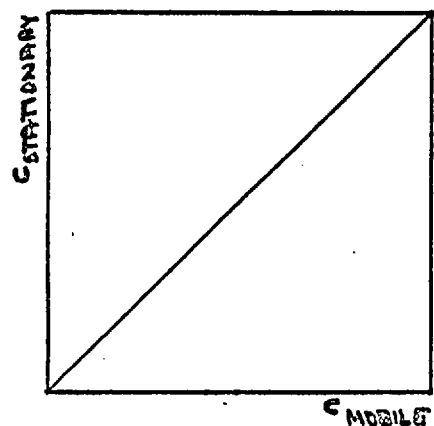
$$\lambda_i = \frac{\text{quantity of component } i \text{ per unit wt. of exchanger}}{\text{quantity of component } i \text{ per unit volume of liquid}} = \frac{\bar{C}}{C} \quad (1)$$

Now consider zone 'y' where there is an overlap of the two saturated exchange forms. The total concentration in either phase remains constant, so that the overall concentration is equal to the influent concentration  $C_0$ . Therefore the  $\lambda$ 's of  $C_1^+$  and  $C_2^+$  are the same in their saturated zones, 'x' and 'z' respectively, and are independent of the nature of the counterion. The value is given by  $\bar{C}/C_0$  and  $C_1^+$  and  $C_2^+$  in their own zones move at equal rates. The migration rate increases with increase in feed concentration, decreases with increasing concentration of fixed ionic group and is proportional to the flowrate. In the overlap region the preferred ion has the larger distribution coefficient and so moves at the slower rate. Hence the exchanger and operating conditions should be chosen to favour the ion in the feed.

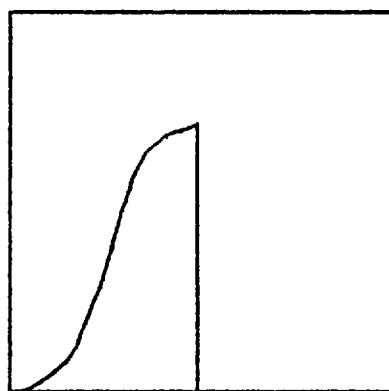
By plotting  $\lambda$  (Dorfner 1972) the exchange isotherm is revealed, which will be one of three types, one linear and two non-linear. Figure 8 shows the three distinct types, and also shows the respective chromatographic bands resulting from the said isotherm. A symmetrical band corresponds to isotherm A, one with a sharp leading front gives a convex isotherm B, and a concave isotherm is produced by a band with a sharp trailing edge. Investigations have shown that the distribution coefficient is linear for a low external concentration and low capacity.

**OPERATING CONDITIONS** - Affects the boundary sharpness. Any volume element only has a finite contact time with any given section of a bed and this is usually insufficient for equilibrium to develop. The boundary may, however, be sharpened by adopting a slow flow rate and a high exchange rate.

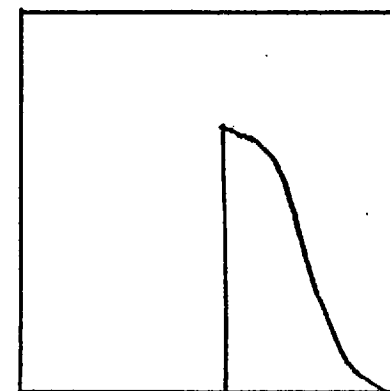
**FLOW RATE** - The curve becomes sharper and breakthrough capacity is



SYMMETRICAL



SHARP LEADING FRONT



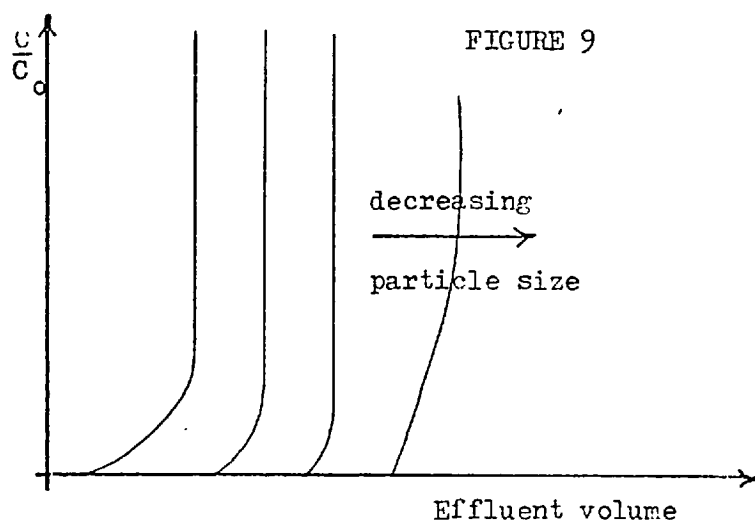
SHARP TRAILING FRONT

THE THREE POSSIBLE EXCHANGE ISOTHERMS AND RESPECTIVE SHAPES OF THE ELUTION BANDS, FIGURE 8

higher the lower the flow rate. It has been shown that the flow rate is  $f(\text{particle size, exchanger})$ . There being a small influence on changing the flow rate for an open network structure exchanger, but where there is high cross-linking the change may be considerable, especially for coarse particles. <sup>This is</sup> Easy to understand as network structure and particle size are of utmost importance to exchange velocity. For very dilute solutions, or where a risk of decomposition is evident it may be necessary to use a high filtration rate.

- NOTE: i) after operating for some time the rate will decrease, so exchanger should be removed and agitated so that fine particles can be separated,
- ii) swelling changes may occur and clog the filter so it may pay to use a wide filter and introduce the exchanger into the column whilst it is in it's largest form.

PARTICLE SIZE - highly important. Exchange breakthrough capacity increases with decreasing size. For quantitative uptake it is necessary to use fine particles.



TEMPERATURE - Increased temperature leads to an increase in the rate of both ion exchange and breakthrough capacity and sharpens the breakthrough curves. Note that the viscosity decrease with temperature, and diffusion increase with temperature; both suggesting that a higher temperature should be adopted. If the solution tends to irreversible hydrolysis an increase in temperature would not be advisable, and for a solution tending to decomposition at ordinary temperatures lowering

the temperature may well be worth trying.

CONCENTRATION - usually relatively low concentrations as uptake of ions increases with dilution. In very dilute solutions, or higher concentrations, where there are risks of complications by hydrolysis it may be possible to avoid difficulties by increasing the flow rate or by adding sufficient acid to the solution

ACIDITY - In general the quantitative separation can be performed by filtering even very acid solutions through  $H^+$  saturated filters. The breakthrough capacity is, however, usually reduced by a decreasing pH (Kihsk and Hassan, 1973; Lee; Demumbrum and Jackson, 1956). Keay and Wild (1961), however, report differently for the case of exchange on vermiculite. They say that pH 4 to 9 showed no affect, whilst below pH 4 the rate was increased due to the presence of the oxonium ion, and above pH 9 precipitation of  $Mg(OH)_2$  decreases the exchange rate.

COLUMN SIZE AND SHAPE - Increasing the length brings about an increase in breakthrough and overall capacities, so the degree of utilization increases if favourable equilibrium. On the otherhand, if the exchange is unfavourable it adopts the proportionate pattern (ie. non-sharpening) and breakthrough shifts to the right and spreads out. In this case the increase in length brings about no useful change. An obvious disadvantage is the extra resin required and the extra flow resistance.

The ASPECT RATIO (L/D) if high (at constant flow rate and bed volume) improves the utilization if the equilibrium is favourable, and has little effect if unfavourable. Disadvantages are the high flow resistance and so low flow throughput, and for too small a diameter the problem of maldistribution because of the wall effects.

Note that the boundary may be distorted by irregularities in packing and hydrodynamic phenomena (flow maldistribution, channelling,

fingering), so careful packing and uniform particle size are essential for a sharp boundary.

In general there is a high degree of column utilization if:-

- i) there is a strong preference of the ion exchanger for the feed counterion
- ii) small and uniform particle size
- iii) high volume capacity
- iv) low degree of cross-linking
- v) elevated temperature
- vi) low flow rate
- vii) low concentration of counter-ion in feed
- viii) high column length or aspect ratio
- ix) suitable pH.

Note that the gain in column efficiency may be offset by undesirable side effects, but the above mentioned are in agreement with experimental results (Dorfner, 1972).

### 3.3.1 LABORATORY APPARATUS

Due to the wide range of operating conditions that have to be accommodated in the laboratory the literature describes numerous designs for ion exchange columns. Usually for analytical work the ratio of height to diameter is in the range 1:10 - 1:20, lower if required to work quickly, and a diameter of 8 to 15 mm is selected (Samuelson, 1953). Obviously, whatever design is adopted it must allow easy flow through the column.

A simple column can easily be made from a glass-tube with bored stoppers at each end (see figure 10A) (Samuelson 1953; Dorfner, 1972; Stock and Price, 1974). The bottom is attached to a capillary dropping attachment via a flexible tube connection; the dropping rate being controlled by a pinch cock. The top of the column is provided with an ordinary dropping funnel as a reservoir. Inert packing material (cotton or glass wool, quartz, cellulose, etc.) are placed at both ends of the resin to prevent plugging of the discharge tube by 'free' ion exchange particles and to prevent turbulence of the bed at the top end. Figure 10B shows a more refined version made by glass blowers. Here ground glass joints are used and reservoirs of different sizes may be attached. A further refinement would be to include an overflow tube, figure 10C, at the bottom in order to prevent drainage of the column during operation.

Countercurrent columns are also said to offer some advantages, and the apparatus of figure 10D can be used in both descending and ascending flow. This is achieved by means of the control offered by the three-way stop-cock. The main advantage (Dorfner, 1972) is that materials which have been exchanged near the top of the bed do not need to cover the distance through the entire column and can thus be eluted more easily. The same end is achieved very simply by the Wickhold inversion column, figure 10E.



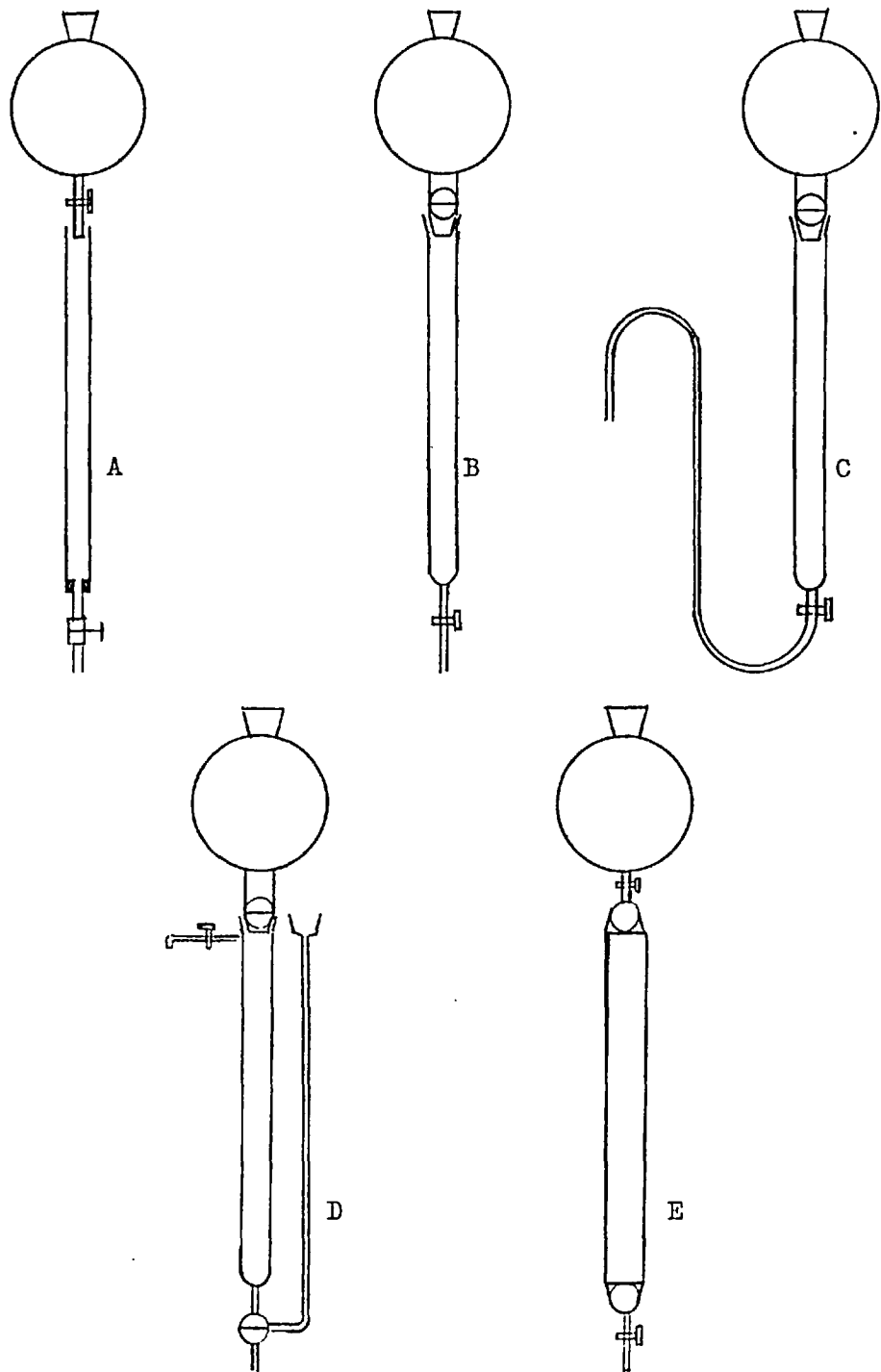


FIGURE 10

- A. Simple homemade ion exchange column
- B. Ion exchange column with ground joint
- C. Ion exchange column with overflow
- D. Countercurrent ion exchange column
- E. Wickbold inversion column

Very often a burette is used in the laboratory, figure 11, the only adaption being made for loading and unloading solutions. Where high temperatures are to be employed the column may simply be fitted with a temperature regulating jacket, figure 12.

In parallel studies with ion exchange resins means that a column system may be adopted. Here several <sup>columns</sup> columns are joined together by a distribution system, see figure 13. Obviously each could have its own reservoir acting independently.

Larger columns may be constructed in a similar way to these simple versions, glass being used as the main material of construction. Dimensions of 50 mm diameter and 800 mm length are recommended (Dorfner, 1972). In this case acid-washed sand or quartzite is usually used as the support for <sup>the</sup> resin. Experiments on this scale can often be directly scaled-up.

Seedhouse (1957) reported the use of vermiculite in columns of 5 ft. diameter which were satisfactory in downward or upward flow. Each column was capable of handling 900 gallons per hour (gph) ( $3.74 \text{ ml.cm.}^{-2} \text{ min.}^{-1}$ ), but it was found best not to exceed 600 gph ( $2.49 \text{ ml.cm.}^{-2} \text{ min.}^{-1}$ ). Bed depth was found to be best at 18 in. as there was no improvement for depths greater than this. Tests were reported that showed vermiculite will support algae growth, although unlikely in plants using demineralised water, and it is therefore necessary to ensure that airborne material and sunlight are avoided. However if it does grow it can of course be destroyed with hypochlorite.

Charging the ion exchanger into the column is easily done with practice. First the resin must be treated with water so that any swelling occurs whilst outside the column so that rupture of the column is avoided. Two hours are usually sufficient for swelling (Dorfner 1972). The exchanger is then charged into the column; rapid charging leading to uniform packing of the different sized exchanger

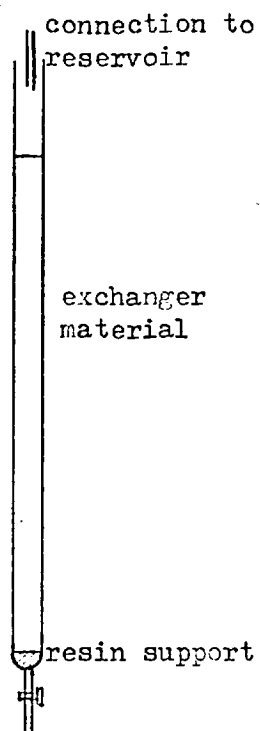


FIGURE 11

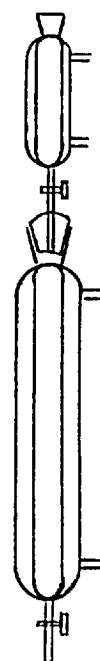


FIGURE 12

HEATABLE COLUMN

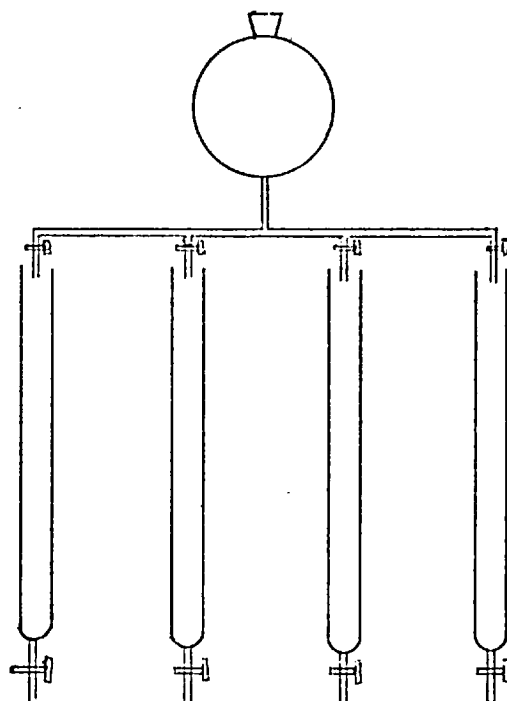


FIGURE 13

SCHEMATIC REPRESENTATION OF  
A COLUMN SYSTEM.

particles. It must be ensured that the bed is always covered with water (Dorfner 1972; Samuelson, 1953) but the excess is continually removed. If by chance too much water is taken from the column and air enters the packing it is usually sufficient to add water and swirl the bed by tipping the column. Finally the inert material is placed on top of the packing.

Three parameters (Dorfner, 1972) serve to describe the dynamic and chemical processes taking place in an exchange column, i.e. flow rate, pressure drop, and breakthrough capacity.

Usually flow rate is expressed in  $\text{ml.cm.}^{-2}\text{min.}^{-1}$ . If the flow is given in  $\text{ml.min.}^{-1}$  the column diameter must also be supplied. The linear flow rate of  $\text{cm.min.}^{-1}$  or  $\text{cm.sec.}^{-1}$  are frequently used.

The resistance produced by friction leads to pressure drop as the solution flows through the column, so that flow rate is limited. The pressure drop is obviously applicable to both cationic and anionic exchange processes and is a function of apparent density, particle size and shape.

Breakthrough capacity has already been discussed in some detail above.

On the industrial scale the process is often continuous in a counter-current column. A characteristic of such processes is that a large part of the upper ion exchange bed remains in the column without utilization during the run, while the lower portion performs the exchange (Dorfner, 1972).

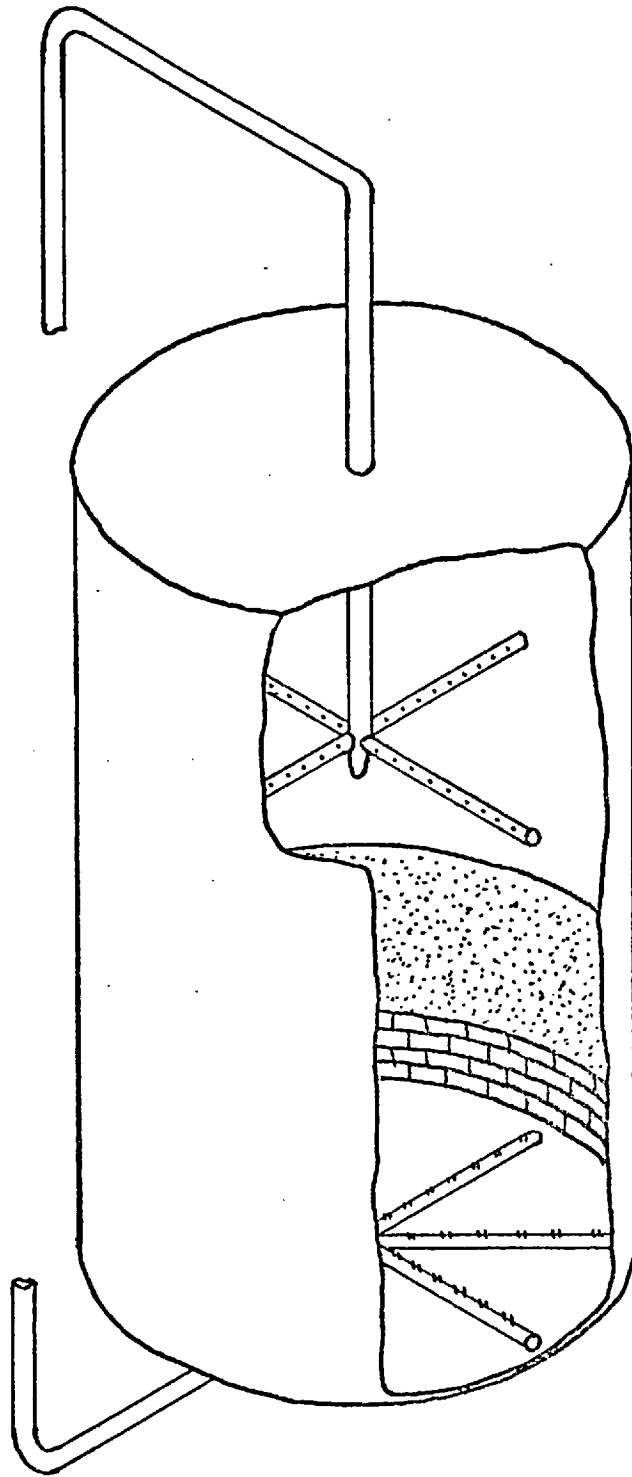
### 3.3.2 INDUSTRIAL EQUIPMENT - COLUMNS IN INDUSTRY

The column process is the most important industrial technique, although it is very rare that laboratory operations can be directly scaled-up. For column operation the most important feature is the total capacity for it is this value which determines the amount of exchanger; usually with operation being based upon a 50-70% usage. Usually the exchange material must have high selectivity, small size, and high porosity together with suitable physical conditions, and often a column of high aspect ratio, i.e. length/diameter, is adopted. It must be noted that the nature and control of regeneration essentially determines how the column capacity is attained, but, for the work being considered here regeneration has not to be considered as the exchanger will be replaced after each run.

The hydraulics of the process should be considered as uniform flow through the whole column and even distribution at inlet and outlet are of importance. Darcy's law serves to describe the pressure drop and Stoke's law deals with the expansion of the bed (Dorfner, 1972).

After charging the column backwashing is usually adopted to remove any small particles and to layer in order of decreasing size the exchanger. The exchanger solution can then be loaded until the column is 'exhausted' whence cleaning-out and recharging can be carried out.

To achieve such an operation uniform flow, as mentioned above, is required to ensure that the whole filter bed is used. Hence the column must have such a configuration and necessary equipment to ensure the operation can be accommodated. Figure 14 shows a typical ion exchange column. It consists of a cylindrical tank containing a layer of porous material (eg. quartz, gravel, etc.) on which the ion



A SIMPLE ION EXCHANGE FILTER FOR  
A COLUMN PROCESS

FIGURE 14

exchanger may be loaded until it has reached a level some what above the mid-point of the tank. Often stainless steel, or another suitably acid resistant material, is used in the construction. More complex systems for the column process are discussed fully in Dorfner (1972) and Coulson & Richardson (1971).

To be able to produce absorbate-free effluent, a bed must be long enough to contain the whole sorption zone, see figure 10. It must also be long enough to give the zone a residence time at least equal to the required on-line time; 8, 12 or 24 hours being normal in conventional designs, but periods may be as short as ten minutes in others.

The advantage of a fixed bed is that it is simple and easy to construct, but there are a couple of disadvantages which arise from the very simplicity that makes it attractive:-

- i) because it is discontinuous it has to be switched to regeneration at regular intervals. This may be done manually or automatically, the control system being activated by effluent concentration,
- ii) in order to give the sorption zone a convenient residence time and to provide a stand-by bed, much more sorbent is tied up in the unit than is actually being used at any one time. This also leads to a higher pressure drop than is necessary.

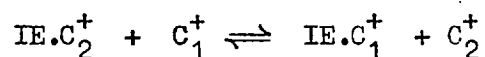
Distribution and discharge are of great importance with uniformity being the main essential. This ensures that parts of the column are not missed altogether or only partially used due to local high flow rates. Typical units are depicted in the diagram, and note that during back-washing the tasks are reversed. The maximum efficiency is obviously a function of this feature.

Process control has to be developed for each unit as there are such a variety of designs and operating features.

#### 4. THEORY

##### 4.1 ION EXCHANGE EQUILIBRIA

Ion exchange equilibrium is attained when an ion exchanger is contacted, for a sufficient time, with a solution containing a counterion different to the one contained in the exchanger itself. The exchange is both reversible and stoichiometric, and in the simplest case may be represented by:



where:

'IE' denotes the ion exchanger

and  $\text{C}_1$ ,  $\text{C}_2$  are the counterions of valence one.

Obviously, at equilibrium the solution and exchanger both contain the ions  $\text{C}_1^+$  and  $\text{C}_2^+$ .

So, by formal application of the Law of Mass Action, equilibrium may be represented, in terms of activities, by:

$$K = \frac{a_{rC_1} \cdot a_{sC_2}}{a_{rC_2} \cdot a_{sC_1}} \quad \dots (2)$$

where:

$a_{sC_1}$  &  $a_{sC_2}$  are the activities of ions  $\text{C}_1$  &  $\text{C}_2$  in solution

and  $a_{rC_1}$  &  $a_{rC_2}$  are the activities of ions  $\text{C}_1$  &  $\text{C}_2$  in the resin.

Then the activities may be replaced by the product of concentration and activity coefficient, thus:

$$K = \frac{f_{rC_1} \cdot f_{sC_2} \cdot q_{C_1} \cdot C_2}{f_{rC_2} \cdot f_{sC_1} \cdot q_{C_2} \cdot C_1} \quad \dots (3)$$

where:  $q$  denotes the concentration in the resin phase

$C$  denotes concentration in the solution



$f$  denotes activity coefficient

Then, by noting that the total concentration in the solution remains constant at  $C_o$  and denoting the total capacity of active exchange sites by  $Q$ , we can replace the concentration as shown below:

$$\begin{aligned} q_{C_1} &= q & C_1 &= C \\ q_{C_2} &= Q - q & C_2 &= C_o - C \end{aligned} \quad \dots (4)$$

which on substitution gives:

$$K = \frac{1 - C/C_o}{C/C_o} \cdot \frac{q/Q}{1 - q/Q} \cdot \frac{f_{rC_1} \cdot f_{sC_2}}{f_{rC_2} \cdot f_{sC_1}} \quad \dots (5)$$

The ratio  $f_{sC_2}/f_{sC_1}$  is approximately unity, and  $f_{rC_1}/f_{rC_2}$  is difficult to compute, and so it is grouped with the constant  $K$  to give an empirical constant  $K'$ , as shown below:

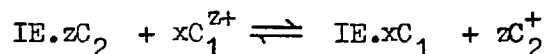
$$\frac{q/Q}{1 - q/Q} = K' \cdot \frac{C/C_o}{1 - C/C_o} \quad \dots (6)$$

This equation is plotted in figure 15, for different values of  $K'$ .

The use of Mass Action has been justified experimentally (Drew/Hoopes, 1958). It has also been shown (Drew/Hoopes, 1958), that for organic resin exchangers,  $K$  varies with changes in resin density that occur progressively during exchange. High concentrations in the solution phase lead to an appreciable uptake of unbound ions by the resin structure, and this uptake also affects the apparent equilibrium. Further, the activities of the exchanging ions in solution will change with changing ionic strength; for two ions of equal valence, the changes in activity coefficients will often be almost equivalent, and for these cases  $K$  will be nearly independent of the total ionic concentration of the solution.

These factors make it difficult to obtain a completely general relation for exchange of heterovalent ions. But Mass Action, again, gives the best approximation. Note that in this case the concentrations should be expressed in equivalents rather than in moles.

In a more general form the exchange may be represented by:



where the counterions  $\text{C}_1$  and  $\text{C}_2$  are of different valence, namely 'z' and 'x' respectively. In this case, proceeding as above, the Law of Mass Action yields:

$$K' = \frac{q_{\text{C}_1}^x \cdot c_2^z}{q_{\text{C}_2}^z \cdot c_1^x} \quad \dots (7)$$

and for  $x = 1$ ,  $z = 2$ , it can be shown that:

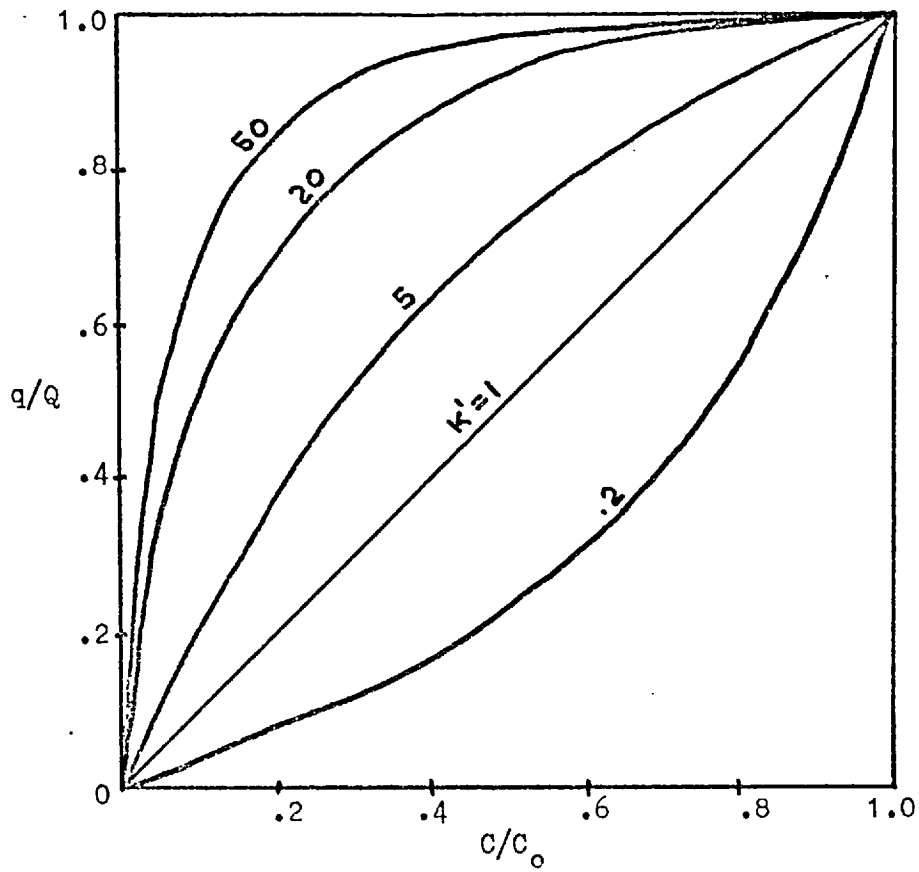
$$\frac{q/q}{(1 - q/q)^2} = \frac{K' q \rho_a}{c_o} \cdot \frac{c/c_o}{(1 - c/c_o)^2} \quad \dots (8)$$

This is plotted in figure 16, with  $K' q \rho_a / c_o$  as parameter.

Note,  $\rho_a$  is the apparent density of the exchanger in g. dry H form/cm<sup>3</sup> and the ratio of the solution phase activity coefficients have again been taken as unity.

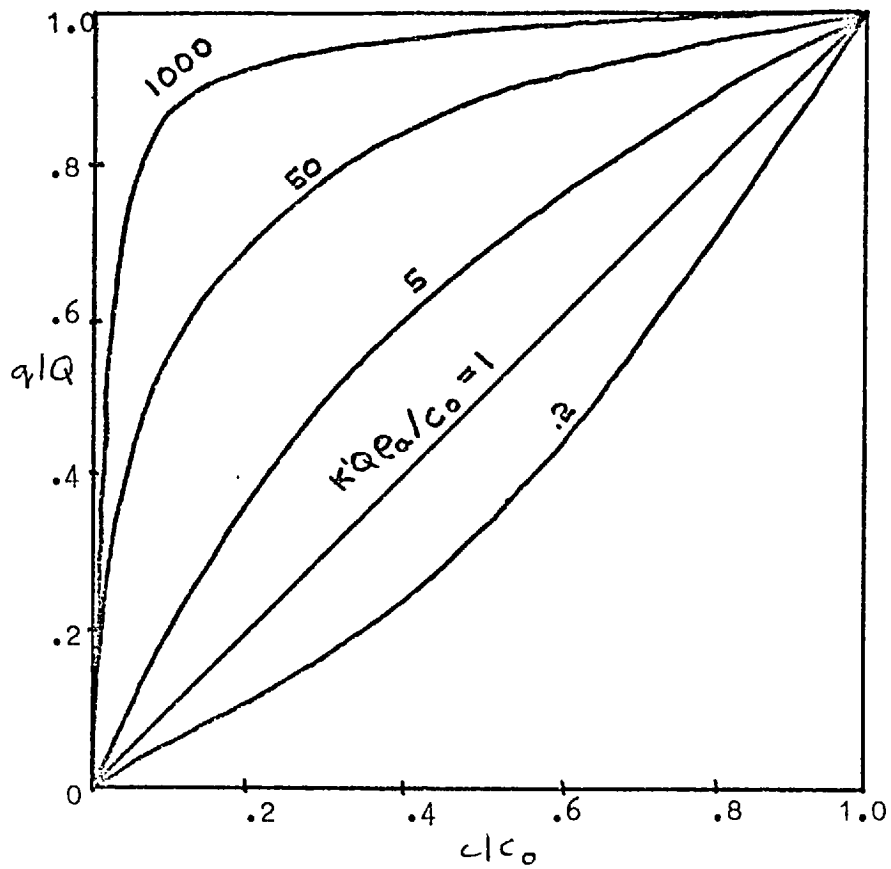
Bauman and Eichhorn (Nachod/Schubert, 1956) have shown that the above results could be obtained by regarding the resin and liquid phases as being separated by a semipermeable membrane which confined the exchange active groups, and applying the principle of Donnan equilibrium to the diffusable ions.

THE EFFECT OF CONCENTRATION - From the theoretical relationship it can be seen that when ions of different valence are exchanging the equilibrium parameter is a function of total concentration. This is



THE GENERALISED EQUILIBRIUM PLOT .....  
for the exchange of ions of equal valence

FIGURE 15

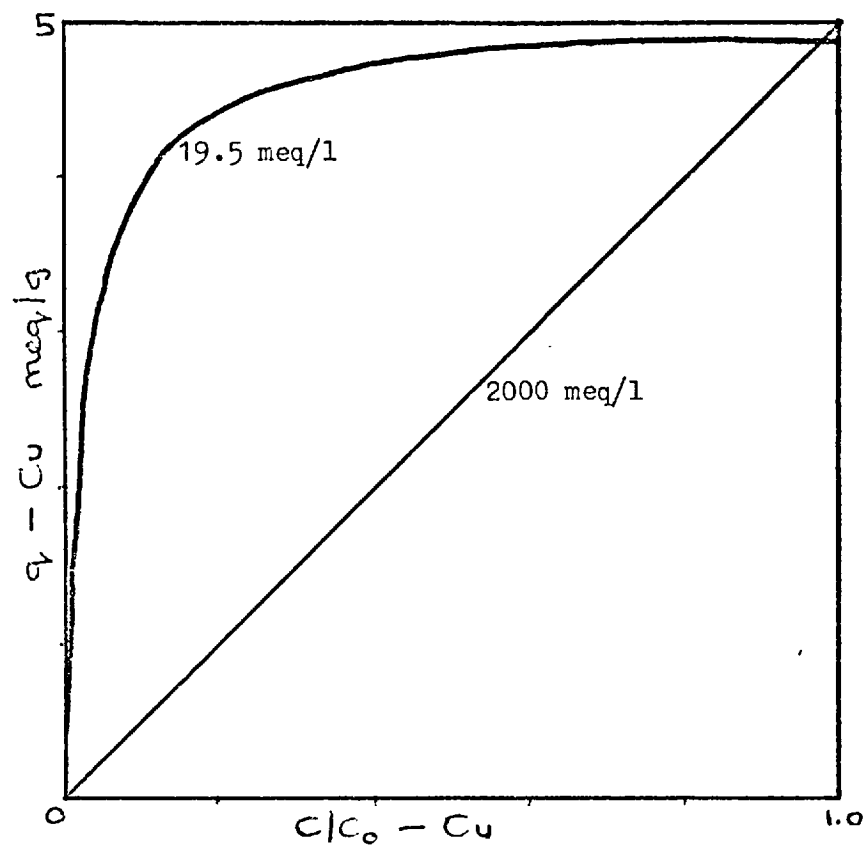


THE GENERALISED EQUILIBRIUM PLOT .....  
for divalent-monovalent exchange

FIGURE 16

similar to the equilibrium constant for a gas phase reaction written in terms of mole fractions, the equilibrium constant being dependent on the total pressure in a manner known in qualitative form as Le Chatelier principle. Hence, in the exchange of univalent for divalent ions, the equilibrium parameter is shifted to favour pickup of the univalent ions by an increase in concentration.

This is very important for industrial scale operations as regenerants are usually univalent and if dilute solutions were employed regeneration would be ineffectual. Higher concentrations mean that the equilibria are more favourable in the desired direction. This is illustrated in figure 17.



EFFECT OF CONCENTRATION - COPPER-HYDROGEN EXCHANGE,  
AMBERLITE IR-120

FIGURE 17

#### 4.2 ION EXCHANGE KINETICS

Obviously, for practical reasons the rate of reaching equilibrium is of great importance, as if the rate is slow, the time required is high and so in the case of column operation a slow flow rate has to be adopted.

Essentially an ion exchange resin is a three-dimensional cross-linked network of chain compounds which carry fixed ionic groups, the charge of which is balanced by mobile ions of opposite charge. These are the COUNTER IONS, and they are free to diffuse within the resin network. The ion exchange process results in the resin taking up some solvent and additional mobile ions (counter ions and co-ions, the latter having the same charge sign as the fixed ionic groups). The result is the exchange of the originally present counter ions by a different species. So each stage of the diffusion, whether in the resin or solution phase, must be accompanied in the presence of an ion of opposite charge, for the law of electroneutrality must be obeyed at all times. Even at low dilutions, the Donnan conditions are such that the situation is satisfied.

But, it is also possible to have an ion enter into the exchange within the resin phase without the presence of an equivalent number of oppositely charged ions. Jenny's (Kunin, 1958) contact exchange theory must be adopted here. It may clearly be assumed that an ion that can enter into exchange reactions reversibly is dissociated when in the exchange complex. This ion can therefore oscillate a finite distance and may be considered to be occupying an oscillation volume. According to Jenny's concept, exchange results whenever these two oscillation volumes overlap. This can take place between the exchange surfaces of two particles or within an ion exchange particle. This concept may therefore account for exchange without the entry of free electrolyte within the resin phase. A system consisting of a resin

having a high fixed ion concentration and an extremely low bulk-solution concentration may require such a mechanism, for the amount of free electrolyte entering the resin phase would be ridiculously small.

So considering an exchange pellet located in a solution there are five rate controlling steps for the reaction (Salmon/Hale, 1959):



These are:-

- i) the diffusion of  $\text{C}_1^+$  ions through the solution up to the surface of the ion exchange resin particles,
- ii) the diffusion of  $\text{C}_1^+$  ions through the resin particle to the exchange sites,
- iii) the replacement of  $\text{C}_2^+$  ions by  $\text{C}_1^+$  ions at an exchange site,
- iv) the diffusion of  $\text{C}_2^+$  ions back through the resin particles toward the solution,
- v) the diffusion of  $\text{C}_2^+$  ions away from the surface of the resin particles into the bulk solution.

These processes occur simultaneously, and by assuming electro-neutrality of solution and resin during the exchange processes (i) and (v), together with (ii) and (iv), can be linked together resulting in three rate controlling steps, as listed below:-

- i) the diffusion of  $\text{C}_1^+$  ions up to the surface of the resin particle and simultaneous diffusion of  $\text{C}_2^+$  ions away from the resin surface,
- ii) the diffusion of  $\text{C}_1^+$  ions through the resin network towards the exchange sites and simultaneous diffusion of  $\text{C}_2^+$  ions back through the resin towards the solution,
- iii) replacement of  $\text{C}_2^+$  ions by  $\text{C}_1^+$  ions at exchange sites



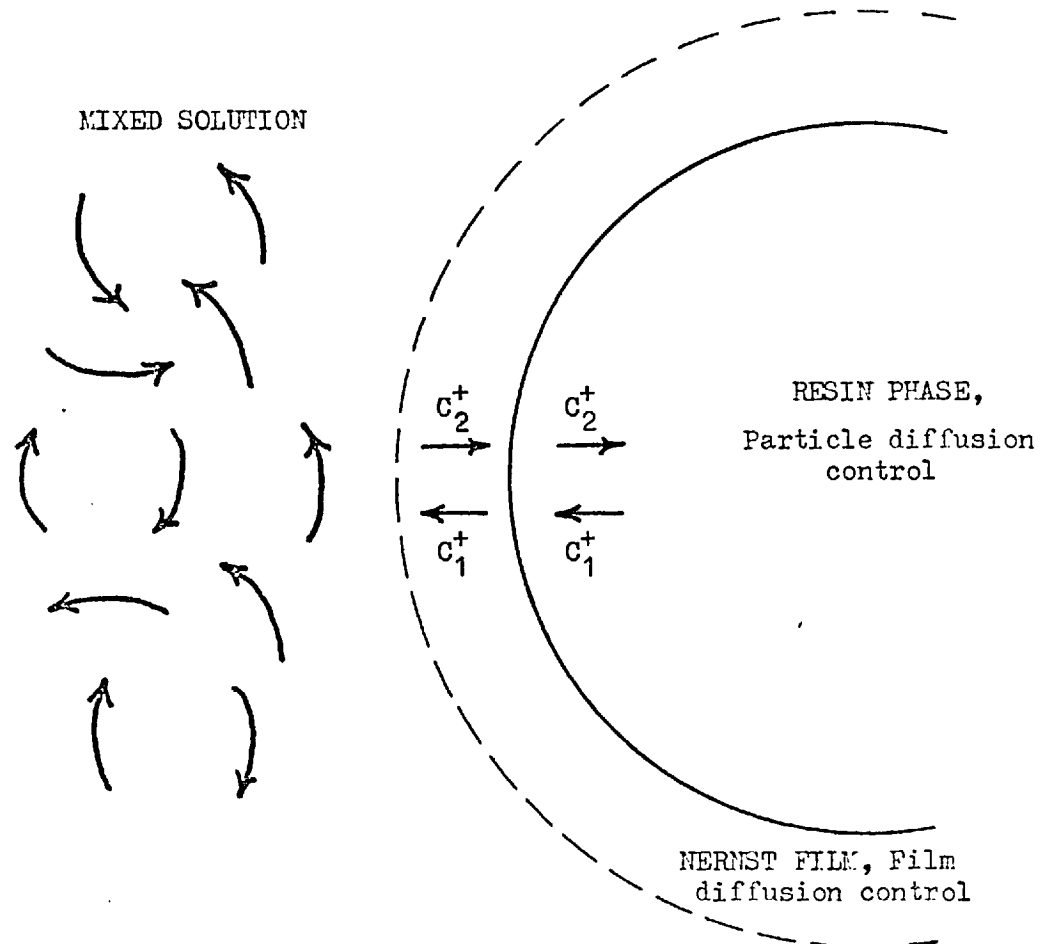
These processes occur simultaneously, and it is obviously the slowest which determines the rate. It has been shown (Helfferich & Plesset, 1958; Marcus & Kertes, 1969; Boyd et. al., 1947) that diffusion is the rate controlling step, ie. steps (i) or (ii).

Now, step (i) depends on the degree of mixing of the bulk solution, which is usually considered as perfectly mixed. But hydrodynamic conditions lead to the adoption of a theory that assumes a thin film of unmixed solution around the pellet itself. See figure 18. This is the 'Nernst Film', and is considered to have thickness  $\delta$  which is dependent on the degree of agitation for a batch process, or the flow rate of a column process. The faster the mixing the thinner the film. The usual thickness of the Nernst Film is of the order  $10^{-2}$  to  $10^{-3}$  cm. (Kitchener, 1957; Rieman/Malton, 1970), but of course this is impossible to measure. The rate of film diffusion is increased by:-

- i) reducing the thickness by increased agitation or flow rate,
- ii) increasing the concentration of exchanging ions in the solution,
- iii) increasing the surface area, by decreasing the particle size,
- iv) increasing the temperature.

Process (ii) on the otherhand, involves the diffusion of ions through the resin and is termed 'particle diffusion'. If the rate of film diffusion is high, the surface of the resin particles will be almost in equilibrium with the solution and the rate of particle diffusion will be determined by conditions inside the particle. Hence particle diffusion is increased by:-

- i) increasing the porosity of the resin - ie. decrease cross-linking,
- ii) decrease the particle size,
- iii) raise the temperature.



SCHEMATIC REPRESENTATION OF THE RATE  
CONTROLLING STEPS OF ION EXCHANGE

FIGURE 18

Salmon and Hale (1959) report that film diffusion is usually controlling at low concentrations, whereas at high concentrations it is usually particle diffusion. Under ordinary conditions, i.e. moderate stirring and a moderately or highly swollen resin, diffusion through the film is the slow step with solutions of the order of 0.01N or less, while diffusion in the resin is ordinarily the slow step with solutions of the order 0.1N or more (Rieman/Walton, 1970). Samuelson (1953) reports that in most cases the diffusion of the ions through the resin particles is the rate-determining factor. The rate of exchange with multivalent ions is more likely to be controlled by particle diffusion. Large organic ~~molecules~~<sup>ions</sup> usually exchange very slowly and the rate is controlled by particle diffusion at all concentrations.

Marcus and Kertes (1969) state that diffusion is improved by increasing the valency of the counter ion and by decreasing the hydration tendency of the ions. Kunin (1958), on the other hand, reports that the effect of charge is to decrease, roughly ten fold, the diffusion rate for each increase in unit charge.

At normal degrees of cross-linking for commercial resins, the self diffusion constants are approximately 1/5 to 1/10 of the constant in free solution. Inczedy (1966) takes these approximations further, and states that the diffusion constant in the resin ( $D_p$ ) for univalent cations at room temperature with common ion exchange resins is in general 1/3 to 1/10, for bivalent cations 1/5 to 1/100 and for trivalent cations 1/10 to 1/1000 part of the diffusion constant ( $D_0$ ) measured in aqueous solution. However, as the degree of cross-linking is decreased the rate of diffusion within the resin approach those in free solution.

Note that the rate determines the steepness of breakthrough curves, the sharpness of elution peaks and the degree of overlap in

chromatographic separations. Also, if dry resins are employed the reaction is slower than for resins which have been kept under water for some time (Samuelson, 1953).

The diffusion coefficients, for diffusion in free solution, can be taken to be given by (Cupta, 1973):-

$$D_i = 2.66 \times 10^{-7} \times \frac{\lambda_{oi}}{Z_i} \text{ cm}^2.\text{sec}^{-1} \quad \dots (9)$$

where  $\lambda_{oi}$  = limiting ionic conductance (Parsons, 1959)

$Z_i$  = valency

The estimated values are given in the table below.

TABLE 5

CATIONS AT 25°C	LIMITING IONIC CONDUCTANCE Ohm <sup>-1</sup> cm. <sup>2</sup>	DIFFUSION IN WATER cm. <sup>2</sup> .sec. <sup>-1</sup>
Cu <sup>2+</sup>	56.6	7.53 x 10 <sup>-6</sup>
Zn <sup>2+</sup>	52.8	7.02 x 10 <sup>-6</sup>
Cr <sup>3+</sup>	67	5.9 x 10 <sup>-6</sup>

### 4.3 RATE DETERMINING MECHANISMS

1. FLUID-PHASE EXTERNAL DIFFUSION (FILM DIFFUSION). The counter diffusion of '1' from the bulk fluid to the outer surface of the solid particle and of '2' from the particle to the bulk fluid.

The rate of transfer of '1' into the particle may be expressed as:

$$\frac{dq_i}{dt} = k_f a_p \frac{\epsilon}{\rho_b} (C_1 - C_1^*) \quad \dots (10)$$

where  $k_f$  = fluid-phase mass-transfer coefficient

$a_p$  = external area of particles / unit bulk volume of packed column

$\epsilon$  = fraction of external voids

$t$  = time

$\rho_b$  = bulk density of packing

2. FLUID-PHASE PORE DIFFUSION. In porous bodies where the pores are freely accessible to the bulk fluid outside. Counter diffusion of '1' through the pores of the particle to the point where exchange occurs and '2' from the point of exchange in the pore surface back to the outer surface of the particle.

The pore diffusion rate is given for a sphere by Vermeulen (Drew/Hoopes, 1958) as:

$$D_{\text{pore}} \left( \frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right) = \chi \frac{\partial C_i}{\partial t} + \rho_p \frac{\partial q_i}{\partial t} \quad \dots (11)$$

where  $D_{\text{pore}}$  = diffusivity in pore (given by  $D_o / 2$ )

$\chi$  = internal porosity of solid particles

$\rho_p$  = density of adsorbent particle

$C_i$  = fluid phase concentration of component within particle at radius  $r$

$$q_i' = q_i - C_i, \text{ equilibrium value with } C_i$$

The mean concentration of the entire particle, of total radius  $r_p$ , is

$$q = \frac{3}{r_p^3} \int_0^{r_p} q_i r^2 dr \quad \dots (12)$$

These equations are usually written in terms of the component being adsorbed.

3. REACTION OR PHASE CHANGE. Desorption of '2' from the solid phase at pore surface or at the outer surface, and adsorption of '1' in its place.

For exchange between two components, usually from the liquid phase:

$$\frac{d(q_1)_i}{dt} = k_i(C_1((q_1)_0^* - (q_1)_i) - r(q_1)_i(C_0 - C_1)) \quad \dots (13)$$

Here  $q_i$  or  $(q_1)_i$  is the solid-phase concentration at the surface and  $k_i$  is the rate of surface reaction. The latter is not known by experiment as the rates are so fast, and therefore this is usually not a rate controlling step.

4. SOLID PHASE INTERNAL DIFFUSION (PARTICLE DIFFUSION). Diffusion through a homogeneous, permeable (ie. absorbing), non-porous solid; diffusion in a mobile, adsorbed phase covering the pore surfaces of a porous solid whose crystalline portion is impermeable; or diffusion in an absorbing liquid held in the pores spaces of a solid.

The rate is expressed by

$$D_p \left( \frac{\partial q_i}{\partial r^2} + \frac{2}{r} \frac{\partial q_i}{\partial r} \right) = \frac{\partial q_i}{\partial t} \quad \dots (14)$$

where  $D_p$  = particle diffusion coefficient

$q_i$  = particle phase concentrations at radius  $r$

This equation has been solved only for irreversible- and linear-equilibrium cases of fixed bed operation (Drew/Hoopes, 1958). It is usually approximated by the linear driving force relation:

$$\frac{dq_1}{dt} = k_p a_p (q_1^* - q_1) \quad \dots (15)$$

where  $k_p a_p = 60D_p/d_p^2$  is the mass transfer coefficient

$q_1$  = concentration of 1 averaged over the entire particle

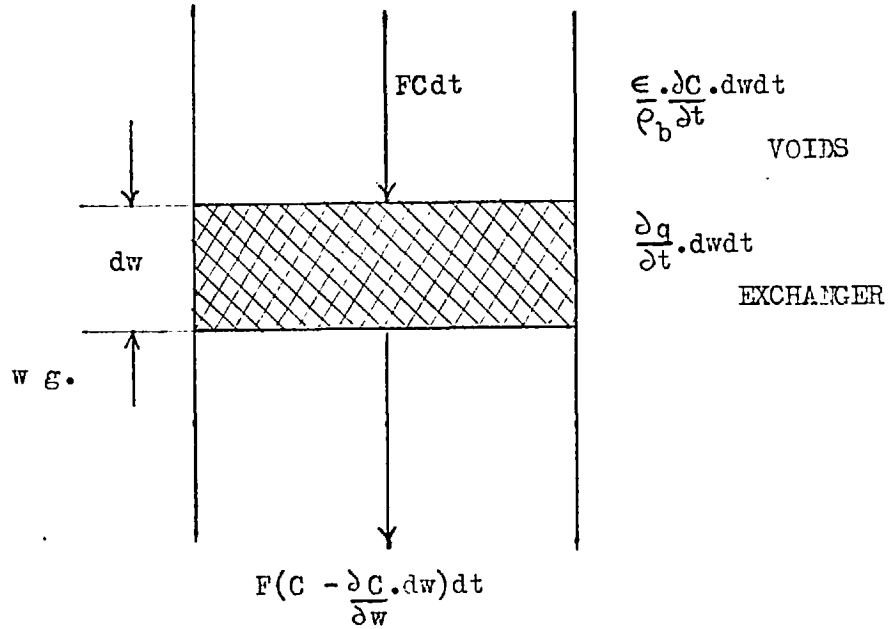
$q_1^*$  = concentration the particle would have if it were in equilibrium with the instantaneous, fluid phase

concentration at the outer surface of the particle

The sequence of steps will be (1)-(2)-(3) in ion exchange with synthetic resin particles, and in partition absorption or extraction. For simple adsorption, (or ion exchange on inorganic zeolites), the sequence will usually be (1)-(2)-(3), occasionally (1)-(3)-(4), and rarely (1)-(2)-(3)-(4) (Drew/Hoopes, 1958).

4.4 MATHEMATICAL MODELS

Figure 19



$F$  - Flow rate,  $\text{cm}^3 \cdot \text{sec}^{-1}$

$\epsilon$  - void fraction,  $\text{cm}^3 \text{ void (g. dry exchanger)}^{-1}$

$w$  - bed weight, g.

$C$  - concentration in liquid,  $\text{meq} \cdot \text{cm}^{-3}$

$q$  - concentration of exchanging ion in exchanger phase,  $\text{meq} \cdot (\text{g dry H form})^{-1}$

$\rho_b$  - apparent density of a particle of exchanger,  $\text{g} \cdot \text{cm}^{-3}$

$t$  - time

**MATERIAL BALANCE** - If an element  $dw$  of bed of unit cross-sectional area normal to flow is considered, as shown in the figure, the following material balance may be written:

$$FCdt = F(C - \frac{\partial C}{\partial w})dt + \frac{\epsilon \cdot dw \cdot \partial C}{b \partial t} \cdot dt + \frac{\partial q}{\partial t} \cdot dw dt \quad \dots (16)$$

which reduces to



$$F \cdot \frac{\partial C}{\partial w} = \frac{\epsilon}{\rho_b} \cdot \frac{\partial C}{\partial t} + \frac{\partial q}{\partial t} \quad \dots (17)$$

and by substituting the variable

$$Y = Ft - \frac{\epsilon w}{\rho_b} \quad \dots (18)$$

the material balance equation becomes:

$$\frac{\partial C}{\partial w} \Big|_Y + \frac{\partial q}{\partial Y} \Big|_w = 0 \quad \dots (19)$$

or in the form used by Vermeulen (Drew/Hoopes, 1958)

$$\frac{\partial C}{\partial v} \Big|_V - v\epsilon + \rho_b \frac{\partial q}{\partial V} \Big|_v = 0 \quad \dots (20)$$

Then by defining the following parameters (dimensionless):

- i) The Solution Concentration Ratio,  $x$ , expresses the ratio of solute concentration at any downstream point to the feed value (which is assumed constant), that is:

$$x = C/C_0 \quad \dots (21)$$

- ii) The Solid Concentration Ratio,  $y$ , expresses the ratio of solute concentration on the solid to the maximum attainable concentration, ie. the cation exchange capacity, so

$$y = q/Q \quad \dots (22)$$

- iii) The Throughput Ratio,  $Z$ , which reaches unity when the volume of feed that has passed through the column becomes stoichiometrically equivalent to the exchange capacity of the column. The stoichiometric volume,  $V_{\text{stoic}}$ , can be defined by the relation :

$$C_0 V_{\text{stoic}} = Q \rho_b v \quad \dots (23)$$

The throughput parameter is then:

$$Z = \frac{V - v\epsilon}{V_{\text{stoic}}} = \frac{C_o(V - v\epsilon)}{Q_{fb}v} \quad \dots (24)$$

the equation becomes

$$-\frac{\partial x}{\partial v}\bigg|_{Zv} = \frac{\partial y}{\partial Zv}\bigg|_v \quad \dots (25)$$

and by introducing the number of transfer units, as defined below, the resulting equation is dimensionless and has the form:

$$-\frac{\partial x}{\partial N}\bigg|_{ZN} = \frac{\partial y}{\partial ZN}\bigg|_N \quad \dots (26)$$

Note that it is this equation of continuity, rather than the rate equation used with it, that reflects the special behaviour of the fixed-bed systems.

- iv) The Number of Transfer units,  $N$ . For fixed bed operation it is desirable to obtain a steep, by comparison with the total volume of solution handled, breakthrough curve. In this case it is possible to utilize the greatest amount of bed.

The relative steepness increases as the volume of bed increases and also as the exchange rate increases. These two factors may be combined into a common, dimensionless, column capacity parameter  $N$ , the number of transfer units.

For external diffusion controlling:

$$N_f = k_f a_p v\epsilon / F \quad \dots (27)$$

If pore diffusion contributes or controls,  $k_f$  is replaced by  $k'_f$ .

Whilst for solid phase internal diffusion controlling:

$$N_p = k_p a_p Dv\epsilon / F \quad \dots (28)$$

with  $k_p a_p = 60D_p/d_p^2$  (Drew/Hoopes, 1958). For both resistances appreciable, the overall number of transfer units (NTU's) are defined by:

$$N_{Of} = \frac{b_f v}{\left(\frac{1}{k_f a_p} + \frac{1}{k_p a_p D}\right)F} \dots (29)$$

$$N_{Op} = \frac{b_p D v}{\left(\frac{D}{k_f a_p} + \frac{1}{k_p a_p}\right)F} \dots (30)$$

where  $b_f$  and  $b_p$  are coefficients with values usually near unity.

#### 4.4.1. LIMITING CASES OF EQUILIBRIUM BEHAVIOUR

1. PROPORTIONATE-PATTERN CASE (UNFAVOURABLE EQUILIBRIUM). A classical theory of chromatography, and has been treated by many workers (Drew/Hoopes, 1958). It is assumed that equilibrium is maintained everywhere in the column, ie. the number of transfer units (N) approaches infinity, due to the high mass-transfer rates or long residence times.

Rewriting the conservation equation (25)

$$\frac{\partial x}{\partial v} \Big|_{Zv} = \frac{\partial x}{\partial Zv} \Big|_v \cdot \frac{dy}{dx} \quad \dots (31)$$

and rearranging

$$\begin{aligned} \frac{dy}{dx} &= \frac{\partial x / \partial v \Big|_{Zv}}{\partial x / \partial Zv \Big|_v} = \frac{\partial Zv}{\partial v} \Big|_x \\ &= v \frac{\partial Z}{\partial v} \Big|_x + Z \quad \dots (32) \end{aligned}$$

This may be integrated, as done by Devault (Drew/Hoopes, 1958), at constant x and constant dy/dx, to give:

$$\frac{dy}{dx} = Z + \frac{a}{v} \quad \dots (33)$$

where 'a' is a constant of integration which may be evaluated with the aid of the material balance integral (Drew/Hoopes, 1958):

$$\int_0^\infty (C_0 - C) \cdot d(v - v_e) = Q \rho_b v \quad \dots (34)$$

$$\text{or } \int_{Z=0}^{x=1} (1-x) \cdot dZ = 1 \quad \dots (35)$$

this relation is comparable to equation (25) but is written for the whole column rather than a differential section of it.

For a constant separation factor, r, Vermeulen gives (Drew/

Hoopes, 1958)

$$\frac{dy}{dx} = \frac{r}{((1-r)x + r)^2} \dots (36)$$

and to  $a = 0$ . Combining equations (33) and (36)

$$x = \frac{(r/Z)^{\frac{1}{2}} - r}{1 - r} \dots (37)$$

The limits of validity are  $x = 0$  at  $Z = 1/r$ ;  $x = 1$  at  $Z = r$ . It provides a proportionate pattern as  $x$  depends only on  $Z$ , and not on  $N$  or  $v$ . The relative sharpness of the breakthrough curve cannot be increased by lengthening the column.

If the equilibrium becomes favourable, with  $r < 1$ ,  $dx/dZ$  will take on a negative slope which is prohibited by the material balance. So the breakthrough curve for 'equilibrium' must be drawn vertical<sup>ly</sup> for the concentration region for which  $r \leq 1$ .

At  $r < 2$ , the equilibrium-limit breakthrough given by equation (37) is approached only at high values of  $N$  ( $> 500$ ). For  $r \geq 10$ , however, this limit will apply at nearly all  $N$  values ( $\geq 10$ ).

2. CONSTANT PATTERN CASE (FAVOURABLE EQUILIBRIUM). It is assumed that there are a region of  $r$  values for which the effluent concentration pattern is independent of column length. This is equivalent to  $\partial Zv/\partial v|_x$  a constant.

With this assumption equation (33) still applies and integration gives

$$y = (\text{const.}) x \dots (38)$$

and since  $y$  and  $x$  have the same limits

$$y = x \dots (39)$$

This is the continuity equation for this example.

In order to obtain realistic concentration-history curves, the rate can no longer be assumed infinite. Instead the breakthrough is dependent on rate.

a) EXTERNAL DIFFUSION. For irreversible adsorption ( $r=0$ ) equations (9) and (39) lead to

$$\frac{dx}{dt} = k_f a_p D x \quad \dots (40)$$

where  $D$  is as defined below.

v) The Distribution Ratio,  $D$ , is the limiting value reached as saturation is approached. For simple binary exchange:

$$D = \frac{Q P_b}{C_o \epsilon} \quad \dots (41)$$

Integration for a column of given  $v$ , as described by Vermeulen (Drew/Hoopes, 1958) produces the following result

$$1 + \ln x = k_f a_p D (V - v \epsilon - v_{stoic}) / F \quad \dots (42)$$

or

$$\ln x = N_f (Z - 1) - 1 \quad \dots (43)$$

Equation (43) applies between  $Z = 1/N_f$  (below which  $\ln x = -N_f$ ) and  $Z = 1 + 1/N_f$ , at which  $x$  becomes unity. Vermeulen (Drew/Hoopes, 1958) also gives the result of Michaels, which is for the case of a constant separation factor

$$\frac{1}{1-r} \ln \frac{x_2(1-x_1)}{x_1(1-x_2)} + \ln \frac{(1-x_2)}{(1-x_1)} = N_f (Z_2 - Z_1) \quad \dots (44)$$

b) INTERNAL SOLID-PHASE DIFFUSION. An exact solution for the irreversible constant pattern breakthrough has been provided by various workers and described by Vermeulen (Drew/Hoopes, 1958):

$$x = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2(\gamma N_p(Z-1) + 0.97)) \quad \dots (45)$$

where  $N_p$  is again given by  $60D_p Dv\epsilon/Fd_p^2$ . For this case ( $r=0$ ),  $\gamma = \pi^2/15$ . The linear driving force approximation is also given, which on integration for the irreversible case becomes

$$x = 1 - \exp(-N_p(Z-1) + 1) \quad \dots (46)$$

If used in this form this equation gives a good fit to (45) for the lower part of the curve, when  $0 < x \leq 0.6$ .

Boyd et. al. (1947) give the solution for the case where the adsorbent particles are slabs, rather than spheres:

$$x = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp(-(2n-1)^2 \gamma N_p Z) \quad \dots (47)$$

where, in this case  $N_p = 60D_p Dv\epsilon/Fx_0^2$  and  $\gamma = \pi^2/240$ . Since the adsorbent particles in their experiments were far from being exact spheres, it was thought possible that a better fit would be obtained with the slab equation. On examination both were found to agree closely with the experimental data, but the equation for the spherical case gave the better approximation.

The formula for partially irreversible adsorption, one of highly favourable equilibrium with a constant separation factor, is that of Glueckauf and Coates (Drew/Hoopes, 1958):

$$\frac{r}{1-r} \ln \frac{x_2(1-x_1)}{x_1(1-x_2)} + \ln \frac{(1-x_1)}{(1-x_2)} = N_p(Z_2 - Z_1) \quad \dots (48)$$

The limits of validity are the same as those for equation (44).

Further solutions are also discussed by Vermeulen (Drew/Hoopes, 1958), including a quadratic driving force approximation which integrates to:

$$x = (1 - \exp(-\gamma(N_p(Z-1) + 0.93)))^{\frac{1}{2}} \quad \dots (49)$$

This equation is also given by Coulson and Richardson (1971), but in different form.

c) PORE DIFFUSION. The fluid phase concentration in the pores is assumed negligible compared to the solid phase value. Equation (10) then becomes:

$$\frac{D_{\text{pore}}}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_i}{\partial r} \right) = \rho_b \frac{\partial q_i}{\partial t} \quad \dots (50)$$

Differentiation of equation (11) gives

$$\frac{\partial}{\partial r} \left( \frac{dq}{dt} \right) = \frac{3r^2}{r_p^3} \frac{\partial q_i}{\partial t} \quad \dots (51)$$

Combination of these two expressions and considering the irreversible case; where the concentration wave entering the particle will saturate each spherical particle layer before it penetrates further. That is,  $C_i$  cannot exceed zero at a particular radius  $r_i$  until  $q_i$  at that radius has become equal to the saturation value  $q_m$ . With  $C/C_o = q/q_m = 1 - (r_i/r_p)^3$  by material balance over one particle we obtain (Drew/Hoopes, 1958):

$$\frac{dr_i}{dt} = - \frac{k_{\text{pore}}}{15} \frac{r_p^2 + r_p r_i + r_i^2}{r_i} \quad \dots (52)$$

where 
$$k_{\text{pore}} = 60 D_{\text{pore}} C_o / (R q_m d_p^2) \quad \dots (53)$$

Integration of equation (53) can be followed by numerical evaluation of  $x$ . The result fits the empirical relation:

$$x = 0.557(N_{\text{pore}}(Z - 1) + 1.15) - 0.0774(N_{\text{pore}}(Z - 1) + 1.15)^2 \quad \dots (54)$$

where 
$$N_{\text{pore}} = 60 D_{\text{pore}} v / r_p d_p^2 \quad \dots (55)$$

Note that at  $x = 0$ ,  $Z = 1 - (1.15/N_{\text{pore}})$  and at  $x=1$ ,  $Z = 1 + (2.43/N_{\text{pore}})$ .



d) COMBINED EXTERNAL AND INTERNAL-DIFFUSION RESISTANCES. Where these processes have similar rates, external diffusion will tend to predominate at low extents of breakthrough and internal diffusion will have more of a retarding effect as full saturation is approached. The describing equation according to Vermeulen (Drew/Hoopes, 1958) is:

$$k_f(x - x_i) = k_p D \frac{y_i - x^2}{2x} \quad \dots (56)$$

In the initial stages of breakthrough, under irreversible conditions,  $x_i = 0$  and  $y_i = 1$ , so that breakthrough follows the external diffusion curve, equation (43). Eventually  $y_i$  reaches unity, and abruptly  $x_i$  becomes finite, equation (46) then applies. Equation (56) can be solved for  $x$  at the transition point.

## 5. EXPERIMENTAL

### 5.1 THE EXPERIMENTAL DETAILS

The vermiculite used in the experiments was exfoliated and graded, by Mandoval Ltd., as 'superfine' and 'micron'. It originated from the Palabora deposit in the North East Transvaal. In contrast to Miss Mohn's work (1973), where the vermiculite was dried overnight at 110°C, it was decided to use the vermiculite as it was, straight from the bag.

Although exfoliated vermiculite absorbs a considerable amount of water it was found to have poor wetting properties and so weighed samples were allowed to stand, in contact with water, overnight for ease of charging the column. The batch experiments were carried out by charging the dry vermiculite to the stirred vessel.

The transition metal ions investigated in this study were copper ( $\text{Cu}^{2+}$ ), zinc ( $\text{Zn}^{2+}$ ), nickel ( $\text{Ni}^{2+}$ ) and chromium ( $\text{Cr}^{3+}$ ). In all cases analytical grade sulphate was used to supply the ion, as below:-

Copper	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Zinc	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Nickel	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
Chromium	$\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$

Solutions were prepared with distilled water, of pH approximately 4.9, and for batch experiments the volume used was 500 ml.

BATCH EXPERIMENTS - The quantity of vermiculite used per sample varied from 0.1 to 0.3 g. and the metal ion concentration ranged from 25 ppm to 200 ppm (by weight).

Conical flasks were charged with 500 ml. of standard solution and mixed by magnetic stirrer. The weighed, dry vermiculite was then charged. Stirring was allowed to continue for 20 hours (Mohn (1973) determined 18 hours was sufficient to achieve equilibrium), whereupon

samples were taken, diluted and analysed by means of atomic absorption techniques (see Appendix 2). Different grades of vermiculite were employed. Investigations with nickel were not carried out.

**CATION EXCHANGE CAPACITY DETERMINATION** - Conical flasks were charged with standard solutions of the ions, concentration 500 ppm. Weighed samples, 0.5 g., of vermiculite were added and stirred for 20 hours. The samples were then left for 20 days, stirring at regular intervals; to ensure the cation exchange capacity was being determined. The solutions were then diluted and analysed by atomic absorption techniques (see appendix 2). Different grades of vermiculite were employed.

**COLUMN OPERATION** - The quantity of vermiculite used was generally 15 g., 10 g. in the twelve hour experiments, and usually the initial concentration was 100 ppm; two experiments being carried out at 50 ppm.

It was decided to use a simple column process, outlined schematically in figure 20. The standard solution was charged to the storage tank 'A' and pumped by means of a peristaltic pump 'B'. The constant head device 'C' was employed to help with the control which was carried out by means of two taps 'E' and 'F'. The solution then passed through the column of vermiculite, supported on glass wool, and out of the bottom where samples were taken at half-hourly intervals (hourly in the twelve hour experiments), diluted and analyzed by means of atomic absorption techniques (see Appendix 2). Different grades of vermiculite were employed.

The column itself was made of glass, its dimensions being given in Appendix 1.

Note that the top of the bed was covered by a plug of glass wool to help prevent turbulence of the bed which would result from the drops of liquid falling into the top of the column.

The flow rate was measured by recording the time taken, by means of a standard stop-watch, to collect 50 ml. of effluent. This procedure was repeated several times and the average value taken.

NOTE: All experiments were carried out at room temperature.

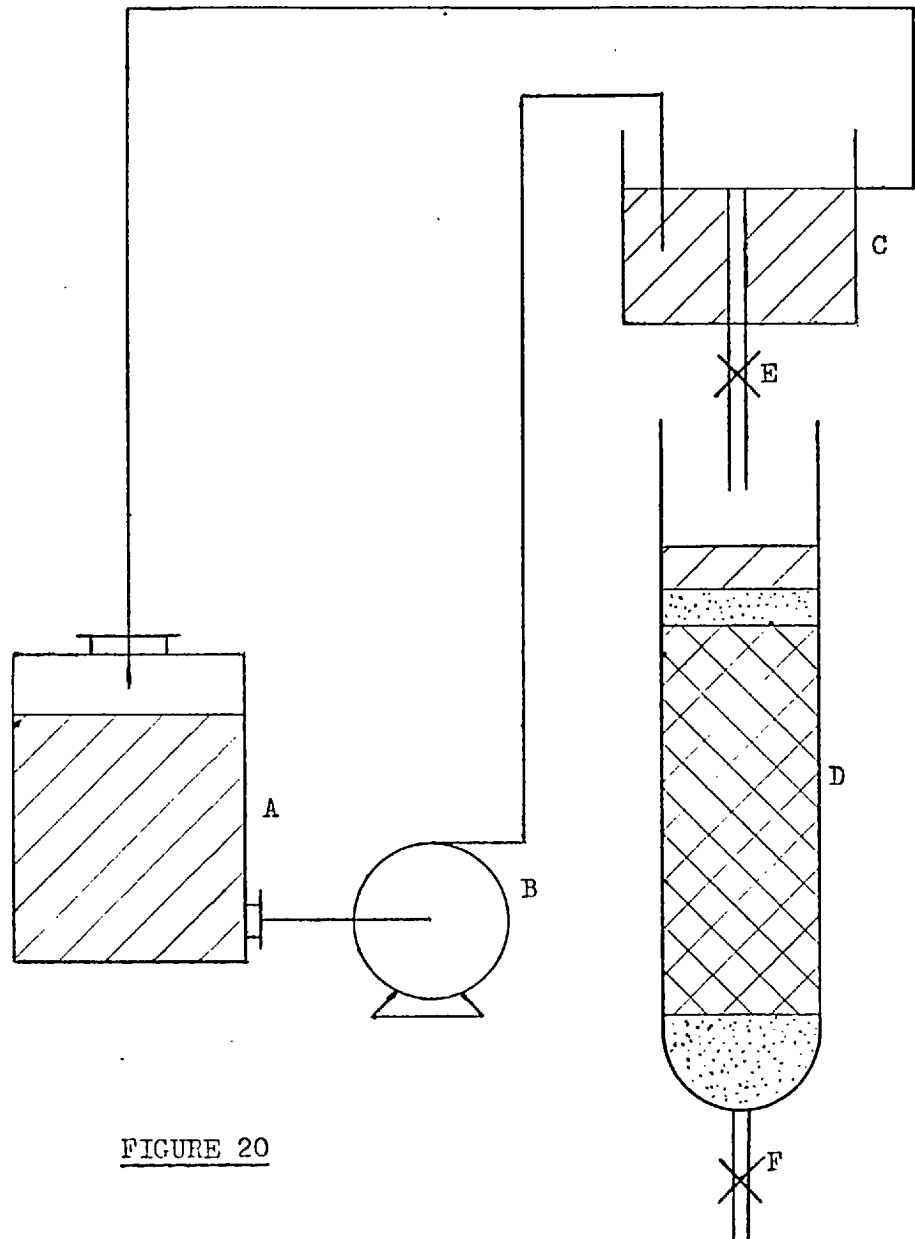


FIGURE 20

SCHEMATIC DIAGRAM OF APPARATUS  
Flow rates controlled by means  
of valves E and F.

## 5.2 THE EXPERIMENTAL RESULTS

### 5.2.1 BATCH RESULTS

The results of the batch experiments are depicted as shown in Table 6 below.

TABLE 6

ION	GRADE OF VERMICULITE	GRAPHICALLY	DATA
Cu <sup>2+</sup>	Micron	Fig. 21	Appendix 1 Table 12
Cu <sup>2+</sup>	Superfine	Fig. 22	Appendix 1 Table 13
Zn <sup>2+</sup>	Micron	Fig. 23	Appendix 1 Table 14
Zn <sup>2+</sup>	Superfine	Fig. 24	Appendix 1 Table 15
Cr <sup>3+</sup>	Micron	Fig. 25	Appendix 1 Table 16
Cr <sup>3+</sup>	Superfine	Fig. 26	Appendix 1 Table 17

From the graphs it is clear that micron grade vermiculite gives the better separation and further that Cu<sup>2+</sup> is preferred to Zn<sup>2+</sup>, which in turn is preferred to Cr<sup>3+</sup>. Both as shown by the higher values for a given C/C<sub>0</sub>. In fact the graph for Cu<sup>2+</sup> (micron vermiculite) is pretty close to that for linear equilibrium, see figure 16 which is similar.

All these values are recorded as higher than those obtained by Miss Mohn (1973) (but within the bounds met by other workers, Table 4). On the otherhand CEC values are in close agreement with her work, in fact for chromium they agree exactly. The difference I can only presume is due to the different grade of vermiculite used (Miss Mohn used grade 'fine') and to the method of measurement used as she used a colourimetric method (ASTM D1688, D1687, D1691) whereas I used atomic absorption techniques (ASTM D.2576, Appendix 2), which should, presumably, give the more accurate results.

All the results indicate that the exchange is unfavourable in all cases.

FIGURE 21. COPPER EXCHANGE / MICRON VERMICULITE

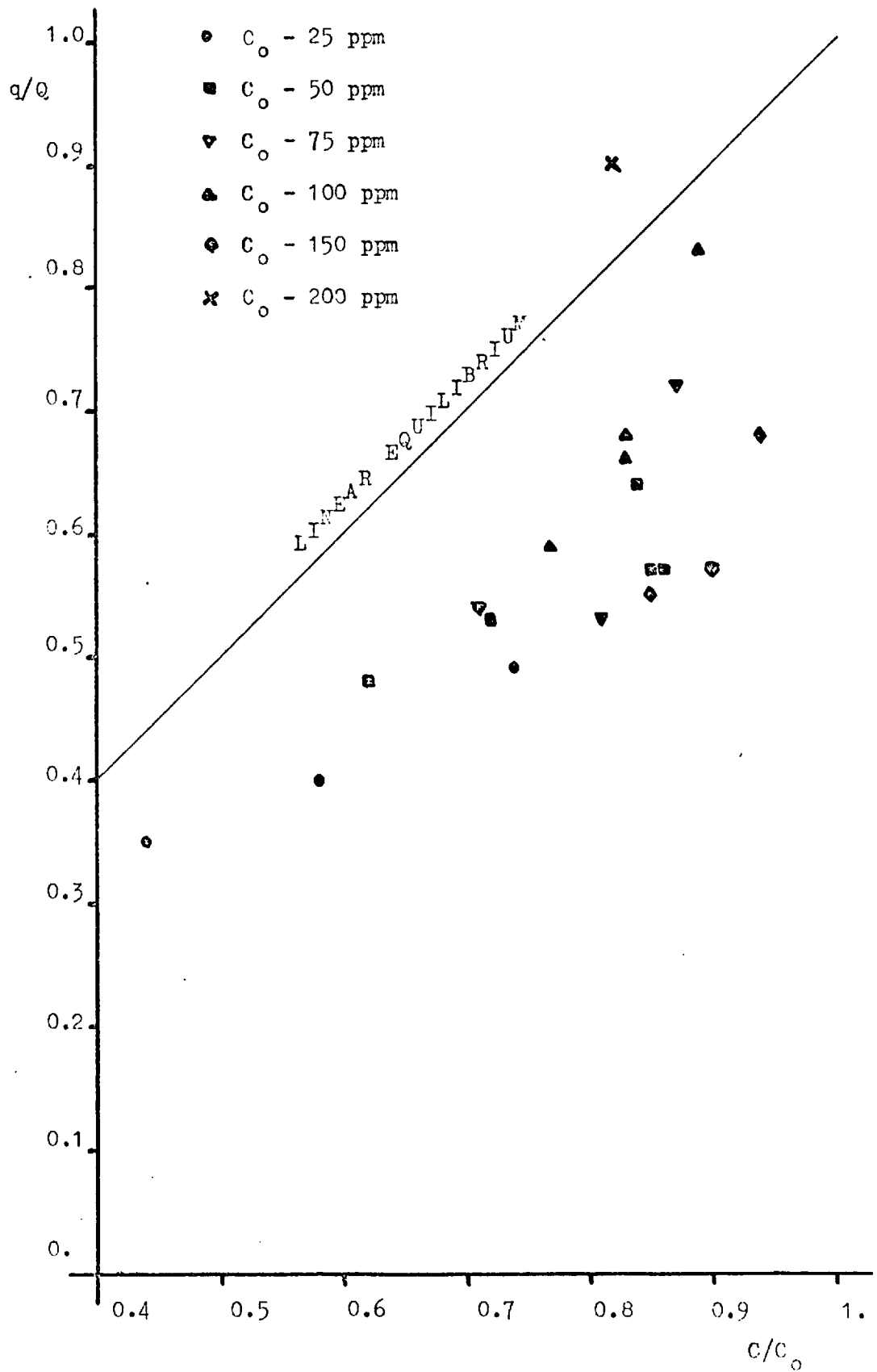


FIGURE 22. COPPER EXCHANGE / SUPERFINE VERMICULITE

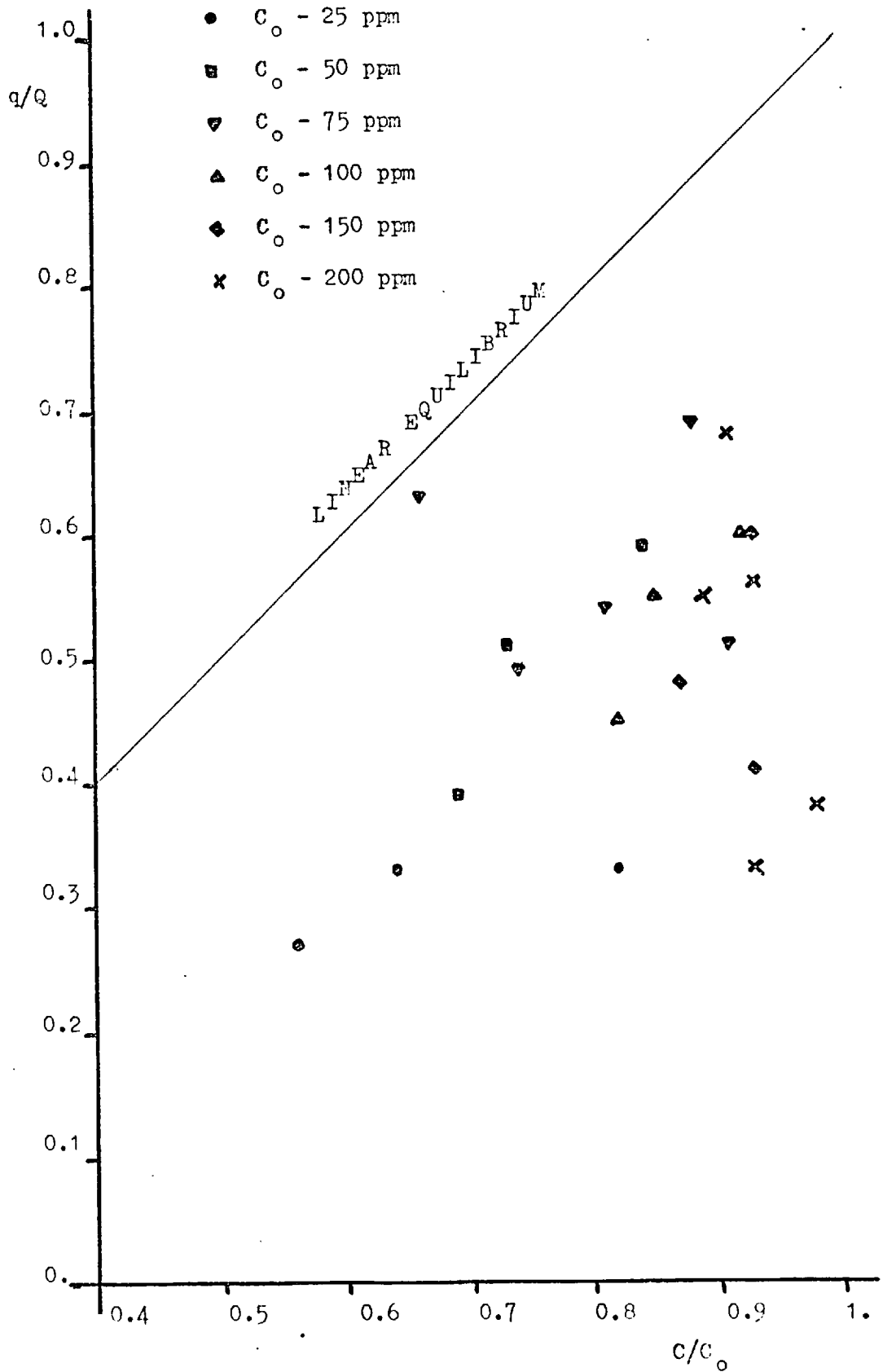




FIGURE 23. ZINC EXCHANGE / MICRON VERMICULITE

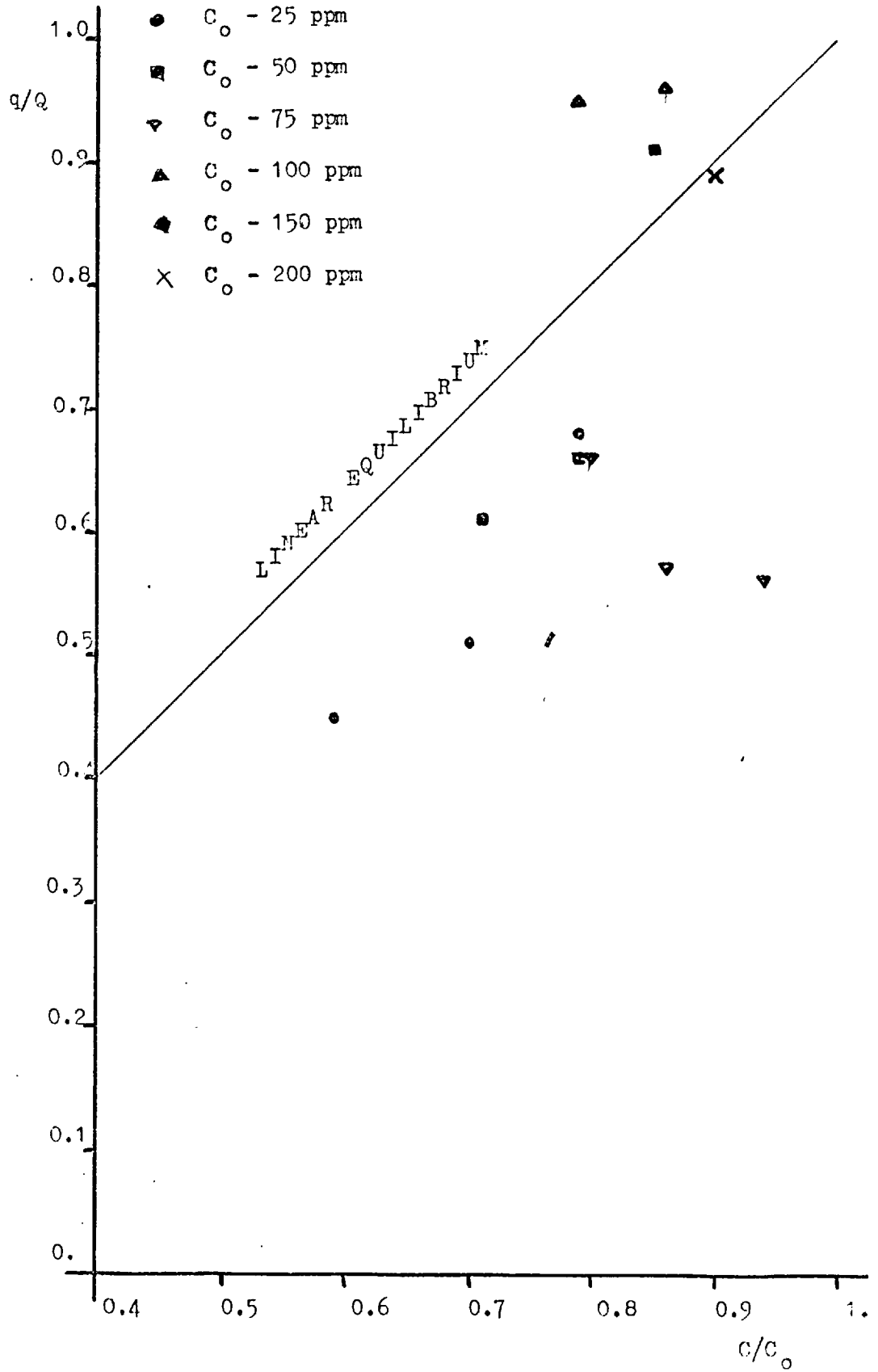


FIGURE 24. ZINC EXCHANGE / SUPERFINE VERMICULITE

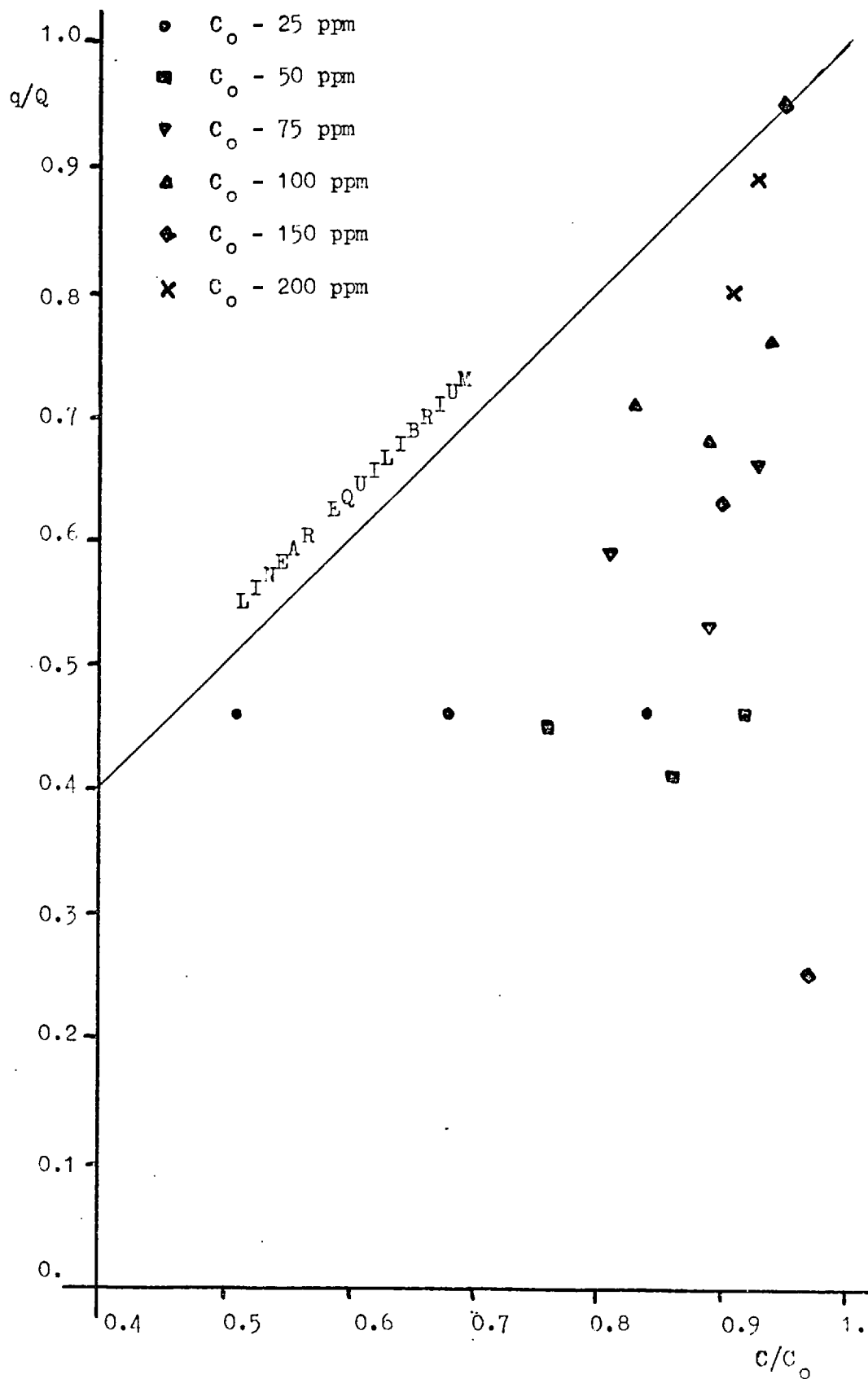


FIGURE 25. CHROMIUM EXCHANGE / <sup>137</sup>CESION VERMICULITE

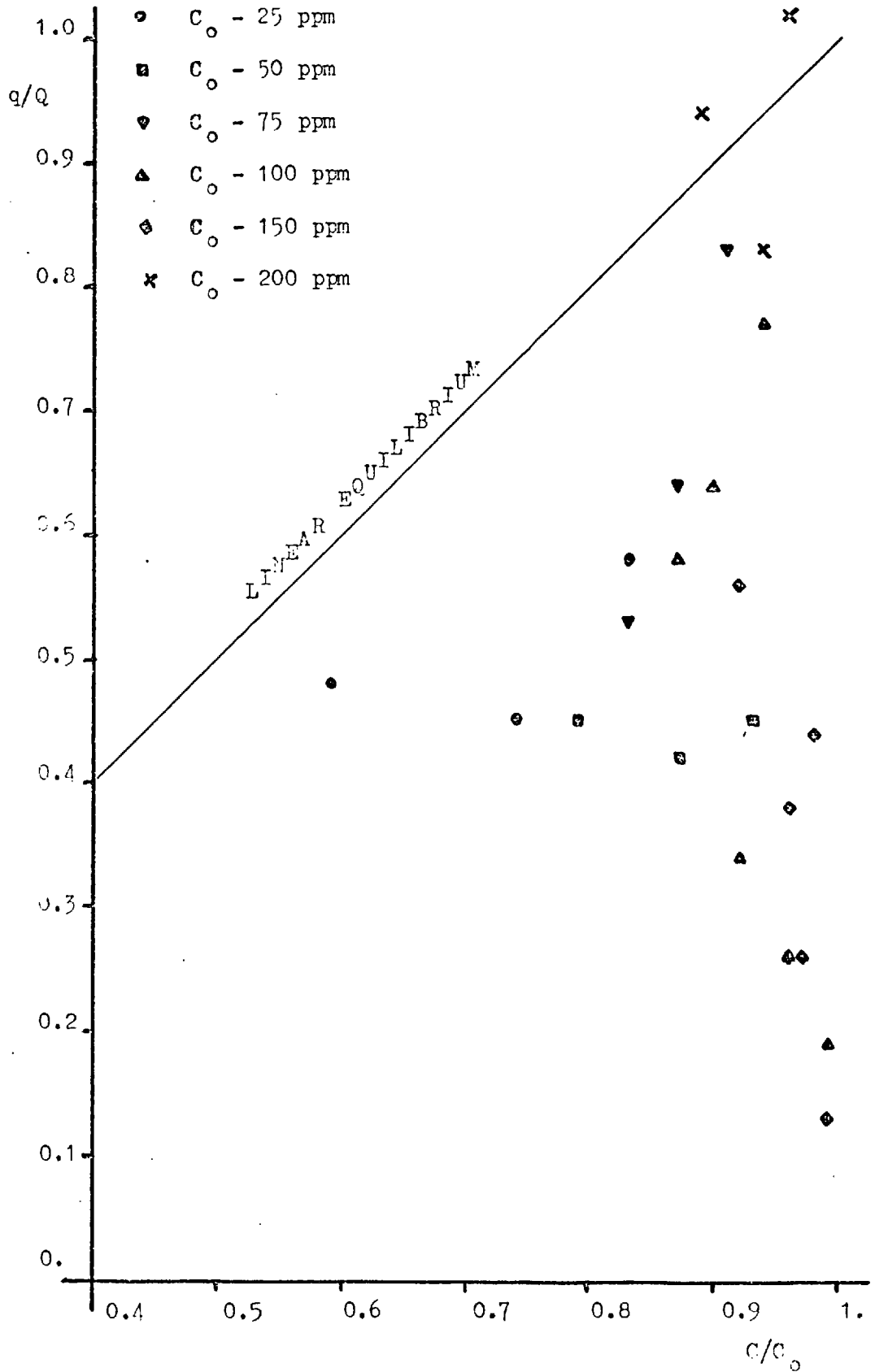


FIGURE 26. CHROMIUM EXCHANGE / SUPERFINE VERTICULITE

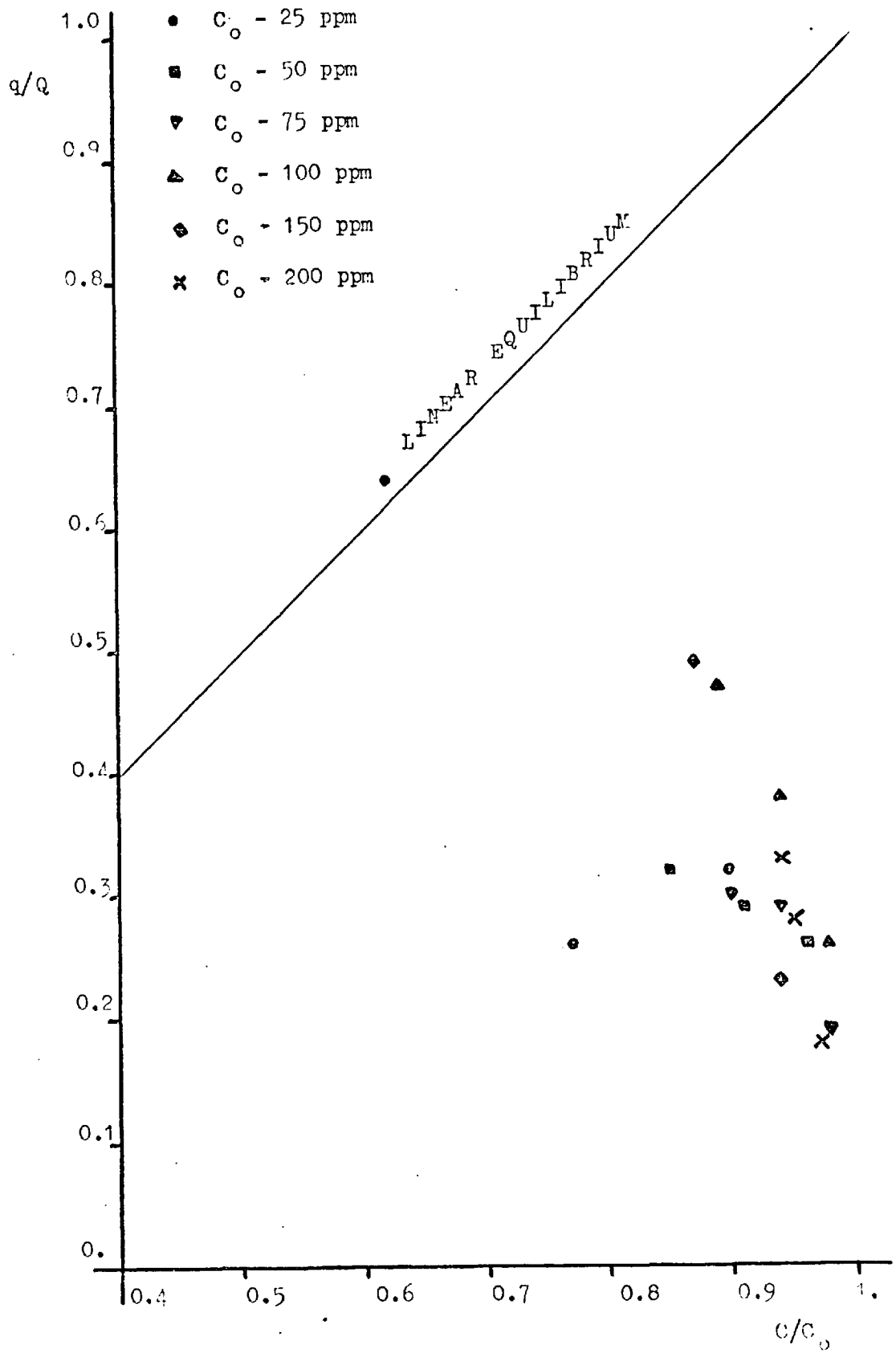


FIGURE 27. SMALL COLUMN RESULTS / SUPERFINE VERMICULITE (Cu)

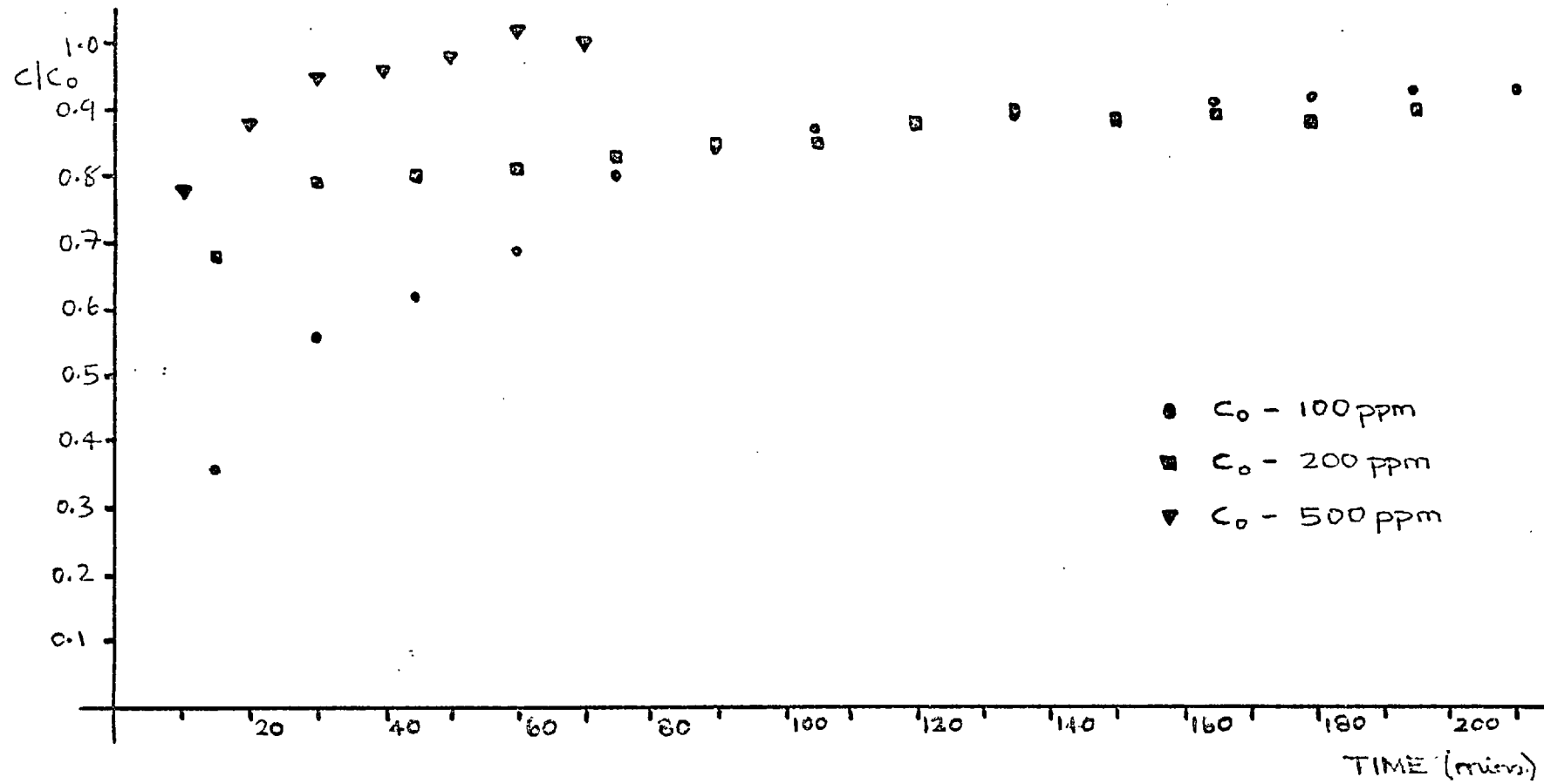


FIGURE 28, ZINC 12 HOUR EXPERIMENTS

- 1.57 ml. cm<sup>-2</sup> min.<sup>-1</sup>, 100 ppm, micron vermiculite
- 1.39 ml. cm<sup>-2</sup> min.<sup>-1</sup>, 100 ppm, superfine vermiculite
- ▼ 2.02 ml. cm<sup>-2</sup> min.<sup>-1</sup>, 50 ppm, micron vermiculite
- ▲ 1.79 ml. cm<sup>-2</sup> min.<sup>-1</sup>, 50 ppm, superfine vermiculite

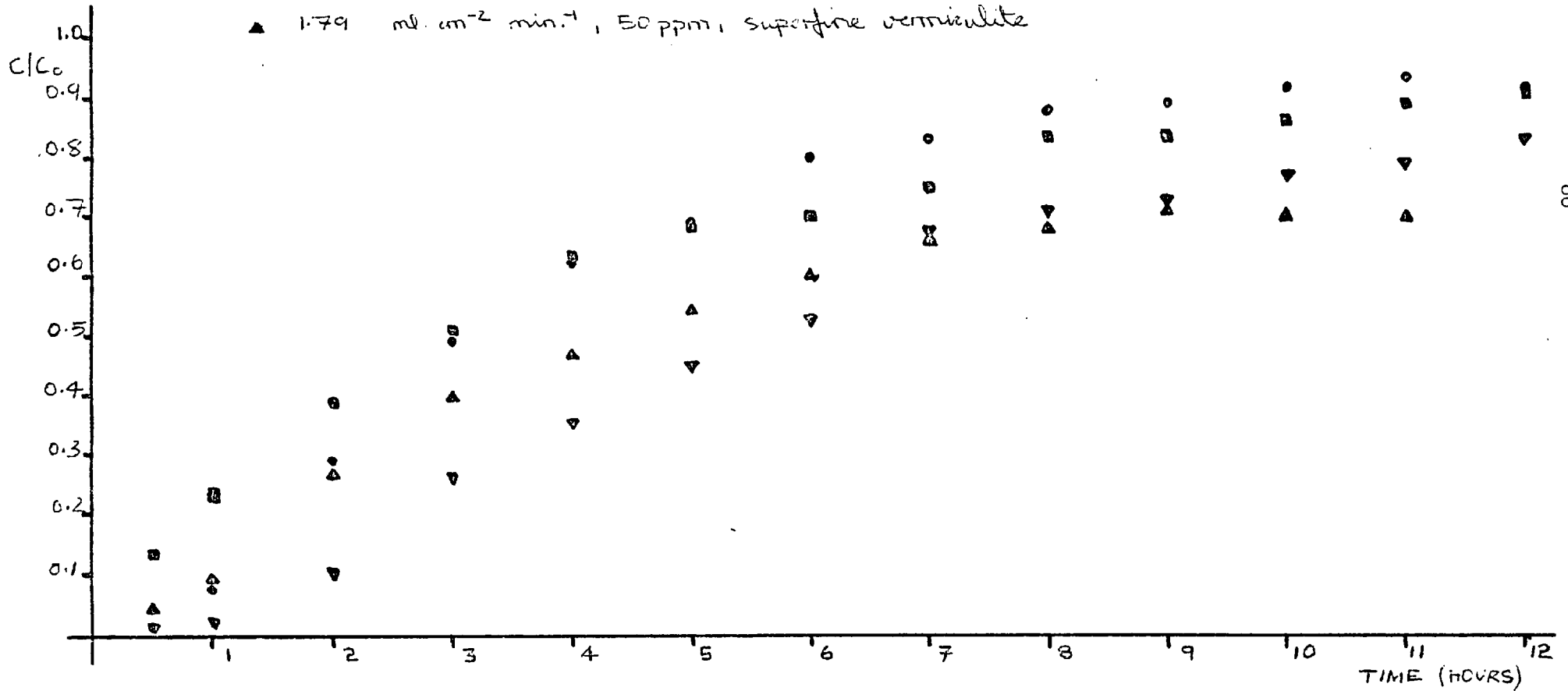


FIGURE 29. EFFECT OF PARTICLE SIZE ON ION EXCHANGE IN A COLUMN

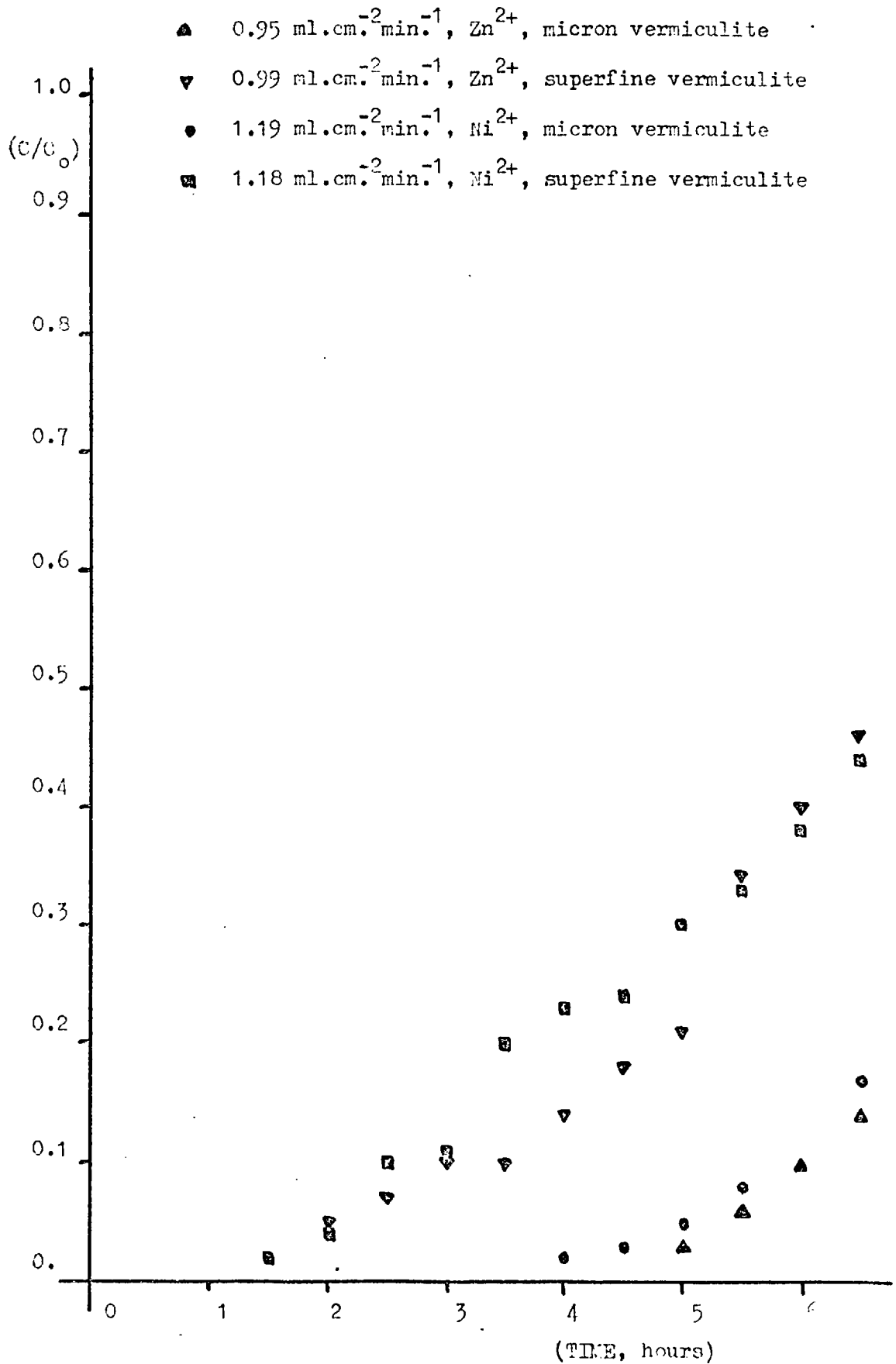


FIGURE 30.  $C/C_0$  VS. TIME FOR SIMILAR FLOW RATES FOR THE DIFFERENT IONS. MICRON VESICULITE.

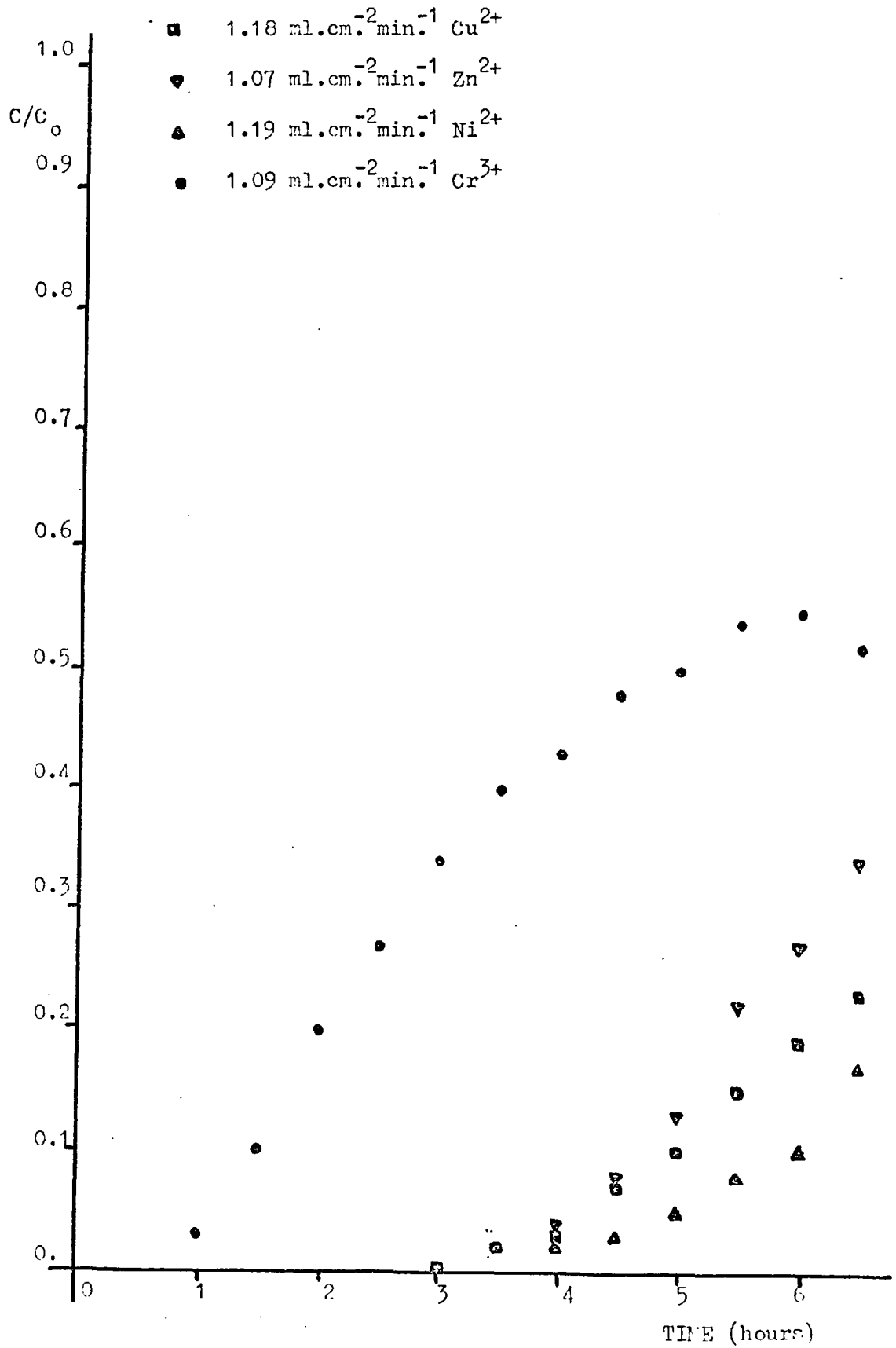




TABLE 7

The approximate degree of utilization of the column for the various ions for approximately the same flow rate (see figure 30).

Micron grade vermiculite.

ION	DEGREE OF UTILIZATION
$\text{Cu}^{2+}$	12%
$\text{Zn}^{2+}$	15%
$\text{Ni}^{2+}$	29%
$\text{Cr}^{3+}$	5%

FIGURE 31. COLUMN OPERATION, COPPER / MICRON VERMICULITE

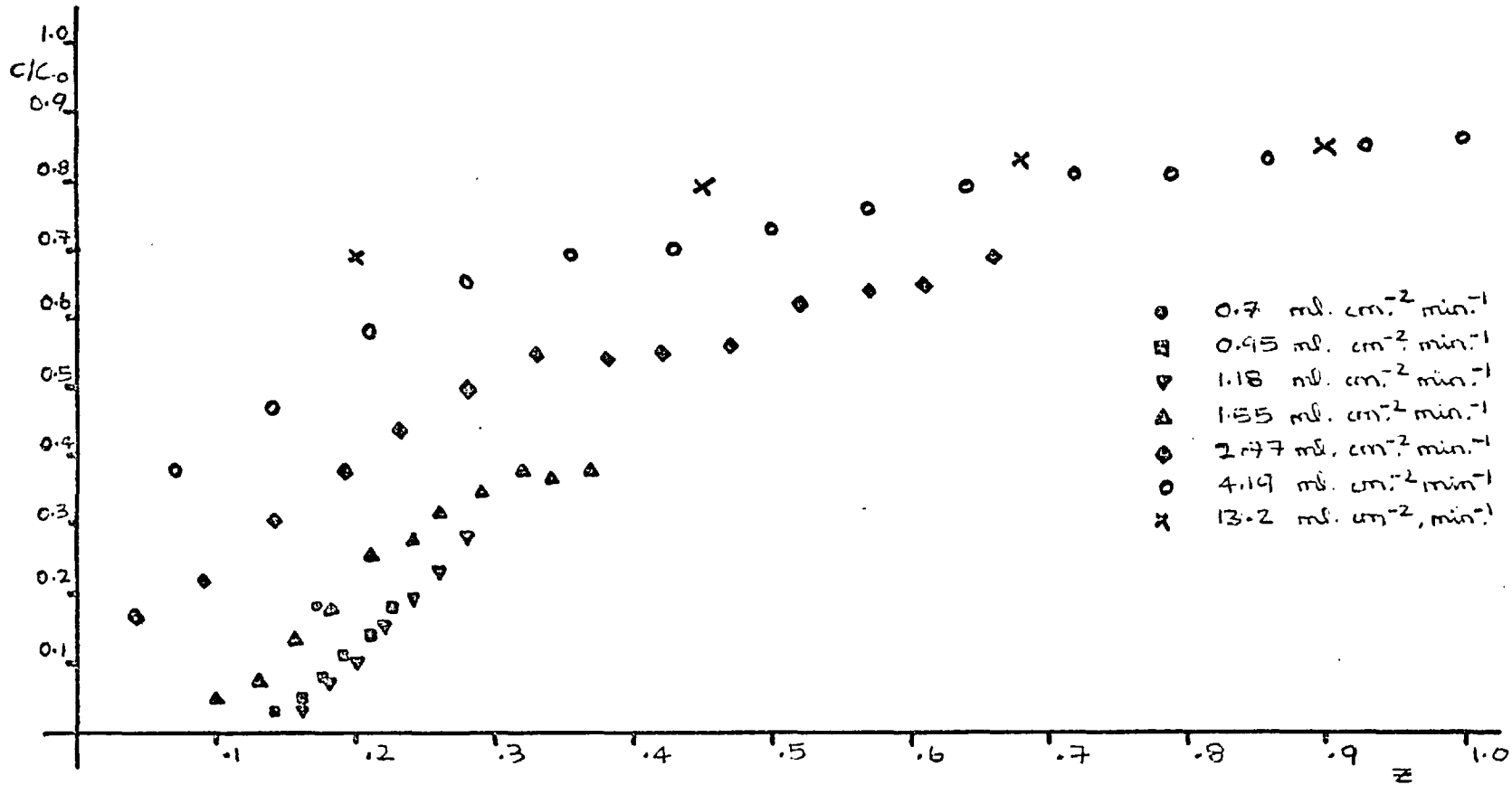


FIGURE 32. COLUMN OPERATION, COPPER / MICRON VERMICULITE

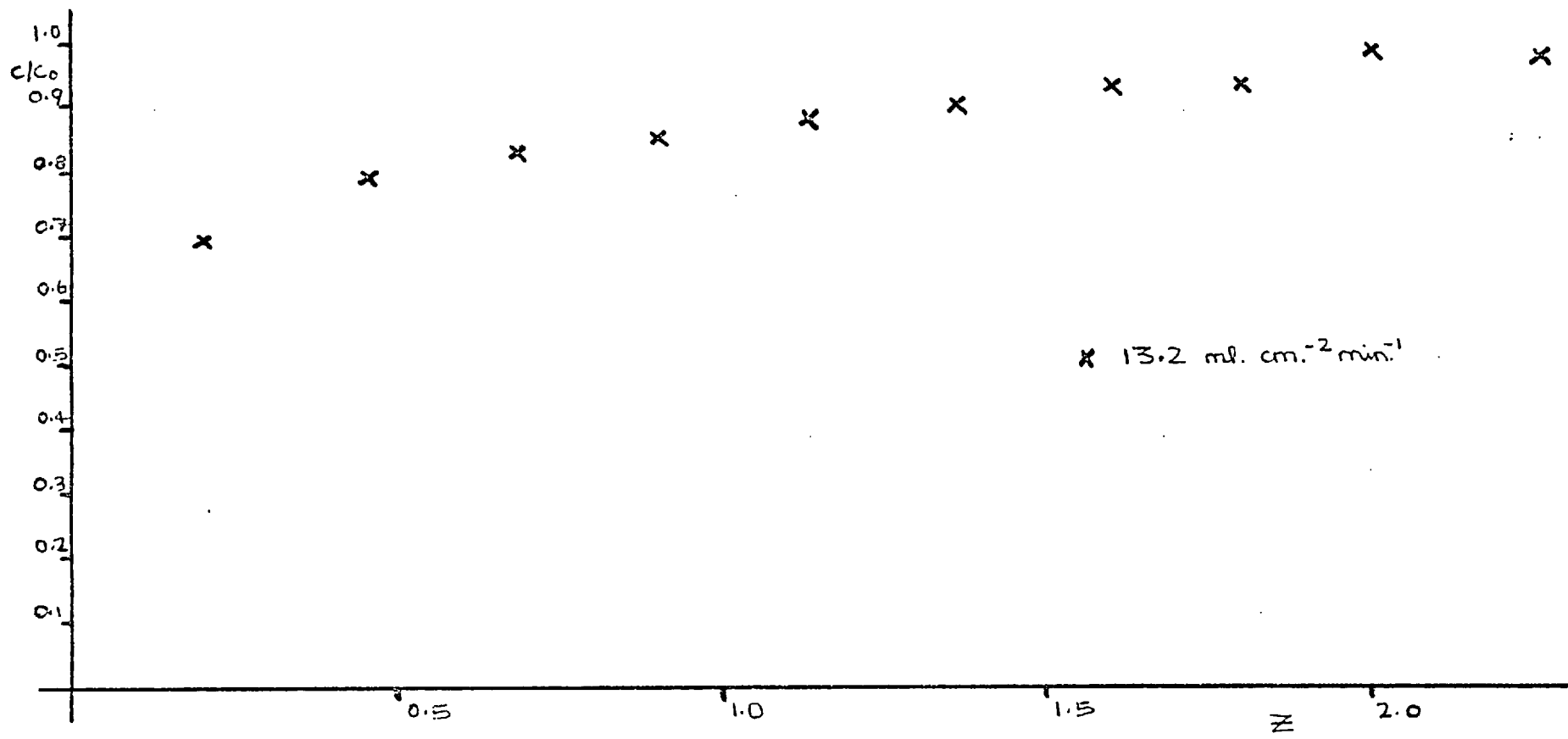


FIGURE 33. COPPER / SUPERFINE VERMICULITE

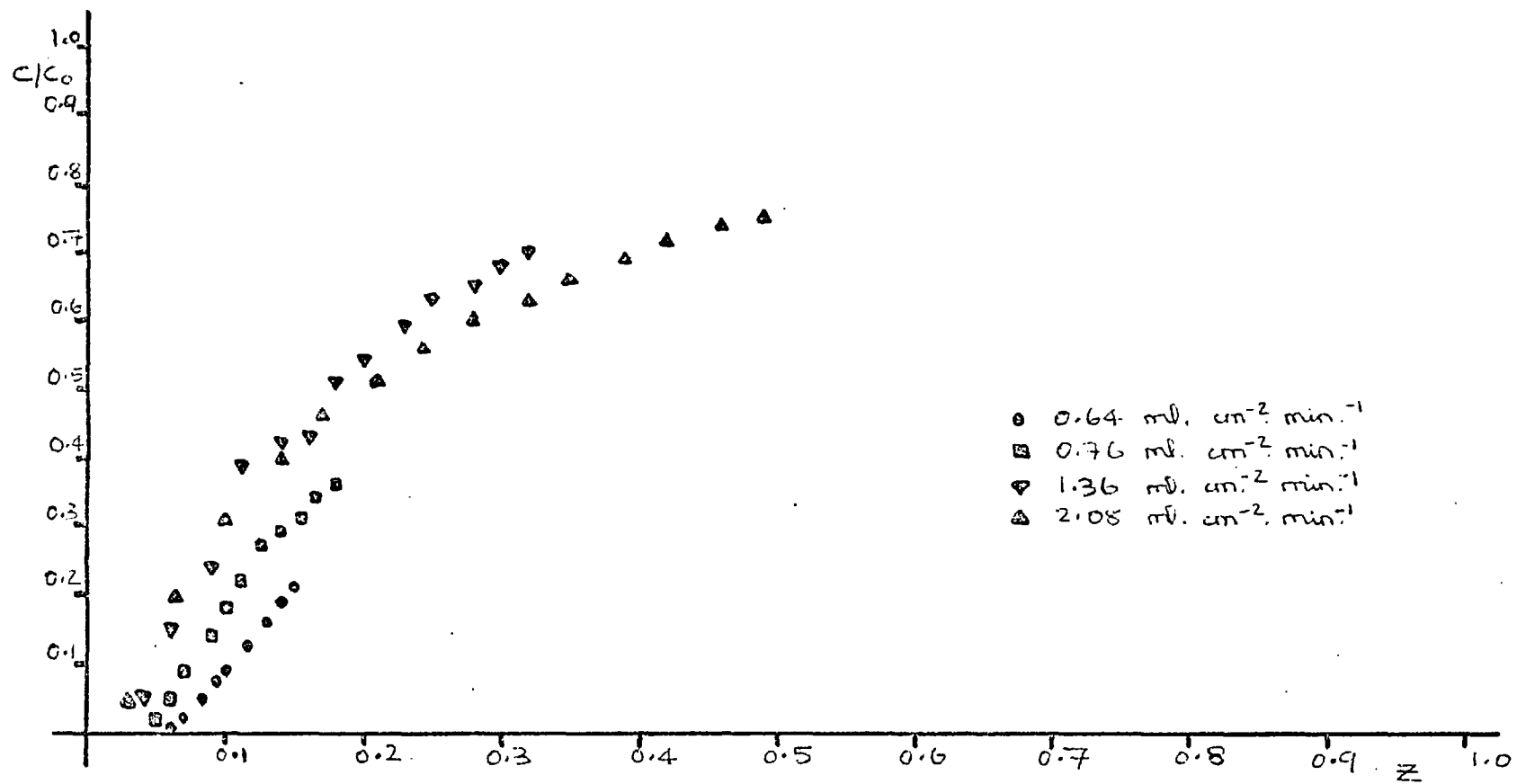


FIGURE 34. COLUMN OPERATION, ZINC / MICRON VERMICULITE

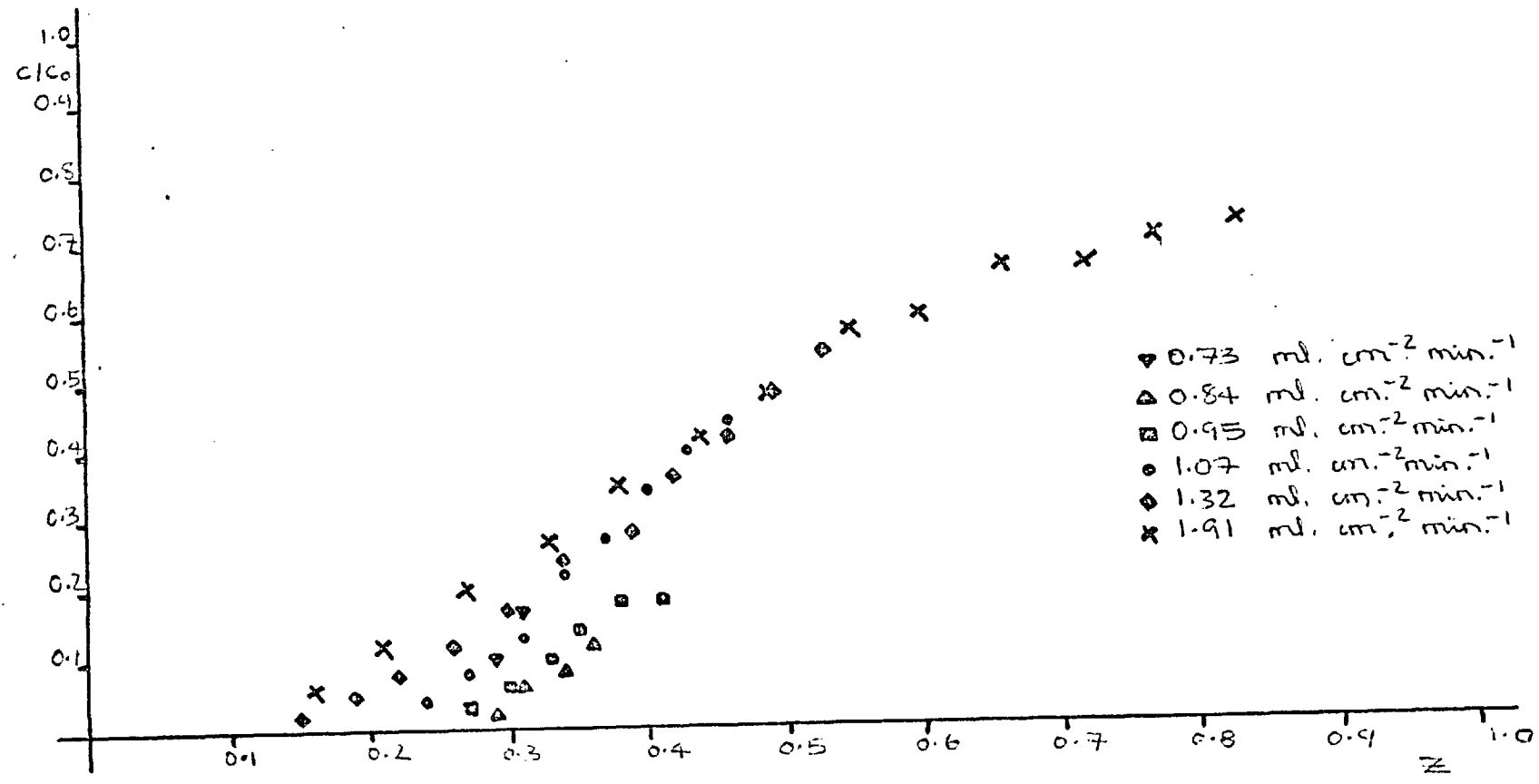


FIGURE 35. COLUMN PROCESS, ZINC / SUPERFINE VERMICULITE

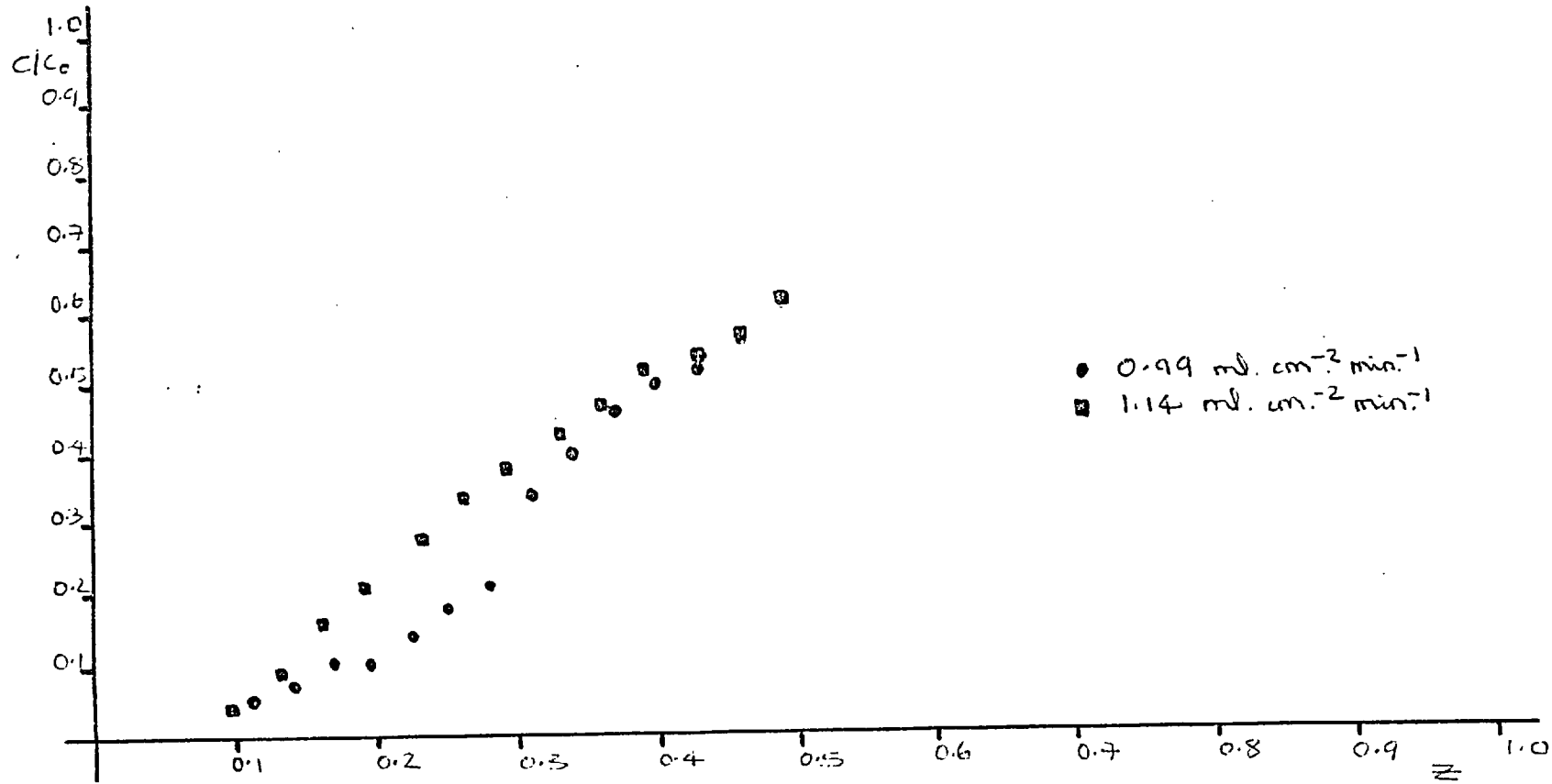


FIGURE 36. COLUMN OPERATION, NICKEL / MICRON VERMICULITE

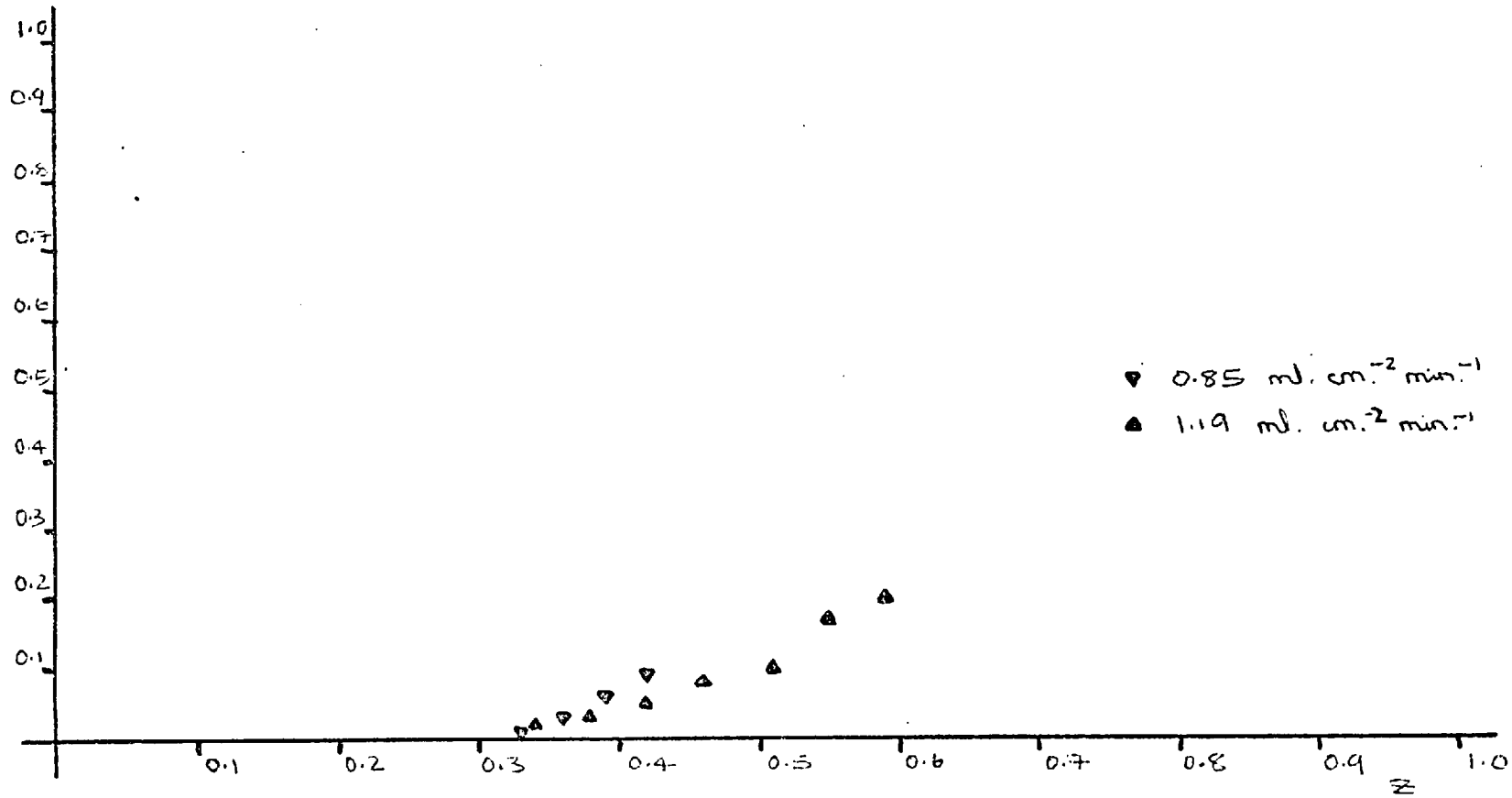


FIGURE 37 COLUMN PROCESS, NICKEL / SUPERFINE VERMICULITE

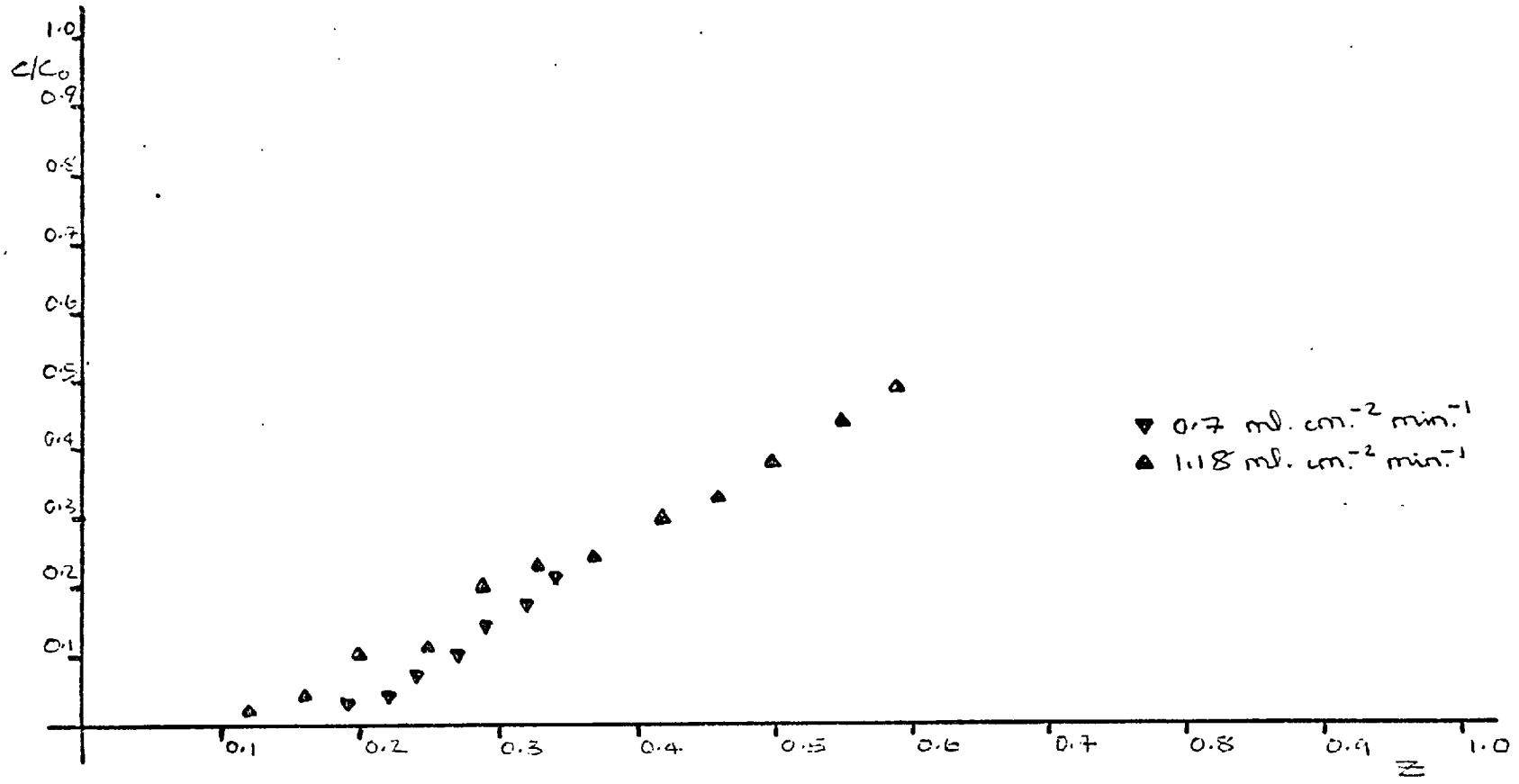




FIGURE 38. COLUMN PROCESS, CHROMIUM | MICRON VERMICULITE

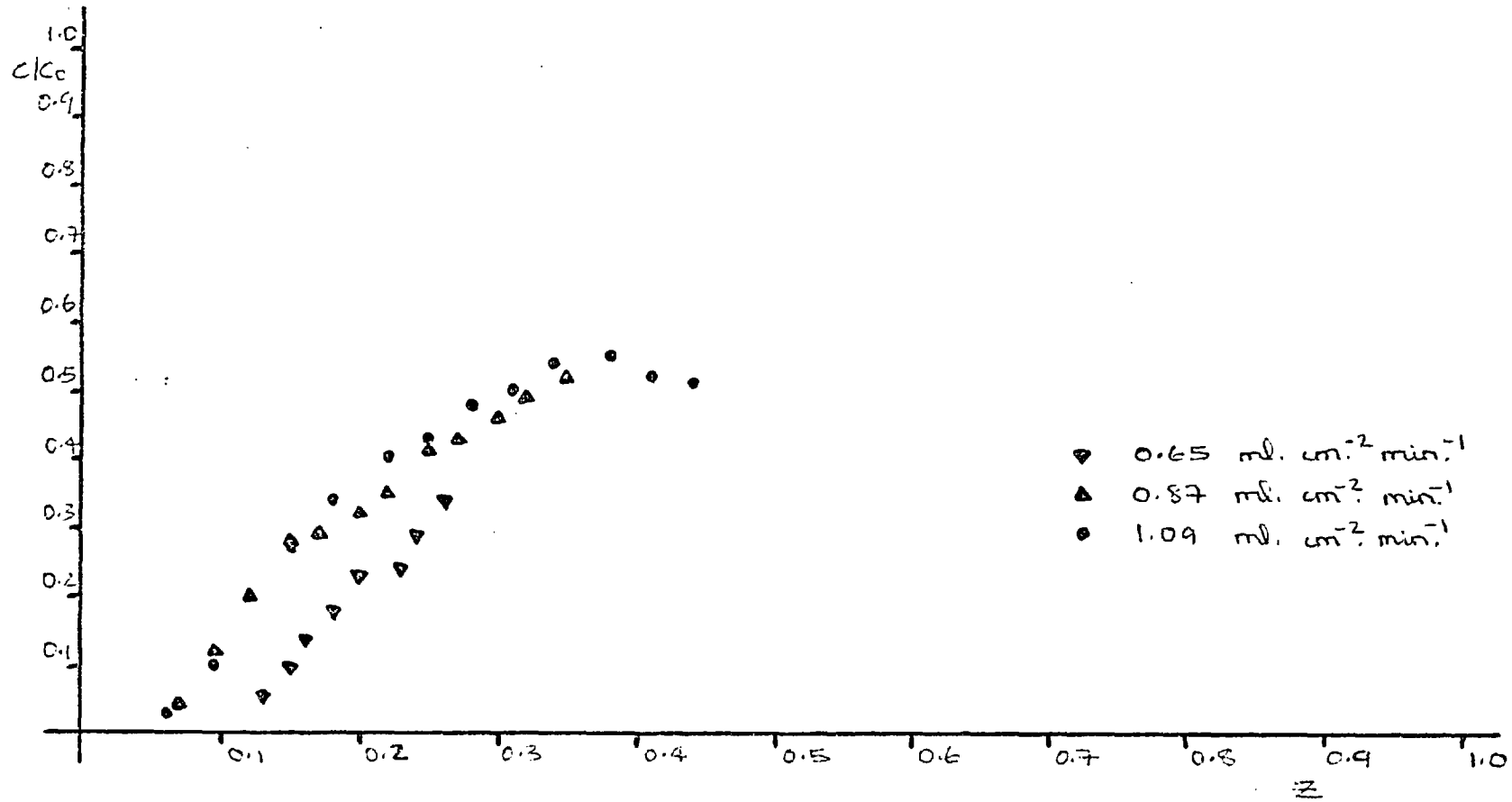
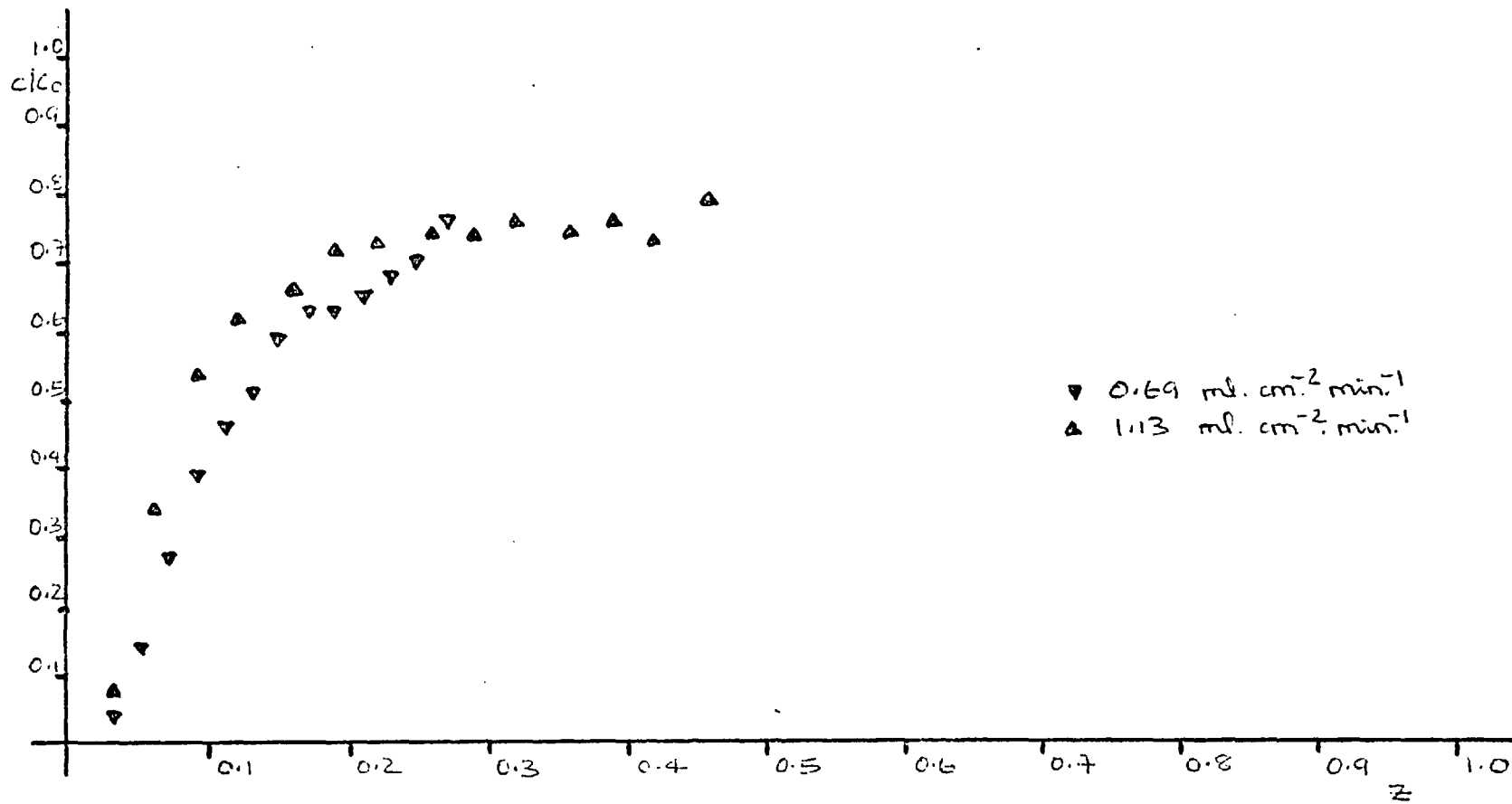


FIGURE 39. COLUMN PROCESS, CHROMIUM | SUPERFINE VERMICULITE.



## 5.2.2 COLUMN RESULTS / THE MODEL AND ESTIMATION OF DIFFUSION

### COEFFICIENTS

The column data is shown graphically in figures 27 to 39 and shown in tabular form in Appendix 1, Tables 18 to 28. From these results, especially figure 30, it is clear that breakthrough is in the order  $Ni^{2+} > Cu^{2+} > Zn^{2+} > Cr^{3+}$ .

The best fit to the data was found to be given by equation (49) for low flow rates, ie. less than about  $1.5 \text{ ml.cm}^{-2}\text{min}^{-1}$ , that is

$$x = (1 - \exp(-\psi(N_p(Z - 1) + 0.93)))^{\frac{1}{2}}$$

which on rearranging gives

$$\ln(1 - x^2) = \psi N_p(1 - Z) - 0.93\psi \quad \dots (57)$$

So a plot of  $\ln(1 - x^2)$  vs  $(1 - Z)$  should be a straight line, see figures 40-47. This equation allows the prediction of the solid phase diffusion coefficients. The value of  $\psi$  can be found from the intersection on the  $\ln(1 - x^2)$  axis (ie.  $0.93\psi = \text{intersection value}$ ) and the value of  $\psi N_p$  may be estimated from the gradient. Thus  $N_p$  may be found. Then equation (28) gives:

$$N_p = k_p a_p D_p v_e / F$$

and after substituting for  $k_p a_p (=60D_p/d_p^2)$  and  $D$  (equation (41)), this may be rearranged to give:

$$D_p = N_p d_p^2 C_o F / 600M \quad \dots (58)$$

Note that the particle phase diffusion coefficient is a function of flow rate.

The estimated values of the diffusion coefficients for a particular flow rate are given below. For copper they seem to vary

considerably with the grade of vermiculite employed, but otherwise they are fairly consistent.

TABLE 8. Estimated diffusion coefficients (Flow rate = 1.2 ml.cm.<sup>-2</sup>min.<sup>-1</sup>)

ION	MICRON VERMICULITE	SUPERFINE VERMICULITE
Copper	$5.4 \times 10^{-10}$	$2 \times 10^{-9}$
Nickel	$1.7 \times 10^{-9}$	$5 \times 10^{-9}$
Zinc	$1.2 \times 10^{-9}$	$3.9 \times 10^{-9}$
Chromium	$1.7 \times 10^{-9}$	$5 \times 10^{-9}$

The values of the constants,  $\psi$  and  $\psi_{N_p}$ , estimated from the data are given in Table 9 below:

TABLE 9. Values of Model Constants

ION	MICRON VERMICULITE		SUPERFINE VERMICULITE	
	$\psi$	$\psi_{N_p}$	$\psi$	$\psi_{N_p}$
Copper	0.8	0.88	2.2	2.5
Zinc	1.18	1.66	1.34	1.58
Nickel	0.22	0.37	0.66	0.85
Chromium	1.45	1.53	3.48	3.33

Note that the value of  $\psi$  and  $\psi_{N_p}$  for the superfine grade vermiculite are usually higher than the corresponding values for the micron grade.

The relations for  $D_p$  as a function of flow rate are given below:

TABLE 10. Relations for the diffusion coefficients as a function of flow rate

ION	MICRON VERMICULITE	SUPERFINE VERMICULITE
Copper	$7.7 \times 10^{-11} F$	$2.8 \times 10^{-10} F$
Zinc	$1.7 \times 10^{-10} F$	$5.6 \times 10^{-10} F$
Nickel	$2.4 \times 10^{-10} F$	$7.1 \times 10^{-10} F$
Chromium	$1.24 \times 10^{-10} F$	$4.6 \times 10^{-10} F$

NOTE: here the flow rate (F) is expressed in ml.min.<sup>-1</sup>

NOTE: these values are only correct for an initial concentration of 100 ppm.

FIGURE 40. COPPER EXCHANGE / MICRON VERTICULITE / MODEL

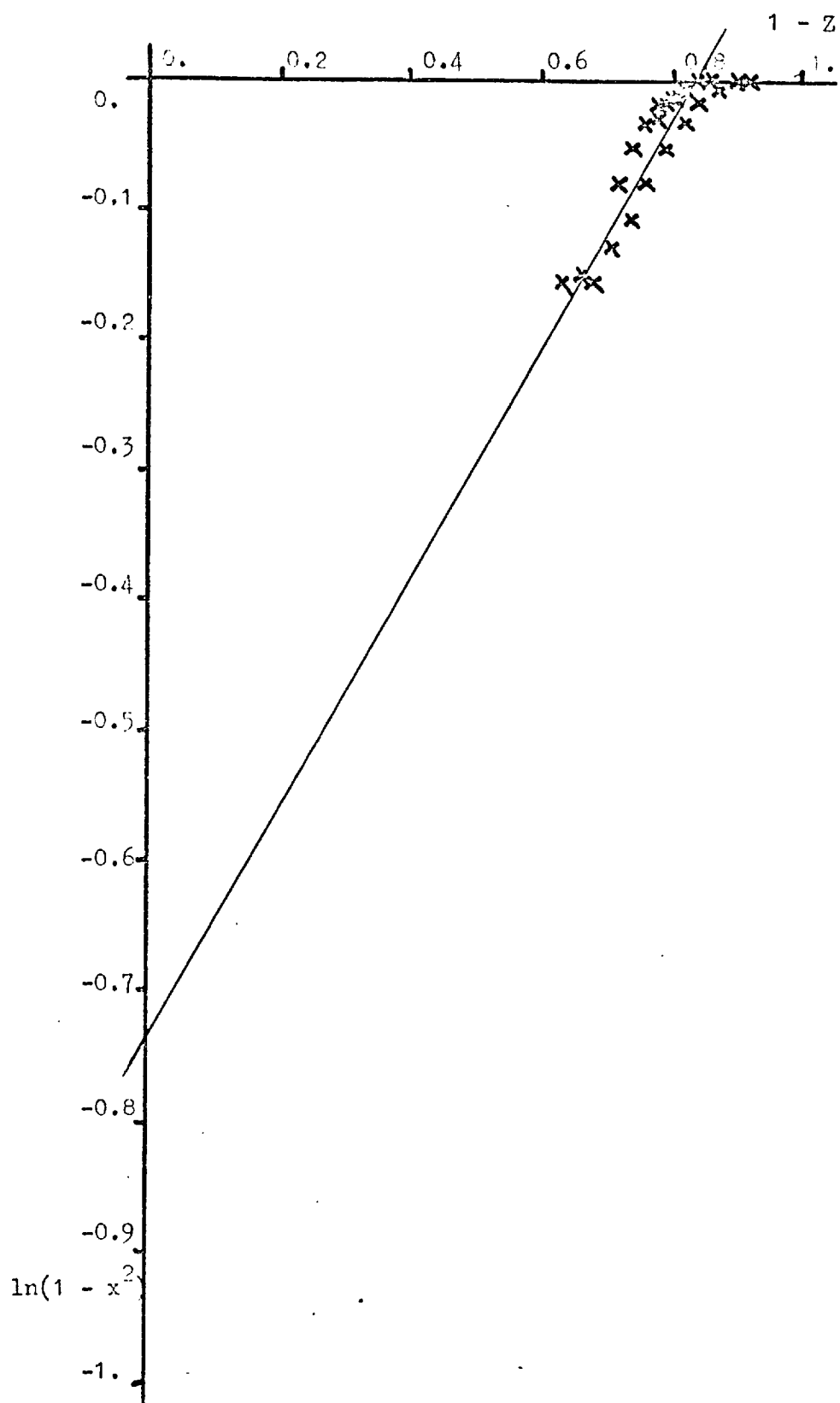


FIGURE 41. COPPER EXCHANGE / SUPERFINE VERTICULITE / MODEL

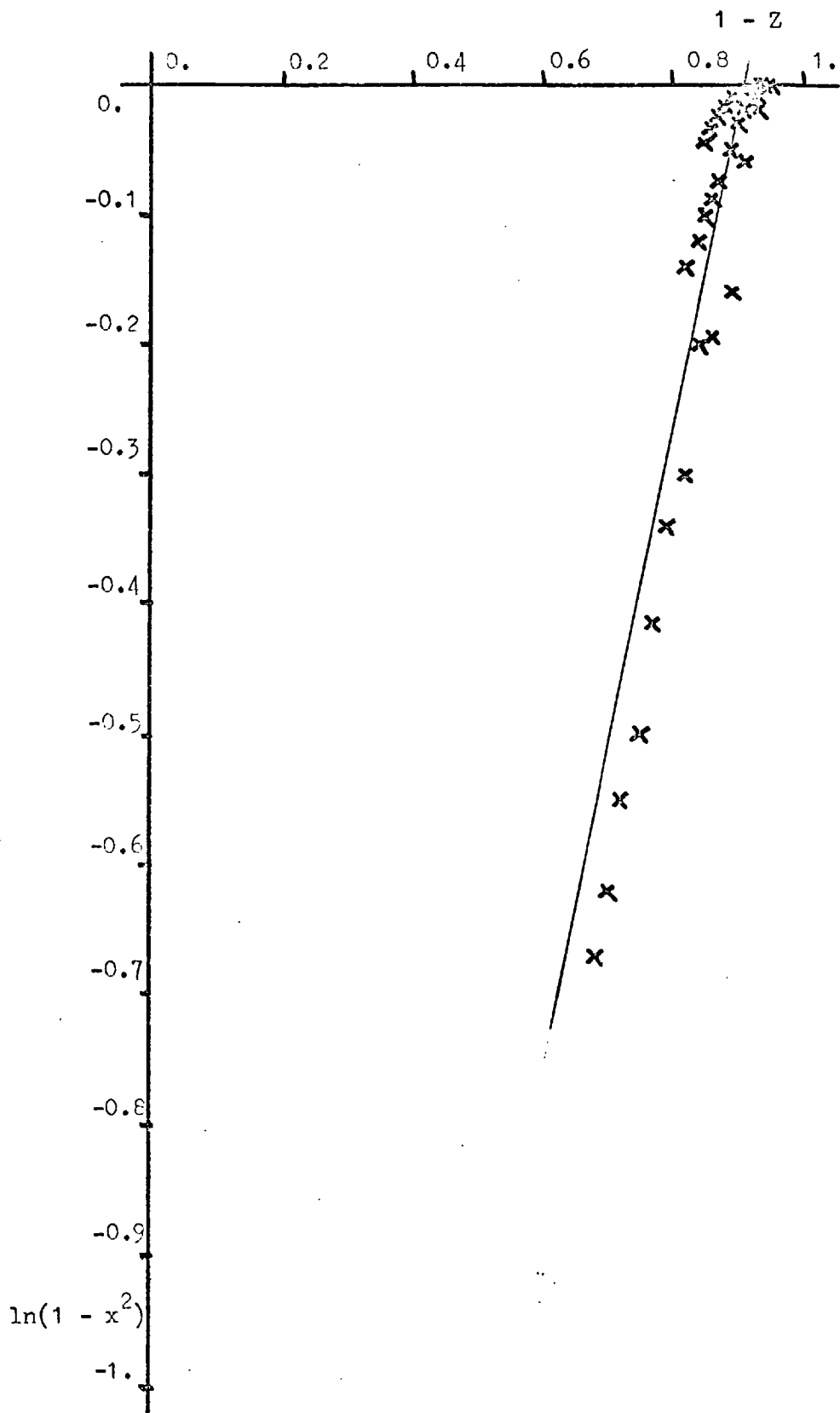


FIGURE 42. ZINC EXCHANGE / MICRON VERMICULITE / MODEL

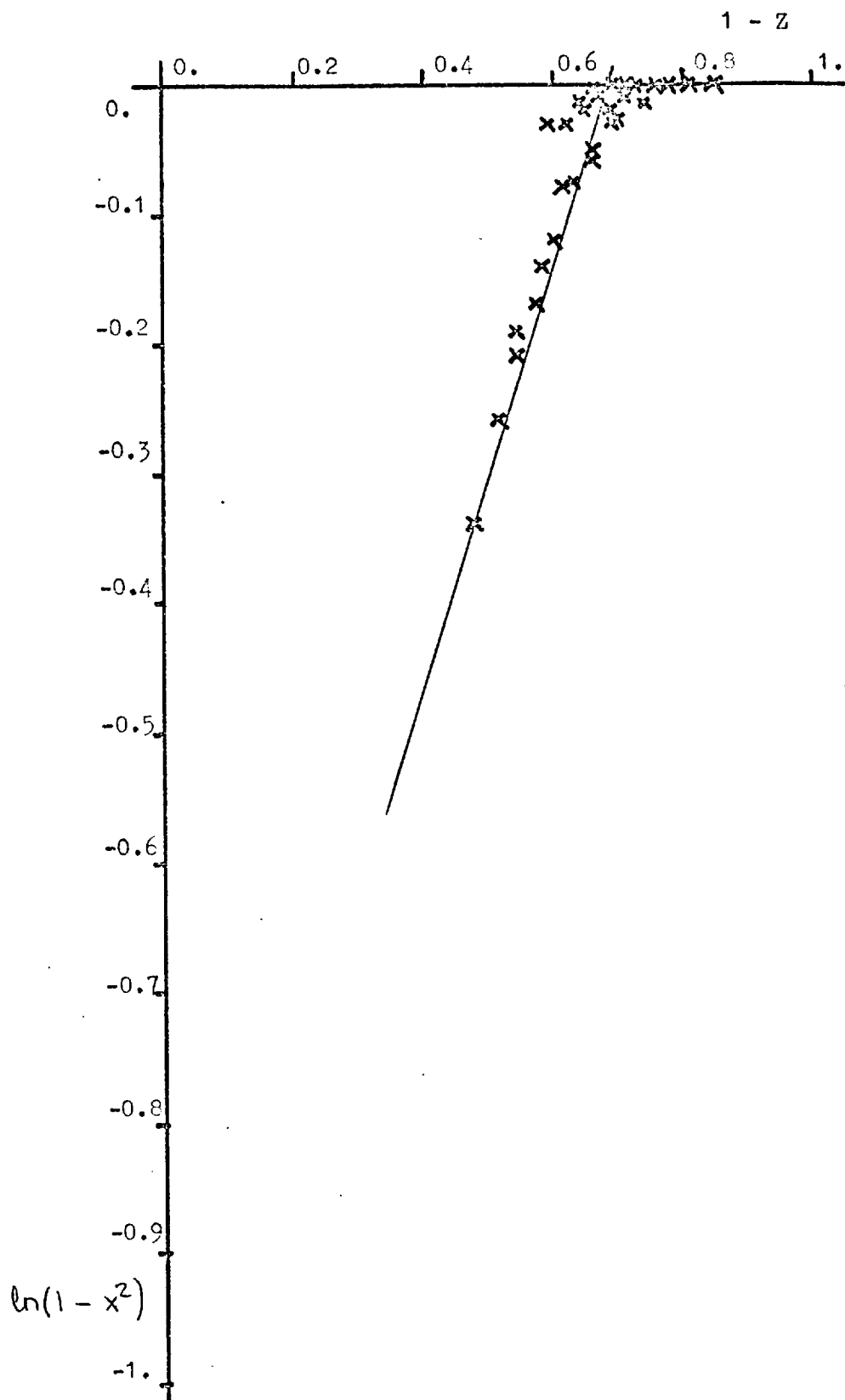


FIGURE 43. ZINC EXCHANGE / SUPERFINE VERTICULITE / MODEL

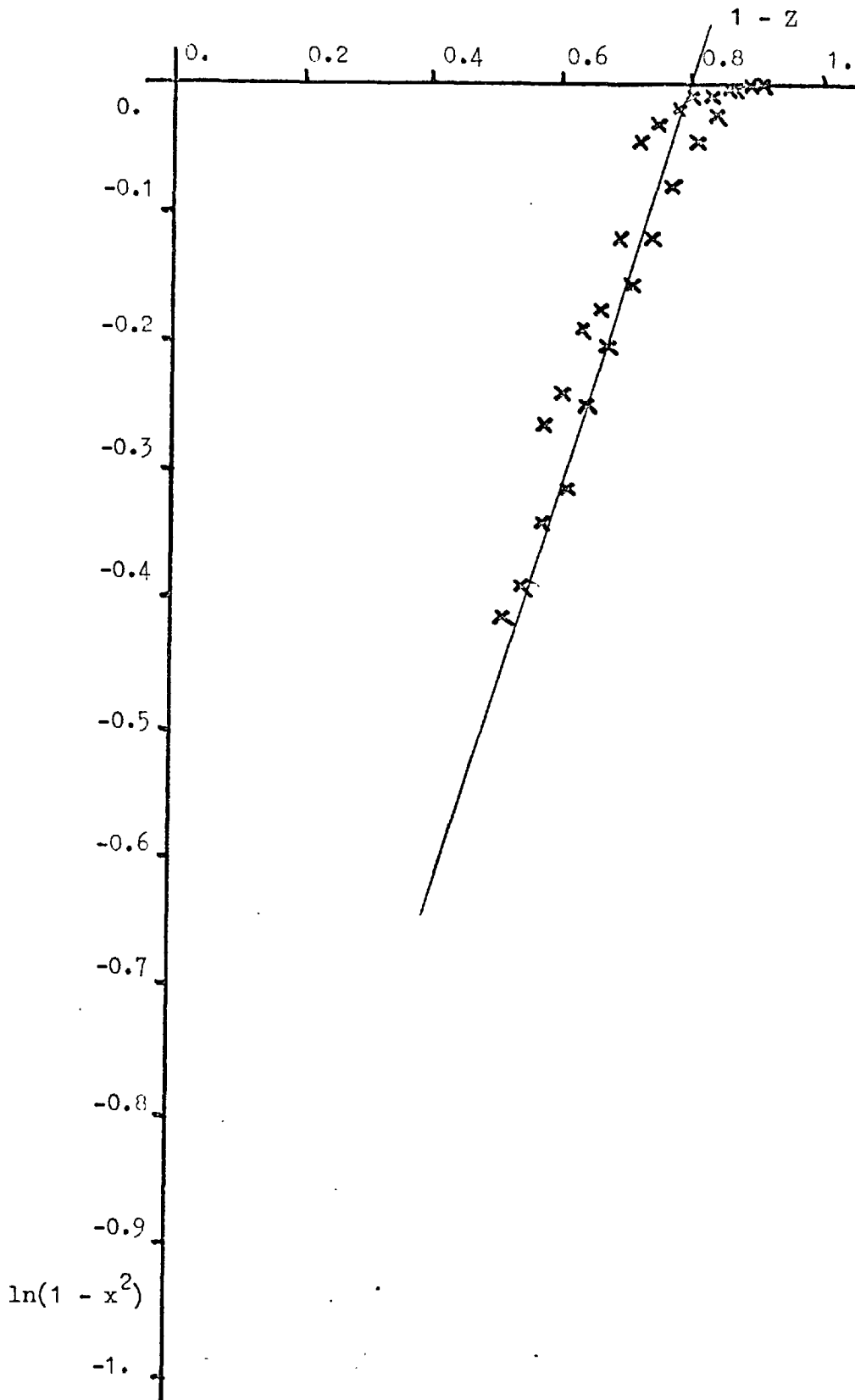




FIGURE 44. NICKEL EXCHANGE / MICRON VERMICULITE / MODEL

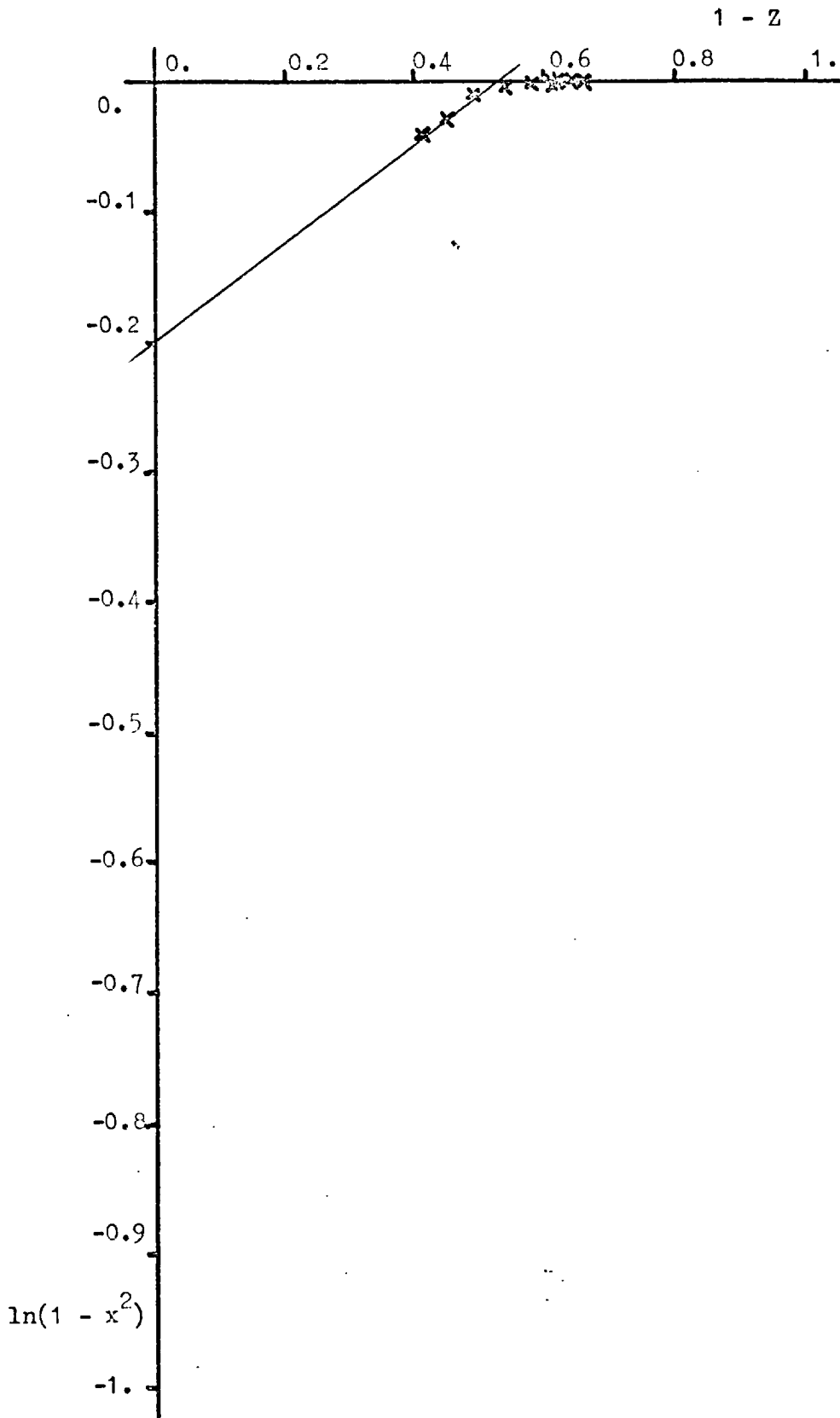


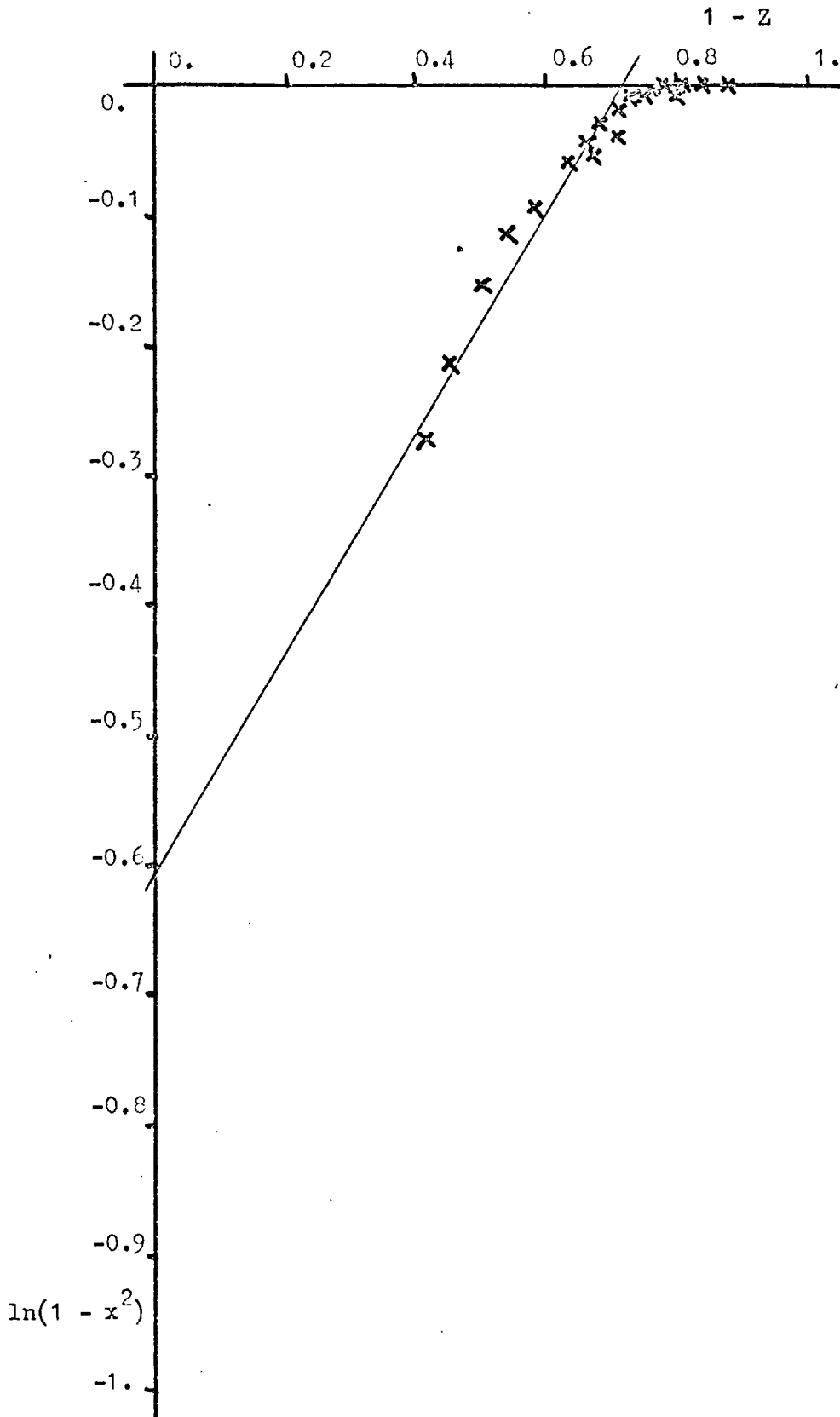
FIGURE 45. NICKEL EXCHANGE / SUPERFINE VERMICULITE / MODEL

FIGURE 46. CHROMIUM EXCHANGE / MICRON VERMICULITE / MODEL

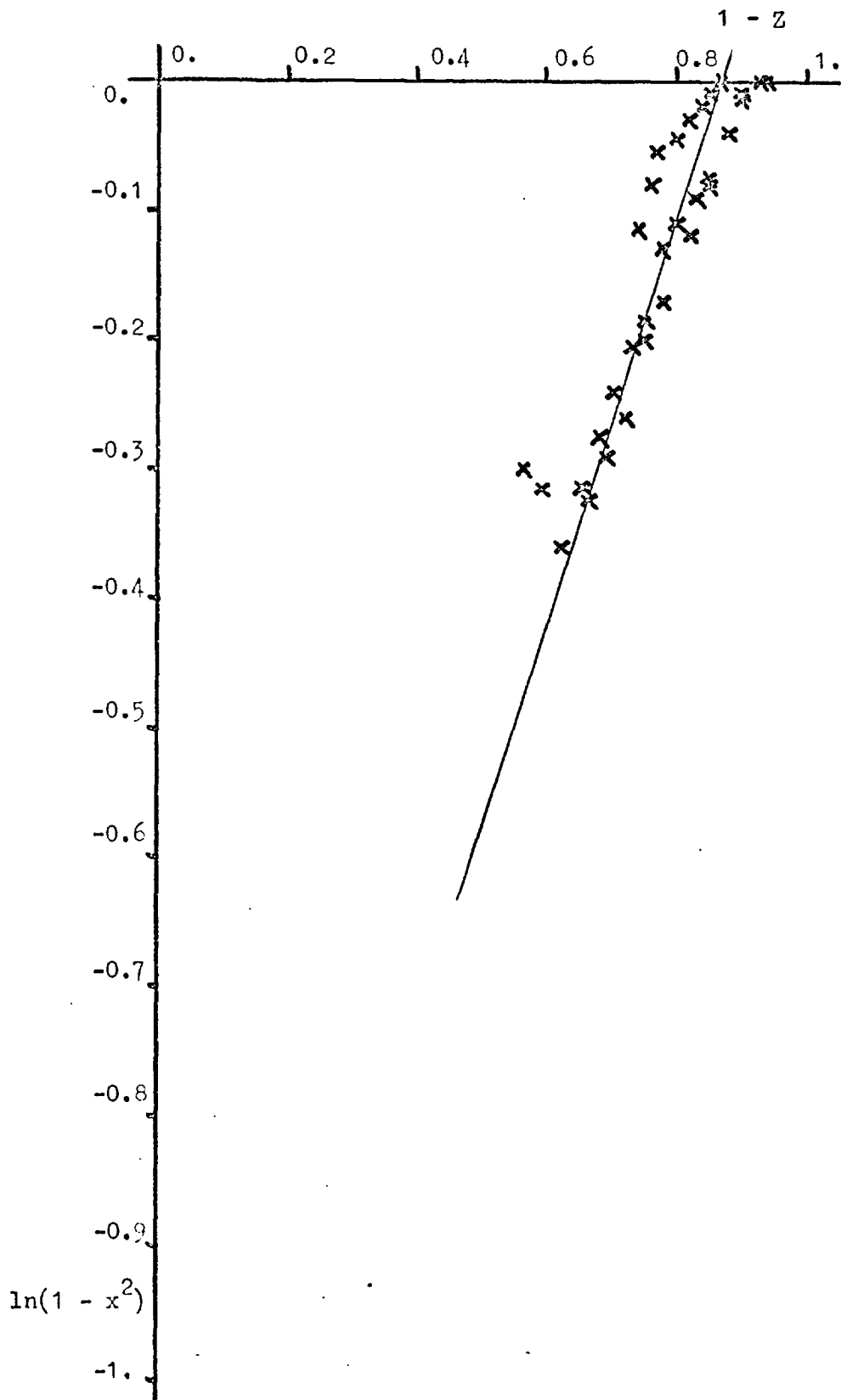
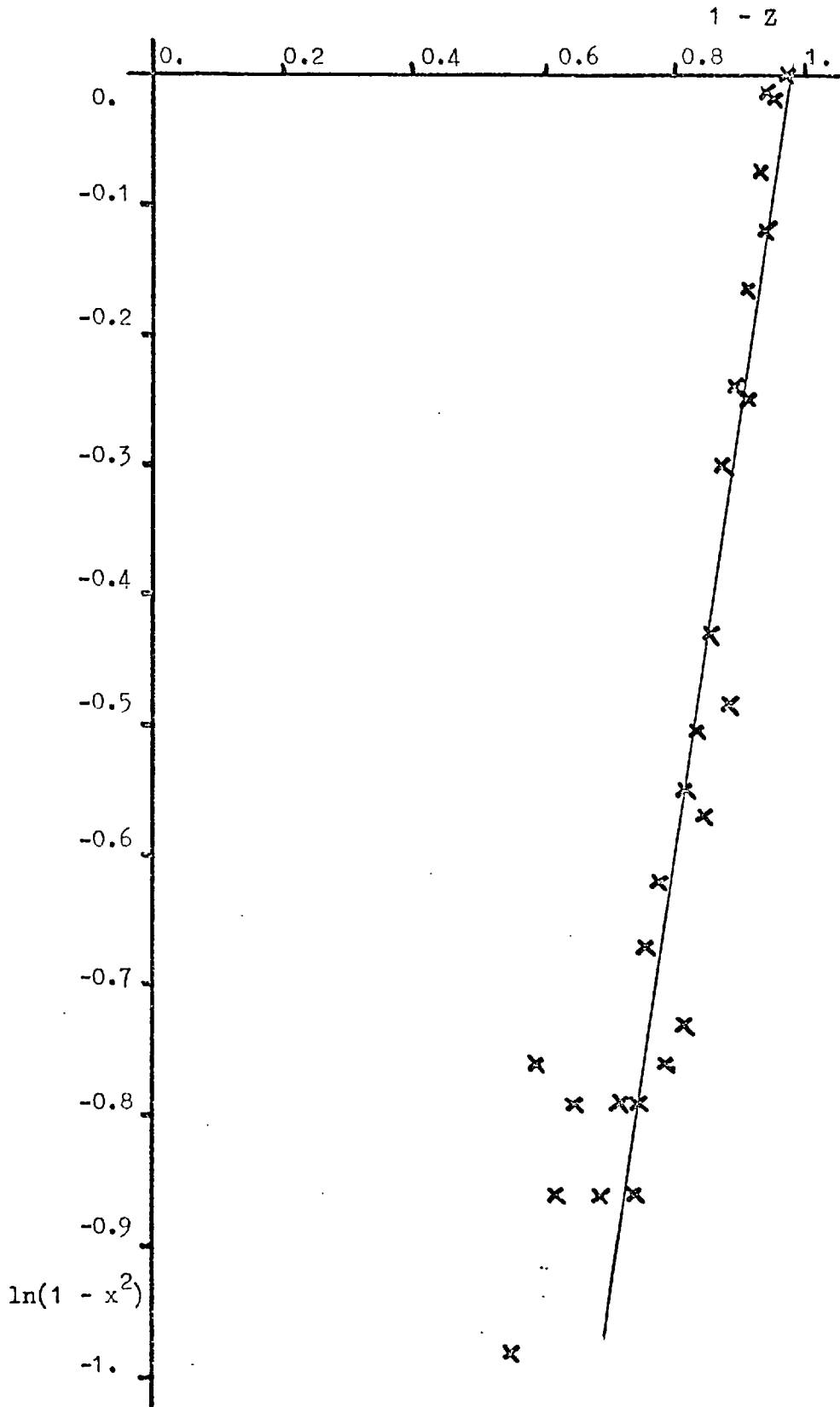


FIGURE 47. CHROMIUM EXCHANGE / SUPERFINE VERMICULITE / MODEL



6.1 EXAMPLE DESIGN

Supposing it is desired to treat  $200 \text{ gal. hr.}^{-1}$  of an aqueous effluent containing 100 ppm of  $\text{Cu}^{2+}$  with micron grade exfoliated vermiculite. The desired exit concentration not exceeding 10 ppm and the bed to be replaced after 24 hours operation.

From the graph (20) (or the model equation (57)) we can find the value of  $(1 - Z)$ , and hence  $Z$ .

$$\text{ie. } \ln(1 - x^2) = \ln(1 - 0.1^2) = \ln 0.99 = -0.01$$

$$\text{so } (1 - Z) = 0.83$$

$$Z = 0.17$$

Then equation (24) may be rearranged to give the volume of the bed, ie.

$$v = C_0 V / (Z Q \rho_b + C_0 \epsilon)$$

where

$$C_0 = 10^{-1} \text{ mg.ml.}^{-1}$$

$$V = 200 \times 24 \text{ gals.} = 2.2 \times 10^7 \text{ ml.}$$

$$Z = 0.17$$

$$Q = 66.3 \text{ mg.g.}^{-1}$$

$$\rho_b = 0.15 \text{ g.cm.}^{-3}$$

$$\epsilon = 0.39$$

hence 
$$v = 1.3 \times 10^6 \text{ cm.}^3 = \text{volume of bed}$$

Now to find the diameter of the bed we note that the flow rate must not exceed  $1.5 \text{ ml.cm.}^{-2} \text{ min.}^{-1}$

$$\begin{aligned} \text{so Area of bed} &= 2.2 \times 10^7 / 24 \times 60 \times 1.5 \text{ cm.}^2 \\ &= 1.02 \times 10^4 \text{ cm.}^2 \end{aligned}$$

$$\begin{aligned} \text{hence } d_b &= (1.02 \times 10^4 \times 4/3.142)^{\frac{1}{2}} \\ &= 1.15 \times 10^2 \text{ cm.} \end{aligned}$$

and bed height is given by  $\text{Volume/Area} = 1.3 \times 10^6 / 1.02 \times 10^4$   
 $= 1.27 \times 10^2 \text{ cm.}$

Therefore the desired column size is 127 cm high by 115 cm diameter.

Now, the volume of the bed is  $1.3 \times 10^6 \text{ cm}^3$

so the mass of the bed =  $\frac{1.3 \times 10^6}{0.15} \text{ g.}$   
 $= 8.67 \times 10^6 \text{ g}$

hence total capacity of bed = mass  $\times Q$

$$= 8.67 \times 66.3 \times 10^6$$

$$= 5.7 \times 10^8 \text{ mg}$$

and the breakthrough capacity =  $2.2 \times 10^4 \times 90 \text{ mg}$   
 $= 1.98 \times 10^6$

so Degree of utilization =  $1.98 \times 10^6 / 5.7 \times 10^8$   
 $= \underline{0.34\%}$

## 6.2 DISCUSSION OF RESULTS AND CONCLUSIONS

The experiments gave the value of the cation exchange capacity of copper of the order  $2 \text{ meq.g.}^{-1}$  whereas that of chromium was  $2.2 \text{ meq.g.}^{-1}$  and those of zinc and nickel were of the order  $1 \text{ meq.g.}^{-1}$ . These values are in close agreement with those of Mohn (1973) and other workers, see Table 4. The high value of the exchange capacity of copper may be due to the precipitation of  $\text{Cu}(\text{OH})_2$ . Note that the same value was found for the two grades.

Higher values were found than those of Mohn (1973) in the batch experiments; this can only be assumed to be due to the finer grades of vermiculite that were employed in this study. Grade 'Fine' being used in her work whereas 'micron' and 'superfine' were used in this work.

The batch results indicate the preference for the ions to be  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$ , see figures 21-26. This trend does not, however, agree with that found by Mohn (1973) who found the order to be  $\text{Cr}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+}$ . I also mentioned in the text that other workers, Wild and Keay (1964), found that vermiculite has a greater preference for the higher valent ions. So there seems to be a contradiction of results. I can only assume, that if my values are correct, the lower value for chromium is due to the fact that far fewer sites are occupied by the ion in the network than are occupied by the divalent ions.

By looking closely at figures 21-26 and comparing the results for superfine and micron grade vermiculites it can clearly be seen that the smaller particles achieve a much closer approach to linear equilibrium.

The batch results also show that the exchange is unfavourable in all cases.

None of the column experiments carried out reached saturation point, see figures 27 & 28 for example, although the 500 ppm case of figure 27 approached this closely. This was true even when the column was run for twelve hours, figure 28. In fact a study of the figures shows that the reaction seems to slow down considerably and it appears that it would take many hours for saturation to occur. This suggests that exfoliated vermiculite would have to be used as a 'low capacity' exchanger and so a large column or frequent changes of vermiculite would be required for purification on an industrial scale.

Figure 30 shows plots of breakthrough curves using micron vermiculite and similar flow rates. See also figures 31 to 39. From these graphs it is clear that the divalent ions are much preferred to the chromium, a point in favour of the batch results. It also shows that breakthrough for the divalent ions occurs almost simultaneously, the major difference being in the slope of the curve. The actual order of breakthrough times is found to be  $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+}$  which is the same order as found for the preference of these ions.

The degree of utilization has also been estimated from the figure 30, see Table 7. From these results it is clear that this value is low, especially for chromium. It is, however, much higher than the value estimated from the model design calculation, which suggests that the design may well be over specified. Since the breakthrough with superfine vermiculite occurs earlier than with micron vermiculite it is obvious that the degree of utilization would be lower for the larger grade.

The particle control constant pattern model adopted seems to fit the data reasonably accurately, see figures 40-47, even though it is for favourable equilibrium. It must be noted, however, that the flow rate must not exceed  $1.5 \text{ ml.cm}^{-2} \text{ min}^{-1}$ , which is rather low. The lower parts of the curve are not fitted exactly but the concentrations



are very low here anyway, generally less than 5 ppm.

The diffusion coefficients estimated by this model are very low, of the order  $10^{-9}$  to  $10^{-10}$   $\text{cm}^2\cdot\text{sec}^{-1}$ , which was much lower than I had expected ( $10^{-7}$  to  $10^{-8}$   $\text{cm}^2\cdot\text{sec}^{-1}$ , see text). Lutze and Miekeley \* carried out an investigation into the diffusion of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  in vermiculite disks. They discovered that the results could not be interpreted by the simple theory of Helfferich but by making suitable adaptations agreement could be found between experiment and theory. Their results showed that the diffusion coefficient is of the order  $10^{-7}$ , but this does not mean my results are in error. It is possible that one of us has been working with the hydrated ion diffusion and the other with the unhydrated ion diffusion. This could well result in the  $10^2$  difference between the two sets of results.

An example design calculation is given for 100 ppm.  $\text{Cu}^{2+}$  influent. The size of the contactor given should theoretically give the desired separation but further experiments should be carried out to see if such a scale-up is valid, as usually larger scale equipment should be used when scale-up is the intention. Note that more experiments are required - to evaluate the constants for the model - before this method can be applied to the design for different influent concentrations.

\* Lutze, W, ; Miekeley, N.

Ion Exchange Kinetics in Vermiculite,  
J. Phys. Chem., 75, 2484 (1971)

### 6.3 SUGGESTIONS FOR FURTHER WORK

Further work should involve studies of the kinetics, preferably in a different way than tackled in this report.

Some work should be done on the use of centrifuge operation and of fluidised beds.

Larger scale operations should be employed so that scaling up could be carried out with a greater degree of confidence. A column size suitable for this is suggested in the text.

As  $Z$  is a function of initial concentration, experiments should be carried out to determine  $\tau$  and  $\tau_{N_p}$  as a function of initial concentration then the model can be used for prediction of results for different influent concentrations.

To complement this work experiments should be carried out with actual waste waters to determine if the presence of other ions and organic material, especially ammonia and amines, have any affect on the exchange capacities. Variation of pH and temperature should also be considered but it must be remembered that, for copper anyway, a lower pH would result in the precipitation of  $\text{Cu}(\text{OH})_2$ .

7. NOMENCLATURE

- a - activities
- $a_p$  - effective mass-transfer area between fluid and particles ( $\text{cm}^2 \cdot \text{cm}^{-3}$ )
- C - concentration of ions in solution ( $\text{mg} \cdot \text{l}^{-1}$  (ppm),  $\text{meq} \cdot \text{l}^{-1}$ )
- $C_o$  - total initial concentration of ion in solution ( $\text{mg} \cdot \text{l}^{-1}$ ,  $\text{meq} \cdot \text{l}^{-1}$ )
- $d_p$  - diameter of sphere equal in volume to actual particle (cm.)
- $D_p$  - diffusivity in particle ( $\text{cm}^2 \cdot \text{sec}^{-1}$ )
- $D_o$  - diffusivity in free solution ( $\text{cm}^2 \cdot \text{sec}^{-1}$ )
- f - activity coefficients
- F - volumetric flow rate ( $\text{cm}^3 \cdot \text{sec}^{-1}$ )
- k - rate coefficient for kinetics ( $\text{cm}^3 \cdot \text{sec}^{-1} \cdot \text{g} \cdot \text{mole}^{-1}$ )
- K - equilibrium constant for exchange or adsorption, in appropriate concentration or pressure units
- M - mass of bed (gs.)
- n - integer in infinite series
- q - concentration of solute in particle phase ( $\text{mg} \cdot \text{g}^{-1}$  or  $\text{meq} \cdot \text{g}^{-1}$ ) of air dried particles
- Q - cation exchange capacity for adsorption ( $\text{meq} \cdot \text{g}^{-1}$ ,  $\text{mg} \cdot \text{g}^{-1}$ )
- r - radial distance within spherical particle (cm)
- $r_p$  - radius of exterior surface of particle (cm.)
- S - cross-sectional area of contactor ( $\text{cm}^2$ )
- s - distance along bed (cm.)
- t - time (sec.)
- u - intergranular fluid velocity ( $\text{cm} \cdot \text{sec}^{-1}$ )
- v - bulk packed volume of contactor ( $\text{cm}^3$ )
- V - volume of saturating feed entering column ( $\text{cm}^3$ )
- w - bed weight (gs.)
- $z_i$  - valency

## DIMENSIONLESS GROUPS

- D - distribution parameter, or ratio of concentration in particles and fluid phase
- N - number of transfer units
- r - equilibrium parameter
- x - ratio of fluid phase concentrations of a component to that of all components  $C/C_o$  ( $x_A$ , etc.)
- y - ratio of particle phase concentration of a component to total for solid at saturation with feed  $q/Q$
- Z - throughput parameter, or ratio of actual volume of effluent to stoichiometric volume

## GREEK LETTERS

- $\delta$  - film thickness (cm.)
- $\epsilon$  - ratio of void space outside particles to total volume of contacting zone
- $\lambda_i$  - distribution coefficient
- $\lambda_{oi}$  - limiting ionic conductance ( $\text{Ohm}^{-1} \text{cm}^2$ )
- $\rho$  - density ( $\text{g.cm}^{-3}$ ) - usually fluid density;  $\rho_b$  = bulk density of air dried particles,  $\rho_p$  = density of adsorbent particles
- $\gamma$  - numerical correction factor for solid phase diffusion
- $\chi$  - internal porosity of adsorbent particles

## SUBSCRIPTS

- 1,2,3,.... - instantaneous times of measurement
- a - apparent
- b - bulk
- f - fluid phase
- i - interior or interface
- o - overall
- o - initial or entrance conditions, or in free solution

p - particle phase

pore - fluid phase. pore diffusion

r - resin phase

s - solution phase

stoic - stoichiometric proportions

t - given time

$\infty$  - at infinite time

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APPENDICES

APPENDIX 1

TABLES OF RESULTS

TABLE 11. CATION EXCHANGE CAPACITIES

ION	CAPACITY	
	mg.g. <sup>-1</sup>	meq.g. <sup>-1</sup>
Cu <sup>2+</sup>	66.3	2.1
Zn <sup>2+</sup>	39.5	1.2
Ni <sup>2+</sup>	32.5	1.1
Cr <sup>3+</sup>	39.	2.25

TABLE 12. COPPER EXCHANGE IN BATCH EXPERIMENT / MICRON VERMICULITE

WT. VERM. (g.)	$C_0$ (mg.l. <sup>-1</sup> )	$C$ (mg.l. <sup>-1</sup> )	$C/C_0$	$q$ (mg.g. <sup>-1</sup> )	$q/Q$ (meq.g. <sup>-1</sup> )	$q/Q$
0.1	25	18.6	0.74	32.	1.	0.48
0.1	25	17.8	0.71	36.	1.13	0.54
0.2	25	14.4	0.58	26.5	0.83	0.4
0.3	25	11.	0.44	23.3	0.73	0.35
0.1	52.5	44.	0.84	42.5	1.34	0.64
0.1	52.5	45.	0.86	37.5	1.15	0.57
0.1	50.4	42.8	0.85	38.	1.2	0.57
0.2	50.4	36.4	0.72	35.	1.1	0.53
0.3	50.4	31.2	0.62	32.	1.	0.48
0.1	74.5	65.	0.87	47.5	1.49	0.72
0.1	74.5	65.	0.87	47.5	1.49	0.72
0.1	75.	67.5	0.9	37.5	1.18	0.57
0.2	75.	61.	0.81	35.	1.1	0.53
0.3	75.	53.5	0.71	35.9	1.13	0.54
0.1	104.	86.5	0.83	87.5	2.75	1.32
0.1	104.	87.	0.84	85.	2.67	1.28
0.1	102.5	85.	0.83	43.8	1.38	0.66
0.1	100.	89.	0.89	55.	1.73	0.83
0.2	100.	82.5	0.83	45.	1.42	0.68
0.3	100.	76.5	0.77	39.2	1.23	0.59
0.1	155.	134.	0.87	105.	3.3	1.58
0.1	147.	138.	0.94	45.	1.42	0.68
0.2	147.	132.	0.9	37.5	1.18	0.57
0.3	147.	125.	0.85	36.7	1.15	0.55

TABLE 12. continued.

WT. VERM. (g.)	$C_o$ (mg.l. <sup>-1</sup> )	C (mg.l. <sup>-1</sup> )	$C/C_o$	q (mg.g. <sup>-1</sup> )	q (meq.g. <sup>-1</sup> )	q/Q
0.1	205.	184.	0.9	105.	3.3	1.58
0.1	199.	180.	0.9	95.	2.99	1.43
0.2	199.	171.	0.86	70.	2.2	1.05
0.3	199.	163.	0.82	60.	1.89	0.9



TABLE 13. COPPER EXCHANGE IN BATCH EXPERIMENT / SUPERFINE VERMICULITE

WT. VERM. (g.)	$C_0$ (mg.l. <sup>-1</sup> )	C (mg.l. <sup>-1</sup> )	$C/C_0$	q (mg.g. <sup>-1</sup> )	q (meq.g. <sup>-1</sup> )	q/Q
0.1	24.2	19.8	0.82	22.	0.69	0.33
0.2	24.2	15.4	0.64	22.	0.69	0.33
0.3	24.2	13.6	0.56	17.8	0.56	0.27
0.1	50.	42.	0.84	40.	1.26	0.6
0.2	50.	36.4	0.73	34.	1.07	0.51
0.3	50.	34.4	0.69	26.	0.82	0.39
0.1	75.6	68.8	0.91	34.	1.07	0.51
0.3	75.6	56.	0.74	32.7	1.03	0.49
0.1	74.4	65.2	0.88	46.	1.45	0.69
0.2	74.4	60.	0.81	36.	1.13	0.54
0.3	74.4	49.2	0.66	42.	1.32	0.63
0.1	99.5	91.5	0.92	40.	1.26	0.6
0.2	99.5	85.	0.85	36.3	1.14	0.55
0.3	99.5	81.5	0.82	30.	0.94	0.45
0.1	146.	138.	0.93	40.	1.26	0.6
0.2	146.	135.	0.93	27.5	0.87	0.41
0.3	146.	127.	0.87	31.7	1.	0.48
0.1	200.	195.	0.98	25.	0.79	0.38
0.2	200.	185.	0.93	37.5	1.18	0.56
0.3	200.	178.	0.89	36.7	1.15	0.55
0.1	198.	177.	0.89	105	3.3	1.58
0.2	198.	180.	0.91	45.	1.42	0.68
0.3	198.	185.	0.93	21.7	0.68	0.33

TABLE 14. ZINC EXCHANGE IN BATCH EXPERIMENTS / MICRON VERMICULITE

WT. VERM. (g.)	$C_0$ (mg.l. <sup>-1</sup> )	C (mg.l. <sup>-1</sup> )	$C/C_0$	q (mg.g. <sup>-1</sup> )	q (meq.g. <sup>-1</sup> )	q/Q
0.1	26.2	20.8	0.79	27.	0.83	0.68
0.2	26.2	18.2	0.7	20.	0.61	0.51
0.3	26.2	15.5	0.59	17.8	0.54	0.45
0.1	49.2	42.	0.85	36.	1.1	0.91
0.2	49.2	38.8	0.79	26.	0.8	0.66
0.3	49.2	34.8	0.71	24.	0.73	0.61
0.1	78.	73.6	0.94	22.	0.67	0.56
0.2	78.	67.	0.86	22.5	0.69	0.57
0.3	78.	62.4	0.8	26.	0.8	0.66
0.1	106.4	92.4	0.87	70.	2.14	1.77
0.2	106.4	91.2	0.86	38.	1.16	0.96
0.3	106.4	84.	0.79	37.3	1.14	0.95
0.1	155.	136.	0.87	95.	2.91	2.4
0.2	155.	129.	0.83	65.	1.99	1.64
0.3	155.	125.	0.81	50.	1.53	1.27
0.1	199.5	189.	0.95	52.5	1.61	1.33
0.2	199.5	182.	0.91	43.8	1.34	1.1
0.3	199.5	178.5	0.9	35.	1.09	0.89

TABLE 15. ZINC EXCHANGE IN BATCH EXPERIMENTS / SUPERFINE VERMICULITE

WT. VERM. (g.)	$C_0$ (mg.l. <sup>-1</sup> )	C (mg.l. <sup>-1</sup> )	$C/C_0$	q (mg.g. <sup>-1</sup> )	q (meq.g. <sup>-1</sup> )	q/Q
0.1	22.6	19.	0.84	18.	0.55	0.46
0.2	22.6	15.4	0.68	18.	0.55	0.46
0.3	22.6	11.6	0.51	18.3	0.56	0.46
0.1	45.	41.4	0.92	18.	0.55	0.46
0.2	45.	38.6	0.86	16.	0.49	0.41
0.3	45.	34.4	0.76	17.7	0.54	0.45
0.1	74.	68.8	0.93	26.	0.8	0.66
0.2	74.	65.6	0.89	21.	0.64	0.53
0.3	74.	60.	0.81	23.3	0.71	0.59
0.1	100.	94.	0.94	30.	0.92	0.76
0.2	100.	89.2	0.89	27.	0.83	0.68
0.3	100.	83.2	0.83	28.	0.86	0.71
0.1	150.	142.5	0.95	37.5	1.15	0.95
0.2	150.	146.	0.97	10.	0.31	0.25
0.3	150.	135.	0.9	25.	0.77	0.63
0.1	198.8	186.9	0.94	59.5	1.84	1.5
0.2	198.8	184.8	0.93	35.	1.07	0.89
0.3	198.8	179.9	0.91	31.5	0.96	0.8

TABLE 16. CHROMIUM EXCHANGE IN BATCH EXPERIMENTS / MICRON VERNICULITE

WT. VERM. (g.)	$C_0$ (mg.l. <sup>-1</sup> )	$C$ (mg.l. <sup>-1</sup> )	$C/C_0$	$q$ (mg.g. <sup>-1</sup> )	$q$ (meq.g. <sup>-1</sup> )	$q/Q$
0.1	27.	22.5	0.83	22.5	1.3	0.58
0.2	27.	20.	0.74	17.5	1.01	0.45
0.3	27.	15.8	0.59	18.7	1.08	0.48
0.1	49.5	46.	0.93	17.5	1.01	0.45
0.2	49.5	43.	0.87	16.3	0.94	0.42
0.3	49.5	39.	0.79	17.5	1.01	0.45
0.1	75.	68.5	0.91	32.5	1.88	0.83
0.2	75.	65.	0.87	25.	1.44	0.64
0.3	75.	62.5	0.83	20.8	1.2	0.53
0.1	100.	94.	0.94	30.	1.73	0.77
0.2	100.	90.	0.9	25.	1.44	0.64
0.3	100.	86.5	0.87	22.5	1.3	0.58
0.1	100.	98.5	0.99	7.5	0.43	0.19
0.2	100.	96.	0.96	10.	0.58	0.26
0.3	100.	92.	0.92	13.3	0.77	0.34
0.1	153.	152.	0.99	5.	0.29	0.13
0.2	153.	149.	0.97	10.	0.58	0.26
0.3	153.	140.	0.92	21.6	1.25	0.56
0.1	146.	142.6	0.98	17.	0.98	0.44
0.2	146.	140.	0.96	15.	0.87	0.38
0.3	146.	140.	0.96	10.	0.58	0.26
0.1	200.	192.	0.96	40.	2.31	1.02
0.2	200.	187.	0.94	32.5	1.88	0.83
0.3	200.	178.	0.89	36.6	2.11	0.94

TABLE 17. CHROMIUM EXCHANGE IN BATCH EXPERIMENTS / SUPERFINE VERMICULITE

WT. VERM. (g.)	$C_0$ (mg.l. <sup>-1</sup> )	$C$ (mg.l. <sup>-1</sup> )	$C/C_0$	$q$ (mg.g. <sup>-1</sup> )	$q/Q$ (meq.g. <sup>-1</sup> )	$q/Q$
0.1	26.	23.5	0.9	12.5	0.72	0.32
0.2	26.	16.	0.62	25.	1.44	0.64
0.3	26.	20.	0.77	10.	0.58	0.26
0.1	48.5	46.5	0.96	10.	0.58	0.26
0.2	48.5	44.	0.91	11.3	0.65	0.29
0.3	48.5	41.	0.85	12.5	0.72	0.32
0.1	72.	70.5	0.98	7.5	0.43	0.19
0.2	72.	67.5	0.94	11.3	0.65	0.29
0.3	72.	65.	0.9	11.7	0.67	0.3
0.1	100.	98.	0.98	10.	0.58	0.26
0.2	100.	94.	0.94	15.	0.87	0.38
0.3	100.	89.	0.89	18.3	1.06	0.47
0.5	144.	135.	0.94	9.	0.52	0.23
0.5	144.	135.	0.94	9.	0.52	0.23
0.5	144.	125.	0.87	19.	1.1	0.49
0.5	201.	194.	0.97	7.	0.4	0.18
0.5	201.	190.	0.95	11.	0.64	0.28
0.5	201.	188.	0.94	13.	0.75	0.33

TABLE 18. SMALL COLUMN RESULTS

INTERNAL DIAMETER 4.8 cm. (Cross-section 2.55 cm.<sup>2</sup>)  
5 g. vermiculite.

100 ppm Cu<sup>2+</sup>, Flow rate = 29.1 ml. min.<sup>-1</sup> = 11.4 ml.cm.<sup>-2</sup>min.<sup>-1</sup>  
15 minute interval between samples

SAMPLE	0	1	2	3	4	5	6	7
C	97.5	35.5	55.5	62.3	69.5	80.	84.	86.5
C/C <sub>0</sub>		0.36	0.55	0.62	0.7	0.8	0.84	0.87

SAMPLE	8	9	10	11	12	13	14
C	88.	88.5	89.3	90.8	91.5	92.5	93.
C/C <sub>0</sub>	0.88	0.89	0.89	0.91	0.92	0.93	0.93

500 ppm Cu<sup>2+</sup>, Flow rate = 26. ml. min.<sup>-1</sup> = 10.2 ml.cm.<sup>-2</sup>min.<sup>-1</sup>  
10 minute interval between samples

SAMPLE	0	1	2	3	4	5	6	7
C	460.	360.	406.	437.	440.	450.	470.	460.
C/C <sub>0</sub>		0.78	0.88	0.95	0.96	0.98	1.02	1.

200 ppm Cu<sup>2+</sup>, Flow rate = 26.4 ml. min.<sup>-1</sup> = 10.4 ml.cm.<sup>-2</sup>min.<sup>-1</sup>  
15 minute interval between samples

SAMPLE	0	1	2	3	4	5	6	7
C	210.	142.	166.	169.	170.	175.	178.	179.
C/C <sub>0</sub>		0.68	0.79	0.8	0.81	0.83	0.85	0.85
SAMPLE	8	9	10	11	12	13		
C	184.	189.	184.	186.	185.	190.		
C/C <sub>0</sub>	0.88	0.9	0.88	0.89	0.88	0.9		

TABLE 19. RESULTS ON EXPERIMENTS WITH THE LARGER COLUMN ARE SHOWN IN THE FOLLOWING TABLES, THIS TABLE GIVES THE DETAILS OF THE COLUMN USED.

INTERNAL DIAMETER 2.7 cm. (Cross-section  $5.73 \text{ cm}^2$ )

15 g. of vermiculite (usual charge) - 7 hour experiments

Bed Height - 18 cm.

Aspect Ratio - 6.7

10 g. of vermiculite (charge) - 12 hour experiments

Bed Height - 13 cm.

Aspect Ratio - 4.8

TABLE 20. COLUMN PROCESS, COPPER EXCHANGE / MICRON VERMICULITE

FLOW RATE ml.cm. <sup>-2</sup> min. <sup>-1</sup>		TIME (hours)							
		$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
0.51	C C/C <sub>0</sub>	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.
0.7	C C/C <sub>0</sub>	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.
0.95	C C/C <sub>0</sub>	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.
1.18	C C/C <sub>0</sub>	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0.5 0.01	1.5 0.02	3. 0.03
1.55	C C/C <sub>0</sub>	0. 0.	0. 0.	0. 0.	5. 0.05	7.5 0.08	13.5 0.14	18.5 0.19	23. 0.23
2.77	C C/C <sub>0</sub>	16.5 0.17	21.5 0.22	31. 0.31	38. 0.38	44. 0.44	49.5 0.5	55. 0.55	54. 0.54
4.19	C C/C <sub>0</sub>	38. 0.38	47. 0.47	58. 0.58	65. 0.65	69. 0.69	70. 0.7	73. 0.73	76. 0.76
13.2	C C/C <sub>0</sub>	68.5 0.69	79. 0.79	83. 0.83	85. 0.85	88. 0.88	90. 0.9	92.5 0.93	93. 0.93
		TIME (hours)							
		$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7	$7\frac{1}{2}$	
0.51	C C/C <sub>0</sub>	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	
0.7	C C/C <sub>0</sub>	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	0. 0.	1.8 0.02	
0.95	C C/C <sub>0</sub>	3. 0.03	4.5 0.05	8. 0.08	11. 0.11	14. 0.14	18. 0.18		
1.18	C C/C <sub>0</sub>	6.5 0.65	10. 0.1	15. 0.15	19. 0.19	22.5 0.23	28. 0.28		
1.55	C C/C <sub>0</sub>	28. 0.28	32. 0.32	34.5 0.35	37.5 0.38	37. 0.37	38. 0.38		
2.77	C C/C <sub>0</sub>	55. 0.55	55.5 0.56	61.5 0.62	63.5 0.64	65. 0.65	68.5 0.69		
4.19	C C/C <sub>0</sub>	79. 0.79	81. 0.81	81. 0.81	83. 0.83	85. 0.85	86. 0.86		
13.2	C C/C <sub>0</sub>	98. 0.98	96.5 0.97	96.5 0.97	91. 0.91	91. 0.91	89.5 0.9		



TABLE 21. COLUMN PROCESS, COPPER EXCHANGE / SUPERFINE VERMICULITE

FLOW RATE ml.cm. <sup>-2</sup> min. <sup>-1</sup>		TIME (hours)							
		$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
0.64	C	0.	0.	0.	0.	0.	1.	2.5	5.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.01	0.03	0.05
0.76	C	0.	0.	0.	2.	5.	9.	13.5	18.
	C/C <sub>0</sub>	0.	0.	0.	0.02	0.05	0.09	0.14	0.18
1.36	C	0.	5.	15.	23.5	38.5	41.5	43.	50.5
	C/C <sub>0</sub>	0.	0.05	0.15	0.24	0.39	0.42	0.43	0.51
2.08	C	4.5	19.5	31.	39.5	46.	51.	56.	59.5
	C/C <sub>0</sub>	0.05	0.2	0.31	0.4	0.46	0.51	0.56	0.6
		TIME (hours)							
		$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7		
0.64	C	7.5	9.5	13.	16.	19.	21.		
	C/C <sub>0</sub>	0.08	0.1	0.13	0.16	0.19	0.21		
0.76	C	22.	26.5	28.5	31.	34.	36.		
	C/C <sub>0</sub>	0.22	0.27	0.29	0.31	0.34	0.36		
1.36	C	54.	58.5	62.5	65.	67.5	69.5		
	C/C <sub>0</sub>	0.54	0.59	0.63	0.65	0.68	0.7		
2.08	C	63.	65.5	69.	72.	74.	75.		
	C/C <sub>0</sub>	0.63	0.66	0.69	0.72	0.74	0.75		

TABLE 22. COLUMN PROCESS, ZINC EXCHANGE / MICRON VERTICULITE

FLOW RATE ml.cm. <sup>-2</sup> min. <sup>-1</sup>		TIME (hours)							
		$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
0.41	C	0.	0.	0.	0.	0.	0.	0.	0.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.
0.73	C	0.	0.	0.	0.	0.	0.	0.	0.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.
0.84	C	0.	0.	0.	0.	0.	0.	0.	0.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.
0.95	C	0.	0.	0.	0.	0.	0.	0.	0.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.
1.07	C	0.	0.	0.	0.	0.	0.	0.	4.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.04
1.32	C	0.	0.	0.	1.6	4.8	7.6	11.6	17.
	C/C <sub>0</sub>	0.	0.	0.	0.02	0.05	0.08	0.12	0.17
1.91	C	0.	0.	5.6	11.6	19.6	27.	35.2	42.
	C/C <sub>0</sub>	0.	0.	0.06	0.12	0.2	0.27	0.35	0.42

		TIME (hours)						
		$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7	$7\frac{1}{2}$
0.41	C	0.	0.	0.	0.	0.	0.	0.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.
0.73	C	0.	0.	0.	0.	3.4	10.8	16.8
	C/C <sub>0</sub>	0.	0.	0.	0.	0.03	0.11	0.17
0.84	C	0.	0.	0.	1.6	5.6	7.6	11.6
	C/C <sub>0</sub>	0.	0.	0.	0.02	0.06	0.08	0.12
0.95	C	0.	3.	5.6	9.6	14.4	18.	18.
	C/C <sub>0</sub>	0.	0.03	0.06	0.1	0.14	0.18	0.18
1.07	C	7.6	12.8	21.6	26.8	33.6	40.	44.
	C/C <sub>0</sub>	0.08	0.13	0.22	0.27	0.34	0.4	0.44
1.32	C	24.4	27.6	36.4	41.6	48.4	53.6	
	C/C <sub>0</sub>	0.24	0.28	0.36	0.42	0.48	0.54	
1.91	C	48.	57.2	59.	66.4	66.4	69.6	71.6
	C/C <sub>0</sub>	0.48	0.57	0.59	0.66	0.66	0.69	0.72

TABLE 23. COLUMN PROCESS, ZINC EXCHANGE / SUPERFINE VERMICULITE

FLOW RATE ml.cm. <sup>-2</sup> min. <sup>-1</sup>		TIME (hours)							
		$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
0.99	C	0.	0.	0.	4.8	7.	10.	10.4	13.6
	C/C <sub>0</sub>	0.	0.	0.	0.05	0.07	0.1	0.1	0.14
1.14	C	0.	0.	4.4	9.0	15.6	21.	28.	34.4
	C/C <sub>0</sub>	0.	0.	0.4	0.9	0.16	0.21	0.28	0.34
		TIME (hours)							
		$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7	$7\frac{1}{2}$	
0.99	C	18.	20.8	34.4	40.	46.4	50.	52.	
	C/C <sub>0</sub>	0.18	0.21	0.34	0.4	0.46	0.5	0.52	
1.14	C	38.	42.8	47.	51.6	54.4	56.8	61.	
	C/C <sub>0</sub>	0.38	0.43	0.47	0.52	0.54	0.57	0.61	

TABLE 24. COLUMN PROCESS, NICKEL EXCHANGE / MICRON VERICULITE

FLOW RATE ml.cm. <sup>-2</sup> min. <sup>-1</sup>		TIME (hours)							
		$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
0.85	C	0.	0.	0.	0.	0.	0.	0.	0.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.
1.19	C	0.	0.	0.	0.	0.	0.	0.	2.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.02

		TIME (hours)						
		$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7	
0.85	C	0.	0.	1.	3.	6.	9.	
	C/C <sub>0</sub>	0.	0.	0.01	0.03	0.06	0.09	
1.19	C	3.	5.	8.	10.	17.	20.	
	C/C <sub>0</sub>	0.3	0.05	0.08	0.1	0.17	0.2	

TABLE 25. COLUMN PROCESS, NICKEL EXCHANGE / SUPERFINE VERMICULITE

FLOW RATE ml.cm. <sup>-2</sup> min. <sup>-1</sup>		TIME (hours)							
		$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
0.7	C	0.	0.	0.	0.	0.	0.	0.	3.
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.03
1.18	C	0.	0.	2.	4.	10.	11.	20.	23.
	C/C <sub>0</sub>	0.	0.	0.02	0.04	0.1	0.11	0.2	0.23
		TIME (hours)							
		$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7		
0.7	C	4.	7.	10.	14.	17.	21.		
	C/C <sub>0</sub>	0.04	0.07	0.1	0.14	0.17	0.21		
1.18	C	24.	30.	33.	38.	44.	48.5		
	C/C <sub>0</sub>	0.24	0.3	0.33	0.38	0.44	0.49		

TABLE 26. COLUMN PROCESS, CHROMIUM EXCHANGE / MICRON VERMICULITE

FLOW RATE ml. cm. <sup>-2</sup> min. <sup>-1</sup>		TIME (hours)								
		$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4	
0.34	C	0.	0.	0.	0.	0.	0.	0.	0.	
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.	0.	
0.65	C	0.	0.	0.	0.	0.	0.	4.3	9.	
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.	0.04	0.09	
0.87	C	0.	0.	4.	12.	20.	27.5	28.5	31.5	
	C/C <sub>0</sub>	0.	0.	0.04	0.12	0.2	0.28	0.29	0.32	
1.09	C	0.	2.5	10.	20.	26.5	34.	39.5	43.	
	C/C <sub>0</sub>	0.	0.03	0.1	0.2	0.27	0.34	0.4	0.43	
		TIME (hours)								
		$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7			
0.34	C	0.	0.	0.	0.	0.	0.			
	C/C <sub>0</sub>	0.	0.	0.	0.	0.	0.			
0.65	C	13.	16.5	21.	23.	28.	33.			
	C/C <sub>0</sub>	0.13	0.17	0.21	0.23	0.28	0.33			
0.87	C	35.	41.	42.5	45.5	48.5	51.5			
	C/C <sub>0</sub>	0.35	0.41	0.43	0.46	0.49	0.52			
1.09	C	48.	50.	54.	55.	52.	51.			
	C/C <sub>0</sub>	0.48	0.5	0.54	0.55	0.52	0.51			

TABLE 27. COLUMN PROCESS, CHROMIUM EXCHANGE / SUPERFINE VERMICULITE

FLOW RATE ml.cm. <sup>-2</sup> min. <sup>-1</sup>		TIME (hours)							
		$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$	4
0.69	C	0.	4.	14.	27.	39.	46.	51.	59.
	C/C <sub>0</sub>	0.	0.04	0.14	0.27	0.39	0.46	0.51	0.59
1.13	C	8.	34.	54.	62.	66.	72.	73.	74.
	C/C <sub>0</sub>	0.08	0.34	0.54	0.62	0.66	0.72	0.73	0.74
		TIME (hours)							
		$4\frac{1}{2}$	5	$5\frac{1}{2}$	6	$6\frac{1}{2}$	7		
0.69	C	63.	63.	65.	68.	70.	76.		
	C/C <sub>0</sub>	0.63	0.63	0.65	0.68	0.7	0.76		
1.13	C	74.	76.	74.	76.	73.	78.5		
	C/C <sub>0</sub>	0.74	0.76	0.74	0.76	0.73	0.79		

TABLE 28. COLUMN PROCESS, ZINC EXCHANGE / 12 HOUR EXPERIMENTS

M -micron, S - superfine

FLOW RATE		TIME (hours) - 100 ppm initial concentration						
ml.cm. <sup>-2</sup> min. <sup>-1</sup>		$\frac{1}{2}$	1	2	3	4	5	6
M 1.57	mg.l. <sup>-1</sup>	1.2	7.6	29.2	49.2	62.4	69.	80.
	meq.l. <sup>-1</sup>	0.04	0.23	0.89	1.51	1.91	2.11	2.45
	C/C <sub>o</sub>	0.01	0.08	0.29	0.49	0.62	0.69	0.8
S 1.39	mg.l. <sup>-1</sup>	13.6	23.2	39.2	51.	63.6	68.	70.4
	meq.l. <sup>-1</sup>	0.42	0.71	1.2	1.56	1.94	2.08	2.15
	C/C <sub>o</sub>	0.14	0.23	0.39	0.51	0.64	0.68	0.7
		TIME (hours)						
		7	8	9	10	11	12	
M 1.57	mg.l. <sup>-1</sup>	83.	88.	88.8	91.6	93.6	91.6	
	meq.l. <sup>-1</sup>	2.54	2.69	2.72	2.8	2.86	2.8	
	C/C <sub>o</sub>	0.83	0.88	0.89	0.92	0.94	0.92	
S 1.39	mg.l. <sup>-1</sup>	75.2	83.6	83.6	86.4	88.8	90.8	
	meq.l. <sup>-1</sup>	2.3	2.56	2.56	2.64	2.72	2.78	
	C/C <sub>o</sub>	0.75	0.84	0.84	0.86	0.89	0.91	
		TIME (hours) - 50 ppm initial concentration						
		$\frac{1}{2}$	1	2	3	4	5	6
M 2.02	mg.l. <sup>-1</sup>	0.8	1.2	5.2	13.2	17.8	22.5	26.6
	meq.l. <sup>-1</sup>	0.03	0.04	0.16	0.4	0.54	0.69	0.81
	C/C <sub>o</sub>	0.02	0.02	0.1	0.26	0.36	0.45	0.53
S 1.79	mg.l. <sup>-1</sup>	2.2	4.8	13.6	20.	23.6	27.2	30.2
	meq.l. <sup>-1</sup>	0.07	0.15	0.42	0.61	0.72	0.83	0.92
	C/C <sub>o</sub>	0.04	0.1	0.27	0.4	0.47	0.54	0.6
		TIME (hours)						
		7	8	9	10	11	12	
M 2.02	mg.l. <sup>-1</sup>	33.8	35.6	36.4	38.4	39.5	41.4	
	meq.l. <sup>-1</sup>	1.03	1.09	1.11	1.17	1.21	1.27	
	C/C <sub>o</sub>	0.68	0.71	0.73	0.77	0.79	0.83	
S 1.79	mg.l. <sup>-1</sup>	33.2	34.2	35.6	35.	35.		
	meq.l. <sup>-1</sup>	1.02	1.05	1.09	1.07	1.07		
	C/C <sub>o</sub>	0.66	0.68	0.71	0.7	0.7		



APPENDIX 2

ANALYSIS PROCEDURE

METALS IN INDUSTRIAL WATER AND INDUSTRIAL WASTE WATER BY ATOMIC  
ABSORPTION SPECTROPHOTOMETRY . . . . . ASTM D.2576

This procedure covers the determination of dissolved metals, detected by atomic absorption spectrophotometry.

TABLE 29

METAL	CONCENTRATION RANGE mg.l. <sup>-1</sup>	WAVELENGTH nm	FUEL	OXIDANT
Chromium (Cr <sup>3+</sup> )	0.2 - 20	357.9	C <sub>2</sub> H <sub>2</sub>	AIR
Copper (Cu <sup>2+</sup> )	0.1 - 20	324.7	C <sub>2</sub> H <sub>2</sub>	AIR
Nickel (Ni <sup>2+</sup> )	0.08 - 20	232.	C <sub>2</sub> H <sub>2</sub>	AIR
Zinc (Zn <sup>2+</sup> )	0.02 - 3	213.8	C <sub>2</sub> H <sub>2</sub>	AIR

NOTE: The concentration ranges for Chromium and Nickel given by this standard could not be achieved, the upper limit had to be about 100 ppm.

The upper limits of detection can, clearly, be increased by dilution and the lowest limit is dependent on the machine being used. The lowest concentration is usually considered to be equal to twice the maximum variation of the background.

METHOD - The method is dependent on the fact that metallic elements, in the ground state, absorb light of the wavelength they emit when excited. When radiation from a given source, of the element under test, is passed through a flame containing ground state atoms of that element the intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the flame. A hollow cathode lamp, whose cathode is made of the element to be determined, forms the standard source of the radiation. The metal atoms to be measured are placed in the beam of radiation by aspirating the specimen into an oxidant/fuel flame. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a

photosensitive device measures the attenuated transmitted radiation.

DEFINITIONS - For definitions of the terms used refer to ASTM D.1129.

INTERFERENCES - No interferences are specifically listed for the metals under test. In general the most common interference is caused by chemical reactions in the flame which prevent the conversion of the metal under test to the atomic state. Certain anions, also, cause low results by forming insoluble compounds in the flame.

INSTRUMENT - The instrument shall consist of an atomiser and burner, suitable pressure regulating devices capable of maintaining constant oxidation and fuel pressure for the duration of the test, a hollow cathode lamp for each metal (multi-element lamps have been found to be satisfactory) to be tested, an optical system capable of isolating the desired line of radiation, an adjustable slit, a photomultiplier tube or other photosensitive device as a light measuring and amplifying device, and a read-out mechanism for indicating the amount of absorbed radiation.

The instrument used was the PYE-UNICAM SP.90 Atomic Absorption Spectrophotometer. This was used in conjunction with hollow cathode lamps supplied by Activion Glass Ltd.

TABLE 30 ACTIVION HOLLOW CATHODE LAMPS

METAL	ABSORBING LINE nm		FILLER GAS	WINDOW	CURRENT mA	
	most sensitive	alternatives			Operating	Max.
Cr <sup>3+</sup>	357.9	429. 520.4 520.8	NEON	QUARTZ	5	25
Cu <sup>2+</sup>	324.8	222.6 244.2 249.2 327.4	NEON	QUARTZ	5	25
Ni <sup>2+</sup>	232.				5	25
Zn <sup>2+</sup>	213.9	307.6	NEON	QUARTZ	15	25

Note. The maximum current must not be exceeded as damage to the cathode would result and also self-absorption or line broadening of the spectral output may occur, which would reduce absorbance readings. The operating current is that recommended for good results and long life.

OXIDANT - Air

FUEL - Commercial acetylene is the usual fuel. The acetone always present can be prevented from entering the system by not using cylinders once the pressure has dropped below 100 psig.

PURITY OF REAGENTS - as specified by ASTM Methods E200, Preparation, Standardisation, and Storage of Standard Solutions for Chemical Analysis.

PURITY OF WATER - As specified by ASTM Specifications D1193, for Reagent Water, Type I.

#### STANDARD SOLUTIONS

- i) CHROMIUM (1ml = 1.0 mg.  $\text{Cr}^{3+}$ ) - 6.369 g of Chromic Sulphate,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ , dissolved in 200 ml. of water and diluted to 1 liter.
- ii) COPPER (1 ml = 1.0 mg.  $\text{Cu}^{2+}$ ) - 1 g. of electrolytic copper dissolved in a mixture of 15 ml.  $\text{HNO}_3$  (sp gr 1.42) and 15 ml. water. 4 ml. of  $\text{H}_2\text{SO}_4$  (1+1) was added and the mixture heated to evolve  $\text{SO}_3$  fumes. After cooling the residue was diluted to 1 liter with water.
- iii) NICKEL (1 ml. = 1.0 mg.  $\text{Ni}^{2+}$ ) - 4.78 g. of Nickel Sulphate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , dissolved in 200 ml. of water and diluted to 1 liter.
- iv) ZINC (1 ml. = 0.1 mg  $\text{Zn}^{2+}$ ) - 0.1245 g of zinc oxide,  $\text{ZnO}$ , dissolved in a mixture of 10 ml.  $\text{HCl}$  (sp gr 1.19) and 10 ml. of water. Then diluted to 1 liter with water.

#### CALIBRATION, STANDARDISATION AND OPERATION

- a) Prepare standard solutions to bracket the expected concentration

of the solution under test. This must be done each time a test is carried out.

b) Operate the instrument in accordance with the manufacturers handbook, but as a guide to operation:

- i) switch on instrument,
- ii) apply current to the cathode lamp and allow time for the instrument to stabilise. Usually 10-20 mins.,
- iii) set slit width as recommended by the manufacturer, and set wavelength for element under test,
- iv) feed fuel and oxidant to burner as recommended and ignite the mixture,
- v) atomise water and check aspiration rate, usually a rate of  $4-5 \text{ ml. min.}^{-1}$  is suitable. Both samples and standards should be exposed to the same rate,
- vi) adjust wavelength to give most sensitive operation,
- vii) atomise standards and note readings. Remember to atomise water between each standard,
- viii) prepare calibration curve by plotting standard values on linear graph paper, absorbance vs standard concentration for each standard,
- ix) atomise sample and record reading. Atomise water between each sample to rinse the instrument,
- x) read off concentrations of sample from calibration curve.

PRECISION - Determined from master solutions. The precision for the metals detected may be expressed by:

$$\text{CHROMIUM (Cr}^{3+}\text{): } S_t = 0.094X + 0.04; S_o = 0.014X + 0.01$$

$$\text{COPPER (Cu}^{2+}\text{): } S_t = 0.038X + 0.03; S_o = 0.020X + 0.02$$

$$\text{NICKEL (Ni}^{2+}\text{): } S_t = 0.024X + 0.04; S_o = 0.010X + 0.03$$

ZINC ( $\text{Zn}^{2+}$ ):  $S_t = 0.050X + 0.01$ ;  $S_o = 0.013X + 0.005$

where  $S_t$  = overall precision,  $\text{mg.l.}^{-1}$   
 $S_o$  = single operator precision,  $\text{mg.l.}^{-1}$   
 $X$  = concentration of metal determined,  $\text{mg.l.}^{-1}$ .

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