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BATCH FLUIDIZED ION-EXCHANGE COLUMN FOR STREAMS CONTAINING SUSPENDED PARTICLES

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SUMMARY

Experiments are described with a fluidized ion-exchange column in which backmixing of the exchanger is prevented by horizontal perforated plates. Over a certain range of liquid velocities the resin distributes itself over a series of fluidized beds between which there is no transfer of resin. This reduces backmixing so that the column can be used for processes involving a fluidized batch of resin.

The break-through of the column can be quite accurately simulated by a numerical model which describes the column as a series of well mixed compartments with a mass-transfer resistance between the phases. Break-through curves for systems with not too low selectivities are sufficiently sharp for many process applications.

The column has disadvantages compared with conventional packed columns: its volume is larger, the separation sharpness is less and the range of operating velocities is limited. However, it has one advantage which may be important: liquids containing fine suspended particles can be processed (if these do not foul the ion exchanger).

INTRODUCTION

Ion exchange is usually carried out in a packed column, where the ions to be removed from the liquid passing through are exchanged with ions from the resin. Such a column is relatively simple to construct, can be used over a wide range of flow velocities and it can give sharp separations. However, a packed column is not suitable for streams containing particles.

If the particles do not play a role in the exchange process they can be removed by filtration. This is an extra process step which is not always necessary. If the particles are formed or dissolved during the exchange they have to pass through the exchanger bed. A packed column is then useless. However, the particles may well pass through a fluidized bed of ion exchanger beads (Fig. 1).

Fluidized beds have applications in continuous countercurrent processes¹, but very little has been published on batch fluidized columns. These may be expected to be useful in cases where relatively small amounts of ions are to be removed and the loading time of the resin is large. The main problem of fluidized beds is the mixing of

the resin. This can cause loaded beads to move up to the exit of the column. They can then exchange their contents again and so drastically reduce the separation sharpness (Fig. 2).



Fig. 1. A packed column will be blocked by particles, a fluid bed will not.

Fig. 2. Fluidized beads can transport sorbed ions to the outlet and lose them again.

This paper describes a column in which a batch of exchanger is fluidized. Horizontal perforated plates are used (Fig. 3) to reduce the backmixing. It might be thought that these would simply damp the turbulent eddies in the fluidized bed. We have found, however, that a very different and much more effective mechanism occurs, at least over a limited range of operating conditions.

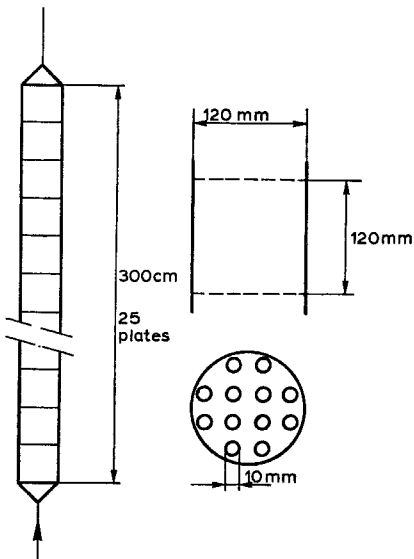


Fig. 3. Column and plate dimensions.

THE COLUMN

The column (3×0.12 m I.D.) (Fig. 3) is fitted with 25 plates with a distance of 0.12 m between each. In most of the experiments described here the plates have twelve holes with a diameter of 10 mm. This gives a free area fraction (FAF) of 0.082.

A few experiments are also included using plates with twelve holes of diameter 4 mm (FAF = 0.013). The column is fed from below; the liquid flow-rate can be adjusted and metered between 0.02 and 0.25 l/sec.

The resin used was an ordinary batch of a strong acid cation exchanger, Lewatit S 100. The bead-size distribution as determined by microscopy is given in Fig. 4. The Sauter-mean diameter is 0.63 mm. The density of the wet beads in the Na⁺ form is 1.304 kg/l, and they have a capacity of 3.5 equiv. per litre of solid phase or *ca.* 2.1 equiv. per litre of settled bed.

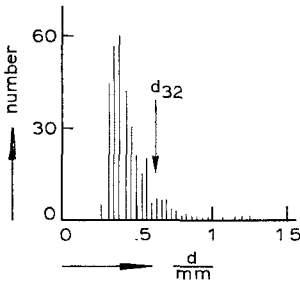


Fig. 4. Size distribution of the resin.

FLOW REGIMES

An expansion curve of the resin fluidized in a tube of diameter 20 mm is given in Fig. 5. The minimum fluidization velocity is 0.8 mm/sec; below this value the resin forms a packed bed with a porosity of 0.38. The porosity increases rapidly with increasing liquid velocity. The smaller beads have a free falling velocity of *ca.* 15 mm/sec; at this point they are driven out of the bed.

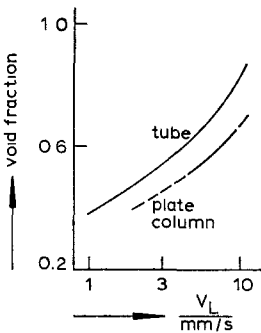


Fig. 5. Expansion of a resin bed as a function of the fluidization velocity.

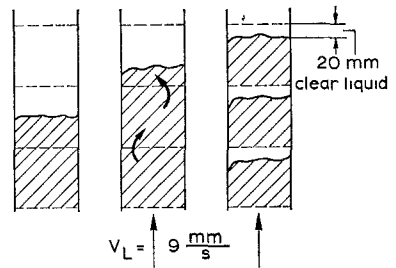


Fig. 6. The way the resin distributes itself when the column is started.

The fluidization characteristics on a tray are similar, but the bed expansions are lower. At liquid velocities above 11 mm/sec a large part of the beds is driven out of the column; also the volume of the column will be poorly utilized as the void fraction is large. At 9.5 mm/sec about one third of the column volume is occupied by the resin. Most experiments described here have been done at this velocity.

It might be thought that the lower operating limit would be the minimum fluidization velocity. But this turns out to be too optimistic. We will come back to this point later.

The column is filled initially to about one half of its height with resin (this corresponds to a volume fraction of one third). The liquid flow is then turned on to its maximum value and the resin passes through the holes of the trays above (Fig. 6). After a short time it is more or less homogeneously fluidized throughout the greater part of the column. As the liquid in the holes has a much higher velocity than that on the tray it entrains beads so that a layer of clear liquid of thickness *ca.* 20 mm develops below each tray. Once this has happened there is no further transport of the resin between the trays. Each tray behaves as a separate compartment. It is this mechanism which eliminates top-to-bottom mixing and allows reasonable separations to be obtained.

Once the column has been started small reductions of the flow-rate have little effect. The velocity in the tray holes is sufficient to prevent beads falling through and the only effect is a decrease of the bed height. With a further decrease of the flow-rate, however, the beads begin to fall through the tray, and this will reduce the separation sharpness (Fig. 7). The ratio between the maximum flow-rate and the "raining-through" limit is very sensitive to the free area fraction of the tray. With the original trays (FAF = 0.082) the liquid velocity could only be reduced from a maximum of 11 mm/sec to 6 mm/sec. Subsequent experiments have shown however that the operating range can be increased substantially. With an FAF of 0.013 no raining through was observed down to a liquid velocity of 0.4 mm/sec. Raining through always starts at a single hole. At the raining point the average hole velocity is still about 1.5 times higher than the free falling velocity of the largest beads. So the raining phenomenon seems to be related to the development of non-uniform flow through the holes.

When the liquid flow is shut off the resin drains to the lower part of the column. This is a very slow process; with trays having an FAF of 0.013 it takes *ca.* 1 h because the falling beads have to displace an equal volume of liquid upward through the tray holes. So short interruptions of the operation are not expected to alter significantly the resin distribution in the column.

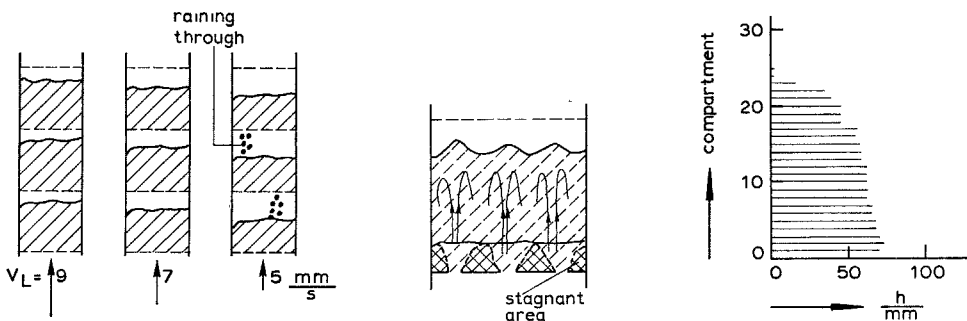


Fig. 7. Effect of reducing the flow-rate.

Fig. 8. The flow pattern on a tray.

Fig. 9. The distribution of resin over the trays (heights of the settled resin beds).

Our column is transparent so the flow on the tray can be observed. It is best described as that of a "multiple spouted bed" (Fig. 8). Jets of liquid entraining beads issue from the holes. The liquid and the beads separate at the top of the bed and the beads are circulated. At flow-rates near the maximum almost the whole bed is in a wavy-eddy type of motion. Only in the lower corners of the tray are small stagnant zones, probably a few percent of the tray volume. At the lower fluidization velocities which can be used with trays having a small free area, larger parts of the bed are stagnant or only moving sluggishly. It is probably better to use velocities greater than 2 mm/sec.

The resin distribution on the trays is not uniform. The relative amounts of resin on the trays can be determined by shutting down the column, allowing the beads to settle on the tray and measuring the bed height before significant raining through has occurred. A typical set of data is shown in Fig. 9. A considerable classification of beads occurs, the smaller ones preferentially occupying the higher trays. It may be possible to improve the distribution by using a narrow bead-size distribution, but we have not investigated this.

PULSE EXPERIMENTS

Further information on the liquid flow pattern in the column can be obtained from pulse-response experiments. In these experiments the column is fluidized by deionized water and the resin is in the sodium form. At a given moment the feed is deflected through a by-pass tube containing 125 ml of a 0.1 *M* NaCl solution. The pulse is detected at the column outlet by a conductivity meter. A typical result is given in Fig. 10. The reproducibility of these measurements is very good.

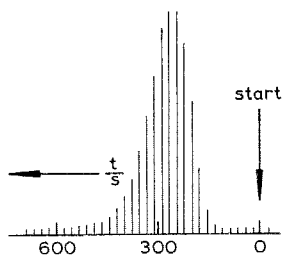


Fig. 10. The response at the outlet of the column to a pulse of NaCl at the inlet.

Because the resin is in the Na^+ form there is no ion exchange as the pulse passes through the column. There does seem to be a little adsorption; the average residence time of the tracer is 9% longer than that of the liquid.

The results can be interpreted as the pulse response of a series of stirred vessels². The number of vessels computed from Fig. 10 (using "the method of moments") is 21. The difference between this and the actual number of stages (25) is probably due to the adsorption noted above.

AN ION-EXCHANGE EXPERIMENT

To test the column we have done a number of experiments in which sodium is displaced by potassium.

The selectivity of the resin for potassium is not large (Fig. 11). If the equilibrium is described by

$$y = \frac{\alpha x^*}{1 + (\alpha - 1) x^*}$$

the separation factor α varies between 1.5 and 1.7 (y and x^* are the fractions of the potassium cations in the resin and in the solution). This low selectivity yields rather broad and unfavourable break-through curves. However, these do allow an accurate assessment of the mass-transfer performance of the column.

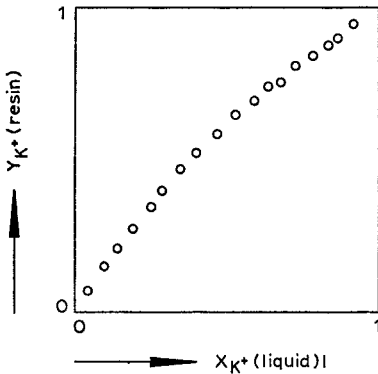


Fig. 11. The equilibrium distribution of K^+ between the resin and the liquid $C_{K^+} + C_{Na^+} = 0.1$ mol/l.

In the experiment described here resin in the Na^+ form is brought into the column and fluidized with deionized water until 23 trays are occupied by beads. One then switches to a 0.100 M KCl solution and K^+ exchanges with Na^+ . Samples of both the clear liquid and the bed contents are taken from compartment 11 every 5 or 6 min. The top compartments are not sampled because they are not so well defined). Also, determination of the complete break-through curve of the column requires 1 m³ of feed solution per experiment, which is more than was available.)

The bed samples are rapidly separated into a resin and a liquid fraction by filtration and subsequent washing. This procedure continues for more than 1 h, when the resin concentration in compartment 11 has reached its saturation value. The liquid samples are analyzed by atomic absorption spectrometry. The resin is treated with a $BaCl_2$ solution to remove the Na^+ and K^+ , which are then determined in the same way.

The superficial velocity of the liquid during the experiments was 9.5 mm/sec. The compartments contained an average of 0.42 l of solids and 0.88 l of liquid each. Results are given in Fig. 12. These have been checked with the sodium balance in the eleven compartments. The difference between the amounts calculated from the resin capacity and from the liquid contents is less than 2%.

A MODEL OF THE COLUMN

The flow observations indicate that the column can be described as a series of well mixed compartments. This suggests using the model shown in Fig. 13. This model has the following features:

- Only upward flow of the liquid between the compartments
- No exchange of the resin between the compartments

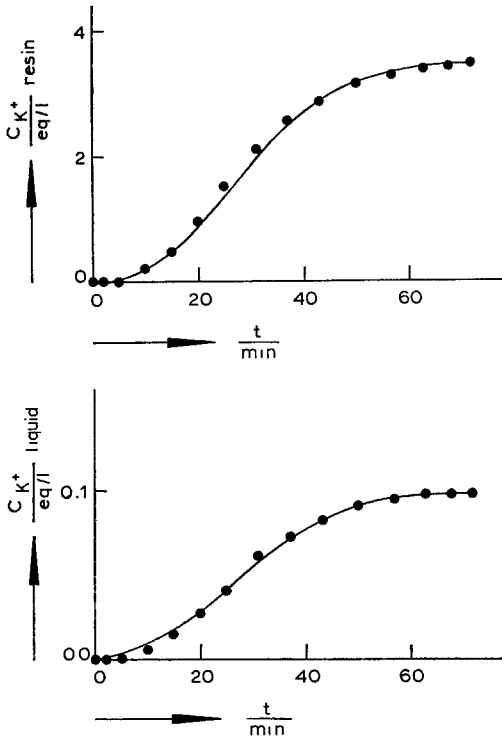


Fig. 12. The potassium concentration of the liquid and the resin in compartment 11. The curves are results of the simulation with $K_{01}a = 0.1 \text{ sec}^{-1}$.

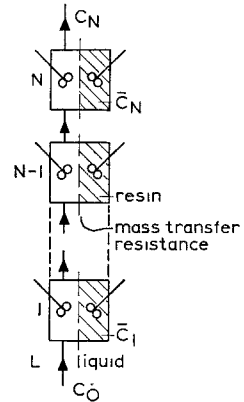


Fig. 13. The model of the column.

The equilibrium distribution of the K^+ is given by a fourth degree polynomial fitted to the data in Fig. 11. From this equation one calculates the concentration c^* of K^+ in the liquid, which would be in equilibrium with the resin concentration \bar{c} :

$$c^* = f(\bar{c})$$

Both phases are well mixed. So each phase is described by a single composition in each compartment

The mass-transfer rate between the liquid and the resin is mainly governed by the diffusional ("film") resistance outside the beads. The transfer rate per unit volume of resin is then given by

$$R = K_{01}a(c - c^*)$$

where c is the liquid concentration of K^+ in the compartment under consideration. The transfer coefficient $K_{ot}a$ is the only fitting parameter in the model.

For each stage one now has the following set of equations:

- the balance of K^+ in the liquid
- the balance of K^+ in the resin
- the balance for the co-ion in the liquid
- the transfer-rate equation
- the equilibrium relation

This set of linear first order differential and non-linear ordinary equations can be solved numerically. Starting with the initial conditions: $t = 0$, $c_0 = 100 \text{ mol/m}^3$, $\bar{c} = c_n = 0 \text{ mol/m}^3$, the evolution of both the liquid and the resin concentrations in the different compartments can be simulated.

The curves in Fig. 12 show the results obtained with the liquid flow-rate and resin capacity as used in the previous experiment. The value $K_{ot}a = 0.1 \text{ sec}^{-1}$ fits the experimental data quite well. (Prior to the experiment, $K_{ot}a$ was estimated from available data³ to have a value of 0.08 sec^{-1} .) The fit can be further improved by including a small concentration-dependent term in the mass-transfer coefficient. This is to allow for the mass resistance inside the beads which is time- and therefore concentration-dependent and not entirely negligible.

CONCLUSION

With the aid of this model we have calculated break-through curves for a larger number of effective compartments ($N = 25$) and higher separation factors such as might be encountered in practice (Fig. 14). Although less favourable than with conventional columns, the attainable separations would seem to be sufficient for many process applications.

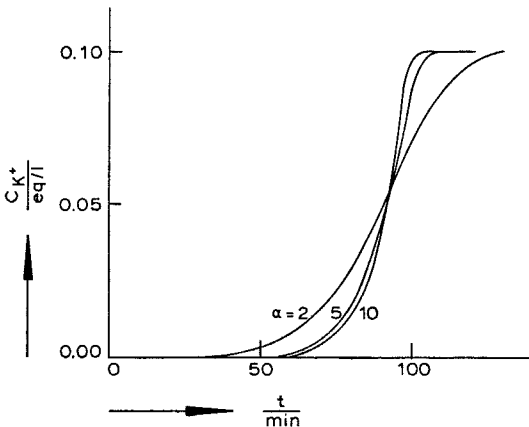


Fig. 14. Break-through curves calculated for different separation factors. $N = 25$; $K_{ot}a = 0.08 \text{ sec}^{-1}$; $V_1 = 9.5 \text{ mm/sec}$.

It is clear that a fluidized plate column has several disadvantages compared with a conventional packed bed:

the separation is not so sharp

the column volume is larger

the system only operates within a limited range of liquid properties and velocities.

It does have one advantage, however: it can process turbid streams. In some cases this may be very important. Of course it will always be necessary to ascertain experimentally that the process streams do not foul the ion exchanger, even though a fluidized bed is "continuously being backwashed".

REFERENCES

- 1 M. J. Slater, *Brit. Chem. Eng.*, 14 (1969) 41.
- 2 O. Levenspiel, *Chemical Reaction Engineering*, Wiley, New York, 2nd ed., 1972.
- 3 M. J. Slater, *Can. J. Chem. Eng.*, 52 (1974) 43.