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COUNTERCURRENT ION EXCHANGE

Final Summary Report

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Final Summary Report

COUNTERCURRENT ION EXCHANGE

I Introduction

The separation or removal of ions by ion exchange operates by transfer between a solid resin phase and a solution phase. Ion separation is concerned with the fractionation of the ions in a solution into two groups, while ion removal involves substantially complete elimination of the ions concerned from the solution. Separations of ions are possible because of differences in affinities of the resin for different ions.

Ion exchange operations are now utilized for treating solutions with ion concentrations of 2500 ppm or less, and are now performed as intermittent processes by passing the solutions through columns of resin, i.e., fixed beds. Stanford Research Institute, however, in an attempt to overcome the usual disadvantages of such cyclic, unsteady-state processes conceived and developed a continuous, countercurrent ion exchange technique.

It seemed evident that the continuous process would be of interest to the Atomic Energy Commission for use in separating materials and in treating waste products. As a result of discussions of this matter, SRI Project CU-337 was established under U.S. AEC Contract AT (11-1)-110, Project Agreement No. 1, on June 25, 1950, and the project was continued until June 30, 1953.

The detailed results of this project are contained in Technical Reports No. I through VIII.* The present report summarizes this information.

II Objectives

The broad and ultimate objective of the project was:

To establish the countercurrent separation or removal of ions by ion exchange as a chemical engineering unit operation.

* A list of the technical reports referred to is appended.

Such a unit operation would have a wide range of application both within and outside the atomic energy field. Moreover, the equipment developed for the process would find application in all fields involving solid-liquid contact, such as adsorption, leaching and catalysis.

More specifically, the project was planned to achieve the following objectives:

1. To develop calculation methods for the design of countercurrent ion exchange equipment.
2. To develop experimental units with good resin-solution contact efficiencies and satisfactory means of transferring the resin between such units.
3. To compare the performance of the experimental equipment with that predicted by the calculation methods.
4. To evaluate the comparative economics of countercurrent ion exchange and of the more conventional fixed bed process.

The first three steps conform to the classic approach in the development of a unit operation or process.

III Theory and Equipment Developments

A. General

A great deal of groundwork preceded the ultimately successful outcome of the project. The early work included studies of a number of calculation methods for countercurrent ion exchange and analogous unit operations. The theory and practice for the better-established fixed bed ion exchange process was also studied to secure a firmer basis for countercurrent process development. The references concerned are listed in the bibliography, Technical Report No. VIII.

On the experimental side, three laboratory models of a continuous countercurrent system were constructed, evaluated, and discarded before satisfactory equipment was developed. Each model was an improvement over the previous one. (The succeeding discussions are concerned with the successful equipment). These preliminary studies are described in Technical Reports No. I and II.

Accurate analytical methods were a prerequisite for the evaluation of equipment. Technical Report No. IV describes the analytical techniques ultimately developed for the ion-resin system used in the experimental program. This system was lithium, potassium, and hydrogen ions exchanging on Chempro C-20 resin with the total metal ion concentration at about 1500 ppm. It was selected for several reasons, mainly because of the ease of analysis and the known separability of the two metal ions.

B. Trace Ion Exchange

In the countercurrent separation of two ions in a feed solution, the ion most strongly held by the resin is selectively removed from the solution. The other ion remains largely in the solution and is contained in the product effluent. The logical first step in an evaluation of this process was to carry out experiments under conditions where the most simple theory applies, so that the results could be interpreted most readily. The simplest case is that in which the ion of interest is very dilute with respect to the total concentration of the solution. Under these conditions--termed "trace"--the equilibrium concentration of the trace ion on the resin is directly proportional to its concentration in the solution, i.e., the equilibrium isotherm is linear.

The separation of trace ions was accomplished in two types of countercurrent resin-solution contactors: an equilibrium stage apparatus and a continuous, countercurrent column.

C. Equilibrium Stage Contactor

In the equilibrium stage contactor, aliquots of resin and solution were mixed together until equilibrium was approached between the two phases. The operation was such that the resin aliquots remained in the several mixing vessels throughout a run, while the solutions were transferred in and out of these vessels automatically to obtain countercurrent resin-solution contact.

For this unit, a theoretical relation was found between the change produced in the concentration of the trace ion, the ratio of the resin and solution aliquot volumes, and the number of contacts between the phases. A number of runs were conducted in which the variables affecting the separation of trace ions were investigated.

Although the performance of the equilibrium stage contactor was predicted accurately and its contact efficiency was practically 100%, it is not as suitable for commercial applications as the continuous column described below. This is because the equilibrium stage contactor is complex equipmentwise, and has the inherent disadvantages of intermittent operations. This leads to high equipment and operating costs. The apparatus appears to be of primary importance in the experimental evaluation of new ion systems for which countercurrent ion exchange is being considered. In this capacity the apparatus can provide the necessary design data, including equilibrium information, quickly and accurately.

The trace theory, the design and operation, and the experimental results for the equilibrium stage contactor are contained in Technical Report No. III.

D. Continuous Column

In the continuous, countercurrent column, contact between the resin and solution occurred in a moving bed of resin, contained in a 4"-diameter glass column. The resin passed downward through the column as a dense moving bed. The feed solution was introduced into the base of the column, flowed continuously upward through the resin bed, and overflowed at the top. This unit incorporated unique resin transfer and dewatering valves to introduce the resin into the top of the column and to remove it at the base.

The continuous column design theory (somewhat analogous to that for the equilibrium stage contactor) relates the change in the concentration of the trace ion with the ratio of the resin and solution flowrates and the number of transfer units.* However, the number of transfer units alone does not fix the design of a continuous column; the height of the moving resin bed represented by each transfer unit must also be known. The height of resin equivalent to a transfer unit is a function of the specific ion system and the design and operating conditions of the column. A correlation was developed which associates the height of a transfer unit with the characteristics of the ion-resin system and the operating variables of the experimental column.

The experimental results of the many continuous column runs correlated well. This indicates that the design method can be used with confidence to calculate the bed height and flow conditions required for countercurrent ion exchange to bring about a specific change in the trace ion concentration.

At low solution-flow velocities, the most favorable resin-solution contact was obtained with an oscillating device that imparted a jiggling motion to the resin bed and which thus reduced channeling. At higher velocities--those of commercial interest--good contact was obtained in the moving resin bed without any such mechanical device.

In general, the continuous column offers the most attractive means for industrial countercurrent ion exchange. No serious scale-up problems are envisioned.

The major aspects of trace exchange in the continuous, countercurrent column are covered in Technical Report No. V.

* The number of transfer units is a mathematical measure of the difficulty of transferring the ion from the solution to the resin. One transfer unit represents an easy exchange; ten, a difficult exchange.

E. Gross Ion Exchange

Ion exchange under gross conditions involves solutions in which the ion of interest is the major constituent. The equilibrium relation between the concentrations of a gross ion in solution and on the resin is no longer linear, and thus the design theory is much more complex. However, since such solutions are frequently treated by ion exchange, it was important to develop equipment design procedures for these applications.

Graphical design methods, similar to those used in distillation design, were developed for predicting the performance of both the equilibrium stage contactor and the continuous, countercurrent column for multi-component gross ion exchange. Feed solutions, containing the same ion species as used for the trace studies but at gross concentrations, were used for experimental runs in both types of laboratory equipment.

The experimental results obtained with the equilibrium stage contactor under gross conditions matched very closely with those predicted by the calculation procedure. Less satisfactory agreement was obtained between the experimental results obtained with the continuous, countercurrent column and the performance predicted by the proposed calculation method. However, the calculated results were of the right order of magnitude, and the method provides something better than an entirely empirical approach to this design problem of gross ion exchange.

The calculation methods for gross ion exchange in both countercurrent contactors, as well as the experimental results, are contained in Technical Report No. VI.

IV Economic Evaluation of Ion Exchange Processes

A. General

The culmination of the project was the comparative engineering evaluation of fixed bed and countercurrent ion exchange processes for the separation and removal of ionic components. This is the subject of Technical Report No. VII. Here all the design procedures described in Technical Reports III, V, and VI were utilized to solve realistic design problems. In this study, fixed bed and countercurrent ion exchange plants were completely designed for given product specifications. At each of these specifications, the total annual costs (fixed charges and operating costs) were determined for each type of plant of the optimum design for the particular product requirement.

B. Separation of Trace Ions

Before discussing the results of the evaluation as it applies to ion separation, it is necessary to point out a fundamental difference between a fixed bed and a single countercurrent unit. The latter is able to achieve only the degree of separation which represents equilibrium between an entering and an exiting countercurrent stream. This theoretical

limit is thus a function of the equilibrium separation factor between the two ions. The degree of separation attainable becomes higher as the ions become more unlike. The fixed bed process, since it operates by a different principle, is not technically limited in the degree of separation attainable with a single unit.

Normally, a high degree of separation would be desired in an ion separation process. If the solution being treated contains easily separated (unlike) ions, so that the separation attainable in a single countercurrent unit is better than that desired, then the continuous unit is cheaper than a fixed bed. Conversely, if the ions of interest are so difficultly separated that the desired degree is greater than is attainable with a single countercurrent unit, multiple units (cascades) would be required, and then the fixed bed process is cheaper. However, if this desired degree of separation is at a point where a single countercurrent unit can be used, even for difficultly separated (similar) ions, then the continuous process is again more economical.

The equilibrium stage contactor was the most expensive throughout the range of separations considered. This was due to its complexity and the intermittent nature of its operation.

C. Ion Removal

The economics of the fixed bed and continuous column were also compared for the removal of both trace and gross ions. Here the continuous process was found to be more economical than the fixed bed for all removal cases, trace and gross, regardless of product specifications. The potential savings offered by the continuous process are greater for gross than for trace removal. When the throughput requirements for trace ion removal were increased, the unit cost was reduced for both processes, the reduction being greater for the continuous process. Thus the use of the continuous column is even more economical at high feed rates.

V Principal Accomplishments and Conclusions

1. Major progress was made toward the ultimate objective of establishing countercurrent ion exchange as a unit operation. The need still remains for pilot-plant or commercial scale operations to assess the scale-up factors involved, and additional work is necessary to perfect the gross calculation methods.

2. Two successful types of countercurrent ion exchange equipment were developed.

3. Separations of unlike ions could be carried out in these contactors over a wide range of solution concentrations and operating conditions.

4. The performance of the equipment was predicted accurately by calculation methods based on fundamental concepts.

5. For commercial-scale removal of ions, the continuous, counter-current process developed on this project is definitely more economical than the traditional fixed bed process.

6. On the other hand, the fixed bed process may sometimes be more economical than the continuous process for the separation of ions, the choice depending on the ion system.

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