

57

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0353035 6

ORNL 1310 *Ja*
Chemistry-Separation Process for
Plutonium and Uranium

DOE 1979 REVIEW OF
DECLASSIFIED REPORTS

This Document is Properly Declassified,
Reviewed by P. S. Eaker
ORNL Classification Officer

DECLASSIFIED

CLASSIFICATION CHANGED BY: *212-1112*
AUTHORITY: *K. Page 4/23/97*

INV. 82

**A COUNTERCURRENT SOLID-LIQUID CONTACTOR
FOR CONTINUOUS ION EXCHANGE**

55
57



CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this document,
send in name with document and the library will
arrange a loan.

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION



POST OFFICE BOX P
OAK RIDGE, TENNESSEE

~~SECRET~~

INTERNAL DISTRIBUTION

- | | | |
|---|-----------------------|----------------------|
| 1. G. T. Felbeck (C&CCC) | 22. E. D. Shipley | 38. W. K. Eister |
| 2-3. Chemistry Library | 23. F. C. Vonderlage | 39. F. R. Bruce |
| 4. Physics Library | 23-24. L. Steahly | 40. F. L. Culter |
| 5. Biology Library | 25. C. Brian | 41. J. O. Davis |
| 6. Health Physics Library | 26. J. Swatout | 42. H. K. Jackson |
| 7. Metallurgy Library | 27. S. Lind | 43. D. D. Cowen |
| 8-9. Training School Library | 28. A. H. Bell | 44. J. Reyling |
| 10. Reactor Experimental
Engineering Library | 29. A. Hollander | 45. J. Higgins |
| 11-14. Central File | 30. M. T. Kealey | 46. J. Roberts |
| 15. C. E. Center | 31. K. Z. Morley | 47. J. E. Blanco |
| 16. E. Larson | 32. J. Felton | 48. K. A. Maus |
| 17. W. B. Humes (K-25) | 33. A. B. Householder | 49. M. J. Skinner |
| 18. L. B. Emlet (Y-12) | 34. C. S. Harrill | 50. S. H. Jury |
| 19. A. M. Weinberg | 35. E. Winters | 51. W. R. Winbro |
| 20. E. H. Taylor | 36. D. W. Cardwell | 52. J. Shacter, K-25 |
| | 37. E. M. King | |

EXTERNAL DISTRIBUTION

- 50-61. Argonne National Laboratory (1 copy to Jack Schubert)
- 62. Armed Forces Special Weapons Project (Sandia)
- 63. Armed Forces Special Weapons Project (Washington)
- 64-70. Atomic Energy Commission, Washington
- 71-74. Brookhaven National Laboratory (1 copy to David Ballantine)
- 75-76. California Research and Development Company
- 77. Carbide and Carbon Chemicals Company (C-31 Plant)
- 78-79. Carbide and Carbon Chemicals Company (K-25 Plant)
- 80-81. Carbide and Carbon Chemicals Company (Y-12 Area)
- 82. Chicago Patent Group
- 83-89. duPont Company (1 copy to G. R. Monet)
- 90-93. General Electric Company, Richland
- 94-95. Hanford Operations Office (1 copy to L. L. Burger)
- 96-99. Idaho Operations Office
- 100. Iowa State College
- 101-104. Knolls Atomic Power Laboratory
- 105-107. Los Alamos
- 108. Massachusetts Institute of Technology (Benedict)
- 109-111. Mound Laboratory
- 112. Naval Research Laboratory
- 113-116. New York Operations Office
- 117-118. North American Aviation, Inc.
- 119. Patent Branch, Washington
- 120. Savannah River Operations Office (Augusta)
- 121. Savannah River Operations Office (Wilmington)
- 122-125. University of California Radiation Laboratory
- 126-127. Vitro Corporation of America
- 128. Stanford Research Institute (N. Heister)
- 129-143. Technical Information Service, Oak Ridge

~~SECRET~~

Table of Contents

Page No.

1.0 Abstract	5
2.0 Introduction	5
3.0 Summary	6
4.0 Acknowledgment	6
5.0 Equipment and Operation	6
5.1 Development of the System	6
5.2 Details of Equipment Operation	7
5.3 Development of the Equipment	8
6.0 Examples of Recovery and Concentration	9
7.0 Examples of Separation	9
8.0 Bibliography	10

Figures

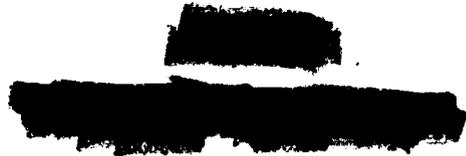
5.1 Schematic diagram of the continuous countercurrent solid-liquid contactor	11
5.2 Original laboratory-scale hand-operated contactor	12
5.3 Laboratory-scale automatic contactor, showing column arrangement and motor-driven resin plug-valves.	13
5.4 Laboratory-scale automatic contactor showing cycle timer, air-driven bellows, and air-driven solution plug-valves.	14
6.1 Recovery and concentration of ferric iron on the continuous ion-exchange contactor.	15
6.2 Recovery and concentration of cerium on the continuous contactor.	16



Figures (continued)

Page No.

7.1 Separation of cesium and uranium with the continuous contactor.	17
7.2 Separation of barium and strontium with the continuous contactor.	18



1.0 ABSTRACT

A continuous countercurrent solid-liquid contactor has been developed which retains the desirable features of the conventional fixed bed and gains the advantages of countercurrent flow. It can be adapted to many solid-liquid mass-transfer processes such as ion exchange, silica gel adsorption, and ore leaching.

2.0 INTRODUCTION

In the last ten years there has been a very rapid development in ion-exchange technology. The ion-exchange method of chemical processing is very attractive because of the high degree of separation possible in simple and compact pieces of equipment. However, practically all applications employ batchwise sorption-desorption with fixed resin beds where neither the exchanger material nor the reagents are used with highest efficiency. For more extensive and economical application of ion-exchange processes to AEC problems, development of a continuous countercurrent flow system seemed necessary. The advantages of continuous over fixed-bed ion exchange should be similar to those found for continuous operation in other mass-transfer systems, such as distillation and solvent extraction. More efficient utilization of resin and chemicals, lower fixed and operating costs, higher degree of separation and concentration, and improved uniformity of products are to be expected.

Several continuous ion-exchange systems have been proposed and developed. Most of the systems involve a "dense" falling bed.^(1-3, 6) Probably the greatest disadvantage of the dense falling bed is the limitation placed on flow rates and solution densities to prevent fluidization or flooding. A device using ion-exchange membranes and electric current to separate ions continuously has been proposed^(1, 4) which achieves many of the advantages to be expected from a continuous ion-exchange process.

The continuous system described in this report retains the fixed-bed advantages of placing almost no limitations on flow rates, solution densities, and resin grading and at the same time gains the advantages of countercurrent flow.



3.0 SUMMARY

A continuous countercurrent contactor for ion exchange, or other solid-liquid mass-transfer processes, has been devised which retains the advantages of the conventional fixed bed and gains the advantages of countercurrent flow. Since the flow is against a packed bed, there is no limiting flow rate, and close control of flow rate is not required. The resin is moved by intermittently stopping the flow of solution and pulling or pushing the resin around in a piston-like manner, with no movement of particles relative to one another. The sorption and desorption sections are so arranged that loaded resin is pulled from the feed end of the sorption column into the solution exit end of the desorption column. Regenerated resin from the feed end of the desorption column is pulled into the solution exit end of the sorption column.

The continuity and superior efficiency of the operation compared to the conventional fixed bed has been demonstrated.⁽⁵⁾ A fully automatic laboratory model has run continuously under steady-state conditions for over 100 hours. Equipment development is continuing to simplify mechanical accessories and to demonstrate the operation of larger scale equipment.

Anticipated application of this device include present ion-exchange processes in which continuous operation is desired and processes previously considered not feasible because of contacting inefficiency. For example, this contactor is simpler than equipment which approximates continuous countercurrent flow by use of multiple columns in series and parallel; also in radiochemical processing the low hold-up times made possible might well eliminate the radiation damage problem.

4.0 ACKNOWLEDGMENT

Recognition is given to A. C. Jealous for suggesting the use of a bellows for metered resin flow. T. A. Arehart and J. R. Parrott procured the equipment and constructed the laboratory automatic contactor. W. E. Shockley operated most of the demonstration runs and aided on equipment set-ups. T. M. Gayle of the Instrument Department designed and built timers and motorized valves. J. T. Roberts planned the "contest" experiments between the continuous contactor and the conventional fixed bed⁽⁵⁾ and developed methods of analyzing the contactor operation.

5.0 EQUIPMENT AND OPERATION

5.1 Development of the System

The conventional fixed ion-exchange bed has several attractive features which should be retained, if possible, in the development of a continuous countercurrent contactor. High throughputs and solution densities are possible, and there is no particular need for closely graded resin. The height



[REDACTED]

of a mass-transfer unit is at a minimum because the particles stay in position relative to one another.

It was discovered that resin in a packed bed could be moved around easily in a column as a solid, unfluidized plug by a sudden jerk applied with either suction or pressure. The movement is like that of a piston. The frictional force between the column wall and the particles being less than that between the particles themselves, the particles cling together and slide in the column as if lubricated by a film of liquid at the wall. The particles remain in the same position relative to one another because the movement is of such velocity that the resistance of liquid flow through the bed does not allow enough liquid to enter to overcome the frictional forces between the particles. Possibly both the fluidizing and the free settling velocities of the resin are exceeded during the movement at such a rate that the particles do not have an opportunity to separate from each other. Fluidization has been discussed by Jury. (6)

Since it is impossible to move the resin in this manner at the same time liquid is flowing through the bed, the solution flows are stopped momentarily to move the resin. This operation would approach true continuous differential countercurrent contact in the limit that the bed were moved instantaneously in infinitesimal increments. In practice this condition is approximated closely by moving a relatively small fraction of the bed at a time and keeping the "off" time small in comparison to the "on" time. The disadvantages of power-driven valves and an automatic timing system in the continuous contactor are balanced against the disadvantages of lower flexibility, closely controlled flow, and closely graded resin needed in the "dense" falling-bed systems.

5.2 Details of Equipment Operation

Figure 5.1 shows, schematically, the equipment arrangement. The ratio of solution to resin flow desired is determined by the pump speed and the amount of resin moved per cycle. The "down-time", to accomplish the resin movement, and the fraction of the bed moved per cycle are inversely proportional and are balanced to keep each at a practical minimum. The timer is arranged to give each operation its proper sequence and duration.

The cycle occurs in the following sequence:

1. The pumps stop. Solution inlet and outlet valves close.
 2. The plug valve between the resin columns opens.
 3. The bellows flex to move the resin bed, which slides as a piston.
 4. The plug valve between the columns closes and the plug valve in the reservoir column opens.
- [REDACTED]

5. The bellows return to their original position, adding a "kick" to the resin settling from the top column to the reservoir of packed resin, which is pulled in at the bottom in step 3.
6. The plug valve in the reservoir leg closes.
7. The pumps start. Solution inlet and exit valves open. The solution flows until the next resin movement period.

5.3 Development of the Equipment

In the original hand-operated equipment, shown in Figure 5.2, flow was controlled by direct measurement of volume throughput. The resin was moved by applying a vacuum at the feed tanks. Valves were operated manually. Several demonstration runs and a "contest"⁽⁵⁾ with a conventional fixed bed were carried out with this equipment.

The use of a power-driven bellows was suggested to give an accurately measured resin flow. This worked out very well on an automatic model, shown in Figures 5.3 and 5.4. A larger contactor is under construction which has a bellows for a 4- to 6-in. column. For columns larger than 1 ft. in diameter, use of a bellows may be impractical and the use of a piston or a hydraulic pump is suggested. When corrosion or leakage from the resin movement mechanism is of concern, an inert liquid which is immiscible with the process solutions may be used in the mechanism.

In the automatic contactor (Figure 5.4) two separate bellows are power driven by means of a rocker arm and one air motor. The column of resin is both pushed and pulled. The same effect can be accomplished by one bellows sealed in a can, but this requires a packing gland around the shaft driving the bellows. It was found possible also to move the resin bed by a single bellows, which either pulls or pushes the resin bed, if bleed valves are opened at the same time. The bleed valves are suggested to eliminate the cost of the second bellows or to eliminate the packing gland in the single canned bellows mechanism. A bellows provides an accurate resin flow and can be adjusted by changing the stroke. The hydraulic pump, although more simple and compact for larger columns, would require a detector to signal how much resin had been moved.

For complete recirculation of the solid it is necessary to have at least one valve to allow passage of the resin bed. The plug-cock type of valve is ideal, but an air-driven pinch valve has also been used successfully. For large-column installations it is not necessary to increase the opening size of this valve proportionately. However, as the column gets larger relative to the valve opening, greater consideration must be given to streamlining. If the solutions in the sorption and scrubbing sections (or scrubbing and stripping) need not be separated from each other, this valve may be placed in the reservoir resin bed, which is kept smaller

to reduce resin inventory. Not only the valve placement but the geometry of the columns will vary with each application, depending on the desired flow rates, equilibration rates, and desired product purities.

6.0 EXAMPLES OF RECOVERY AND CONCENTRATION

Runs were made with the automatic model to demonstrate the recovery and concentration of iron and cerium. In one experiment (Figure 6.1) ferric ion at 1.35 g/liter in 0.25 M HNO_3 was fed at 10 ml/min/cm² to a 17-in. bed of Nalcite HCR. The "loaded" resin was moved from the solution feed end of the sorption section into the solution exit end of a 28-in. desorption ("strip") section. The iron was eluted from the latter section at 11 to 15 g/liter with 0.8 M oxalic acid at a flow rate of about 1 ml/min/cm². Only 0.2% of the iron was lost in the feed waste. This run continued for more than 100 hr almost wholly unattended. Control was accomplished by adjusting the resin movement rate and the oxalic acid strip rate to maintain a dark band of ferric-form resin at the top of the sorption section and at the bottom of the desorption section. In a second experiment (Figure 6.2) cerous ion at 1 g/liter in 0.25 M HNO_3 was fed to a 28-in. column of 50- to 100-mesh Dowex-50, 12% cross-linked, at 10 to 20 ml/min/cm². The cerium was concentrated by a factor of about 15 in a 48-in. strip column using 6 M HNO_3 as eluting agent. About 0.05% of the cerium was lost in the feed waste, but the recovery of this was limited by the background counting of the Ce^{144} tracer. The 15 g/liter product concentration is not considered the maximum possible because the strip-to-feed ratio was limited by the speed range of the pumps used. For recovery-concentration problems where the desired product is present at a low concentration in a dilute (in total electrolyte) feed, it is visualized that the sorption column will be short and wide relative to the desorption column.

7.0 EXAMPLES OF SEPARATION

Two runs were made to demonstrate the separation of two ions, both on the hand-operated contactor. In the first such experiment uranium and cesium were separated in 0.5 M H_2SO_4 , in which the separation factor is 3. The separation section and the stripping section of the column were each 17 in. long. The resin was Dowex-50, 12% cross-linked and 60 to 100 mesh. The relative rates of movement of cesium and uranium down the column with 0.5 M H_2SO_4 had been previously determined on a conventional fixed bed. These ratios of solution to resin flow were incorporated in the operation of the continuous contactor such that uranium continuously moved down the bed and cesium continuously upward. To economized on eluting chemicals and build up the cesium concentration, a portion of the cesium product solution was used as the scrub feed. A continuous product of uranium solution was obtained at a concentration of about 0.4 g/liter; it contained only about 10 to 20 c/min of Cs^{135} , 137 tracer per milliliter. The cesium product contained about 0.005 g of uranium per liter and had an activity of about 5×10^4 c/min/ml. This is one of the runs included in the comparison with the conventional fixed bed to demonstrate the increased

efficiency with countercurrent flow.⁽⁵⁾

Figure 7.2 shows the results of a separation of barium and strontium with a separation factor of 2. The feed contained 10 g/liter each of barium and strontium with Ba¹⁴⁰ and Sr^{89,90} tracer. The separation was made in 2 M HNO₃ on Dowex 50, 12% cross-linked and 60 to 100 mesh. The run was controlled³ by measuring the relative resin and solution flow rates and flame testing the barium and strontium product streams. As shown in the figure, owing to an initial error in operation, the run got out of control but finally leveled off at about 10% of the barium in the strontium product and 0.3% of the strontium in the barium product.

8.0 BIBLIOGRAPHY

- (1) "Plastics that Sort Atoms," Fortune, p. 107, July, 1951.
- (2) Hiester, N. K., "Continuous Separations of Ions by Means of a Moving Ion-Exchange Bed," Stanford Research Institute Report No. COO-41 (March 30, 1951).
- (3) Selke, W. A. and Harding Bliss, "Continuous Countercurrent Ion-Exchange," Chem. Eng. Progress, 47, 529 (1951)
- (4) Dewey, D. R. and J. A. Marinsky, "Ionics Rectification Column," paper delivered at Gordon Research Conference in 1951 (in press).
- (5) Roberts, J. T., "An Experimental Comparison of the Higgins Continuous Ion Exchanger with a Conventional Fixed Bed Column," ORNL CF-52-6-107 (June 18, 1952).
- (6) Jury, S. H., "Continuous Ion Exchange Column Investigations," ORNL CF-50-9-80 (August 31, 1950).


I. R. Higgins

Figure 5.1

Dwg No 15117

"HIGGINS" CONTINUOUS COUNTERCURRENT
SOLID-LIQUID CONTACTOR

Page 11

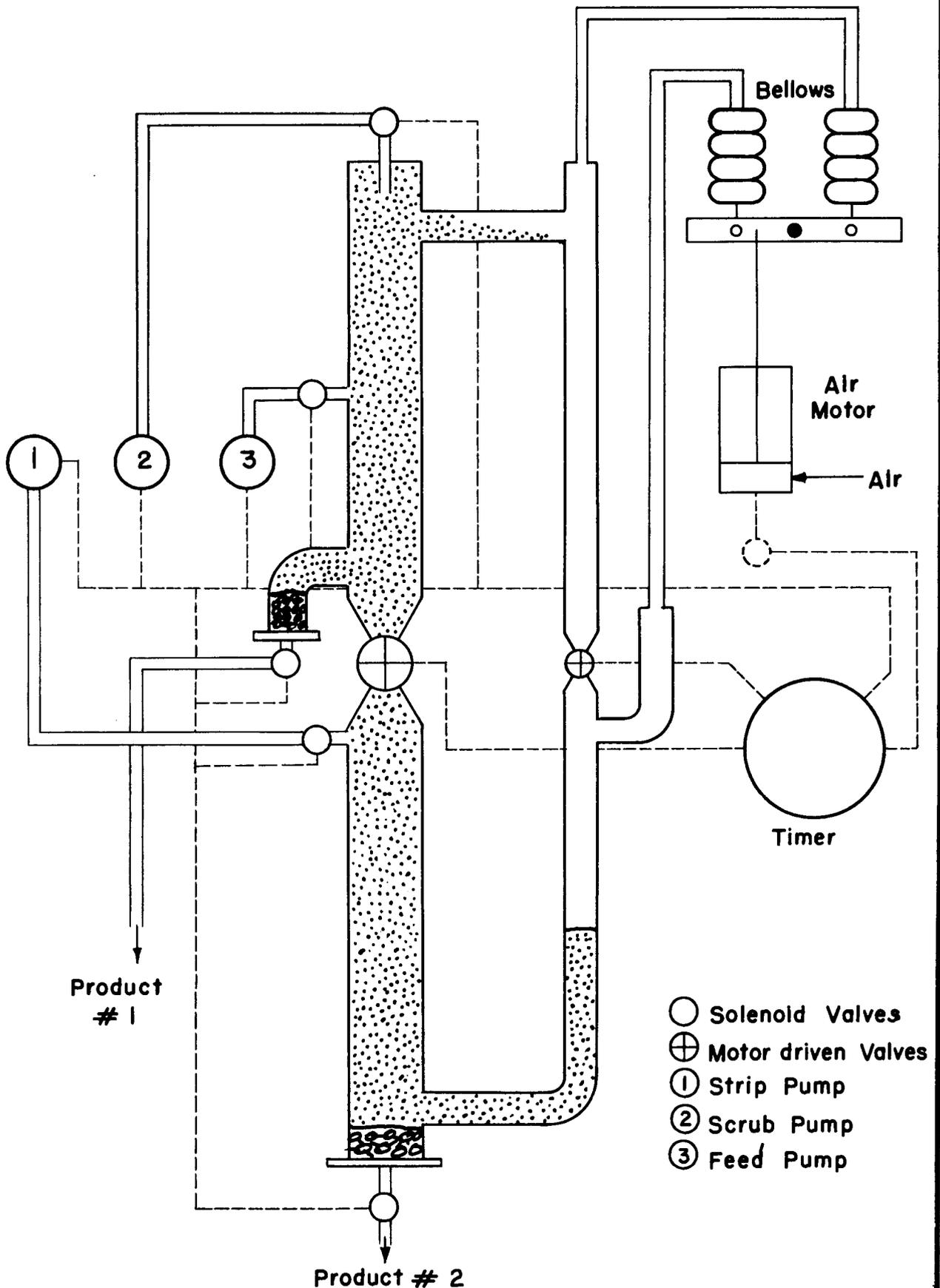


PHOTO 9281

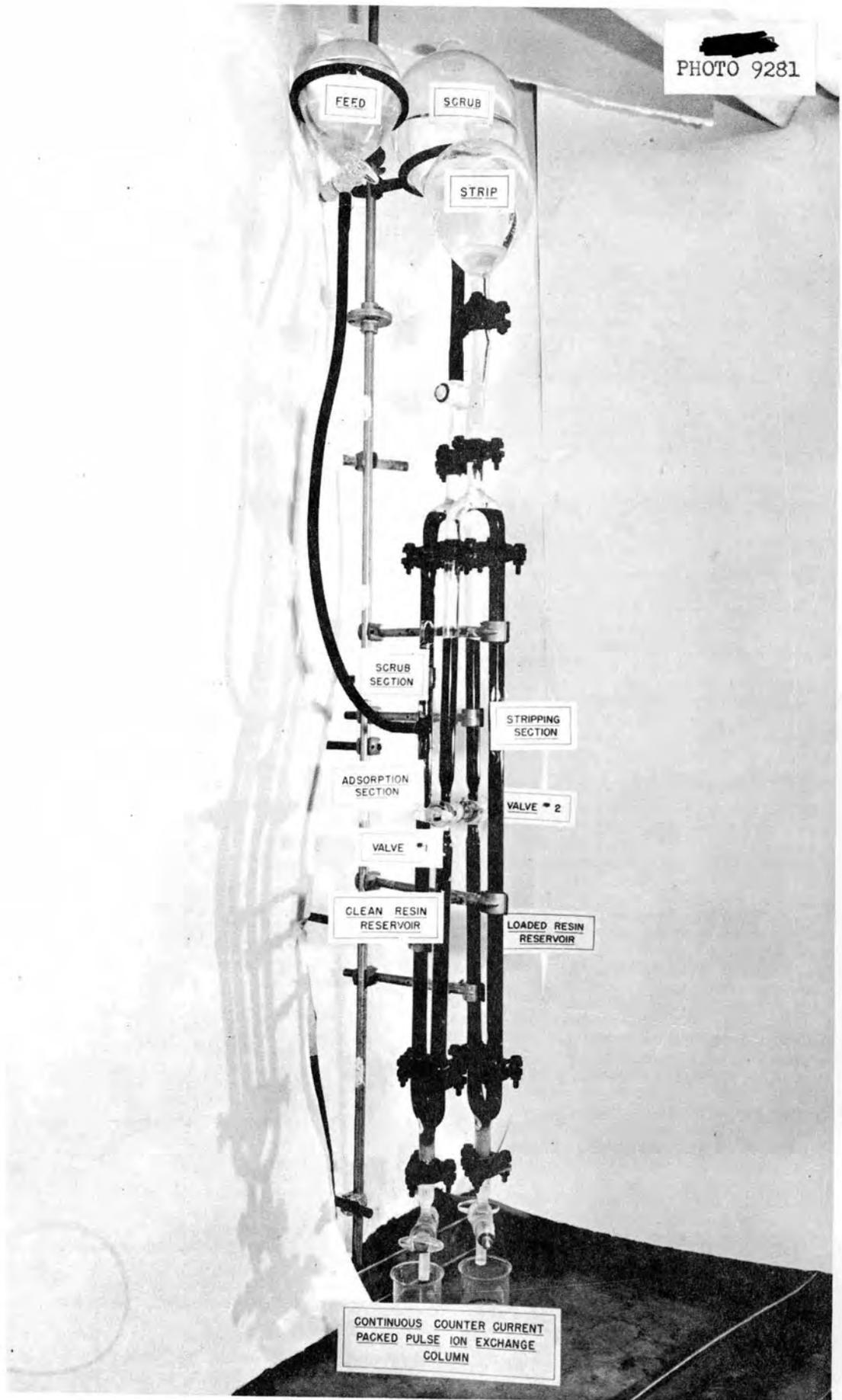


Figure 5.2 Original Laboratory-scale Hand-operated Contactor

PHOTO 10053

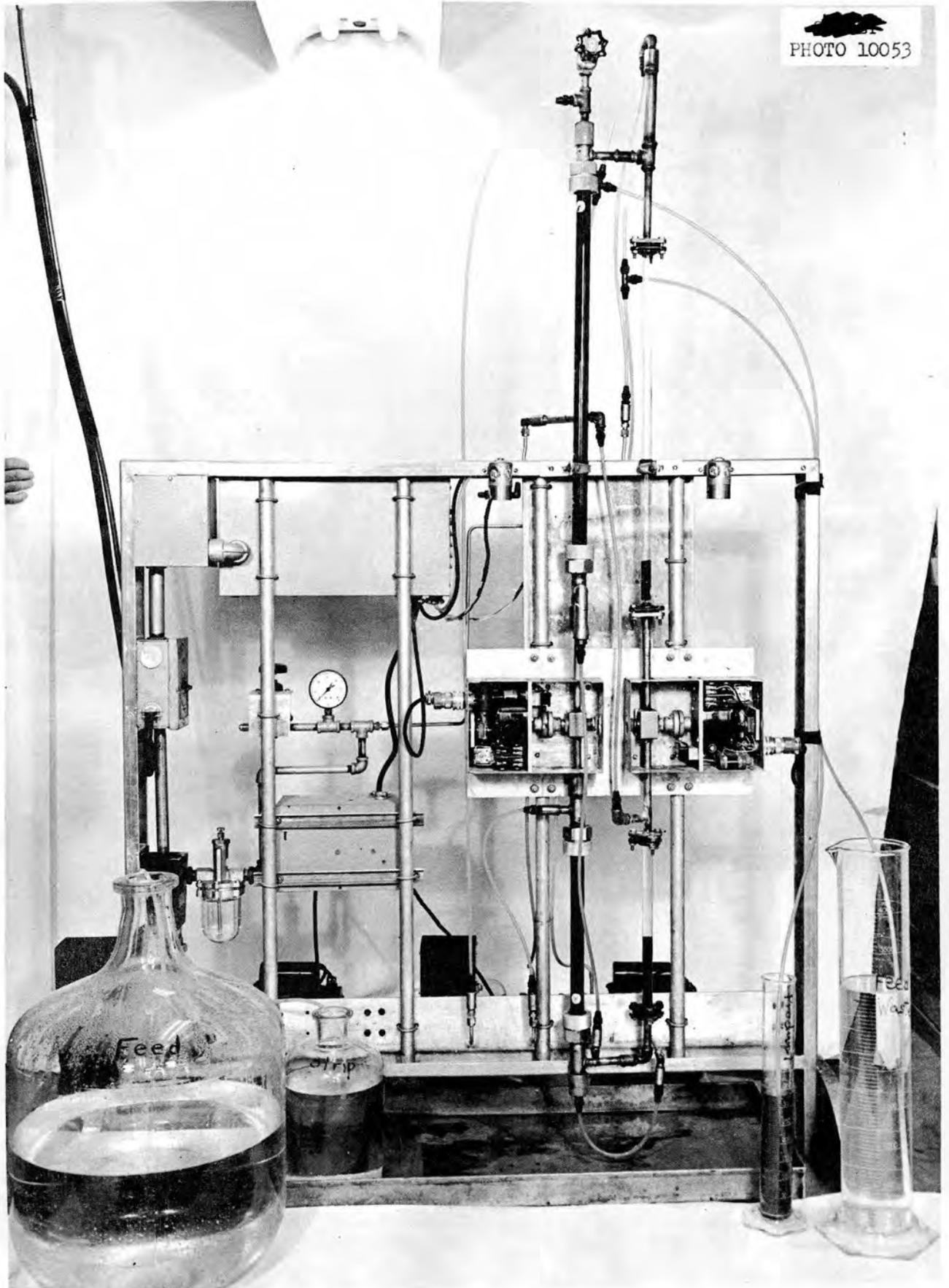


Figure 5.3 Laboratory-scale Automatic Contactor, Showing Column Arrangement and Motor-driven Resin Plug-valves

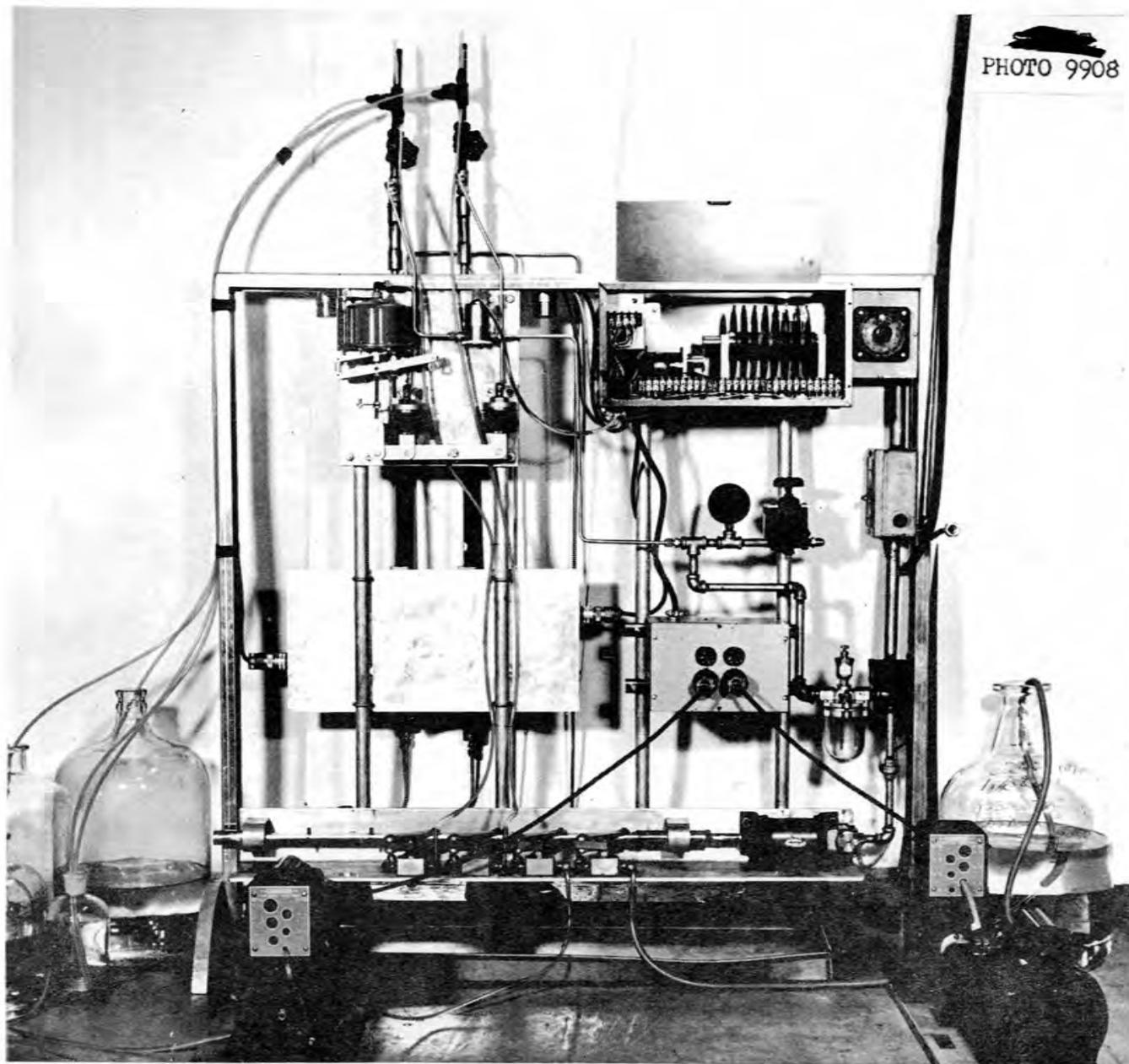


PHOTO 9908

- 14 -

Figure 5.4 Laboratory-scale Automatic Contactor
Contactor Showing Cycle Timer, Air-driven Bellows,
and Air-driven Solution Plug-valves

Figure 6.1
Recovery and Concentration of Ferric Iron
on the Continuous Ion-Exchange Contactor

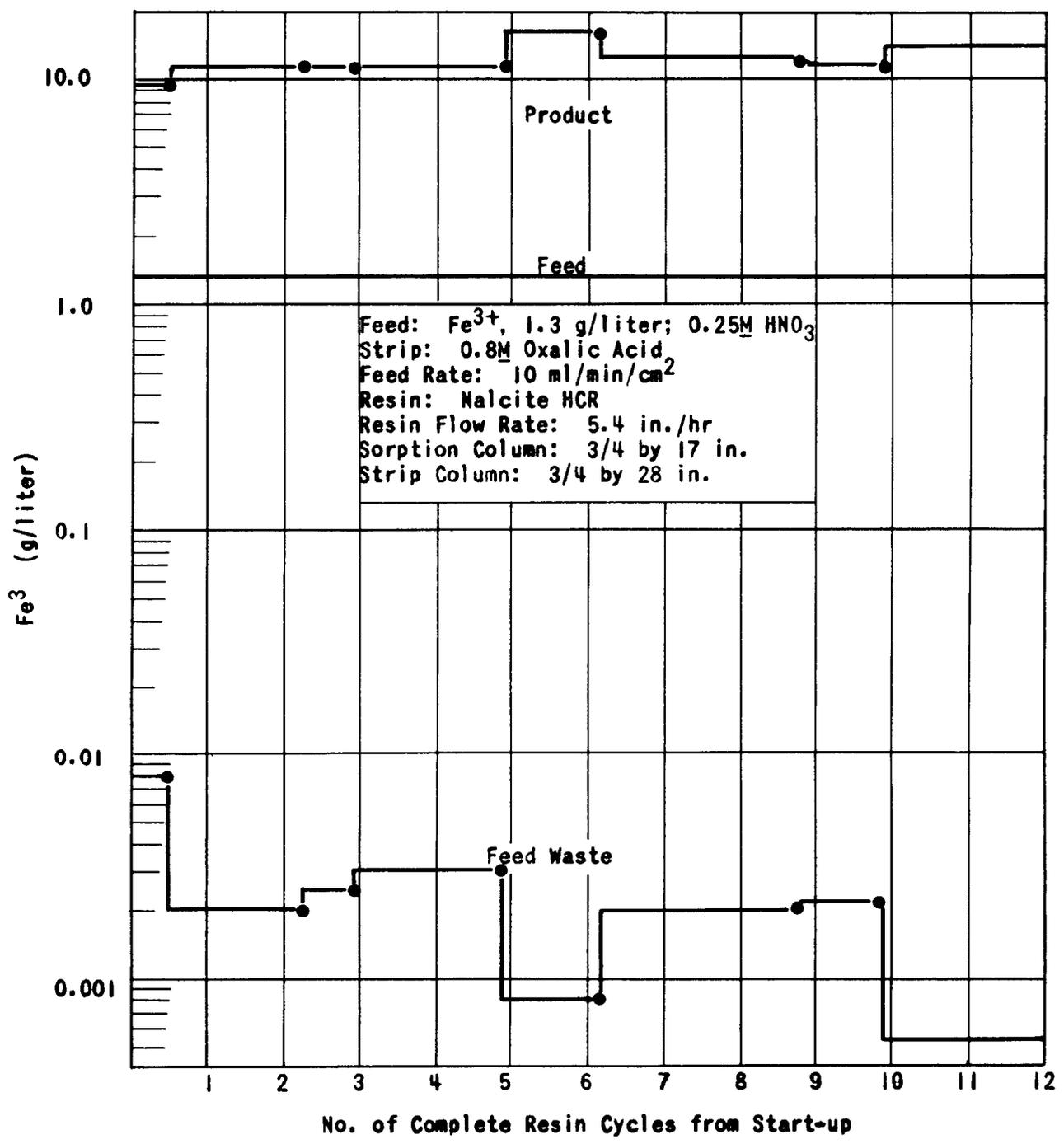


Figure 6.2

DWG. 15642
ORNL-1310

Recovery and Concentration of Cerium
on the Continuous Contactor

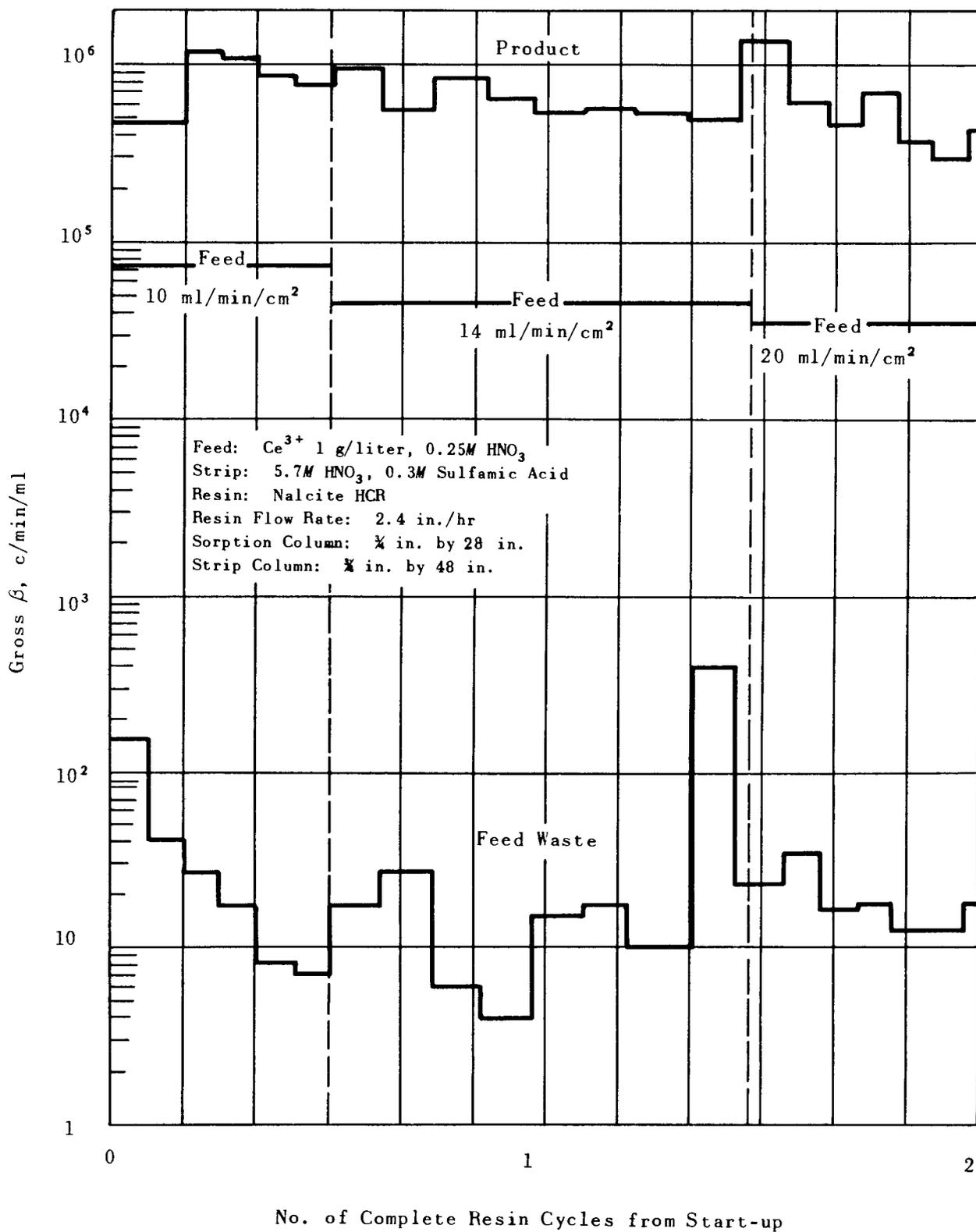


Figure 7.1

DWG. 15643

ORNL-1310

Separation of Cesium and Uranium
on the Continuous Contactor

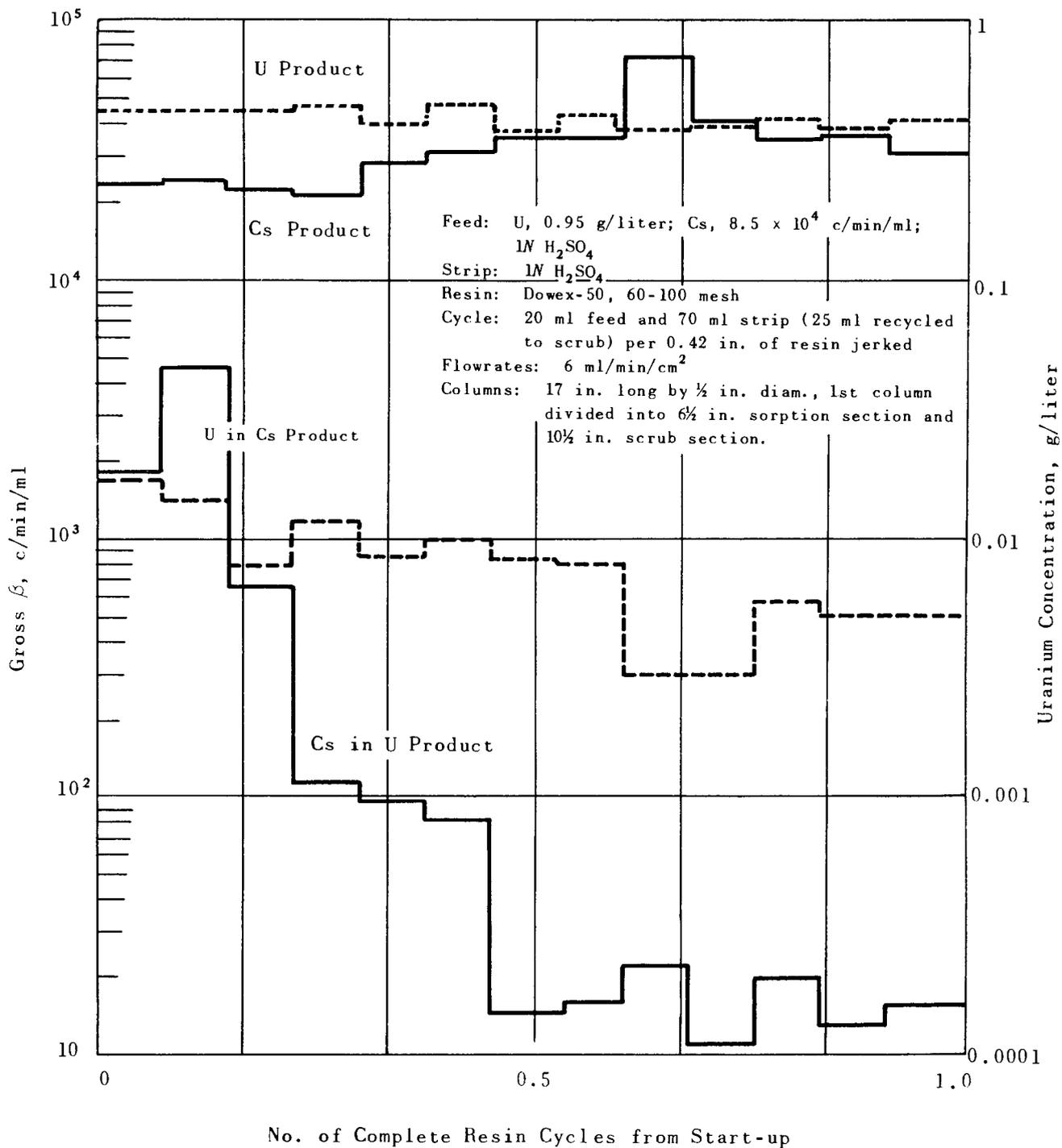


Figure 7.2

SEPARATION OF BARIUM AND STRONTIUM WITH THE CONTINUOUS CONTACTOR

Feed: Ba and Sr, 10 g/liter each; Ba¹⁴⁰ and Sr^{89, 90}, tracer

Scrub: 2M HNO₃

Strip: 6M HNO₃

Resin: Dowex-50, 12% cross-linked, 60 to 100 mesh

