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HIGH-PRESSURE ION-EXCHANGE COLUMN DESIGN FOR REMOTE HOT-CELL OPERATION

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MAY 1974

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CONTENTS

	Page
INTRODUCTION	1
COLUMN DESCRIPTION	1
OPERATING INSTRUCTIONS	4
CONCLUSION	7
REFERENCES	8
APPENDIX A	9
Parts List for HPIE Column Apparatus	9

HIGH-PRESSURE ION-EXCHANGE COLUMN DESIGN FOR REMOTE HOT-CELL OPERATION

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INTRODUCTION

The separation and purification of adjacent rare-earth elements is a frequently encountered problem in the course of radionuclide development. High-pressure ion-exchange (HPIE) elution chromatography, utilizing micron-size cation-exchange resin beads, has been used widely for the rapid, efficient separation of small samples of these chemically similar elements. Radionuclide production operations, on the other hand, often yield highly radioactive rare-earth samples of a few tenths of a gram to a few grams in size that must be separated and purified by remote handling procedures in shielded hot cells. An earlier single-cycle chromatograph apparatus design[1] — a heated resin column connected directly to a high-pressure pump and pressure gauge — was satisfactory for small-scale, bench-top operation where the apparatus could be readily disassembled after each run for resin replacement, but this design required that the column charge and elution solutions be pumped through the pump and past the pressure gauge dead leg which resulted in excessive tailing and poor separation efficiency. When this earlier design chromatograph apparatus was used for more than one or two separations without repacking or replacing the resin, the resin column would pack down so tightly that the column back pressure would exceed the working limits of the pump with resultant pump damage. In order to overcome these difficulties and to accommodate the larger production samples with remote handling requirements, a versatile, compact HPIE column design has been developed. This column allows resin loading and repacking, sample loading, elution, and maintenance to be performed remotely with minimum effort and cross-contamination. To date this new column design has been used for more than 50 rare-earth separations with no equipment failures or sample cross-contamination. The equipment was designed so that more than one operation could be performed simultaneously, enabling completion of the sample loading, elution, resin reconditioning, and column repacking cycles within an eight-hour period.

COLUMN DESCRIPTION

The aims were to develop a safe, compact apparatus providing minimal elution peak tailing, rapid and efficient remote operation and servicing using master-slave manipulators, interchangeable resin columns for greater sample flexibility, and a repackable resin bed for reproducible column performance. The HPIE column apparatus and pump configurations devised to meet these objectives are shown in Figs. 1 and 2, respectively (the numbers shown were included to identify specialized components as listed in Appendix A). This system was designed with the high-pressure pump and low-pressure air supply separate from the column

hardware in order to facilitate operation and to minimize the amount of in-cell equipment and service. All materials that contact the sample solutions directly are either stainless steel (SST) or glass. Commercially available flareless-type tubing fittings were used where practical to reduce fabrication costs and facilitate in-cell servicing. No trouble was encountered in resealing dismantled fittings once they had been set correctly. One-eighth inch OD by 0.035-in. wall SST tubing is used throughout for all high-pressure lines to reduce line void volumes. All high-pressure components are rated for working pressures ≥1800 psi for safety. Aluminum mounting plates provide support for the various components and minimize weight. Mounting brackets fabricated from either angle aluminum or U-bolts, except as noted, are used to hold the various valves, columns, and reservoirs.

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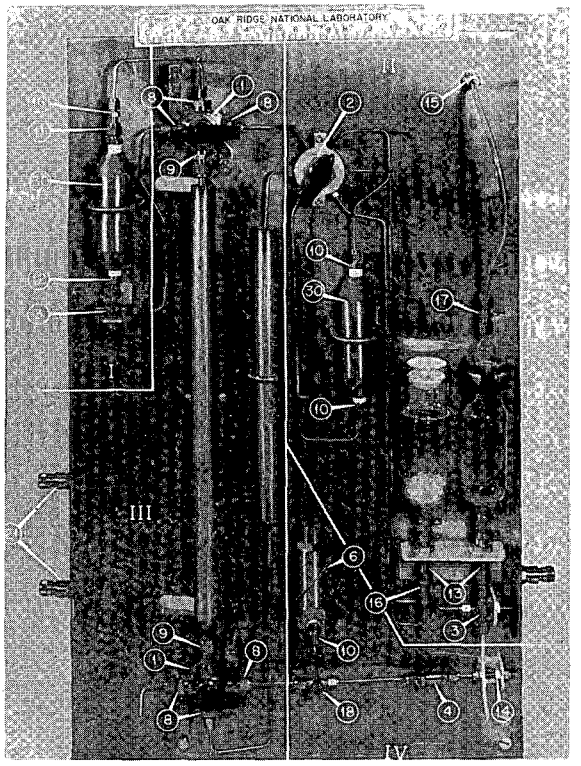

Fig. 1. In-cell Components of High-pressure Ion-exchange Chromatographic Apparatus. Apparatus subdivided into four functional sections: I — resin handling loop; II — sample loading loop; III — resin column; and IV — high-pressure eluent inlet.

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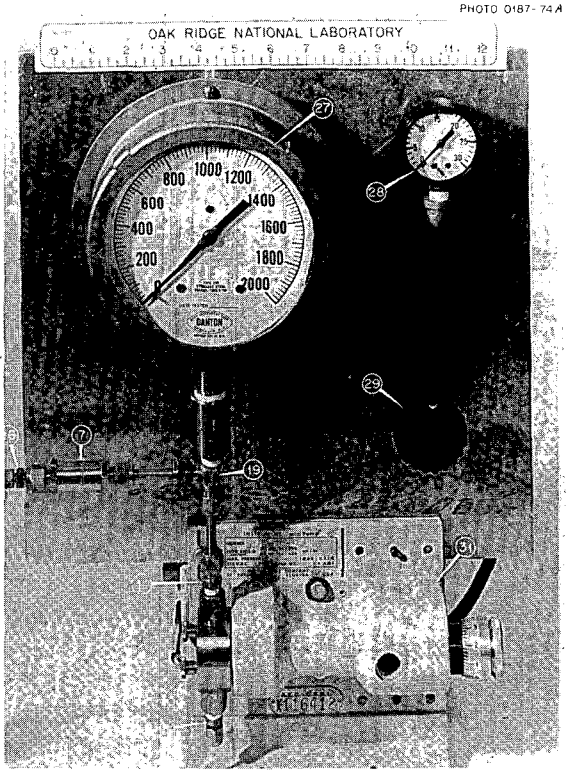

Fig. 2. High-pressure Pump and Low-pressure Air Supply Hardware.

The in-cell components shown in Fig. 1 can be subdivided into four basic functional sections: I — resin handling loop; II — sample loading loop; III — resin column; and IV — high-pressure eluent inlet.

Section I, the resin handling loop, was included for use during resin loading and unloading of the apparatus and during the resin repacking operation. It was found that repacking of the column after each use improved reproducibility of the separation and also prevented the resin bed from packing down so tightly that the 1000-psi limit of the positive displacement pump would be exceeded with resultant pump damage. A sintered SST filter (Part No. 24) was inserted between Part Nos. 11 and 16 at the top of the resin reservoir (Part No. 30) to prevent transfer of the resin into other sections of the apparatus.

Section II, the sample loading loop, was designed for transfer of a rare-earth sample, dissolved in dilute 0.05 *M* HNO_3, from the right-hand low-pressure glass reservoir into the bottom of the high-pressure reservoir (Part No. 30) by means of a slight positive pneumatic pressure. A low-pressure check valve (Part No. 6, not shown in Fig. 1) was inserted in the low-pressure air line between the air inlet (Part No. 22) and the upper bulkhead fitting (Part No. 15) to prevent any possible reverse flow of activity out of the hot cell. Once the initial sample and glass reservoir rinses have been transferred to the high-pressure load reservoir, the low-pressure sample handling loop is valved off *via* the 6-way valve (Part No. 2), and the sample is hydraulically displaced onto the resin column. The equipment was designed to displace the sample out the top of the high-pressure reservoir and thereby purge the lines of any potentially dangerous trapped air before development of the high-pressure head. A 10% w/v $LiNO_3$ solution [spec. gravity = 1.0572 @ 25°C[2]] is used to displace the dilute acid samples onto the resin column (Bio-Rad 50W-X8, 20-35 μm, NH_4^+ form). The apparatus was designed so that after transfer of the sample has been completed, as monitored by an in-cell probe, Section II can be by-passed and the resin converted back to the NH_4^+ form before beginning the elution with a minimum of high-pressure flow. The 3-port ball valve (Part No. 3) was included to facilitate emptying and cleaning of Section II between samples.

Section III, the resin column, is the heart of the apparatus. Stainless steel columns of a uniform 20-in. length and similar in design to those developed by C. D. Scott, *et al.*[3] were fabricated from standard size tubings (e.g., 0.25-in. OD by 0.035-in. wall to 0.75-in. OD by 0.065-in. wall) with welded water jackets for operation at elevated temperatures. Sintered 0.5-micron SST filter elements (Part No. 23) were used to support the resin bed. Special 4-port ball-valve support brackets (see Fig. 3 for design schematic) were used to hold the resin column. These brackets were designed so that the resin column and attached valves could be disconnected remotely and removed without requiring decontamination or handling of the entire apparatus (the slots in the backing plate were required for clearance of the water jacket outlets). Water jacket connections and lines were located on the back of the apparatus (not shown in Fig. 1) to simplify layout requirements. Stainless steel water lines were used in the apparatus pictured, but flexible Tygon tubing lines, which would allow easier removal of the chromatographic column, should serve as well (the parts list in Appendix A does not include the water jacket fittings which are left to the discretion of the user). The eluent is preheated in a small, permanently mounted heat exchanger before passing through the 6-port ball valve onto the resin column. The tubing length between this

6-port ball valve and the upper 4-port ball valve was kept as short as possible in an effort to minimize peak tailing due to sample desorption from surfaces wetted during sample loading.[4]

Section IV, the high-pressure eluent inlet, contains a check valve to prevent reverse flow of possibly contaminated solutions out of the cell and a resealing relief valve set at 1250 psi. The positive displacement high-pressure liquid pump, regulated low-pressure air supply, and constant temperature bath for column heating are all kept outside the hot cell. Connection between the high-pressure pump outlet and apparatus inlet is made with 0.125-in. OD by 0.035-in. wall Teflon tubing, which was found to withstand >1250 psi without failure.

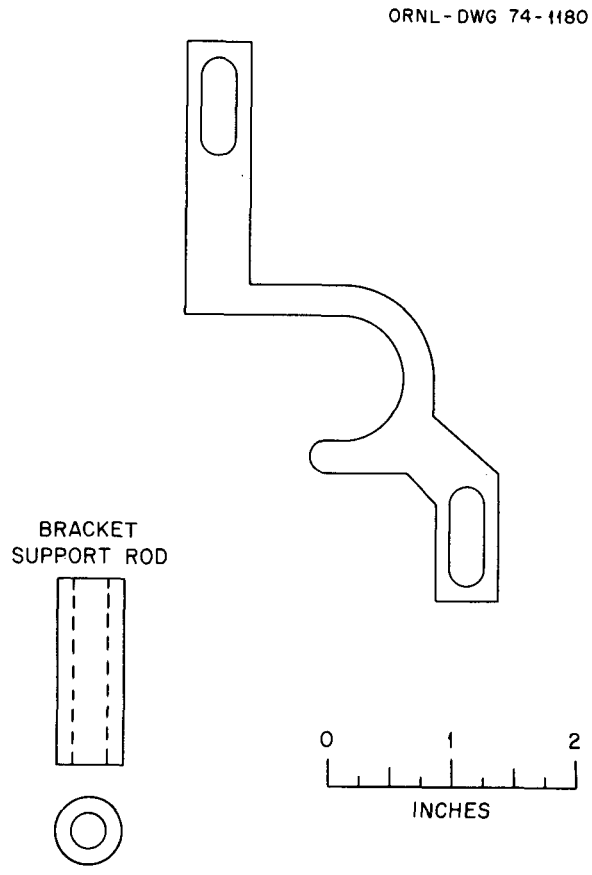

Fig. 3. High-pressure Ion-exchange Column Support Bracket Schematic.

The pump-air supply configuration is shown in Fig. 2. The large surface area SST filter (Part No. 7) was found necessary to prevent pumping foreign material into the system that would eventually plug the 0.5-micron filter unit supporting the resin bed. Under normal operation, this latter filter is reverse flushed and kept clean each time the flow is reversed to transfer the resin bed back to the resin reservoir. Location of the pump unit outside the hot cell greatly facilitates the handling and control of the various reagents required during the separation and resin handling cycles.

OPERATING INSTRUCTIONS

Detailed operating instructions and solution flow patterns for this apparatus design are shown schematically in Figs. 4 thru 9. The arrows in the valve centers represent the valve handle alignments for each operation. Figure 4 depicts the valving sequence for the initial loading of the resin into Section I. In order to prevent overfilling the resin column, the required resin volume was determined by packing a dummy column of the same size as the column to be filled to the required column height and back pressure. This resin was then transferred hydraulically to the high-pressure resin reservoir *via* a 0.125-in. OD by 0.035-in. wall Teflon connecting tube. The resin was retained in the resin reservoir by the sintered SST filter at the top of the reservoir. This operation is the only one during which

the high-pressure flow does not enter *via* Section IV. Once the resin has been transferred to the resin reservoir, the high-pressure flow is connected to the inlet of Section IV (Part No. 14, Fig. 1) and the resin is loaded into the empty resin column as shown in Fig. 5. The same valving sequence is used to transfer the dilute 0.05 *M* HNO_3 rare earth charge solution from the low-pressure glass reservoir into the high-pressure SST load reservoir. Since this loop is separate from the resin repacking loop, both operations could be performed simultaneously if required. The charge solution is first transferred into the high-pressure load reservoir with a slight positive pneumatic pressure (typically 1-2 psig), and then the glass reservoir is washed once or twice with dilute 0.05 *M* HNO_3 to ensure quantitative sample transfer and minimum hold-up in the lines. A 75-ml SST load reservoir was used in construction, so the total charge and rinse volumes were limited to ∿55 ml to prevent losses due to excessive bubbling and sample carry-over into the vent lines. The vent glass reservoir (the left-hand glass reservoir in Fig. 1) was partially filled with raschig rings to prevent any possibility of spray. Figure 6 shows the flow pattern employed to transfer the rare-earth load solution onto the resin column (resin initially in NH_4^+ form). A slightly denser displacing fluid which does not cause premature elution of the rare earths from the column (e.g., 10% w/v $LiNO_3$) is used to displace the load solution out the top of the load reservoir through the 6-port ball valve to the resin column.

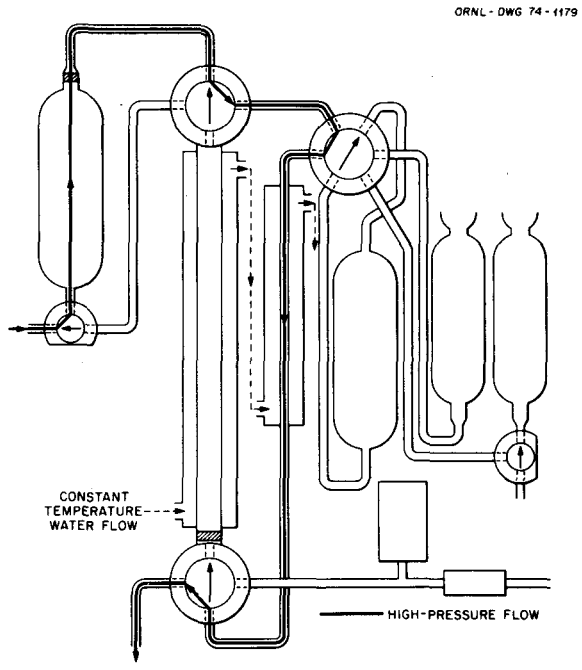

Fig. 4. Initial Apparatus Resin Loading Sequence.

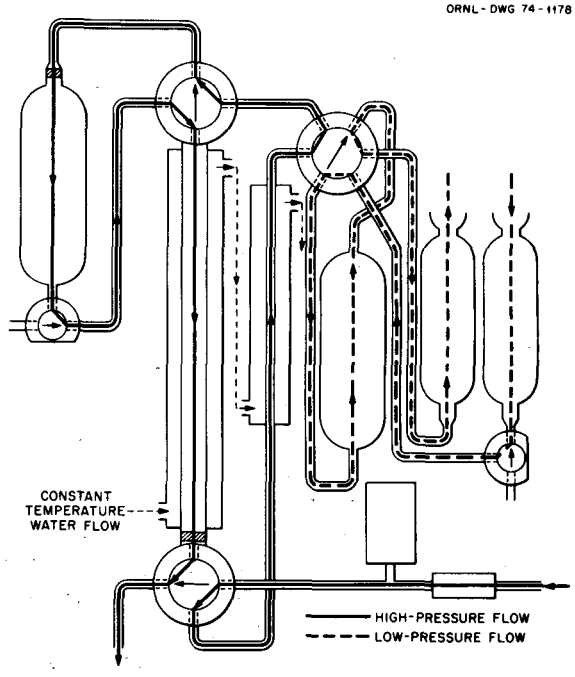

Fig. 5. High-pressure Transfer of Resin into Column and Low-pressure Transfer of Column Charge Solution into High-pressure Load Reservoir.

This flow pattern also allows escape of all trapped air from the system prior to development of the column back pressures, typically 400-700 psi. Recovery of the waste solution from the loading loop after completion of the loading cycle indicated >99% sample transfer for this system design. Once the load solution has been completely transferred onto the resin (as monitored by an in-cell radiation probe), the loading loop, Section II, is valved out of the high-pressure flow as shown in Fig. 7. The resin column is converted back to the NH_4^+ form with 0.25 *M* HNO_3 before the chromatographic separation is begun.

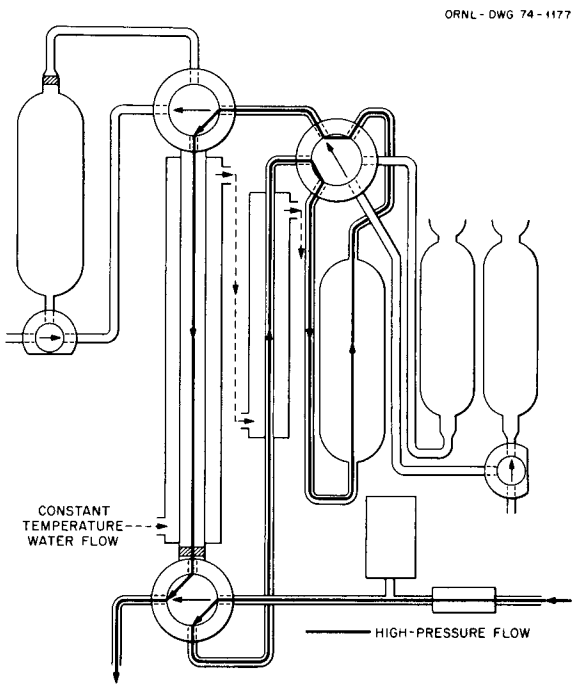

Fig. 6. High-pressure Displacement of Column Charge onto Resin Column.

The choice and concentration of the eluent is determined by the rare-earth elements to be separated. Most of the work performed with this equipment was based on separation conditions estimated from the work of D. O. Campbell,[5] i.e., elution at 85°C with various concentrations of 2-methyllactic acid (α-hydroxyisobutyric acid) at pH 4.4. Chromatographic separations characterized by the development of 700-1000 theoretical plates within the 20-in. column length were typical for this system. The column exit port was either fitted with a simple delivery pipe to collect individual fractions, as shown in Fig. 1, or with a length of 0.125-in. OD Teflon tubing which was passed through an ion chamber for continual effluent monitoring. After completion of the chromatographic separation, the resin was stripped of any residual ions by elution with many column volumes of 3 *M* HNO_3. Once the resin had been stripped, it was converted back to the NH_4^+ form before being backwashed into the resin reservoir

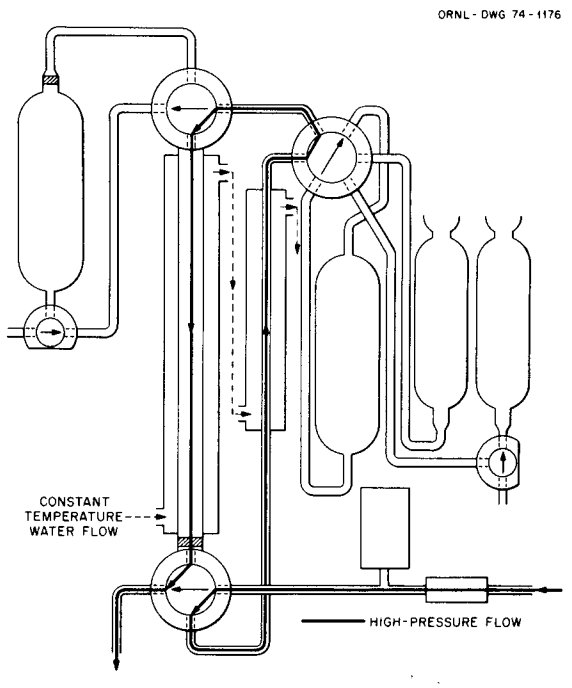

Fig. 7. Resin Column Elution Sequence.

as shown in Fig. 8. The ion exchange resin was reconverted to the NH_4^+ form before being repacked in order to improve column operating performance by minimizing resin shrinkage and packing regeneration, which led to undesirably high column back pressures prior to loading of the rare-earth sample. In order to initiate another separation cycle, one need only return to the valving sequence shown in Fig. 5 and start again. The draining and cleaning sequence for Section II is also shown in Fig. 8. This loop is cleaned with 3 *M* HNO_3 and then emptied before each new sample is started. Figure 9 shows the valving sequence used to remove spent resin from the apparatus once it has been transferred to the resin reservoir.

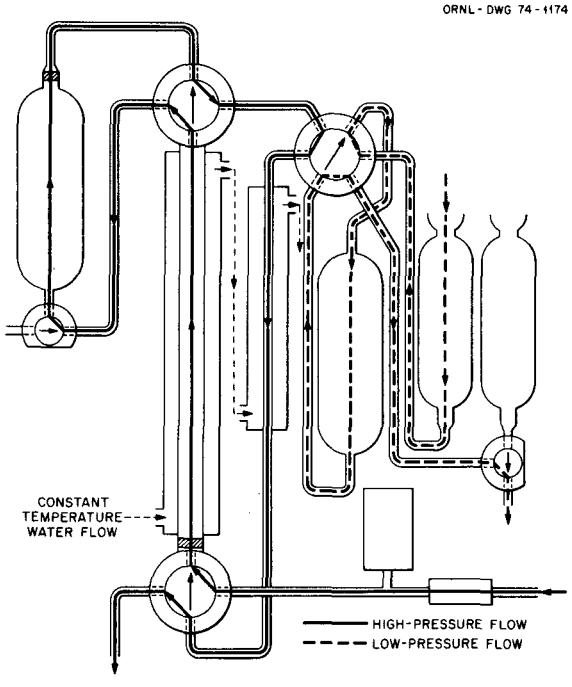

Fig. 8. Resin Back-wash From Column and Load-loop Cleaning Flow Patterns.

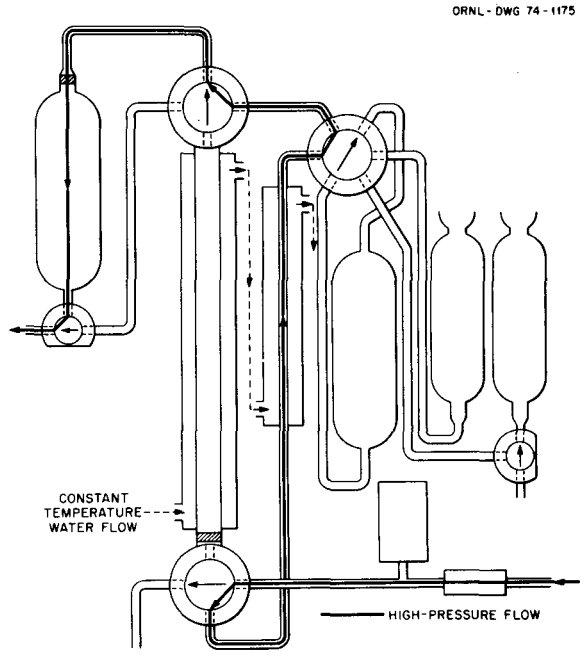

Fig. 9. Removal of Spent Resin From the Apparatus.

CONCLUSION

Even though this system design looks complicated, it has been found to work exceptionally well both in-cell and on the bench top. The movement of solutions can be controlled by a minimum of valve and equipment manipulation, which facilitates remote operation. The system is rapid, efficient, reliable, and easy to service. Resin columns 0.305-in. ID by 20-in. long and filled with 20-35 μm AG50W-X8 cation exchange resin have been used to routinely separate ≥200 mg samples of rare-earth oxides within two hours' elution time. The separation of gram samples should be possible using larger columns and high-pressure pumps with greater flow capacities.

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1. R. E. Lewis, private communication (1970).

2. "International Critical Tables," Vol III, McGraw-Hill Publishing Co., (c) 1928, 78.

3. C. D. Scott, R. L. Jolley, W. W. Pitt, and W. F. Johnson, *Am. J. Clin. Pathology*, 53, 701 (1970).

4. D. O. Campbell, private communication (1971).

5. D. O. Campbell, *J. Inorg. Nucl. Chem.*, 35, 3911 (1973).

APPENDIX A

Parts List for HPIE Column Apparatus

Part No.	Description	Mfr.	Mfr. No.	No. Required
1	Valve, ball, 4-port	WH	SS-43YF2	2
2	Valve, ball, 6-port	WH	SS-43Y6FS2	1
3	Valve, ball, 3-port	WH	SS-41XS2	2
4	Valve, check	NU	SS-2C-10	1
5	Valve, check	NU	SS-2C-1/3	1
6	Valve, relief (set @ 1250 psig)	CS	B5349T2PP(L)1250	1
7	Inline filter (7 μm filter element)	NU	SS-4F-7	1
8	Fitting, tube, O-seal male connector pipe thread	SW	SS-200-1-2-OR	6
9*	O-seal male connector pipe thread	SW	SS-600-1-2-OR	2
10	male connector	SW	SS-200-1-4	4
11	male connector	SW	SS-400-1-4	2
12	adapter tube to pipe	SW	SS-201-A-4	1
13	bulkhead adapter	SW	SS-400-A1-4	2
14	bulkhead union	SW	SS-200-61	1
15	bulkhead union	SW	SS-400-61	1
16	reducer	SW	SS-200-R-4	4
17	union	SW	SS-400-6	1
18	union tee	SW	SS-200-3	1
19	male run tee	SW	SS-400-3-4TMT	1
20	reducing port connector	SW	SS-401-PC-2	2
21	quick-connect, double end shut-off	SW	SS-400-QC-61-DESO	2
22	quick-connect	SW	SS-400-QC-61	1
23*	Snubber element, sintered, 0.5-μ pore size	SW	To fit 3/8" SW fittings	1
24	Snubber element, sintered, 0.5-μ pore size	SW	To fit 1/4" SW fittings	1
25*†	O-ring, Teflon, 3/8 × 1/4 × 1/16 in.	X-10	07-422-8910**	1
26	Insert (for Tygon tubing)	SW	SS-405-2	2
27	Gauge, 0-2000 psig	Y-12	06-033-1050**	1
28	Gauge, 0-30 psig	X-10	06-033-0090**	1
29	Regulator, pressure, 0-30 psig	X-10	06-033-0985**	1
30	Gas cylinders, 75 ml, 1800 psig	HO	4HD-75	2
31††	Pump, liquid metering, 0-1000 psig 460 ml/hr	MR	196-89	1
32	Bath, constant temperature, 20-120°C	HA	1272FE	1

*Parts list developed for a 0.375-in. OD by 0.035-in. wall stainless steel column. These part sizes should be changed to fit OD of column as needed.

**UCCND stock number.

†O-ring inserted between end of stainless steel column and snubber (Part No. 23) to ensure tight seal and no resin leakage.

††This pump has sufficient flow capacity for columns ≤0.375-in. ID.

Manufacturer Code

WH = Whitey Company, 5679 Landregan Street, Oakland, CA 94608

NU = Nupro Company, 15635 Saranac Road, Cleveland, OH 44110

SW = Swagelok-Crawford Fitting Company, 29500 Solon Road, Solon, OH 44139

HO = Hoke Incorporated, One Tenakill Road, Cresskill, NJ 07626

CS = Circle Seal Products Co., Inc., P.O. Box 3666, Anaheim, CA 92803

MR = Milton Roy Company, 1300 E. Mermaid Lane, Philadelphia, PA 19118

HA = Haake Instruments, Inc., 244 Saddle River Road, Rochelle Park, NJ 07662

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