W_0 = initial weight of a single salt particle, lb.
x_s = mole fraction of salt in solution
y = thickness of the laminar film, ft.
z_s = fraction of total mass transfer which is salt, mole basis
α = constant in Equation (13)
θ = time, hr.
μ = viscosity of solution, lb./(hr.)(ft.)
ρ = density of solution, lb./cu. ft.

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Ion Exchange Separation of Gram Quantities of Americium from a Kilogram of Lanthanum

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The separation of 4.5 g. of americium from approximately a kilogram of light rare earths (primarily lanthanum) was achieved on a pilot plant scale by chromatographic displacement of the mixture from Dowex-50 resin with 0.1% ammonium citrate at *p*H 8 into hydrogen-form Dowex-50. The americium collected into a narrow band and was eluted free from lanthanum but contained an equal weight of cerium. A 6- and a 2-in.-diam. column were used in tandem. Use of a final column with a much smaller diameter would have permitted a cleaner separation from cerium, but this was left for a laboratory-scale separation by a different process. Precipitation, which was observed in the columns during the first runs, was later avoided entirely by use of high flow rates both initially and during the transfer between columns. No adverse effects were noted from ~15 curies of alpha activity.

The success of Spedding and Powell (*1*, *2*) in separating kilogram quantities of rare earths by displacement from Dowex-50 using 0.1% ammonium citrate at *p*H 8 suggested that this technique could be applied advantageously to the separation of americium from gross quantities of lanthanum, provided that gram amounts of trivalent americum behaved like a rare earth of intermediate atomic number and, in addition, that several curies of alpha activity would not interfere. Tracer-scale work (*3*) had shown that americium eluted at about the same position as promethium in the elution analysis of a mixture of trivalent rare earths and americium using ammonium citrate and Dowex-50. Thus, in the displacement of a mixture of americium and lanthanum from Dowex-50 using 0.1% ammonium citrate at *p*H 8, the elution positions should be in the aforementioned order after attainment of equilibrium. Furthermore, one would expect that moving the rare earth-americium band through a relatively few equivalent lengths of resin would achieve separation since the problem is essentially that of separating two light rare earths separated by four atomic numbers.

When a macro mixture of rare earths is displaced from Dowex-50 resin with 0.1% ammonium citrate at *p*H 8 into additional hydrogen-form Dowex-50, a series of head-to-tail bands develops, each band containing a substantially pure rare earth with overlap only at the boundaries (*1*, *2*). Furthermore, after equilibrium band lengths are attained, the length of a band is invariant, and elution through additional resin achieves no further separation. Obviously therefore it is preferable to have rare earth bands long with respect to their width, so that cross-contamination by overlap is minimized. This behavior is quite different from that of a mixture of rare earths under *elution analysis* conditions, where bell-shaped rather than flat bands develop and increasing the length of the column increases the distance between adjacent elution peaks.

EXPERIMENTAL

A limit of ⅓ kg. of lanthanum per run was imposed for several reasons: (1) there were restrictions due to the neutron and gamma activity from the americium associated with this amount of lanthanum; (2) ⅓ kg. of lanthanum would load a 2½-ft. resin bed, 6 in. in diameter, to 25% capacity originally and to half its length when the rare earth band had stretched out to equilibrium; (3) some such limit was suggested by the reported (*1*) formation of a precipitate when the initial loading of light rare earths exceeded 1.2 g./sq. cm. of column cross section; (4) exploratory work with a 5-cm. I.D. column and a resin-bed height of 70 cm. showed that lanthanum and americium were separated when the column was loaded to 22% capacity with a portion of the lanthanum-americium mixture to be separated. However, near the leading edge of the original absorbed band precipitation occurred, causing a portion of the americium to be held up. This precipitate dissolved and caught up with the main americium band before its elution.

It has been reported (*2*) that precipitation of the heavier rare earths can be avoided even with very high loading of the resin bed if high initial flow rates are used during spreading out of the rare earth band. After the rare earth band is spread out to its equilibrium length, the flow rate can be lowered. With 0.1% ammonium citrate at *p*H 8 used, the attainment of this equilibrium length involves lengthening of the band from its original absorbed length, in which nearly all the exchange sites are occupied by rare earth, to approximately twice this length (*1*).

There was available about a kilogram of light rare earths, consisting primarily of lanthanum with 5% cerium, in which americium was present to ~0.5 wt. % (4.5 g. of Am^{241}). Consequently, ⅓ kg. of lanthanum would contain only 1.5 g. of americium or ~18.5 meq. of trivalent americium. On a 2-in.-diam. column (20 sq. cm. area), with a resin capacity of 2 meq./cc., the final americium band would theoretically be only ~0.9 cm. long. (With 0.1% ammonium citrate, *p*H 8, the composition of the resin within the equilibrium band is divided about equally between ammonium and rare earth form.) Obviously, with such a length-to-width ratio, one could not anticipate a clean separation from the beginning edge of the rare earth immediately following. Nevertheless, if banding of the americium were obtained comparable to that reported for the rare earths, then adequate separation of the americium from the bulk of impurities would be achieved.

The combination of a 6- and a 2-in.-

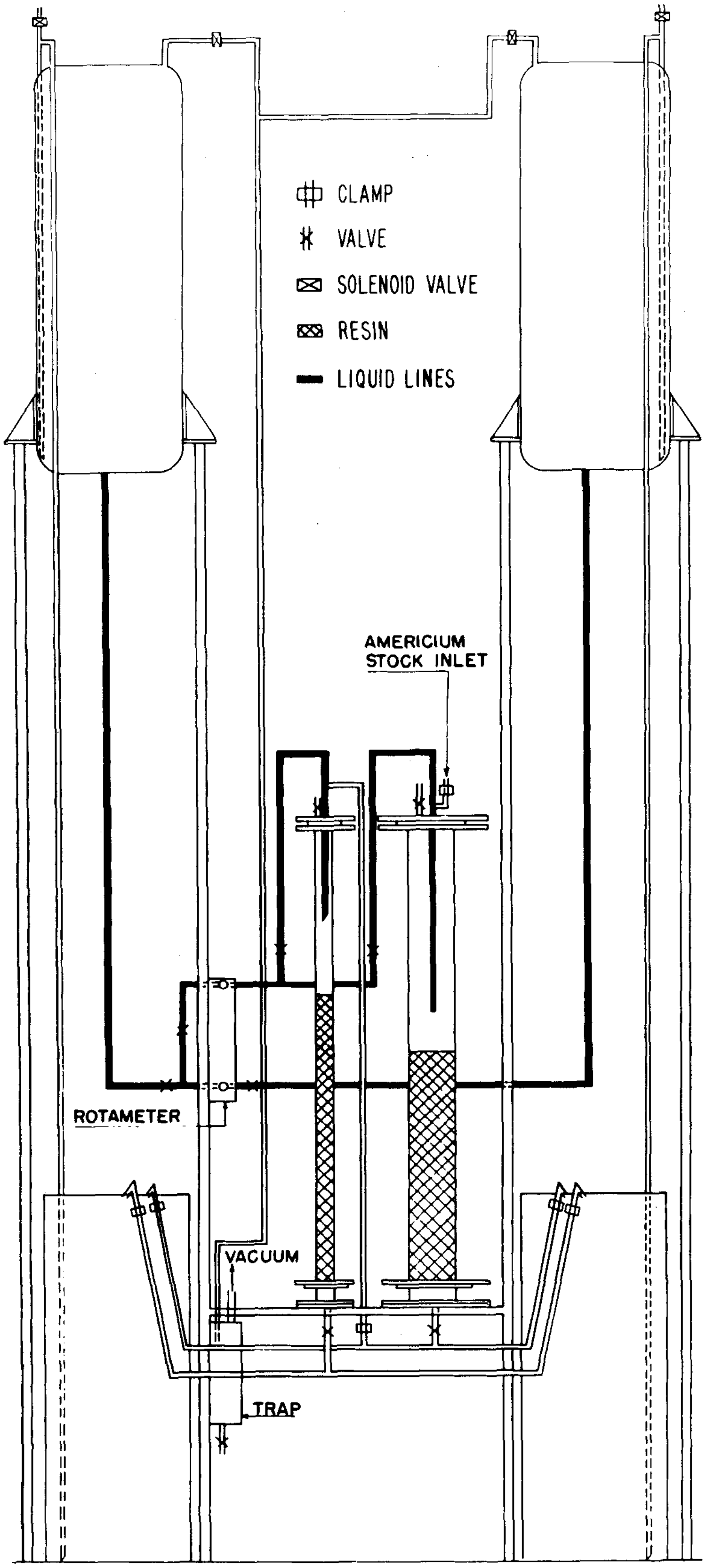

Diagram of apparatus.

diam. column was chosen, as if a 10-to-1 concentration of americium to rare earth was achieved on the 6-in. column, then use of a following 2-in. column would permit nearly the same loading/sq. cm. (9 to 1 area ratio) and should be sufficiently narrow to permit adequate banding of the americium and consequent separation from the bulk of the rare earths when the americium band was eluted.

Equipment

Two 5-ft. Pyrex pipes (one 2- and one 6-in. I.D.) were installed and connected to two 60-gal. overhead feed tanks and two 60-gal. floor tanks with ¼-in. stainless steel pipe. The two columns were connected so that the effluent from the 6-in. column might be fed to either of the floor tanks or to the top of the 2-in. column. A valve manifold allowed the use of any combination of feed and collecting tanks with either column. For recycling, the effluent solution was adjusted to *p*H 8 in the collecting tanks and was then vacuum-lifted (through ¾-in. polyethylene pipe) to the overhead feed tanks. Tygon tubing was used for all other connections.

Because floor space was at a premium, the entire apparatus was placed along the wall of a room with an 18-ft. ceiling and occupied a space only 2 by 8 by 17 ft. The two 60-gal. overhead tanks were strapped to the back wall and each stood on two 12-ft. lengths of 1½-in. standard pipe, bolted to a gusseted flange which was welded to the tank bottoms. The two floor tanks were placed between these pipe legs. The two glass columns were mounted between the two sets of pipe legs and were enclosed in a wooden box with Lucite front; this enclosure was connected to the exhaust system to prevent alpha contamination of the laboratory air. (*See* figure.)

The feed solution was gravity fed at constant head to the columns through a rotameter. Since continuous feed was necessary, the overhead feed tanks were used alternately. At $\sim$25 gal./hr., the fastest feed rate used, there was adequate time to adjust the *p*H of a tank of effluent and vacuum-lift it into the overhead tank before the other feed tank was empty. Air motors and stirrers with 3-in. propellers were used for mixing.

Resin

The ion exchanger was Dowex-50, a sulfonated styrene-divinylbenzene copolymer (8% DVB). Although the mesh size was given as 60 to 100, sieve analysis of the air-dried resin showed that $\sim$20% of the particles were finer than 100 mesh and $\sim$12% were coarser than 60 mesh. Resin for the columns was prepared by slurrying this stock with five times its volume of water and rejecting fractions that settled slower than 7 to 8 in./min. This remaining fraction contained resin coarser than 100 mesh. The effectiveness of water grading was demonstrated by the total retention of this resin by the 100-mesh screen at the base of the columns even after repeated back washing. Although the resin was finer than the $-20 + 30$ mesh size used by Spedding (*2*), it was sufficiently coarse to permit linear flow rates of 6 cm./min. with the effective head (10 ft.). Flow rates up to 9 cm./min. were maintained by connecting the column outlets to partially evacuated 12-gal. carboys.

The capacity of the water-settled, hydrogen-form resin was determined to be 1.95 meq./ml. Resin was loaded into the columns under water to a height of 80 cm. in the 6-in.-diam. column and to 100 cm. in the 2-in.-diam. column. The resin was supported on a 100-mesh stainless steel screen which was held in an inner slot cut partially through a neoprene washer. The gasket was held between a 2-in. glass spacer and the end plate of the column. The resin was conditioned by converting it to the ammonium form with 5% ammonium citrate solution, pH 8. It was then washed with water and converted to the hydrogen form with 2% sulfuric acid (until the effluent tested free from NH_3). The columns were washed with water to remove sulfate, and then the freeboard liquid over the resin was made $0.2N$ in hydrochloric acid.

Preparation of Feed Stock

One third of the americium-lanthanum stock solution was filtered to remove silica, drawn into an 18-liter overhead feed bottle (wrapped with 1/16-in.-lead sheet to reduce the americium gamma radiation), and diluted to 15 liters with hydrochloric acid. Water washes were used to rinse the lines. The resulting clear pink solution was then $0.17M$ in hydrochloric acid, $4 \times 10^{-4}M$ in americium, and $\sim 0.15M$ in rare earth.

The remaining two thirds of the americium stock was passed through chloride-form anion resin to remove an unknown constituent that caused precipitation when the original stock was diluted with water. It was then diluted and placed in the feed bottle in the same manner as the first one third had been handled.

Loading of 6-in. Column

The americium-lanthanum solution was siphoned onto the 6-in. column at a rate of ~1 to 2 cm./min. (3 to 6 gal./hr.). Absorption of americium on the resin was essentially complete, as the effluent contained much less than 1 μg./liter. The column was washed with water until a negative test for chloride ion was obtained. During the addition of the americium feed stock a large cavity in the center of the resin bed was noticed. This had evidently been dug by the stream of entering liquid. In the light of an ultraviolet lamp americium-lanthanum-form resin can be distinguished from the hydrogen form. Prominent spikes 2 to 3 in. long could be seen ahead of the main body of americium-lanthanum–form resin, an indication that absorption was not uniform.

For the two subsequent runs the loading technique was modified as follows. A length of closed-end stainless steel tubing ½ in. O.D. was suspended centrally from the feed pipe by use of Tygon tubing. Two rows of 0.04-in. holes were drilled radially near the closed end of this tube. This "shower-head" arrangement worked better than a baffle plate with the feed liquid jetting out symmetrically to the walls, even at low feed rates, as long as the holes were kept beneath the surface of the liquid over the resin. The dense rare-earth–americium feed solution formed a readily visible layer over the resin, and the less dense washes pushed the feed layer uniformly down into the resin. Absorbing the rare-earth–americium material by this technique gave a flat band with sharp boundaries.

Elution of Americium

Each of the overhead tanks was filled with 55 gal. of 0.1% ammonium citrate, 0.2% phenol, at pH 8. The water used had a conductivity corresponding to 2 p.p.m. (as salt). An auxiliary tank containing 50 gal. of citrate solution was held in reserve for emergency use. Each run required about 400 gal. of eluant; recycling made it possible to work with only 110 gal.

For the first run the 6-in. column was eluted at a linear flow rate of 5.2 cm./min. (15 gal./hr.). Part of the americium precipitated near the top of the column, but the remainder moved down the column as expected. (Later very slow citrate elution of the precipitate on the 6-in. column was successful.) When americium activity appeared in the effluent from the 6-in. column, the stream was diverted onto the 2-in. column at 1.5 gal./hr. Again a portion of the americium gamma activity was found to lag at the top of the 2-in. column, presumably by precipitate formation; however, before the main band of americium reached the bottom of this column, this lagging activity diminished and caught up with the main americium band. During the elution down the 2-in. column the americium formed a *sharp, visible* band about 1 cm. in length, which advanced at a linear rate down the 2-in. column, allowing accurate prediction of its elution time.

During the second run the flow rate through the large column was increased to 25 gal./hr. (8.6 cm./min.) to spread out the rare-earth–americium band and then maintained at 17 gal./hr. until the americium gamma activity was 10 cm. from the bottom. The flow rate was then cut to 8 gal./hr. to sharpen the bands. The 6-in. column (which had been loaded by use of the "shower head" in a very even band) eluted cleanly without perceptible lag of americium activity. However, when the flow rate was dropped to 1 gal./hr. during the passage of americium activity from the 6-in. column onto the 2-in. column, some of the americium activity again lagged at the top of the smaller column behind the main portion. This was avoided during the third run by transferring from the 6-in. column onto the 2-in. column at an increased flow rate, 9 cm./min. (3 gal./hr.) until the americium band had neared the bottom of the second column. The flow rate was then reduced to 0.34 cm./min. to sharpen the americium band prior to its elution.

As long as there is hydrogen-form resin in the column ahead of the eluting bands, ammonium ion (and any americium or rare earth ions) is removed from the 0.1% ammonium citrate and develops ammonium-form resin, leaving citric acid in the effluent, which can be adjusted to pH 8 and reused. Consequently the rate of band front advance is a linear function of the number of millequivalents of ammonium ion passed through each square centimeter of this front. The time rate of band advance depends on flow rate and column area. The time rate of the americium band advance varied with flow rate as predicted. Even with various flow-rate changes, as listed above, the rate of americium band advance per liter of eluant was time independent, as predicted by theory.

Ideally, there would have been americium activity only in the particular effluent fraction from the 2-in. column that contained the main batch of americium. However, in practice it was found that a few micrograms of americium activity was found in all effluent fractions, the amount building the closer americium came toward the bottom of the columns. Furthermore, it was not desirable to switch the effluent from the 6- onto the 2-in. column too soon because of the concomitant lowering in flow rate. Some americium activity therefore leaked through into the effluent stream prior to switching onto the 2-in. column.

RESULTS AND DISCUSSION

High pH citrate elution of an americium-light rare earth mixture from Dowex-50, with H^+ used as a retaining ion, has been demonstrated to be applicable for concentrating gram amounts of americium from amounts of rare earth more than 200 times greater. Formation of precipitate can be avoided by the use of high flow rates. Detailed analysis of the narrow americium band on elution showed that it was a small, flat-topped band, eluting along with the leading edge of the cerium band. Because of its dilution with cerium, americium did not reach its theoretical elution concentration of 8 to 9 meq./liter and required about 2 gal. for elution. No detectable lanthanum was found, but a trace amount of yttrium and ytterbium, too small to form finite-width bands, eluted with the beginning of the americium band. These materials had not been detected in a spectrographic analysis of the feed material but were concentrated along with the americium.

ACKNOWLEDGMENT

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