Separation of Lanthanides and Trivalent Actinides with Pressurized Ion Exchange

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SEPARATION OF LANTHANIDES AND TRIVALENT ACTINIDES
WITH PRESSURIZED ION EXCHANGE

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I. INTRODUCTION

    Certainly, one of the first triumphs of ion exchange chroma-
tography was the separation and identification of fission product
rare earths in the Manhattan Project in the early 1940s. Publi-

cations describing this work were withheld until 1947 when nine
papers from the Oak Ridge National Laboratory and the Ames
Laboratory at Iowa State University appeared simultaneously in the
Journal of the American Chemical Society.[2-10] This work revolu-
tionized the purification and production of rare earths because the
separations were relatively rapid (requiring only hours to days,
compared with years using classical methods) and, for the first
time, small amounts of material, even tracer levels, could be sepa-
rated.

A most important advance in chromatography was the development
and application of what is usually called high-pressure liquid
chromatography in biochemistry during the 1960s. This technique
has led to tremendous advances in those separations which require,
in particular, high resolution or a minimum time. Application of
this method to the separation of trivalent lanthanide and actinide
elements has met with outstanding success, especially for the puri-
fication and separation of extremely radioactive elements. Cur-
rently, pressurized ion exchange is used for the final separation
and purification of essentially all of the heaviest man-made acti-
nide elements which are produced, especially berkelium, califor-
nium, einsteinium, and fermium.

The rare earths include elements of atomic number (Z) 57
through 71; yttrium (Z = 39) is also often included. These ele-
ments are usually trivalent and have very similar chemical proper-
ties. The actinide series of elements differs from the lanthanide
or rare earth series in that the lighter members have stable
valences other than +3 and are chemically less similar to each
other. The term "trivalent actinides" refers to those members of
the actinide series which are usually or always trivalent in aqueous
solutions; this includes the group with $Z \geq 95$. Although some of
these elements, especially americium and berkelium in the actinides
and cerium and europium in the rare earths, exhibit other valence
states, the trivalent state must be dealt with in many practical
cases.

A brief explanation may be in order as to why the method known as high-pressure ion exchange in biochemistry is called pressurized ion exchange here. The reason is entirely practical. In an industry as safety conscious as the nuclear industry, the term "high-pressure" has roughly the same impact as a red flag in a bull fight. The modifier "pressurized" more accurately describes the system, and it does not attract undue attention.

A. Lanthanide and Actinide Separations by Ion Exchange

The initial publications describing rare earth separations[2-10] defined two basic approaches, elution development and displacement development chromatography. In each, the separations were based primarily on differences in complexing of the rare earth elements by citrate solutions during elution through a column of sulfonic acid cation exchange resin. Displacement development was generally used for large-scale separations because larger column loadings were practicable and product concentrations were higher. Elution development was used for small-scale separations (tracer level to many milligrams) because the elements could be completely separated into pure product bands.

A major advance in elution development chromatography resulted from studies of distribution coefficients provided by a large number of complexing agents, which permitted the selection of a suitable agent for any particular separation. For the general separation of all or any of these elements, α-hydroxyisobutyrate[11] (αHIB) is the best because the smallest of the separation factors for all pairs of elements is larger for αHIB than it is for any other known complexing agent. However, other complexing agents may be superior for separation of a particular combination of elements. Most reviews of this subject emphasize the early work with citrate, sometimes to the exclusion of anything else; however, essentially all separations for the past 20 years have been based on αHIB.

Applications have ranged from standard analytical separations to proof of the identities of several new actinide elements (berkelium, californium, einsteinium, fermium, and mendelevium) based on their relative elution positions.[12] The latter work was done on a tracer scale, in some instances utilizing only a few atoms (17, in the case of mendelevium). Elution development chromatography was the only practical method known for separating the trivalent actinide elements, and it was uniformly used for their purification. As the quantities of material being processed increased over the years, problems were encountered because of the intense radioactivity of some of these elements.

Displacement development chromatography progressed in a similar manner. It was demonstrated on a large scale at the Ames Laboratory using citrate,[13] but several other complexing agents were investigated during the early 1950s. Subsequently, various aminopolycarboxylic acid complexing agents (such as nitrilotriacetic acid, NTA; ethylenediaminetetraacetic acid, EDTA; or diethylenetriaminepentaacetic acid, DTPA) have generally been used. An important advance occurred in 1954 with the use of metal ions such as copper[14] and iron[15] to retain the rare earths during elution. These methods have been used for industrial rare earth separations, but the details are largely proprietary and unpublished. A good review was published in 1961 by Powell.[16]

Subsequently, Wheelwright and co-workers[17] at Battelle Northwest Laboratory used displacement development chromatography to separate the trivalent actinide and fission product lanthanide elements from the Shippingsport nuclear reactor blanket. The scale of the operation was large, involving more than 1 kg of americium, 60 g of curium, and 185 g of ^{147}Pm, which were of special interest for heat source applications. This work differed from the initial studies in that EDTA and NTA were used as complexing agents instead of citrate, zinc was used for the barrier ion, and an elevated temperature was employed to improve the kinetics.

B. Actinide Production Programs

During the 1960s a new factor became increasingly important, and this was the extremely high levels of radioactivity which would have to be dealt with. Certain fission product rare earths and most of the actinides are quite radioactive. When decisions were made to devote a substantial effort to the production of the heavy actinide elements by neutron irradiation in nuclear reactors, it was not at all clear that technology was available to separate and purify these elements. Previous experience with gram quantities of americium and curium indicated that the necessary separations could be accomplished only by chromatographic means, but that radiation damage, with conventional ion exchange, for example, might be intolerable.

Large quantities of transplutonium elements, the heaviest elements that have been produced in appreciable amounts, were desired for use by research workers throughout the world. These actinides have been produced in two separate programs. At Oak Ridge National Laboratory two facilities were constructed, the High Flux Isotope Reactor (HFIR) to provide an extremely high neutron flux to cause the successive neutron capture and transmutation reactions to produce the heavy nuclides, and the Transuranium Processing Plant (TRU) to accomplish the recovery and purification of the heavy element products and the recycle of the lighter actinides for additional production.[18]

An oversimplified statement of the goal of this program, with a capital investment of many millions of dollars, is to produce 1 g of californium; in fact, annual production is about 0.5 g of ^{252}Cf at present. The scope of the separation problem in this operation is to process quantities of actinides ranging up to tens of grams of americium and curium, hundreds of milligrams of berkelium and californium, milligrams of einsteinium, and a billion atoms of fermium.

A combination of solvent extraction and anion exchange
processes is used to separate the heavy actinides from the rare
earths and most of the americium and curium, so the total amount of
material processed by cation exchange is small enough that elution
development can be used. With αHIB elution, separation factors for
successive elements generally exceed 1.3, and the extent of sepa-
ration and yield are both desired to be about 99.9% for each ion
exchange cycle. Thus, the requirement is for an ion exchange column
capable of achieving about 500 equivalent theoretical plates with
an initial loading of up to 10 milliequivalents of actinides; this
material will produce a few watts of radiation energy.

Subsequently, a Californium Production Program was initiated
at the Savannah River Laboratory (SRL) to produce more californium
in less time.[19] The initial approach depended on solvent extrac-
tion for all separations of transplutonium elements. Because of
operational problems, ion exchange was later used for the sepa-
ration not only of actinides from each other, but also of actinides
from fission product lanthanides. The separations involved several
kilograms of ^{244}Cm, with individual batches of as much as 100 g of
^{244}Cm, about 200 g of fission product rare earths, and small
quantities of transcurium elements. Radiation damage is a more
severe problem because of the greater column loading. This scale
of work is best done with displacement development; however, the
column resolution again must correspond to a few hundred plates,
as is the case with elution development.

The radiation damage problem is encountered in both the aqueous
phase, where gas bubbles are generated due to radiolysis of water,
and in the organic phase, which loses exchange capacity and swells
because of breaks in polymer chains. Gas formation was so serious
in Wheelwright's work[17] that the resin bed sometimes separated into
segments; this clearly degrades any chromatographic process. Resin
damage is a function of radioactivity of the system and the time of
exposure; for example, experience indicates that Dowex 50 resin

loaded with ^{244}Cm becomes difficult to elute after a number of hours.

The requirements for this work may be summarized as reasonably high (but not extreme) resolution, small to moderate capacity (a few moles), suppression of the effects of radiolytic gassing, and an unusually high speed of separation to minimize the radiation exposure time. These goals are all admirably, and perhaps uniquely, met by pressurized ion exchange.

C.   Development of Pressurized Ion Exchange

It was also during the 1960s, at the same time that these separations problems were being faced, that high-pressure liquid chromatography was being developed, but in the entirely separate discipline of biochemistry. The application of high-pressure chromatography to biochemical separations is an exploding science which has resulted in numerous publications, including review articles in this journal and several books.[20,21] However, it should be pointed out that the rare earth separations work during World War II and the development of high-pressure chromatography are not unrelated events.

Historical reviews of this development (for example, the review by Brown[21]) generally start with Martin and Synge[22] in 1941 and then jump to the work of Cohn[23] in 1949 on the separation of important biochemical materials. These separations were so important that major efforts were devoted to achieving better results, and subsequent work was focused on improving the resolution of the chromatographic system. This led to the use of very small exchange particles, which, in turn, caused low flow rates. Undoubtedly, many attempts were made to overcome this difficulty by increasing the pressure drop along the column, but really successful systems appeared only after dependable hardware (pumps, valves, fittings for connecting components) was introduced commercially. It was

this, rather than any individual genius, which made high-pressure chromatography practical.

Cohn's work in 1949 is generally reported to be the germinal factor which provided the incentive for improved separations methods and led eventually to the high-resolution systems that are so popular today. This work, however, derived from Cohn's earlier involvement with rare earth separations during World War II; he was coauthor of one of the original publications.[2] It was a logical and well-conceived approach to try this new technique in his original field of interest, biochemistry, once the war-time priorities were ended.

Heftmann[24] pointed out that the application of ion exchange elution chromatography to problems in the nucleic acid field followed directly from the invention of the technique and its application to rare earth separations by Tompkins, Khym and Cohn,[2] and that this was the way in which elution chromatography was introduced into biochemistry. Cohn[25] has written that the nucleic acid separations represent a "direct translation of the principles evolved" in his earlier work on ion exchange separations of fission products. The remainder of the story is well recorded. The intriguing fact is that the technology which eventually resulted from this work was applied some 20 years later to the separation of the actinide elements which are so closely related to the rare earths.

II. LANTHANIDE AND ACTINIDE SEPARATIONS BY ELUTION DEVELOPMENT

Because of the apparent advantages of pressurized ion exchange for actinide separations, a program was started in 1967 at Oak Ridge National Laboratory to develop this technique for use in the TRU facility. Nearly all the actinide elements emit alpha radiation, and safety considerations require that such materials be handled in glove boxes with unusually good containment. The

resulting difficulty of the experimental work has led to the common practice of using rare earths as stand-ins in process development work, since the behavior of rare earths can be extrapolated to that of actinides with considerable confidence. For this reason, more detailed experimental data are often available for rare earths, while most information about actinides is derived from production-scale separations.

Elution development separations generally use αHIB eluent and either Dowex 50W-X8 or Dowex 50W-X12 resin. In this resin-eluent system, both actinides and lanthanides are eluted in reverse order of their atomic numbers, that is, heavy members first and light members last. The two series overlap, however; and, although separation factors always exceed 1.3 within each series, they may be very small for interseries separations.[11] Some work has been done using liquid-liquid chromatography, which is especially useful in certain separations because the elution orders are changed.

A. Rare Earth Separations

Campbell initially used pressurized ion exchange to separate rare earths on a scale projected for actinide separations in the TRU facility, and then demonstrated the separation of fermium, einsteinium, californium, berkelium, and curium on a smaller scale.[26] The most detailed studies were made with neodymium and praseodymium and with samarium, gadolinium, and europium, each group including one of the more difficult pairs of rare earths to separate.[27] Quantities up to 200 mg (1.3 millimoles) were successfully separated in times well under an hour, and this easily met the requirements anticipated for the projected actinide production.

The equipment used in initial experiments was similar to that developed by Scott for biochemical separations,[28] consisting of 50- to 150-cm-long glass and stainless steel columns containing 10-20 or 20-40 μm Dowex 50W-X12 resin. Through the years, the systems have been gradually modified to fit better the requirements

for actinide separations; these differ from biochemical separations
primarily with regard to the greater emphasis on speed of separation,
even at the expense of loss of resolution, and the necessity to
separate much larger quantities in many cases. In particular,
higher flow velocities and somewhat larger resin particles are
usually used to minimize processing time and radiation damage.
Columns are usually about 2 ft long for use in glove boxes or 4 ft
long for use in shielded cells because manipulators for remote
operation cannot reach both ends of longer columns; the diameter
is chosen to provide adequate resin volume for the quantity of
metal to be separated.

The rare earths were eluted with αHIB at much higher flow
velocities[29] than those typically used for conventional ion exchange
separations (i.e., up to 25 cm/min vs a few tenths of a centimeter
per minute). Operation at elevated temperature (80°C) resulted in
only very slightly better separation, but the lower pressure drop,
resulting from decreased viscosity, was of more value. Good sepa-
rations were generally achieved with loadings up to 200 mg, which
corresponds to about 6% of the column capacity; with a 25% loading,
band shapes were distorted and substantial overlap occurred.
Precipitation which was observed in glass columns with very high
loadings apparently resulted from the limited solubility of com-
pounds formed between the rare earths and the eluent. It is
generally recognized that resin loadings should not exceed about
10% of the total column exchange capacity with the elution develop-
ment approach.

Since several percent of the resin is usually loaded with
trivalent metals, tests were made to determine whether it would be
advantageous to completely load a small column (0.17 cm^2 by 2.3 cm
long), which could then be eluted through a long chromatographic
column. Results showed that it was practical to load quite short
columns at flow velocities up to 50 cm/min; even with unusually
fine resin (3–18 μm), pressure drops were reasonably low because

of the short length. The use of such a loading (or preabsorption)
column was advantageous for other reasons in addition to the high
flow rate and moderate pressure drop. A major reason was that many
impurity ions which have some tendency to load on the resin are
displaced or eluted during the loading cycle. Nearly all ions, in
contrast, are loaded if the column feed is pumped to the entire
chromatographic column.

One factor which can degrade the separation is the presence of
H^+ ion on the column during elution. The eluent is a buffer
solution that is prepared by partial neutralization of α-hydroxy-
isobutyric acid with NH_4OH. Acid on the resin will decrease the pH
of the eluent within the column; this decreases the concentration
of the αHIB^- ion which complexes the rare earths and causes them to
elute. The result is that elution is delayed and bands move slowly
with little separation until excess acid is neutralized by the
eluent. The column may provide much poorer resolution than it
would if the H^+ ion were not present.

In this work the feed to the column often consists of a sub-
stantial volume of dilute nitric acid solution (a few tenths molar),
which loads by displacing ammonium ion from the resin. It is
important that any such H^+-form resin be converted back to the NH_4^+-
form after loading and before elution. This can be accomplished by
washing the loaded column with several bed volumes of dilute NH_4NO_3
solution; in addition, the problem is greatly diminished by using a
small loading column. Acid loading has been the cause of nonrepro-
ducible elutions and poor resolution in many cases, particularly in
production separations.

Typical separations of neodymium and praseodymium are shown in
Figure 1, which compares results from two experiments which were
identical except for loading. With the higher loading (lower curves)
the first band, neodymium, starts at the same eluent volume but runs
longer. The second band, praseodymium, is delayed by the increased
loading. Thus, with appreciable loadings, band positions are not
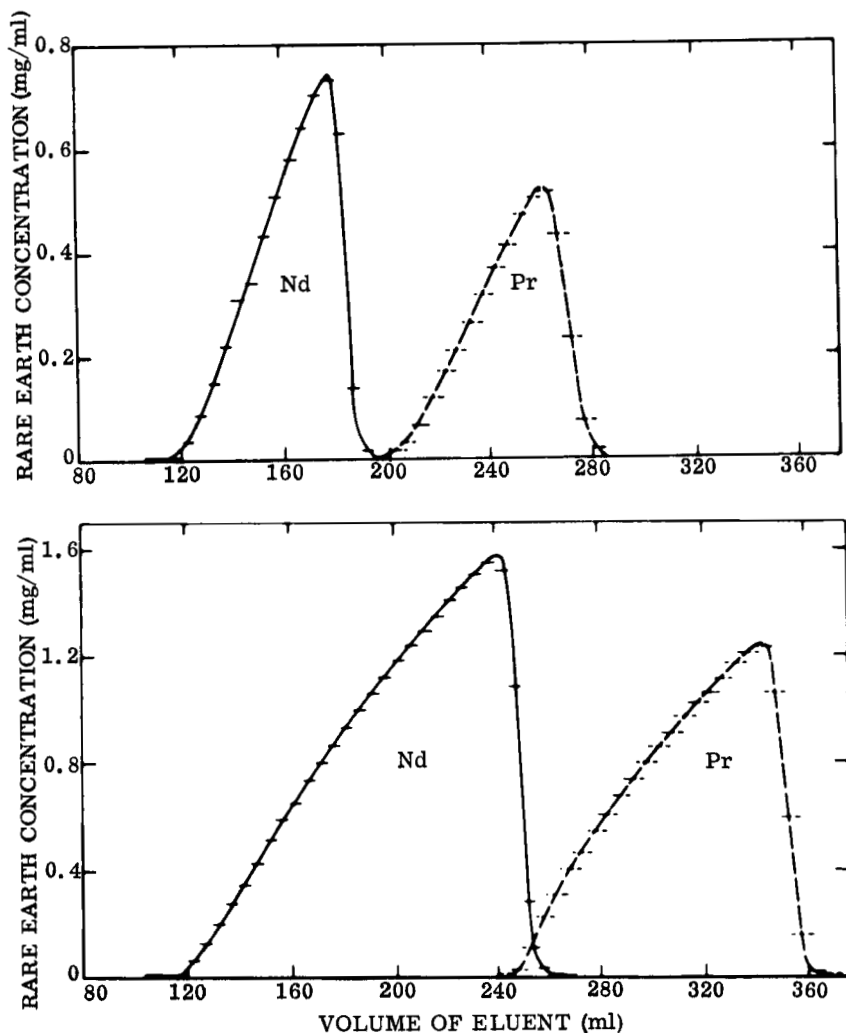
FIGURE 1

Separation of Neodymium and Praseodymium. Conditions: 0.43 $\underline{M}$, pH
4.4 αHIB; 0.66 cm x 150 cm column; Dowex 50W-X12, 20-40 μm resin;
80°C., 8 ml/min.   Top – 25 mg Nd + 17.5 mg Pr; Bottom – 119 mg Nd +
82 mg Pr.   Reprinted with permission from D. O. Campbell and S. R.
Buxton, Ind. Eng. Chem., Process Design Develop., $\underline{9}$, 89 (1970).
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determined simply by distribution coefficients; they also depend on
loading. The unsymmetrical band shapes shown are characteristic of
all such elutions with substantial resin loading; a Gaussian shape
is approached as loading decreases.

Campbell and Ketelle[30] investigated the feasibility of applying
this technique to very rapid tracer separations which might be
useful for purifying short-lived products of nuclear reactions.
They used small columns, 6.3 to 25 cm long, containing 0.25 to 1.00
ml of 10-20 μm Dowex 50W-X12 resin. Studies of the band width of
eluted [141]Pr tracer as a function of flow rate demonstrated that
adequate resolution for separations of adjacent rare earths could
be achieved in times as short as 5 min in the worst case, and about
1 min in many instances (Figure 2).

Separations of several rare earths are required for certain
analytical purposes, and the separation of all of them is an ulti-
mate test. Pressurized ion exchange was first applied to this
problem by Sisson, Mode, and Campbell.[31] In this work, 5 mg each
of nine rare earths and yttrium, plus tracer quantities of several
others, were separated using αHIB elution with a concentration
gradient. Of the several variables studied, including flow rate,
resin cross-linkage, and particle size, the most critical was the
shape of the eluent gradient. Most of this work was done with a
0.63-cm-diam by 24-cm-long column containing 7.5 ml of 25 ± 7 μm
AG50W-X12 resin. Flow velocities up to 13.5 cm/min were used.

Generally, good separations were obtained as long as the
gradient was suitable. Final conditions were defined which gave
adjacent element resolution[32] averaging 1.28 for all elements and
0.96 for the poorest case, the lutetium-ytterbium separation. The
specified procedure required less than 5 hr for separation of all
the rare earths; the same type of separation required 42 to 48 hr
prior to the use of pressurized ion exchange.

Subsequently, Campbell[33] studied the separation of all 15 rare
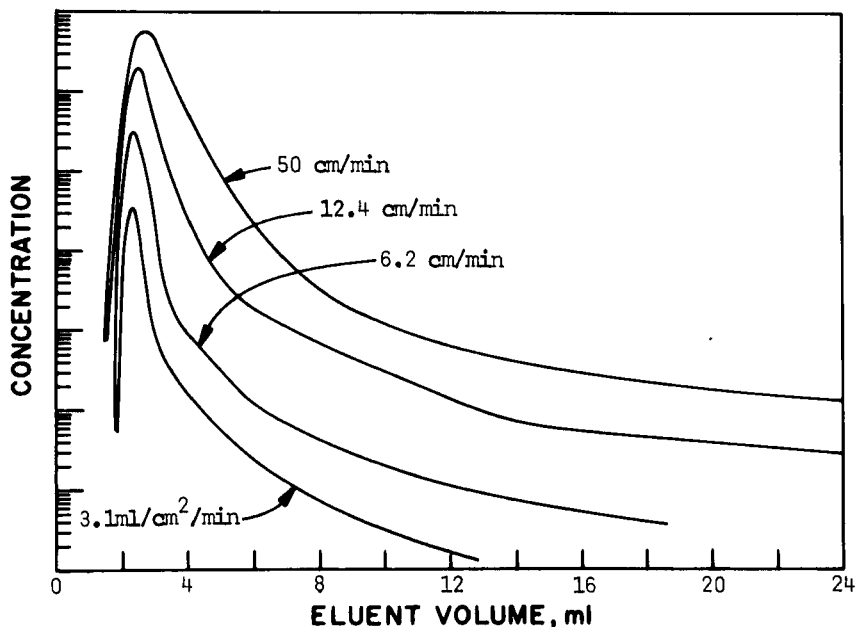earths in quantities of 5 mg or 20 mg of each element (except tracer

FIGURE 2

Effect of Flow Rate on Band Width. Conditions: Tracer Pr eluted
with 0.57 M, pH 4.4 αHIB; 0.16 cm x 12.5 cm column; Dowex 50W-X12,
10-20 μm resin; 25°C. The ordinate scale is arbitrary. Reprinted
with permission from D. O. Campbell and S. R. Buxton, Ind. Eng.
Chem., Process Design Develop., 9, 89 (1970). Copyright by the
American Chemical Society.

promethium). The column was 0.64 cm^2 x 33 cm and contained 22 ml
of 25-60 μm Dowex 50W-X8 resin in most tests; however, both longer
and shorter columns containing the same resin were used in some
cases. Resin loadings were 3 or 12%. Flow rates up to 15.7 cm/min
were used, and excellent separations were obtained in times as short
as 1.5 hr with the smaller resin loading (Figure 3).

Again, the selection of the eluent gradient was a very impor-
tant (and empirical) variable. With a suitable gradient, excellent
separations were achieved with the smaller loading and the maximum
flow rate available; resolution for successive bands varied from
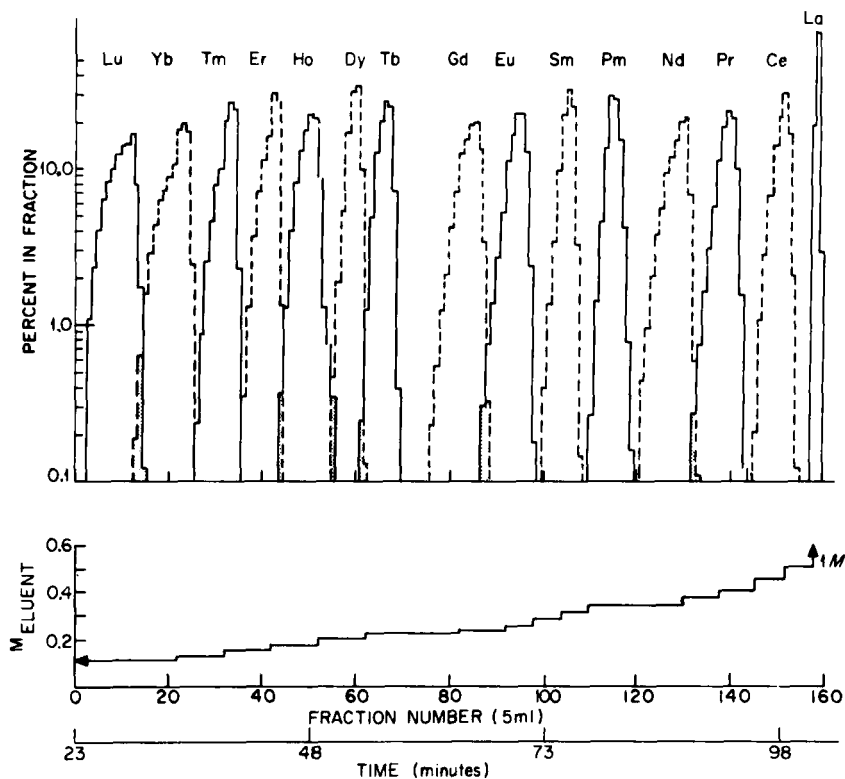
FIGURE 3

Separation of All Rare Earths Using Gradient Elution. Conditions:
pH 4.4 αHIB; 0.9 x 33 cm column; Dowex 50W-X8, 25-60 μm resin; 80°C.,
10 ml/min; 5 mg each element except for tracer-level Pm. Reprinted
from D. O. Campbell, J. Inorg. Nucl. Chem., **35**, 3911 (1973).

1.30 to >2. With the larger loading (12% of the resin), poorer

separations were obtained, especially during the first half of the

elution; resolution varied from 0.5 to >2, being <1 for four pairs.

The use of lower flow rates or a longer column had very little

effect on resolution. A column only 11.7 cm long gave much poorer

results which, however, were markedly improved at lower flow rates.

It was concluded that such a short column containing smaller-

particle resin should permit good separations in substantially less

time, well under an hour. The pressure drop was only 50 psi with this column at the maximum flow rate available; hence it would be reasonable to use substantially smaller resin and a higher flow rate.

It was also pointed out that systems of this type, although small, have a rather substantial time-average throughput. In this work, quantitative separations were obtained in times and on a scale corresponding to 100 g of rare earths per day per liter of resin. **This compares very favorably with the throughput of the** displacement development chromatographic systems normally used for larger-scale work.

A pressurized ion exchange system essentially identical to the systems commonly employed for biochemical separations was used by Karol[34] to study the relative advantages of αHIB and α-hydroxy-α-methylisobutyric acid for rare earth separations. In contrast to the common procedure of loading and eluting in separate steps, a sample injection valve was used in this work to inject a small volume of tracer rare earths into the flowing eluent. **The flow** velocity was 5.4 cm/min. **This procedure yielded excellent repro-**ducibility, and the difficulties often encountered in such studies were effectively eliminated.

Another application of pressurized ion exchange is the separa-tion and purification of rare earths for the determination of their energy levels and other nuclear properties. **For example, Pinajian** et al.[35] used the method developed by Campbell and Buxton[27] to sepa-rate ^{156}Tb which was produced by proton bombardment of stable ^{156}Gd in a cyclotron; tracer quantities of the product must be separated from about 100 mg of the target rare earth. **Other carrier-free** isotopes produced by this method include ^{156}Eu, ^{149}Eu, ^{148}Eu, ^{148}Pm, and ^{151}Gd. **In such work, it is generally observed that cleaner** separations are obtained in less time and with more dependability than when conventional ion exchange is used.

B. Trivalent Actinide Separations

Elution development with conventional ion exchange systems has
long been used to separate small quantities of transplutonium
actinides for the simple reason that no other general method has
been available. Generally, good separations have been achieved with
tracer or very small loadings, while poorer results have been
observed with multimilligram quantities. In all cases flow veloci-
ties were low, typically a few tenths of a centimeter per minute;
and elution times were correspondingly long. Although the method
was used to purify multigram quantities of americium,[36] yields of
pure product were undesirably small and much recycle was necessary.

The application of pressurized ion exchange to this problem
has resulted in a large reduction in the time required for the
separation, a major improvement in both the yield and purity of
product, and a substantial increase in the quantity of material
which can be satisfactorily processed. In fact, scale-up appears
to offer no special problem and can be predicted from the results
of small-scale experiments; however, displacement development is
still generally used for large-scale production work.

It is perhaps an overgeneralization, but the use of small resin
in pressurized ion exchange systems permits an improvement in per-
formance by a factor of probably between 10 and 100. This improve-
ment may be realized via one or a combination of several factors,
including high flow rate and short separation time, or better reso-
lution. However, for the highly radioactive actinides, the major
advantage is that the range of usefulness of the ion exchange chro-
matographic method is extended to materials more radioactive by this
factor of 10 to 100.

1. Laboratory-Scale Separations

Actinide separations were first demonstrated by Campbell[26,37]
using small amounts of all the transplutonium elements which can be

produced by neutron irradiation (americium, curium, berkelium, cali-
fornium, einsteinium, and fermium). The columns, which were
installed in a glove box, were 66 cm long and contained either 5.35
or 11.2 ml of Dowex 50W-X12 resin, 10-20 or 20-40 μm. Flow veloci-
ties up to 25.6 cm/min were used. After the equipment had been
tested with several synthetic mixtures, small amounts of process
solutions from the TRU operations were separated for demonstration
purposes.

A separation of the six transplutonium elements is shown in
Figure 4. Amounts of the elements varied from about 0.5 mg each
of americium and curium, down to 0.07 μg of californium, 0.3 ng of
einsteinium, and $<10^7$ atoms of fermium, but all the transcurium
elements were reasonably well separated from each other. The curve
labeled "β" is a mixture of berkelium and europium, which were not
resolved. The goal of this work is to separate each of the trans-
curium elements and a curium-americium mixed fraction which is
returned to the reactor to produce more transcurium elements. Thus,
the separation of curium from americium is not an overall objective,
and the eluent concentration is increased to effect more rapid
elution. This separation required substantially less than 1 hr.

It should be pointed out that the ordinate in Figure 4 is a log
scale, and that the bands are reasonably Gaussian over a concentration
range of three orders of magnitude or more. However, at lower con-
centrations each band shows tailing to the right, which extends more
or less indefinitely. Any tailing to the left results from material
remaining from the previous run with the same equipment. This
tailing, which is probably characteristic of all separations utilizing
reasonably complex equipment, is not usually reported or observed
because of insufficient sensitivity of the detection methods. In
this work, for example, curium can easily be followed over a con-
centration range of a factor of 10^7.

Typically, tailing begins at a concentration varying from about
1000-fold less than the peak maximum for a poorly engineered system
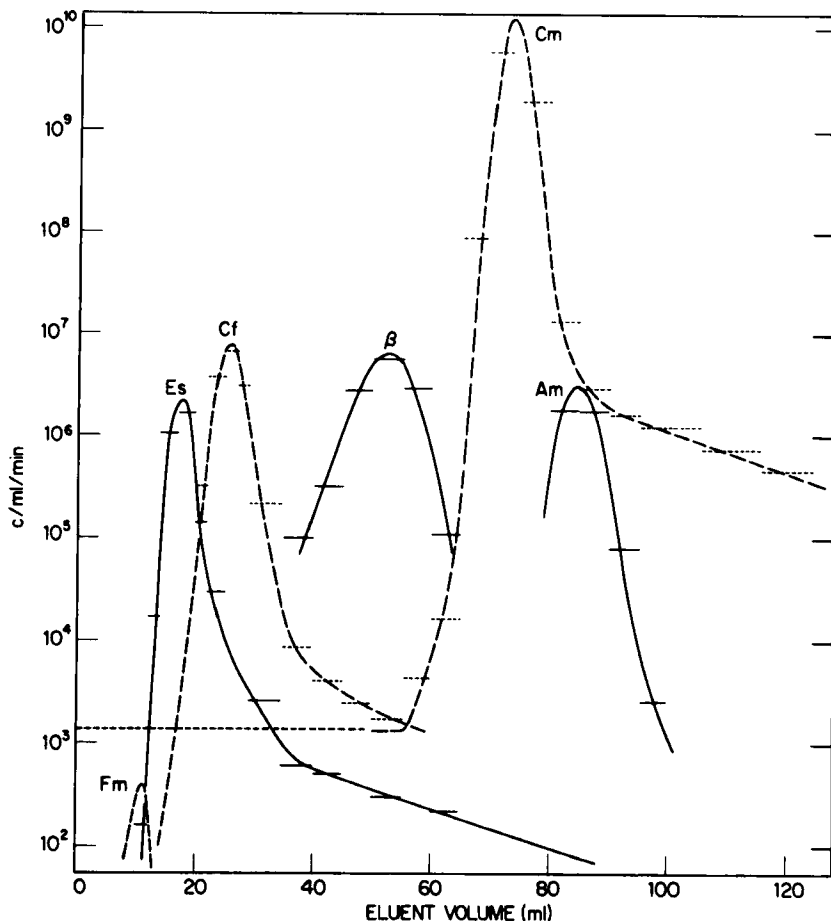
FIGURE 4

Separation of Transplutonium Actinides. Conditions: pH 4.4 αHIB;
62 ml 0.26 $\underline{M}$ followed by 0.32 $\underline{M}$; 0.32 cm x 66 cm column; Dowex
50W-X12, 20–40 μm resin; 80°C., 2 ml/min. Reprinted with permission
from D. O. Campbell, Ind. Eng. Chem., Process Design Develop., $\underline{9}$,
95 (1970). Copyright by the American Chemical Society.

to 10^4-fold less for a simple system; the concentration then drops

slowly with volume throughput. This behavior has also been observed

with conventional ion exchange, and it was shown that it can be

reduced by carefully cleaning all surfaces above the resin bed after

loading and before elution.[38] Tailing ultimately limits the degree
of purity that can be achieved in a single ion exchange cycle, so
that resolution greater than that required for a 10^3 to 10^4 purifi-
cation factor is unwarranted.

2. Production-Scale Separations

     This method was immediately applied to production-scale sepa-
rations in the TRU facility at ORNL.[39] In this facility, conven-
tional solvent extraction and conventional ion exchange processing
are used to prepare a fraction containing all of the transcurium
actinides, part of the americium and curium, and very little of the
rare earths. Pressurized ion exchange is used to separate and
purify further the elements berkelium, californium, einsteinium,
and fermium, which are the major products of the operation.

     The first separation cycle results in five major fractions con-
taining, successively, fermium (if enough is present), einsteinium,
californium, berkelium, and finally the americium-curium fraction
which is recycled to the reactor for further irradiation. The
californium and berkelium products are further purified in additional
ion exchange cycles, and fermium and einsteinium are purified
additionally in subsequent cycles, but with much smaller equipment.

     Since TRU is a production facility, no analytical data for
definition of elution curves are available; but product analyses show
that ion exchange column performance is excellent. An elution curve
derived from an in-line alpha radiation monitor is shown in Figure
5; this detector cannot distinguish one element from another and
is insensitive to berkelium which emits very little alpha radiation.
Nevertheless, the successive peaks clearly indicate the fermium,
einsteinium, californium, and curium elution bands (berkelium appears
between californium and curium).

     Ion exchange columns used in the TRU facility are a maximum of
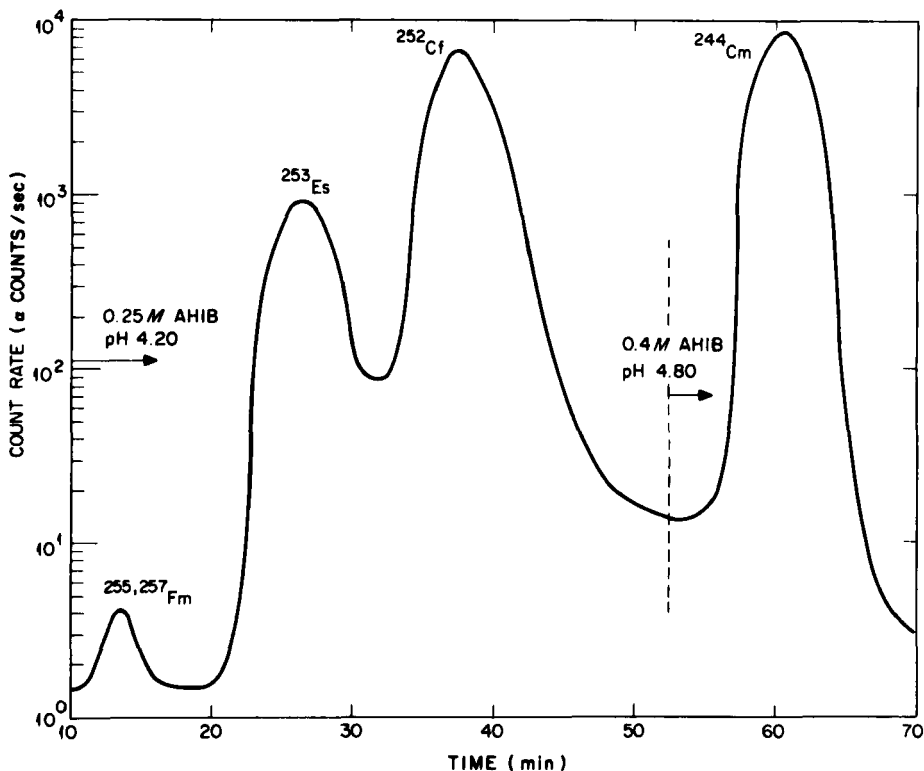4 ft long because they must be operated with remote manipulators.

FIGURE 5

Production-Scale Separation of Transplutonium Elements as Measured
by In-Line Alpha Detector. Conditions: 0.77 cm x 122 cm column;
Dowex 50W-X8, 25-50 μm resin, 80°C., 5 ml/min.

A photograph of a typical equipment rack installed in TRU is shown

in Figure 6; several such racks are used, and this one served for

a 5-year period. Such systems are constructed and tested prior to

installation in the shielded cells. Two jacketed elution columns

can be seen at the left, along with a short, unjacketed column for

loading. Other equipment includes valve manifolds, product col-

lection bottle racks, a vacuum pump for solution transfer, and

glass vessels for solution adjustment and storage. It is standard

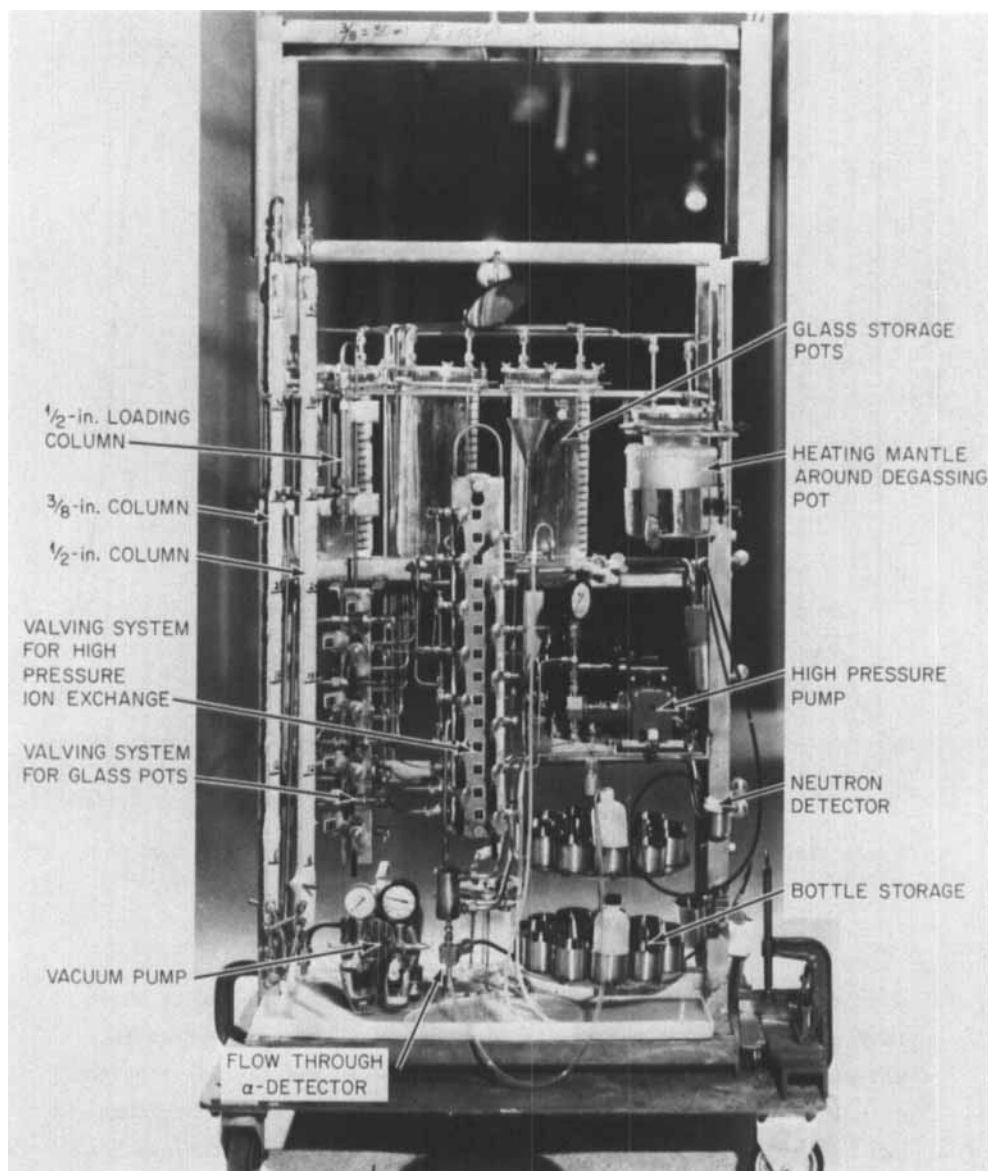practice to replace resin periodically by pumping water to carry

Figure 6
Typical Pressurized Ion Exchange Equipment Rack Used in TRU Processing.

LANTHANIDE AND ACTINIDE SEPARATIONS

the old resin out of the columns and then to displace new resin from a reservoir into the columns.

Columns with diameters up to 1.5 cm are used for the primary separation; however, most columns are made from 3/8- and 1/2-in.-OD stainless steel tubing and contain 50 and 105 ml of resin, respectively. The smaller column is used for loadings up to about 300 mg, and the larger up to 750 mg; thus, loadings are generally less than 5% of the resin capacity. The use of a loading column to load the feed rapidly is extremely important for separations involving high radiation levels. It is then washed with dilute ammonium nitrate solution and eluted through one of the 4-ft columns. Subsequent purification cycles for einsteinium and fermium are carried out in similar but smaller equipment.

The concentration of the eluent, αHIB, may be changed stepwise two or three times during an elution, usually immediately after an element has been eluted. The resin normally used is Dowex 50W-X8, although Dowex 50W-X12 has also given good results. Particle sizes are typically 25-50 or 70-100 μm, and a fairly narrow size fraction is preferred. Flow rates are 15 cm/min for loading and 12 cm/min for elution. The separation of transcurium elements requires about 2 hr, while second-cycle separations of two elements and purifications of individual elements require less time.

Actinide loadings for individual runs may be as high as 750 mg, although some, such as fermium-einsteinium separations, are done on a much smaller scale. The major source of radiation damage is californium, and californium loadings of up to 120 mg have been processed in individual runs. Larger amounts could be handled with the existing procedure, and the separation time could be further reduced, if necessary; this would permit the processing of larger amounts of californium. Present annual production rates are about 500 mg of ^{252}Cf, 50 mg of ^{249}Bk, 2.5 mg of ^{253}Es (20.5-day half-life), and 1 pg of ^{257}Fm (2×10^9 atoms) per year. Fermium-257 is

the heaviest isotope of reasonably long half-life (94 days) which
can be produced by nuclear reactor irradiation. Although the plant
capacity would permit this production to be doubled, present demand
does not justify such an increase.

Larger-scale separations were demonstrated by Thompson,[40] who
purified ^{242}Cm from americium. The 163-day half-life of ^{242}Cm pro-
vides probably the highest specific radioactivity of any element
processed in gram quantities. Because the separation factor for
the curium-americium separation is only 1.4, this is one of the
more difficult pairs to separate; even so, the curium was success-
fully purified using elution development with αHIB in a pressurized
ion exchange system.

The equipment used for curium purification consisted of a
9-in.-long loading (preabsorption) column and a 45-in.-long elution
column, each made of 2 in. sched 40 stainless steel pipe. The
feed, which contained about 0.5 g of ^{242}Cm and was 0.5 $\underline{M}$ in total
cations, was loaded at 22 cm/min; elution was carried out at 4 cm/
min. The radioactivity of ^{242}Cm corresponds to 122 W of decay
energy per gram. The same resin was used for six runs, after which
poor loading occurred. This deterioration in performance was
probably a result of radiation damage; radiolytic gassing was not
a problem.

A single pressurized ion exchange column was used by Burney
et al.[41] to separate milligram amounts of californium from multi-
gram quantities of americium and curium. The column used for this
work, 5.1 cm in diameter by 122 cm long, contained 2.4 liters of
20-40 μm Dowex 50W-X8 resin. It was operated at 75°C at a flow
velocity of 8 cm/min. In this work, the pH of the αHIB eluent was
increased stepwise, usually shortly after each element was eluted.

An elution curve for a run with 35 g of curium-americium is
shown in the lower curve of Figure 7; this corresponds to a loading
of slightly more than 10% of the resin. Good separations are
obtained for californium; berkelium, which is in the leading edge
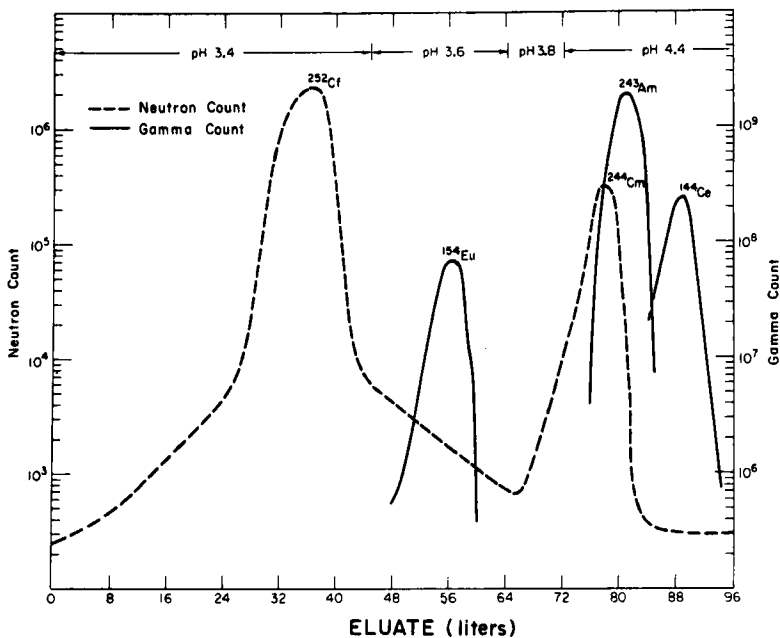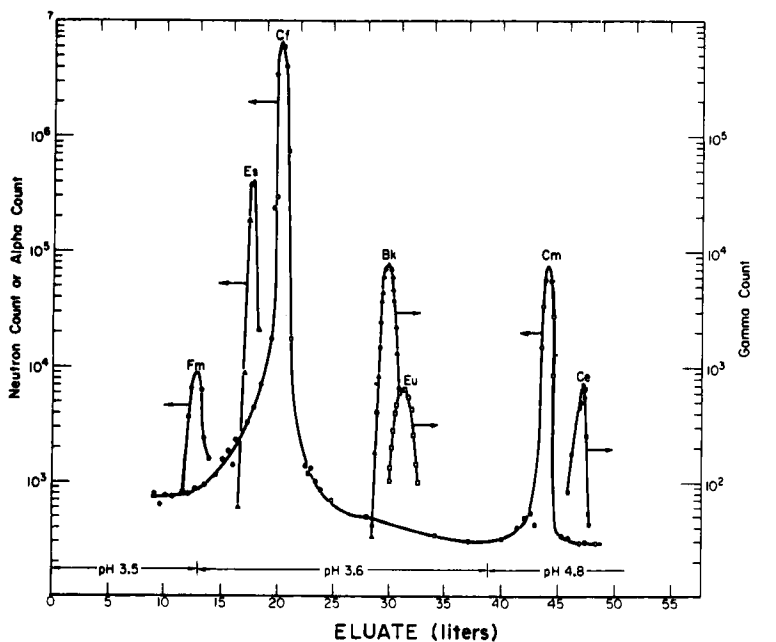
FIGURE 7

Multi-Gram Actinide Separation with Elution Development. Conditions: 0.4 M αHIB; 5 cm x 122 cm column; Dowex 50W-X8, 20–40 μm resin; 70°C., 160 ml/min. Upper – 1.5 g Cm, 1.5 mg Cf, tracer Bk, Es, and Fm; Lower – 21 g Am, 14 g Cm, and 1 mg Cf. Reprinted with permission from G. A. Burney and R. M. Harbour, Radiochim. Acta, 16, 63 (1971).

of the europium band; and the curium-americium recycle material,
which is used to fabricate new irradiation targets. Transcurium
elements, if present, would be well resolved before the californium
band appears. Band tailing is apparent, at a factor of about 1000
below the peaks. It was stressed that displacement of acid by
washing the column with dilute ammonium nitrate solution after
loading was important to good resolution of the californium peak;
it would be even more important for the resolution of transcalifor-
nium elements.

     With smaller column loadings, product bands were much sharper
and better separated. This is clearly demonstrated in the upper
curve of Figure 7, which shows the separation of 1.5 mg of cali-
fornium and smaller quantities of other elements from about 1.5 g
of ^{244}Cm. This represents a loading of less than 1% of the resin.
The feed for this separation was derived from an elution product
using displacement development with DTPA, as described later.

     The important conclusion from this work, however, is that
elution development can be applied successfully to the separation
of such large quantities, many tens of grams, a scale of operation
which is usually conceded to displacement development. Historically,
the scale of operation was almost always either very small or
rather large, but recently more and more problems are appearing
which involve an intermediate scale (i.e., several grams to hundreds
of grams). With proper conditions elution development, as well as
displacement development, can be used for such separations. For
extremely high radiation levels, in particular, elution development
may be the preferred choice because the bands can be maintained at
a lower concentration and can probably be eluted at a greater
velocity, thereby diminishing the effects of radiation damage to
some extent.

3. Analytical Applications

     The first analytical application of pressurized ion exchange
was the determination of berkelium,[42] which had previously pre-

sented considerable difficulty. Berkelium-249 is a beta-emitter
which cannot be determined directly in the presence of the highly
active beta-emitting fission products; decontamination factors up
to 10^{10} are necessary. It may be determined by measuring the in-
growth of its alpha-active daughter, ^{249}Cf, but this requires several
weeks. The chemistry of berkelium is very similar to that of either
cerium or europium, depending on whether it is in the +4 or +3 oxi-
dation state; and both cerium and europium are intense beta-emitting
fission products.

In this application, pressurized ion exchange was used first to
separate berkelium from other actinides and fission products except
europium, and berkelium was then oxidized to +4 and extracted with
thenoyl trifluoroacetone for separation from europium. Separation
factors were >10^{5} for europium, americium, curium, and einsteinium,
and >10^{10} for cerium. The entire procedure required about 6.5 hr.

The other actinides may be easily separated for analytical
purposes with the use of small pressurized ion exchange systems as
described above. All these actinides except berkelium may be
determined by alpha energy analysis; thus an extremely high degree
of separation is not necessary as it is for berkelium.

4. Extraction Chromatography

Extraction (sometimes called reverse-phase) chromatography has
been used for special applications in pressurized ion exchange
systems. Excellent tracer-scale separations had been commonly
obtained with conventional systems, but the exchange capacity was
usually low and separations on the multimilligram scale were not
satisfactory. Baybarz and Knauer[43] extended this approach to
larger-scale separations to obtain pure ^{248}Cm daughter from the
^{252}Cf parent. This curium isotope, which is relatively long-lived,
is in great demand for research purposes; however, it must be
unusually well separated from the very radioactive neutron-emitting
californium. With the normal αHIB elution procedure, californium

is eluted before curium, and the tail from the californium band
contaminates the curium product.

Extraction chromatography using di(2-ethylhexyl)orthophosphoric
acid (HDEHP) as the fixed phase and aqueous nitric acid as the mobile
phase results in a reversal of the elution order, and the curium may
be obtained relatively free of contamination from californium. In
this work 200-325 mesh Bio-Glas (Bio-Rad Laboratories) was used to
support 400 mg of HDEHP per gram of support. The column was easily
dry packed, and the exchange capacity was 1.3 meq/ml, approaching
that of organic ion exchange resins. No loss of exchange capacity
was observed, even after large volumes of nitric acid had been run
through the column.

Both curium and californium were loaded from 0.15 $\underline{M}$ HNO_3 at
10 cm/min; the curium was eluted with 0.5 $\underline{M}$ HNO_3 at 5 cm/min, and
finally californium was recovered with 2 $\underline{M}$ HNO_3. After two
purification cycles the curium product was decontaminated from
californium by factors $>10^{10}$. This procedure is routinely used
in the TRU facility to milk ^{248}Cm from californium neutron sources
which are old enough that a significant fraction of the californium
has decayed. Presently, about 100 mg of ^{248}Cm is produced each
year. A typical scale of operation is the separation of 60 mg of
curium from several milligrams of californium.

Recently, Horwitz et al.[44] have reported rapid separations of
tracer actinides using very small pressurized extraction chromato-
graphic columns. The support consisted of totally porous micro-
spheres 4-6 μm in diameter; extractants were HDEHP or tricaprylmethyl
ammonium chloride, nitrate, or thiocyanate; and eluents were hydro-
chloric or nitric acid solutions. The columns were only 2 cm long
and 2 to 3 mm in diameter. These authors reported that such columns
provide 500 to 1000 equivalent theoretical plates at flow veloci-
ties of 2 to 4 cm/min, and about 200 plates at 60 cm/min. Column
capacities were 0.3 to 1 millimole of extractant per milliliter of
bed volume, and up to 10% of this capacity could be loaded while

maintaining a good separation. Separations of americium and curium
or berkelium and californium into extremely pure form were achieved
in a matter of minutes.

In earlier work Horwitz and Bloomquist[45] studied the separation
of a number of elements with Z >79 using 1% tricaprylmethyl ammonium
salts on Zipax CSP, a porous layer support. The system was pressur-
ized with N_2 gas to give flow velocities as high as 75 cm/min.
Typically, two to four elements could be separated in times of
approximately 1 min to a few minutes. The columns used were 3 to
5 cm long and 0.28 cm in diameter. They concluded that Zipax
packing is much superior to other materials, such as Celite and
porous plastic, for these separations, and that elution times could
be reduced by factors of 10 to 100. Decontamination factors were
>10^5 for elements eluting later and 10^3 to 10^5 for elements eluting
prior to each product. The goal of this work was to develop rapid
separation methods that could be applied to the search for possible
super-heavy elements which are predicted to exist in the range of
Z = 110 to 114.

The capabilities of extraction chromatography columns are
generally similar to those of ion exchange columns with the same
size of packing. In both cases, small-sized packing and high flow
rates yield better separations, and the time requirement can be
reduced by a factor of 10 to 100. Elution orders may be different
in the two systems, and certainly there is a greater choice of
extractants than of ion exchange resins. Extraction chromatography
is clearly superior for special applications. For separations on
a scale greater than milligrams, however, the high cost of the
packing appears to preclude general use until the cost of a ready-
to-use medium is reduced to near that of ion exchange resin.

III. LANTHANIDE AND ACTINIDE SEPARATIONS BY
DISPLACEMENT DEVELOPMENT

The separation of larger (multigram) quantities of rare earths
and actinides is generally achieved using displacement development

following the chemistry developed and applied by Wheelwright and
co-workers[17] with conventional ion exchange systems. By coincidence,
Wheelwright reported on the recovery of promethium, americium, and
curium from irradiated uranium,[46] and Campbell reported the initial
pressurized ion exchange work[26] in the same session of the April,
1968, American Chemical Society meeting. The pressurized ion ex-
change method has been applied to displacement development primarily
at SRL, and a rather large-scale production capability has been
demonstrated.

Most of the displacement development work has been done with
DTPA elution, although NTA has been used in a few cases. The
barrier ion has nearly always been zinc. This process is used to
separate trivalent actinides, primarily americium and curium but
also small amounts of californium, from fission product rare earths,
which are essentially those elements from lanthanum up to and
including gadolinium. The elution order with DTPA, pH 6, is
copper, nickel, fermium, einsteinium, californium, berkelium,
zinc, lead, curium, ytterbium, thulium, erbium, holmium, dysprosium,
lutetium, americium, terbium, gadolinium-europium, samarium, yttrium,
promethium, neodymium, praseodymium, cerium, and lanthanum.[47] Thus,
curium and americium are eluted immediately before all the fission
product rare earths except those elements heavier than gadolinium,
which occur in extremely small quantity.

In displacement development the successive products are eluted
at a nearly constant concentration; hence there are overlap regions
between each pair of bands. If only a small amount of a given
element is present, it may all appear in such overlap zones and,
consequently, no pure product will be obtained. It is common practice
to use several ion exchange columns in series, each of successively
smaller diameter, to decrease the overlap region. A typical flow-
sheet[48] from the work at Savannah River is shown in Figure 8.

Displacement development is not appropriate for analytical
separations because these normally involve small quantities of the
elements; in such cases, successive bands overlap and pure products
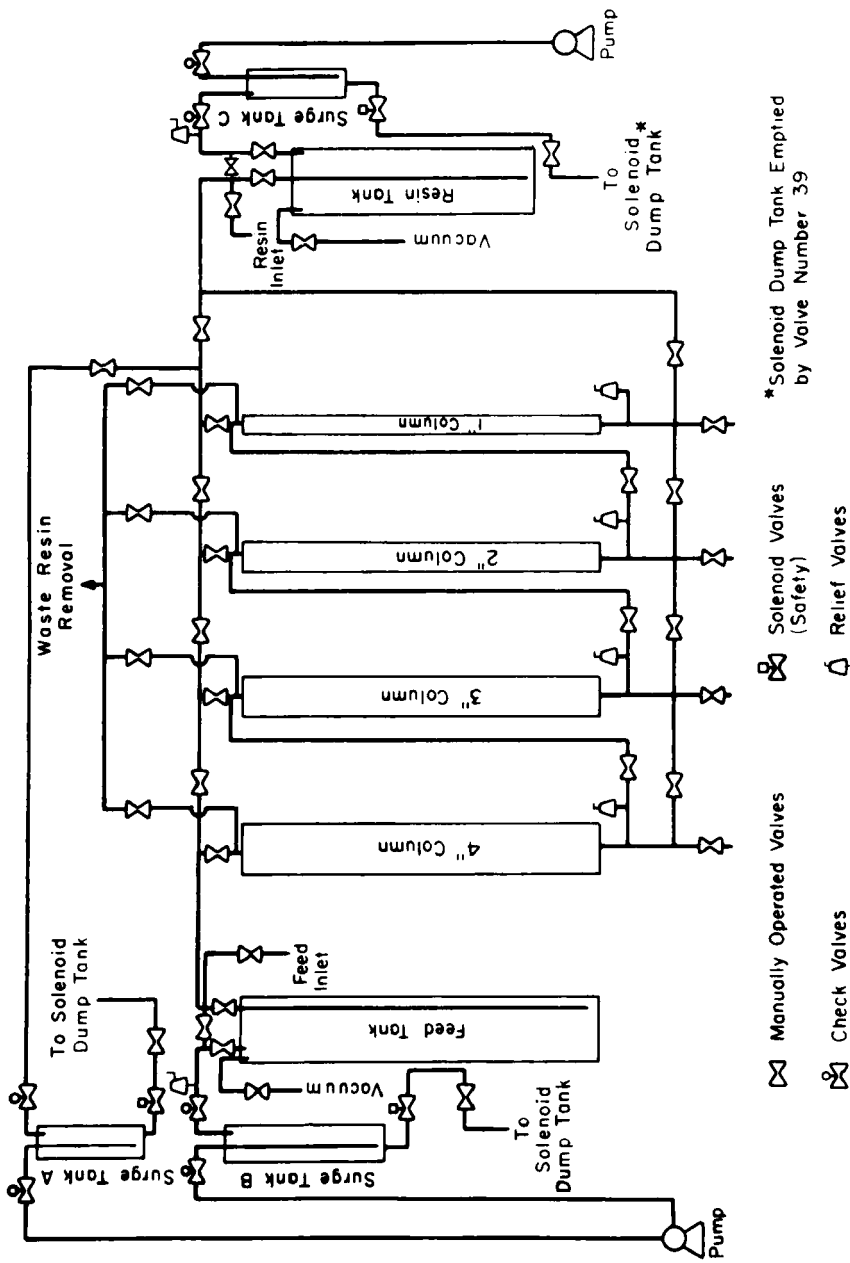
FIGURE 8. Flow Diagram for Displacement Development Separation of Actinides on the 100-g Scale. Reprinted with permission from J. T. Lowe, W. H. Hale, Jr., and D. F. Hallman, Ind. Eng. Chem., Process Design Develop., 10, 131 (1971). Copyright by the American Chemical Society.

are not obtained. Such small-scale separations are always best accomplished with elution development.

No reference has been found in which the extraction chromatographic technique has been used with displacement development. Since displacement development is generally used for larger-scale work, the unavailability of inexpensive and well-characterized column packing materials may be the reason. It is possible that useful separations processes could result from this approach.

A. Rare Earth Separations

Rare earth separations have been made primarily to test the system and to define operating parameters prior to operation with radioactive materials. On a few occasions, recovery of radioactive ^{147}Pm has been the goal. For example, Lowe[49] used four columns of decreasing diameter from 4.75 to 0.79 cm, each 150 cm long, that contained 30-60 μm Dowex 50W-X8 resin. Gram quantities of promethium were separated from the much larger amounts of other fission product rare earths by elution with DTPA at 15 cm/min.

The separation of samarium, neodymium, and praseodymium was studied by Lowe[48] in process development work leading to actinide purifications. Dowex 50W-X8 resin, 30-60 μm, was used with 0.05 $\underline{M}$ DTPA, pH 6, eluent. It was found that the height of an equivalent theoretical plate (HETP) decreased sharply with increasing temperature, and increased by a factor of about 3 when flow velocity increased from 11 to 19 cm/min at 70°C. In most cases the HETP was in the range of 0.6 to 1.5 cm.

In similar studies Kelley[50] determined that higher flow velocities could be used at lower pH of the DTPA eluent. At 16 cm/min the HETP did not change greatly with pH; at 32 cm/min, however, it decreased by a factor of 2.5 between pH 6 and 3. He reported that at pH 3 the HETP was about the same at 16 and 32 cm/min. Satisfactory separations were obtained in tests made at flow velocities up to 50 cm/min with 0.05 $\underline{M}$ DTPA, pH 3, using a 5-ft-long by

0.5-in.-diam column with 200-400 mesh Dowex 50W-X8 resin at 70°C.
This indicates that there is potential for a substantial increase in
the flow velocity while still obtaining adequate performance, if
that should be desired.

Presently, pressurized ion exchange separations of the stable
rare earths and other elements characteristic of fission product
mixtures are being studied by the author to develop processes which
can be applied to the recovery or removal of actinides (particularly
americium and curium) from highly radioactive nuclear wastes. A
total of 1 to 5 g of rare earth elements of the composition of
fission products are separated in about 4 hr. This problem requires
the separation of much smaller amounts of actinides, relative to
rare earths, than the usual actinide purification and production.
Holmium, a stand-in for americium and curium, is well separated from
the rare earths representative of fission products.

B.   Trivalent Actinide Separations

The separation of transplutonium actinide elements has been
developed and applied on a large scale at SRL, and this work was
reviewed in 1972.[51] Hale and Lowe[52] first demonstrated the process
by separating about 1 g of ^{243}Am and ^{244}Cm from 2.8 g of fission
product lanthanides by elution with DTPA; partial separation of
curium and americium was obtained. Subsequently, elution with NTA
was used to purify up to 5 g of curium from small amounts of
americium. Rare earths were reduced in the actinide products by
factors $>10^3$ for europium and $>10^5$ for cerium.

The ion exchange system consisted of three stainless steel
columns in series, each 2.5 ft long by 0.87, 0.43, and 0.18 in. in
diameter, respectively, containing 276, 67, and 11.5 ml of 25-55 μm
Dowex 50W-X8 resin in the zinc-form. Feed was loaded at 20 cm/min,
and the metals were eluted with DTPA or NTA at 16 to 20 cm/min. The
curium-americium band overlap corresponded to a HETP of only 0.44 cm.

Lowe, Hale, and Hallman[48] expanded this work to the hundred-gram scale for americium and curium. Typically, 100 g of americium-curium and 0.1 mg of californium were separated from 1.6 moles of rare earths with a total of 1500 Ci of radioactivity. A maximum of 190 g of curium and 0.25 mg californium was separated from rare earths in a single run. In all, more than 40 runs were made to purify 3 kg of ^{244}Cm, 1.3 kg of ^{243}Am, and 8 mg of ^{252}Cf.

This production system consisted of four ion exchange columns, each 4 ft long by 4, 3, 2, and 1 in. in nominal diameter (see Figure 8). Dowex 50W-X8 25-55 μm resin was used in the zinc-form at 70°C initially. Subsequently, 40-110 μm resin was used in the three larger columns, and 20-40 μm was used in the smallest column.[51] With the smaller resin, the design flow velocity of 16 cm/min could not be met in the two larger columns with the 1000-psig pump available. Adequate resolution was obtained when 20-40 μm resin was used only in the last (and smallest) of the four columns.

The top 30 to 40% of the largest column was loaded with the mixture to be separated. Feed was loaded by water displacement from a tank inside the process cell; therefore, the pump did not transfer radioactive solutions directly. All resin was initially in the zinc-form. The metals were eluted with DTPA, 0.05 $\underline{M}$, pH 6, at 70°C by pumping eluent directly to the column. As the bands moved down the columns, the successively smaller columns were valved in series (and the flow rate was decreased) until the products were eluted from the smallest column. Actinide products were obtained in approximately 12 hr, while a complete run required about 16 hr. Runs were made every 2 to 3 days, as feed was available. A typical elution is shown in Figure 9.

Because of radiation damage to the resin, it was necessary to replace resin frequently when large quantities of curium were involved. As a result of operating experience, resin was replaced after every two runs in the two larger columns and after every run in the two smaller columns in which the curium band is more
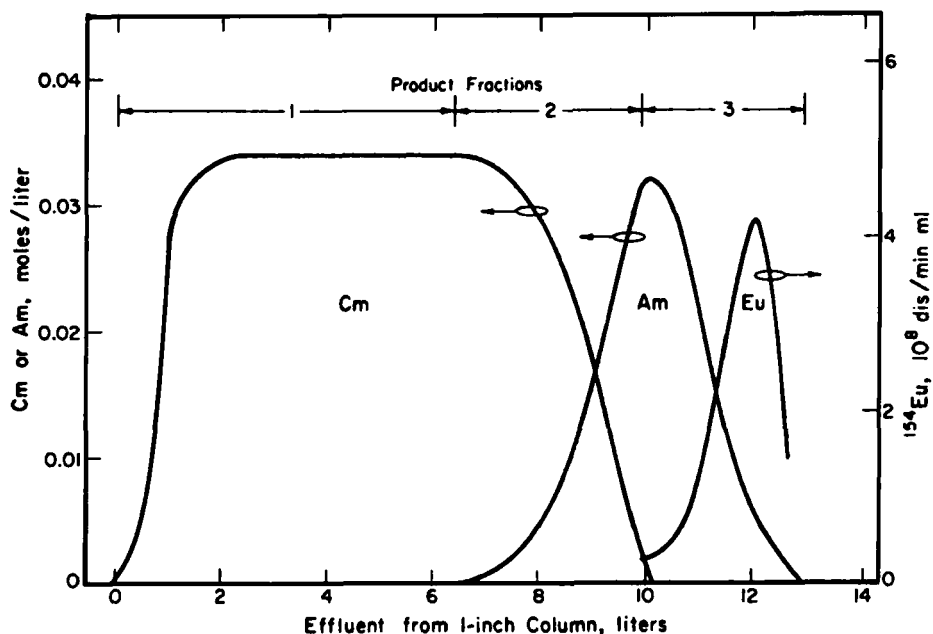
FIGURE 9
Typical Elution Diagram for Separation Using Displacement Development
with DTPA in System Shown in Figure 8. Reprinted with permission
from J. T. Lowe, W. H. Hale, Jr., and D. F. Hallman, Ind. Eng.
Chem., Process Design Develop., 10, 131 (1971). Copyright by the
American Chemical Society.

concentrated. When the resin was changed less frequently, the
pressure drop increased, and the curium band became less compact.

Excess acid in the feed solution loads on the resin and may
degrade the separation during elution, but not to the extent
observed with elution development. In this case, the acid may be
removed by pumping several bed volumes of 0.05 $\underline{M}$ $Zn(NO_3)_2$ solution
through the system after loading, which effectively converts the
resin back to the zinc-form without moving the actinides down the
column. Acid primarily affected the californium band.

Because californium is not retained by zinc in this system, the
small amount of californium runs out into the large volume of zinc

eluate, ahead of the curium and americium bands. This permits excellent separation of californium from curium; otherwise, all the californium would appear in the early part of the curium band and would not be separated from curium. Other barrier ions, such as Ni^{2+} or even Zn^{2+} mixed with H^{+}, will retain californium if that is desired.

The amounts of curium and americium found in the overlap fraction between the two bands decreased substantially subsequent to the early production runs. This improvement in performance was associated with improved resin grading (sizing) techniques.

Kelley[50] developed a process for separating americium and curium from each other and from fission products in a lanthanide-actinide concentrate containing appreciable amounts of ^{242}Cm. Generation of radioactive heat within the ion exchange resin bed would be so great under the conditions defined for the previously discussed ^{244}Cm production (because of the shorter half-life of ^{242}Cm) that the two smaller columns, 2 and 1 in. in diameter, would boil. It was necessary to operate with a high flow rate, and this could only be accomplished with a pressurized ion exchange system.

The problem involved separation of 7 moles of americium, 3 moles of curium, and 167 moles of fission product lanthanides. The 20 g of ^{242}Cm and 700 g of ^{244}Cm produce some 4400 W of alpha-decay energy, and the rare earths produce an additional 9 kW of beta-gamma energy. The ion exchange system used an 8-in.-diam, 5-ft-long column to load some 20 moles of actinide + lanthanide, and three 4-ft-long separations columns with diameters of 6, 4, and 2 in. Dowex 50W-X8 resin, approximately 80 µm, was used. The flow velocity was 32 cm/min for the 2-in. column and 16 cm/min for the three larger columns. Full-scale separation was demonstrated using dysprosium and terbium as stand-ins for curium and americium, and other stable rare earths to duplicate the concentrations of fission product elements.

   It is not clear whether or not this process and equipment have
been used for actinide separations. However, the development work
indicated the direction that might be followed in case it should
become necessary to process larger quantities of highly radioactive
materials, especially of very high specific decay power. Radiation
damage and heating can be controlled by using high eluent flow
velocities, but the rate of advance of the product bands cannot be
too great without degrading the separation. The use of small resin
particles alleviates the resolution problem, but the combination of
unusually high flow velocities and small resin requires high opera-
ting pressures. The eventual limit of such separations, in regard
to the amount of radioactivity that can be dealt with, is not yet
defined.

IV. FUTURE DEVELOPMENTS

   At the present time both production and demand for the trans-
plutonium elements are stable, and pressurized ion exchange processes
are routinely used to separate and purify these elements. Three
areas can be identified which might require an extension of the
methods that are now being used successfully. These are: (1) very
small or tracer-scale separations in minimum time — for example, for
study of new elements or very short-lived isotopes produced by
nuclear reactions; (2) separations similar to those accomplished
presently but on a very much larger scale — for example, because of
increased demand for heat sources or for radioactive waste process-
ing; and (3) separations on a larger scale of the short-lived
isotopes of high specific decay power, such as ^{242}Cm, ^{252}Cf, ^{253}Es,
and others.

   The direction for the first area is already well established.
It would involve the use of small columns with very fine particles
of ion exchange resin or an appropriate porous support in an
extraction chromatographic system. A porous layer support or

pellicular ion exchange resin would probably be advantageous. Very
high flow velocities would be used. It appears that only limited
extension of present techniques would be required to permit tracer
separations corresponding to several hundred equivalent theoretical
plates in times well under 1 min.

The second area is primarily a matter of engineering to scale
up existing techniques. As indicated in the previous section, this
problem has already been addressed at SRL. An example of a design
study for a large-scale separation based on extrapolation of demon-
strated processing (large-scale separations with conventional ion
exchange at Battelle Northwest Laboratory[17] and the pressurized ion
exchange work described in the previous section) is the recovery of
americium and curium from a commercial nuclear reactor fuel repro-
cessing plant, which was considered by Wheelwright.[53] If the
recovery of actinides (americium and curium) from radioactive waste
solutions proves to be desirable, or even necessary, very large-
scale separations of this sort may be required, with the added
restraint that actinide losses during processing must be extremely
small.

The third area presents the greatest challenge. The use of
very small columns is precluded because appreciable amounts of these
materials may have to be processed, perhaps tens to hundreds of
milligrams of ^{253}Es or many grams of isotopes with half-lives of
less than a year, such as ^{242}Cm. It seems likely that columns will
be moderately short with rather small length-to-diameter ratios,
and, of course, that very small particles will be used with unusually
high flow velocities. Pressurized ion exchange presently permits
successful processing of materials up to 100 times more radioactive
than those which can be processed by conventional ion exchange, and
this problem would require an additional factor of 10. It is not
clear what the ultimate limits may be.

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