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Purification of plutonium by a chromatographic method

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PURIFICATION OF PLUTONIUM BY A CHROMATOGRAPHIC METHOD

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I. INTRODUCTION

One of the problems involved in the preparation of fissionable material suitable for production of atomic power is the separation of a very small amount of the desired substance from large quantities of inactive, dangerous, or harmful materials. This may be done in some cases by physical methods utilizing the slight difference in weight of various isotopes or it may be done by chemical methods if the desired substance is chemically different from the other elements which may be present. It will be recognized that the former applies to U^{235} and the latter to plutonium manufactured by a nuclear reaction in the chain reacting piles.

Uranium, when bombarded by neutrons, in addition to undergoing fission of the U^{235} (present to 0.7%) also experiences capture of the neutrons by U^{238}. A radioactive isotope is produced which in turn decays to produce other members of the series in the following manner:

$$U^{238} \xrightarrow{n, \gamma} U^{239} \xrightarrow{\beta} Np^{239} \xrightarrow{\beta} Pu^{239} \xrightarrow{\alpha} U^{235}$$
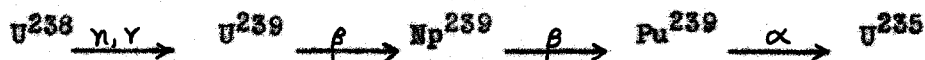
The Pu^{239} when isolated and purified serves as material for production of atomic power. For each pound of plutonium, there is produced at the same time approximately one pound of fission products from the fission of the U^{235}. Table 1 (1) shows the amounts of the different elements produced for various times of cooling after one hundred days operation expressed as grams of element per one hundred grams of Np^{239} and Pu^{239}. It can be seen from this table that the splitting of the uranium atom is not symmetrical but produces radioactive elements in two groups.

Table 1

Weights of Fission Products for Various Times of Cooling
after One Hundred Days Operation Expressed as Grams of
Element per One Hundred Grams of Np^{239} + Pu^{239}.

Element	Time of Cooling in Days					
	0	1	5	10	30	60
Se	0.1	0.1	0.1	0.1	0.1	0.1
Br	0.06	0.06	0.06	0.06	0.06	0.06
Kr	1.6	1.6	1.6	1.5	1.6	1.6
Rb	1.8	1.8	1.8	1.8	1.8	1.8
Sr	4.9	4.9	4.9	4.8	4.6	4.3
Y	2.9	2.9	3.3	3.7	3.4	5.0
Zr	10.7	10.6	10.6	10.6	10.6	10.6
Cb	4.2	4.3	4.3	4.4	4.6	4.9
Mo	7.9	7.9	7.9	8.1	8.5	8.7
42	2.8	2.8	2.9	2.9	2.9	2.9
Ru	6.0	6.0	6.0	5.9	5.8	5.6
Rh	0.7	0.7	0.7	0.8	0.8	1.0
Pd	0.5	0.5	0.5	0.5	0.5	0.5
Ag	0.06	0.06	0.06	0.06	0.08	0.09
Sb	0.02	0.02	0.02	0.02	0.02	0.02
Te	1.6	1.6	1.4	1.4	1.5	1.5
I	0.7	0.7	0.7	0.7	0.6	0.7
Xe	11.9	11.9	11.9	11.9	11.9	11.9
Cs	11.4	11.4	11.4	11.4	11.6	11.6
Ba	5.1	5.1	5.0	4.8	4.5	4.4
La	4.5	4.5	4.4	4.4	4.4	4.4
Ce	12.4	12.4	12.4	12.4	12.1	11.7
Pr	5.3	5.3	5.3	5.2	5.2	5.2
Nd	9.6	9.7	9.8	10.1	10.7	11.3
61	----	----	----	----	----	----
Sm	3.3	3.3	3.3	3.3	3.3	3.3
Eu	0.4	0.5	0.5	0.5	0.5	0.5
Cd	0.02	0.02	0.02	0.02	0.02	0.02
Np	4.2	3.4	2.3	1.1	1.0	1.0
Pu	96.7	97.5	98.6	99.8	100.0	100.0

The fraction of total activity present due to the various radio-active species is given in Table 2 (2) for the case of a pile in operation for 100 days. The various columns give the fraction of the total activity present after 120 days cooling for beta activity, for gamma activity, and for total activity.

It is evident from the figures in Tables 1 and 2 that the plutonium must be separated from many other elements, especially those of atomic number 87 to 44 and 52 to 62. However, the lighter elements up to atomic number 36 and those occurring between the two peaks, from 44 to 52, as well as the heavier elements with the exception of uranium are present in such small amounts that they cause no problem.

The fission products when first produced are extremely active and therefore very dangerous unless suitable precautions are taken in handling the materials. As an example if the uranium is left in the Hanford pile for 100 days and cooled for 16 days, each kilogram of plutonium is accompanied by 800 curies of beta and gamma activity. As a rough approximation the gamma ray intensity may be considered equal to that of the beta rays. The gamma ray energies range from 0.1 to 2.1 Mev while the beta ray energy maxima are in the average range of 0.1 to 5.2 Mev. Immediately after removal the average half life of decay is fairly short, so the uranium cylinders (the so-called "slugs") are usually allowed to decay or cool for 60 days, after which time the average half life is about 45 days. The greatest advantage of this waiting period is that during this time some of the gamma rays of short half life and therefore of ex-

tremely hard energy decay almost completely. On the average only about
0.025% of the uranium is converted to plutonium. The removal of plutoni-
um from the vast quantity of uranium present and the subsequent purifica-
tion from the various fission products must be accomplished by some series
of more or less complicated operations. The general procedure followed
in nearly all methods has been given in detail in several secret reports
and is outlined below. The steps are usually designated as:

    a. Separation, or removal of the uranium.

    b. Decontamination, or removal of most of the fission products.

    c. Concentration, or reduction of amount of carrier.

    d. Isolation, or final separation of product from last trace of
       carrier.

    e. Purification, or removal of every other objectionable element.

In procedures involving precipitation of the plutonium a large amount
of carrier must be added in the first two steps. Thus, for these methods,
the concentration step is important. In other procedures, especially the
adsorption process, no carrier for the plutonium is added since there are
no quantitative precipitations of the product. Consequently the concen-
tration step may be omitted when the adsorption process is used.

In the first step (separation) the plutonium is removed from the
uranium by chemical methods using either the dry or wet procedures. Next,
in the decontamination step, the plutonium is removed from the dangerous
fission products in order that it may be handled with relative safety.
The degree of removal is usually expressed as a decontamination factor
(abbreviated D. F.). This is calculated as the ratio of the original con-

centration of fission products to the final concentration. The first two steps are carried out by remote control, but the final steps are done with less elaborate precautions. Therefore, in the first two steps the decontamination factor must be high enough to make the material safe for handling at relatively close range. The decontamination factor desired is from 10^8 to 10^9. The plutonium may be decontaminated by one of the following procedures:

a. A dry method involving differences in volatility of various salts.

b. A wet method in which the plutonium is first precipitated in a lower oxidation state in the presence of carrier. The precipitate is brought into solution and the plutonium is oxidized. The same precipitating agent is added but this time the plutonium is not precipitated since it is in the oxidized form. The fission products are precipitated and centrifuged off and thus separated. The plutonium is reduced and again precipitated in the presence of added carrier. The efficiency of this method depends on the fact that practically all of the more trouble-some fission products have only one stable valence state. This procedure on a small scale is described in detail in the case of the "Wet Fluoride Method".

c. Liquid-liquid extraction columns possibly involving oxidation-reduction cycles using a solvent which extracts the plutonium only in the one valence state.

d. Adsorption methods using ion exchange resins.

Of the various chemical methods the adsorption procedure has several advantages which may be tabulated as follows:

a. The columns are suited for remote control operation since they have no moving parts. The flow may be by gravity, thus requiring no complicated machinery.

b. The columns are ideally suited for removal of a very small amount of the desired material from very large amounts of other ions. The zeolites and other ion exchange adsorbents have been used in industrial installations for similar purposes. Thus small amounts of calcium and magnesium are removed from large amounts of water. The power of the adsorbent to remove an ion depends primarily upon the valence of the ion, and since plutonium is tetravalent, it will be adsorbed very strongly, affording a basis for separation from the mono- and divalent ions. With these advantages in mind various investigators (3,4,5) have developed procedures for the separation of plutonium from the uranium. A very successful step has been worked out by G. E. Boyd (6) and his co-workers.

This paper describes the use of the ion exchange columns for the decontamination of plutonium. It further describes the method of using both the separation step devolved by Boyd and the decontamination steps in a single integrated procedure making possible an all adsorption method for production of the plutonium in a condition suitable for the purification procedures.

II. HISTORICAL

A. Adsorption

The first studies on adsorption were made by Scheele (7) in 1773 in his experiments on the adsorption of gases by charcoal. In 1785 Lowitz (8) discovered that charcoal would remove certain organic materials from solutions. The first use of adsorption columns was by Tswett (9) who noted that certain colored substances were less strongly adsorbed than others and would move more rapidly down a column of a suitable adsorbent. In 1906 he developed a method of analysis using the principles of relative adsorption. Through this method he was able to separate into its constituents a very complex mixture of coloring agents as found in nature. This method was utilized first in the study of leaf pigments. The complex mixture was poured through a column containing the adsorbent and as the solution traveled downwards, several different colored bands appeared. These bands could be developed by washing the column with additional solvent. Because of the appearance of these colored bands on the white adsorption column, this method was called "Chromatographic Adsorption Analysis", and the general procedure was called "Chromatography". These names were later applied to processes using the same general procedure and theory even when no colored bands were formed. Later a great variety of adsorbents was found to be useful and the procedure was developed into a very generally useful method for separation of components of a mixture, even in some cases where these components were isotopes.

B. Ionic Exchange

In 1850 J. Thomas Way (10), consulting chemist to the Royal Agricultural Society of London, made a series of studies on the retention of manure by soils. He found that clay soils removed the soluble ammonium salts from a solution, replacing the ammonium ion by a calcium ion. He reported 26 experiments in which he tested various soils both qualitatively and quantitatively. Way also made the first artificial zeolite, a sodium aluminum silicate. In his general conclusions, however, he stated that the process was irreversible.

In 1858 H. Eichhorn (11) found that these reactions were reversible and the ion exchanger could be regenerated by washing with an excess of solution of the original ion.

In 1906 Robert Gans (12) manufactured the first commercially successful zeolites and suggested their application to water softening. These synthetic zeolites formed usually by fusion of sand, were applicable only in a limited pH range because the silicate lattice was disintegrated when brought into contact with solutions of low pH.

C. Carbonaceous Zeolites

Later a new type of ion exchanger was discovered (13). When carbonaceous materials, such as coal, tannins, or lignin, were treated with concentrated sulfuric acid, the resulting product showed ion exchange properties. Because of the starting material, the ion exchangers formed in this

manner were called carbonaceous zeolites.

One such carbonaceous zeolite in use today is "Zeo-Karb" formed by treating carbonaceous materials with sulfonating agents such as fuming sulfuric acid, sulfur trioxide, or chlorosulfonic acid. The great importance of this new class of ion exchangers rests on the fact that they may be regenerated with acid to give a hydrogen form, known in one case as "Zeo-Karb H". Thus it is possible to exchange all other cations by hydrogen ion. When the original solids present are carbonates or bicarbonates the final product after degasification is de-ionized water comparable to distilled water. It is also possible to operate at very low pH values. The carbonaceous zeolites are very stable and show no loss of capacity even after 600 cycles.

D. Ion Exchange Resins

The next important discovery came in 1934 when Adams and Holmes (14) found that ion exchangers could be made from resins of the phenol formaldehyde or amine formaldehyde type. Later it was found that increased exchange capacity could be obtained by incorporating sulfonic acid groups into the resin. The cation exchange resins are sulfonated derivatives of the phenol formaldehyde type. These resins may be regenerated either with acid or a sodium salt, thus making it possible to replace any ion by either a hydrogen or a sodium ion as in the case of the carbonaceous zeolites. The anion exchange resins are of the amine formaldehyde type and replace other acids by carbonic acid. By using the cation exchange resin in the

hydrogen cycle with the anion exchange resin followed by a degasifier it is possible to remove completely all ions present in a solution. The right of manufacture under the original patents of Adams and Holmes were given to I. G. Farbenstoff A. G. on the continent and to Resinous Products and Chemical Company in the United States. The Resinous Products and Chemical Company now manufacture ion exchange resins under the trade name of Amberlite.

E. Use of Adsorbents on the Project

The first application of the adsorption procedure applied to radio-active materials by members of the project was a method developed by Schubert, Boyd, and Motta (15) for the separation of UX$_1$ and UX$_2$ from solutions of uranyl nitrate by Norite. The same adsorbent was used to remove gadolinium to the extent of 75 per cent. The removal was satisfactory for dilute solutions but failed in the case of saturated uranyl nitrate solutions.

In subsequent reports the same workers tested other materials including silica gel (16) and ion exchange adsorbents (17). By suitable modifications it was possible to fractionate various ions and thus achieve a partial separation of some of the fission products. Some ions, uranyl thorium, barium, mercuric, and silver, were studied in detail and the experimental data were collected and plotted (18). Curves were fitted to these data by the method of least squares and the constants determined

from these curves. These constants served as the basis of research on inorganic chromatographic isolation of the elements.

At a somewhat later date Seaborg, Willard, and others experimented with various adsorbents in an attempt to separate plutonium from uranium. In the first group of experiments they used as adsorbents fullers earth, silica gel, aluminum oxide, Norite, oxine, oxine in weak acid, and filter paper. In several cases as noted in the table below they obtained a preferential adsorption (19).

Table 3

Adsorption of Plutonium and Uranium on Various Adsorbents

Adsorbent	% Pu Adsorbed	% U Adsorbed
Aluminum Oxide	96	0
Oxine	99	-
Cellulose	56	-

Since the results appeared promising this line of research was continued. Both batch and column experiments were tried using Hyflo Super-Cel, silica gel, resins, Amberlite IR-1, barium sulfate, barium carbonate, and Zeo-Karb, in addition to those previously used. A systematic study was undertaken to determine the effect of pH, concentration of uranyl salts, and the height of the column. In one experiment (20) using Hyflo Super-Cel which is 93 per cent silica, over 95 per cent of the plutonium

was adsorbed while 80 per cent of the fission products went on through. The plutonium was subsequently desorbed with 6 normal nitric acid.

The first successful method for separation of plutonium from the uranium was developed by G. E. Boyd and his co-workers. Their procedure (21) consisted of the following steps:

a. The uranyl nitrate in a 5 to 10 per cent solution was neutralized and poured through a column packed with Amberlite IR-1.

b. The column was washed with a 2.5 per cent solution of sulfuric acid to remove the uranium.

c. The plutonium was eluted from the column. In the early experiments phosphoric and nitric acids were used to elute the plutonium, but this method was discarded since the nitric acid decomposed the Amberlite. A 1.25 normal sodium bisulfate solution was then used as an eluant. Although this solution did not attack the Amberlite it desorbed the plutonium only partially unless a very large amount was used. After much experimentation a more concentrated solution (1.5 N) of sodium bisulfate was used.

This procedure gave a very good separation of uranium from the plutonium but the decontamination factor was low, averaging less than 2. These results are summarized in Table 4.

Table 4

Results of Separation Procedure Using Ion Exchange Columns

Solution	% Uranium	% Beta	% Gamma	% Plutonium
Effluent	86	9.5	10.9	very low
Dilute H_2SO_4 Wash	14	2.7	2.5	very low
Eluate (18% $NaHSO_4$)	none	75.7	51.7	97.7

In order to decontaminate the plutonium to a safe level, experiments were tried using a second column packed with zirconium phosphate on glass wool (22). Early trials gave favorable results but later experiments on a large scale proved that this type of column was entirely unsatisfactory mainly because of excessive resistance to flow under practical working conditions (23).

Beaton (24) and others also experimented with complexing reagents in an attempt to find a reagent which would give preferential adsorption of plutonium. Among other reagents they tried oxalic acid, phosphoric acid, ammonium oxalate, potassium cyanide, and citric acid with negligible success. In the most favorable experiment there was a preferential adsorption and elution of fission products giving a decontamination factor of 35. These experiments were discontinued because of the irregular results over several cycles probably due to breakdown of the resin. Some further experiments (25) were tried using a titanium adsorbent. The decontamination factors were high, averaging around 5000 but the yields were only 30

per cent.

Since the adsorption column using Amberlite IR-1 had been so success-
ful for the separation of plutonium from uranium, the greatest emphasis
was placed on its development to a larger scale. Possible methods of
coupling the column procedure with other processes such as those depend-
ent upon precipitations were studied extensively. A large scale procedure
had been described (26) showing the possibility of using these columns for
factory operations processing ton lots of uranium.

III. THEORETICAL

The procedures used in the investigation were predominantly ion exchange methods. Although these are called adsorption columns, the principles are best explained from the standpoint of the mass action equation rather than from the standpoint of adsorption.

The simplest equation to express the relation between the concentration of a component in solution, c, and the amount adsorbed per gram of adsorbent is the so-called Freundlich equation (27) which was first stated by Bemmelen (28):

$$x = kc^n,$$

where k and n are both constants, n being smaller than one. These constants may be evaluated by determining different values of x and c. If x is plotted against c, the resulting graph is called an adsorption isotherm. Since this simple equation does not always give satisfactory results, several modifications have been suggested (29).

In the case of the ion exchange resins, the reactions may be expressed in the following manner:

$$H^+ + NaZ \rightleftharpoons Na^+ + HZ ,$$

the base exchange material being represented by Z^-, the hydrogen form being HZ, and the sodium form being NaZ.

The course of the reaction will depend upon the relative equilibrium constants. Studies of these equilibria by other workers (30) have shown that they depend upon the size of the ion and its valence. The latter factor is the more important. Thus bivalent ions are bound much more

strongly than a univalent ion, and in the specific case of the replacement of sodium by calcium, the reaction proceeds to the right in the following equation:

$$Ca^{++} + 2 NaZ \rightleftharpoons CaZ_2 + 2 Na^+$$
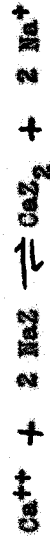
Obviously a tetravalent ion would be bound very strongly and would be replaced only with difficulty. This explains why the plutonium is so strongly adsorbed on the column. Because the reaction is reversible, it is possible by sufficiently increasing the concentration of the sodium ion to make the reaction go the other way, and in this manner replace the higher valent ion by one of lower valence.

Thus, taking advantage of the preferential adsorption of the bivalent ions, one may pour a dilute solution of calcium ions through a column packed with the sodium zeolite. The solution issuing from the bottom of this column is called the effluent. Since the calcium ions have been adsorbed according to the equation given above, the effluent contains only sodium ions. As more and more of the dilute calcium solution is poured through, the concentration of calcium adsorbed on the column increases until finally some of the calcium remains unadsorbed and appears in the effluent. When the ratio of the concentration of the calcium ion in the effluent to the concentration in the feed solution reaches a certain value, usually 2 to 5 per cent, the flow is stopped. This point is called the "break-through". The amount of the ion adsorbed at the break-through point is called the break-through capacity of the column. This is differentiated from the total capacity which is the amount of ion adsorbed when the concentration of ion in the effluent is equal to that in the feed. In some cases the interfering

ion appears to an appreciable extent early in the run. This occurrence, known as "leakage", lessens the value of the process since a less pure product is obtained.

The column is then "regenerated" by pouring a 5 per cent solution of sodium chloride through at a definite flow rate. The large excess of relatively concentrated solution removes or desorbs the calcium ions and changes the zeolite back to the sodium form. The desorption of an ion by a concentrated solution is also called elution. The solution used to elute the ion is called the eluent and the solution issuing from the column is called the eluate. When a solution containing several ions is poured through a base exchange column, it is sometimes desirable to remove some interfering ion before the desired ion is eluted. This may be done by pouring some dilute acid or salt solution through the column. This procedure is called "washing" the column.

By making batch adsorption studies in which a certain amount of the sodium zeolite is shaken with a solution of a salt, as for example a calcium salt, until equilibrium is reached, a value of the equilibrium constant, K, may be obtained. Thus for the equation,

$$2 \; NaZ + Ca^{++} \rightleftharpoons 2 \; Na^{+} + CaZ_2 \; ,$$
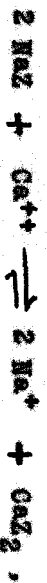
one may calculate K, where

$$K = \frac{\left[Na^{+}\right]^2 \left[CaZ_2\right]}{\left[Ca^{++}\right] \left[NaZ\right]^2} \; ,$$

and in this manner by continuing the studies for different ions obtain the

equilibrium constants and thus predict the qualitative behaviour of the ions on the column. This has been done by a group of workers on the project (31).

The data from the adsorption studies are usually presented in the form of graphs. The two most common graphs are the adsorption isotherms mentioned in the second paragraph of this section, and Schumann curves in which the concentration of the ion in the effluent expressed as per cent of initial activity is plotted against the volume of effluent. The adsorption isotherms are obtained from batch adsorption studies and are valuable for obtaining a large amount of data in a preliminary survey, but they are no substitute for actual column studies. The Schumann curves obtained from actual column runs require more time but provide accurate data.

As was stated above, it is also possible to separate two ions possessing the same valence if they are sufficiently different in size. Thus in the first column of the periodic table, the degree of adsorption is:

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

Cesium is most strongly adsorbed because the size of the ion is smallest.

It is possible to utilize other factors to effect a separation of two ions. One such factor is the relative basicity. Thus, if one has a solution of two ions, one of which is a relatively weak base, at a fairly high pH the weak base will be adsorbed strongly since it will tend to precipitate on the column. In a more general sense if the conditions are such that an ion precipitates out it will be adsorbed or precipitated on the column and bound very strongly. In some cases so strongly that it is desorbed only with the

greatest difficulty. Related to this is the effect of colloidality (32). If the conditions are such that the ion tends to form a colloid, it is readily adsorbed by the resin and desorbed only under drastic conditions. The best examples of this are zirconium and columbium. If the conditions are right, these ions will be adsorbed in the colloidal state at the very top of the column and are not removed even by large amounts of sodium bisulfate (33).

Still another method of separating ions by means of adsorption columns is based on the ability of these ions to form complexes with suitable organic reagents. If a positive ion forms an inner complex compound the positive charge is essentially removed and the ion will not be adsorbed. A very practical way of doing this is to form an inner complex salt, as for example the complex of iron with ferron, which forms a negative ion in solution. Thus the compound formed has a negative charge and can not be adsorbed on a cation exchanger. If two ions form complexes with the same reagent, they may be separated by adjusting the conditions on the column so that one of the complexes is destroyed. This may be done by adjusting the pH to such a value that the complex of the reagent with one of the ions is unstable and as it comes in contact with the resin the ion will be adsorbed. If the complex of the reagent with the other ion is stable at this pH, the ion cannot be adsorbed, but will pass on through in the complexed state, and thus a separation will be effected. In the same manner, by adjusting the conditions, such as pH or concentration of eluant, one ion may be preferentially eluted, leaving the other ion or ions on the column.

IV. RESEARCH

A. Statement of the Problem

When work was started on this problem the Amberlite column had been shown to be very successful for the separation of the plutonium from the uranium, giving complete separation and high yields. The fission product activity was still high, however, and some additional step was needed to reduce this activity to a safe level. Since over 99.9999 per cent of the fission products must be removed without any loss of plutonium, this decontamination could not be effected by simple ion exchange. It was suggested by Dr. F. H. Spedding that the plutonium might be complexed in such a manner that it would not be adsorbed. Thus the uranium solution could be passed through an Amberlite column. The plutonium would be adsorbed and later removed with a suitable eluant. The plutonium in the eluate could be complexed with some reagent and the solution then passed through a second Amberlite column. In this column all ions except plutonium would be adsorbed. The plutonium would go on through and thus be separated from the accompanying fission products.

The investigation was not concerned with developing or improving any of the existing separation procedures since these had been worked out in detail and were very successful. However, there was a definite need for the development of a decontamination procedure which could be coupled with

the separation step.

The research was then resolved into several problems.

a. To find a specific complexing agent for plutonium.

b. To develop an integrated procedure on a laboratory scale.

c. To adapt this procedure to a larger scale and test it on a pilot plant.

d. To determine the partition of fission product activities.

The complexing agent did not necessarily need to be specific for plutonium. To be of value it should meet the following requirements.

a. It should be soluble in water, since it is much easier to add reagents in the form of a solution.

b. The complex should be soluble in water; otherwise it would be precipitated on the adsorbent.

c. The reagent should be stable, especially to radiation and to changes in pH or temperature. If the reagent decomposes to give gaseous products they could cause trouble by building up gas pockets and in this manner increasing resistance to flow. Any decomposition of reagent also is likely to cause a loss of product.

B. Materials and Instruments

1. Ferron

Ferron is a popular name for 7-iodo-8-hydroxyquinoline-5-sulfonic acid.

also known as Yatren.
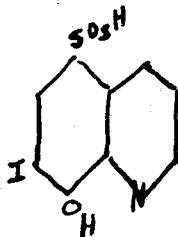
It is used as a specific colorimetric reagent for iron, and has a use in medicine as a substitute for iodoform. It is only slightly soluble in water or other ordinary solvents. The ferron used in the following experiments was obtained from Eastman Kodak Company and from G. D. Searles and Company.

2. Amberlite IR-1

The Amberlite IR-1 is a cation exchange resin having the general formula:
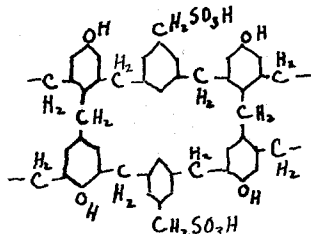
It was manufactured by and was obtained from Resinous Products and Chemical Company, Philadelphia, Pennsylvania.

3. Uranium solutions

The first experiments were carried out using solutions of uranyl nitrate which had been enriched by the addition of a solution containing a known

amount of plutonium. The concentration of plutonium was expressed as counts
per minute per milliliter, which was abbreviated as c/m/ml. In some cases,
to this solution were added other activities such as lanthanum or cerium.

4. Electroscopes

The fission product activities were usually measured on the electro-
scope because of the ease of preparation of the samples and the greater re-
liability of the measurements. The electroscope used was a Lauritsen quartz
fiber instrument rigidly mounted in the cubical housing described by Dr. A.
F. Voigt (34), and having several stages below the instrument on which sam-
ples could be placed. This arrangement made it possible to measure samples
of a wide range of activity. Unless otherwise stated all samples were meas-
ured on the fifth stage. On this stage one division per minute was equiva-
lent to 30,000 disintegrations per minute.

5. Alpha counter

For rough measurements of plutonium or for weak samples, the instrument
used was an ionization chamber and a linear amplifier circuit. The air-filled
counting chamber was mounted by springs on a heavy frame. The sample was
placed on the lower plate which was then screwed into place. Under perfect
conditions it was possible to obtain satisfactory results for samples having
low activity and not too high a contamination of fission products. The max-
imum beta activity allowable was approximately 10^6 disintegrations per minute.

and the loss was about 1 per cent at 1000 counts per minute. The circuits in use during this research were frequently microphonic and subject to extraneous counts from various sources. In order to check the readings an oscilloscope was connected to the amplifier. The ordinary discharge caused by an α-ray gave a regular pattern, but any external disturbance appeared on the oscilloscope screen as an irregular series of hash lines.

6. Proportional alpha counter (35)

The proportional alpha counter was used for precision measurements in the final experiments. The chamber consisted of a block of metal machined in the form of a hollow cylinder. A wire, stretched along the axis of this cylinder, had a potential of about 2500 volts applied to it. The chamber was filled with methane at atmospheric pressure, the methane being slowly bubbled through at the rate of approximately one bubble per minute. The samples to be measured were mounted on platinum disks and placed on a mechanical stage. They could then be raised inside the chamber at a desired distance from the collecting wire. The counter was especially valuable in those cases when the accompanying fission product activity was high. This can be seen from the specifications which stated that the maximum tolerated beta background was 10^9 disintegrations per minute, and that the counting losses were less than one per cent at 10^5 counts per minute.

Before the counter was used its performance was checked. Table 5

gives the agreement of various samples having different activities.

Table 5

Measurement of Samples of Different Activities

Volume of Samples in Microliters	Counts per Minute	Counts per Minute per Microliter
1.552	300	199
1.552	303	
1.552	298	
3.082	591	192
3.082		
7.385	1472	199.5
7.385	1477	
37.960	7215	190
37.960	7297	

The results show that excellent agreement is obtained for samples

ranging from 300 counts per minute to over 7000 counts per minute. These

errors include all errors in transferring of samples, calibration of pi-

pettes, self-absorption, and other mechanical errors in addition to the ac-

tual error of counting. The discrepancy for the 7.385 microliter sample

could be due to faulty calibration of the pipette. The last value repre-

sented the largest amount of solution which could be used.

Figure 1 is a graph showing the plateau curve (counting rate plotted against voltage) when determined with no beta activity present, and the effect of a high beta activity. In the second case it is possible to measure the alpha disintegrations even in the presence of the large amount of beta, but a slight correction factor must be used. The plateau is shortened considerably and shifted slightly. Thus it is wise to re-determine the plateau if an extremely active sample is to be measured.

C. Methods of Analysis

In the early experiments the samples were analyzed for plutonium by the lanthanum fluoride procedure. In this method, 10 milligrams of lanthanum carrier were added to the solution containing not more than 10 per cent of uranyl nitrate. The lanthanum and plutonium were precipitated by the addition of hydrofluoric acid. After a waiting period of thirty minutes to ensure complete precipitation, the lanthanum fluoride was centrifuged off in a lusteroid tube. After washing twice, the lanthanum fluoride was washed out with 10 normal sulfuric acid into a platinum dish and evaporated until fumes of sulphur trioxide were evolved. After cooling, the lanthanum sulphate was taken up in ice water and the plutonium in the solution was oxidized to the plutonyl state with silver nitrate and ammonium persulphate. Additional hydrofluoric acid was added to the solution in order to precipitate the lanthanum. Since only the lower valence states of plutonium form insoluble fluorides, the plutonium remained in solution. After cen-
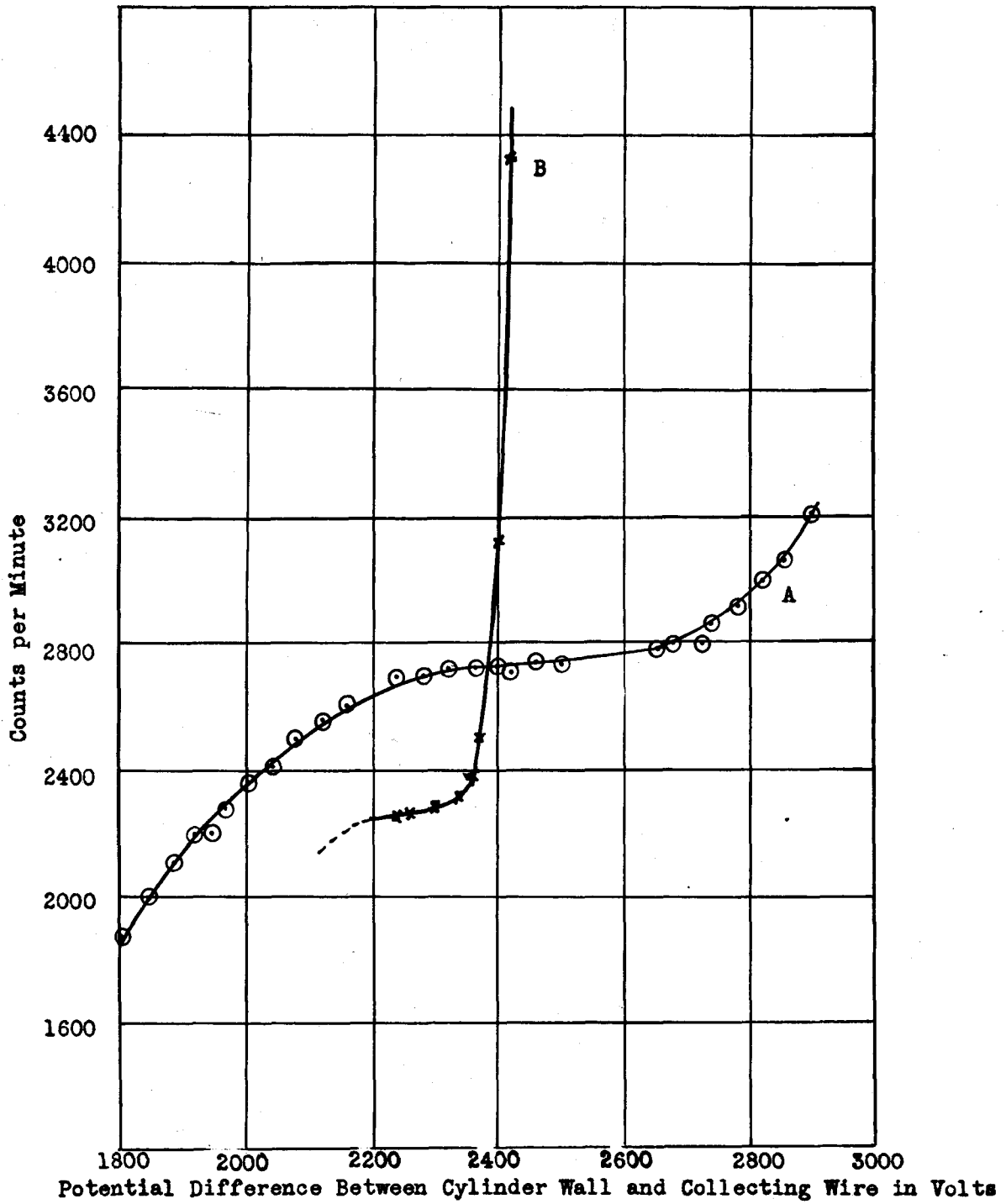
Figure 1. Plateau Curves for Proportional Alpha Counter.
A - No Beta Activity Present
B - Beta Activity Present

trifuging off the lanthanum fluoride, the solution was evaporated to fumes of sulphur trioxide in order to reduce the plutonyl ion. The residue was cooled and taken up in water. About 0.1 milligram of lanthanum carrier was added and precipitated as the fluoride with hydrofluoric acid. The solution was centrifuged and washed in a flat bottomed lusteroid tube. The precipitate in the bottom of the tube was dried with a gentle stream of hot air. The flat bottom was cut off with a razor blade, mounted on cardboard, and counted in an ionization chamber. This procedure was subject to a great many errors, the most serious being the following:

a. Incomplete precipitation or solution.

b. Incomplete oxidation. The last two errors were overcome to a certain extent by having several oxidations and precipitations.

c. Co-precipitation of uranium. The α-rays of uranium could not be differentiated from those of plutonium.

d. Absorption of the alpha rays by the lanthanum fluoride carrier.

e. Discharge between sample and plate in the counter, due to fibers or points in the sample.

f. Instrumental errors or limitations. The counters had a rather narrow range and very active samples had to be diluted. Moreover, the decontamination in the oxidation-reduction cycle had to be high or the beta rays would be counted. Usually an oscilloscope pattern was used to detect a discharge caused by any of the reasons mentioned in e or f.

Because of these errors and limitations the measurements were not of a

very high accuracy but served fairly well for the less active samples.

When the samples were more active or were contaminated with a large amount of fission products as in the later experiments, the lanthanum fluoride procedure was of no value. In these cases the samples with added lanthanum carrier were made 1 normal in sodium hydroxide. The precipitated hydroxides were centrifuged off, washed, dissolved in dilute nitric acid, and made up to a suitable volume, in most cases 10 ml. A 50 microliter aliquot was transferred to a round platinum disk, dried under an infra red lamp, and counted on the proportional alpha counter.

The electroscope was used to measure the fission products. The samples were usually measured on the fifth stage of the electroscope. For total fission product activity a measured sample was placed on a watch glass, evaporated to dryness, and measured. For total rare earths, 10 milligrams of lanthanum carrier were added and this was precipitated with hydrofluoric acid in a flat bottomed lusteroid tube. After drying the sample in an air stream, the bottom of the lusteroid was cut off with a razor blade, mounted on pasteboard, and measured. The activities in one run were all corrected to the date of the analysis of the original solution. The efficiency for measurement of the gamma rays was only 1 per cent of that of the beta rays.

In all the experimental runs using moderately active slugs a major portion of the beta and gamma ray activity occurring in the final steps of the process was due to UX_1 and UX_2. In order to determine the total amount of activity due to UX_1 and UX_2 which is present in the original solution, an analysis of uranium for these activities was carried out in the following

manner.

A sample of uranyl nitrate was dissolved in 50 ml. of water. Lanthanum and thorium carriers were added and the UX_1 precipitated with potassium fluoride and hydrofluoric acid. The precipitate was measured for activity on the same electroscope that was used for measurement of the fission products. After making corrections for background and standard, the following value was obtained:

UX activity $\cong$ 30 d/m per gram of uranium. As was mentioned before, the activities were measured on stage 5 of the electroscope.

D. Batch Adsorption Studies

In order to obtain a great deal of qualitative information of the complexing powers of various reagents, batch experiments were carried out using the procedure described below.

A stock solution containing a known amount of plutonium was prepared. Two ml. of this solution were placed into each of several 150 ml. beakers. A known amount of the reagent to be tested was added and the mixture was diluted to 50 ml. One to 2 grams of the adsorbent were added and the solutions were allowed to stand for a definite time with intermittent stirring. At the end of this time, the supernatant liquid was decanted and the residue washed once with water by decantation. The supernatant and the washings were combined, evaporated to dryness, and then analyzed for plutonium by the usual lanthanum fluoride procedure. The sample was mounted on lusteroid or platinum and counted on an alpha counter. The adsorbent was

destroyed with nitric and sulfuric acids. The residue was mounted, and an analysis of the plutonium was made with an alpha counter.

In Table 6 are listed the results using Zeo-Karb-H as the adsorbent. The destruction of the Zeo-Karb with nitric and sulfuric acids was not very successful since it contained an appreciable amount of inorganic material (mostly silica). This necessitated a more complicated method of analysis, possibly introducing errors.

The plutonium which appeared in the water layer was the portion which was not adsorbed by the Zeo-Karb. The blank gave an indication of the amount present at equilibrium when no complexing or precipitating agent was present.

If any precipitating agent is present, the amount of plutonium in the supernatant should be less than in the blank. On the other hand if the reagent forms a soluble complex, the percentage of the total plutonium appearing in the supernatant should be higher than for the blank. The results indicated that para-hydroxyacetophenone, ferron, pyridine, and perhaps p-dimethylaminoazobenzenearsenic acid and sebacic acid formed soluble complexes and prevented adsorption by the Zeo-Karb.

The experiment was repeated using Amberlite IR-1 giving the results shown in Table 7.

Again ferron and sebacic acid complexed the plutonium and prevented adsorption. Sebacic acid is not so desirable since it is practically insoluble.

Another series of batch adsorption tests was run in the following

Table 6

Distribution of Activities in Batch Adsorption Using Zeo-Karb-H as Adsorbent

Sample	Activity in Solution		Activity on Adsorbent (By Difference)
	Counts per min.	%	%
Blank	282	43.4	56.6
Pyridine	348	53.5	46.5
Quinoline	232	35.7	64.3
Picrolonic Acid	275	42.3	57.7
m-Phenylenediamine	263	40.5	59.5
Ferron	344	53.0	47.0
p-Dimethylaminoazo-benzenearsenic Acid	309	47.5	52.5
Sebacic Acid	321	49.4	50.6
Potassium Thiocyanate	205	31.5	68.5
p-Hydroxyacetophenone	384	59.0	41.0

Table 7

Distribution of Plutonium Between Solution and Adsorbent. Amberlite IR-1 Adsorbent

Sample	Water Extract c/m	Water Extract %	Residue % (By Difference)
Series A			
Blank	360	55	45
Pyridine	260	40	60
Quinoline	high	--	--
Potassium Ferricyanide	425	65	35
Acetylacetone	285	44	56
Ethyl Alcohol	263	40	60
Ferron	637	98	2
p-Dimethylaminoazo-benzenearsenic Acid	350	54	46
p-Hydroxyacetophenone	290	45	55
Sebacic Acid	500	77	23
Potassium Thiocyanate and Hydrazine	95	15	85
Series B			
Blank	417	58	42
Ethyl Alcohol	496	66	34
Pyridine	557	78	22
Quinoline	400	56	44
p-Hydroxyacetophenone	469	66	34
Ferron	750	99	1
p-Dimethylaminoazo-benzenearsenic acid	407	57	43
Nitromethane	413	57	43
α-Nitroso-β-naphthol	571	80	20
m-Phenylenediamine	511	71	29

manner. To 2 ml. of plutonium tracer (1250 c/m) were added 1.5 ml. of complexing reagent. The pH was adjusted to approximately 5 as tested with Hydrion paper. The solution was diluted to 20 ml. and 3 grams of Amberlite IR-1 resin were added. The tubes were corked and shaken intermittently over a period of three hours. In some cases uranyl carrier was added. The results of the experiment are shown in Tables 8 and 9.

Furohydroxamic acid gave positive results showing that some complexing had taken place but it seemed inferior to ferron.

Sodium alizarin sulfonate (Alizarin S) gave very high results showing a strong complexing action. However, it seems to form soluble complexes with the rare earths and would be of little value for separation procedures.

Two azo derivatives resembling ferron, 7-azobenzene-8-hydroxyquinoline-5-sulfonic acid and 8-hydroxyquinoline-5-(p-benzenesulfonic acid), were obtained from Dr. H. Diehl. The former was fairly insoluble in water and formed slightly soluble complexes with uranyl and ferric ions at the proper pH. It gave completely negative results in batch experiments and proved to be of no value. The latter reagent was very soluble and formed insoluble precipitates with ferric, uranyl, and thorium ions. It gave positive results in the batch experiments and would probably serve as a satisfactory complexing reagent.

E. Column Experiments

1. Preliminary studies using zeolite columns

Table 8

Distribution of Plutonium Between Solution and Adsorbent. Amberlite IR-1 Adsorbent

Complexing Reagent	Amount UO_2 Added	Plutonium c/m	Plutonium Not Adsorbed %
Blank	None	562	38.6
Furohydroxamic Acid*	None	495	53.0
Furohydroxamic Acid	5 mg.	820	81.5
Ferron	None	843	90.0
Potassium Iodate	None	529	56.4
p-Hydroxyacetophenone	None	695	74.1
p-Hydroxyacetophenone	5 mg.	916	89.5
Alizarin S	5 mg.	896	94.5
Alizarin S	None	886	93.4
Blank	None	141	15.1
Ferron	None	784	83.7

* The furohydroxamic acid was obtained from F. J. Wolter and H. D. Brown.

Table 9

Distribution of Plutonium Between Solution and Adsorbent. Amberlite IR-1 Adsorbent

Complexing Reagent	Plutonium Not Adsorbed c/m	%
Blank	405	40.0
Ferron	478	47.0
Reagent A*	406	40.1
Reagent B*	631	62.5

* Reagents A and B were obtained from Dr. H. Diehl and have

the following formulas:

Reagent A
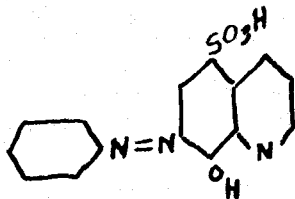
7-Azobenzene-8-hydroxyquinoline-

5-sulfonic Acid

Reagent B
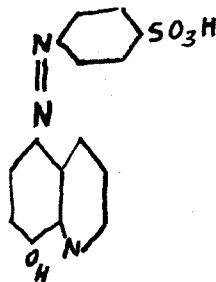
8-Hydroxyquinoline-

5-azo-(p-benzenesulfonic Acid)

Since both Amberlite and Zeo-Karb are very dark, it is impossible to observe the progress of a colored complex ion down the column. However, zeolite (sodium aluminum silicate) is white and the colored ion shows up very well. The action of both zeolite and Amberlite are similar in a qualitative manner for the sodium cycle, and by observing the results for a zeolite column one could extrapolate to an Amberlite column.

Three zeolite columns, one centimeter internal diameter and 30 centimeters high, were prepared for the experiments described below.

a. <u>Iron dipyridyl complex</u>. A solution of iron dipyridyl was

$$\left[Fe \left(\begin{array}{c} N \\ N \end{array} \right)_3 \right]^{++}$$
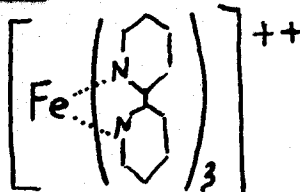
poured through the column. The iron dipyridyl ion was adsorbed on the column very strongly and could be removed only with large amounts of concentrated sodium sulphate.

b. <u>Ferric thiocyanate</u>. A ferric thiocyanate solution was prepared and poured through the column. The iron from the ferric thiocyanate ion, $Fe(CNS)_6^{=}$, precipitated out and was bound on the column. However, the removal of the iron by elution with sodium sulphate was much easier than in the case of the iron dipyridyl.

c. <u>Iron ferron complex</u>. A solution of the iron ferron complex

$$\left(Fe \cdots \left(\begin{array}{c} O \\ N \end{array} \underset{I}{\bigodot} SO_3^{-} \right)_3 \right)$$
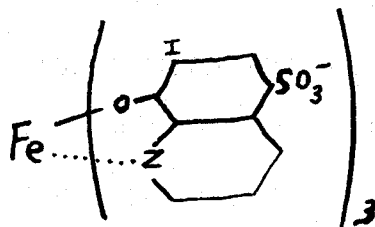
was run through the column. A narrow band of ferric ion was bound at the top of the column but the rest of the unchanged complex went on through. The results of this experiment showed that a suitable complex would prevent adsorption of a cation.

2. **Preliminary studies using Amberlite columns**

a. **Uranyl ferron complex.** An Amberlite IR-1 column, 0.8 square centimeter cross section and 57 centimeters in height with a theoretical capacity of 4 to 5 grams of uranyl ion, was prepared and conditioned in the hydrogen cycle. One gram of uranyl ion was complexed with ferron in a total volume of 250 ml. and run through the Amberlite column. The uranyl ion was completely removed from the complex and was adsorbed on the column. The removal of the uranium was caused by the acid formed by replacement of the sodium ions by hydrogen ions from the column. The complex is stable only in a narrow range and therefore is destroyed by any acid or base.

b. **Plutonium ferron complex.** The experiment was repeated using a solution containing 0.050 gram of uranium and approximately 900 counts per minute of plutonium in 150 ml. total volume with an excess of ferron. The effluent was analyzed and found to contain 5 per cent of the plutonium. The column was eluted with 1.25 molar sulfuric acid to give 96 per cent of the plutonium.

c. **Ferron plutonium solutions (neutralized).** A solution containing 0.050 gram of uranium as uranyl nitrate with 900 counts per minute of plutonium was complexed with ferron and diluted to a volume of 150 ml. This solution was neutralized with sodium hydroxide to a pH of about 7 and then

run through a column filled with Amberlite IR-1 in the sodium form. The effluent was analyzed and found to be very active, showing that the plutonium had remained complexed throughout its passage down the column and had come out unchanged.

The experiment was repeated using a solution containing 0.060 milligram of uranium and 1800 counts per minute of plutonium complexed with ferron at a pH of about 7. At this pH, the uranyl ferron complex is a deep orange red and thus serves as a rough indicator. The effluent from this run was of the same color as the feed solution showing that the uranyl ion had remained in the complexed form. The effluent was analyzed and found to contain approximately 1600 counts per minute showing that over 90 per cent of the plutonium was unadsorbed.

d. <u>Formic acid reduction.</u> An experiment was designed to test the effect of formic acid. If the plutonium is complexed only in the tetravalent state the yields might be increased by first reducing any oxidized plutonium to the tetravalent state with formic acid. Three columns were prepared and the following solutions were run through:

a. A solution containing 0.060 gram of uranium, 1800 counts per minute of plutonium, four drops of formic acid, 10 drops of 10 per cent sodium hydroxide, and an excess of ferron in a total volume of 100 ml.

b. A solution containing 0.060 gram of uranium, 1800 counts per minute of plutonium, 10 drops of sodium hydroxide, and an excess of ferron in a total volume of 100 ml.

c. A blank solution containing 0.060 gram uranium, 1800 counts per minute of plutonium, and 10 drops of sodium hydroxide in a total volume of 100 ml.

The results are given in Table 10. The formic acid used to reduce the plutonium was not necessary and in fact gave lower results.

e. Rare earth complexes. The above experiments showed that ferron did complex the plutonium and thus prevented its adsorption on passage through a column. If the ferron did not prevent the adsorption of the accompanying fission products then this process would serve as a decontamination procedure. To test this, a preliminary experiment was run using lanthanum and cerous ions, since the rare earths are the main constituents of the eluate from the first Amberlite column (Boyd's procedure).

A solution containing 60 milligrams of uranyl, 5 milligrams of lanthanum, and 5 milligrams of cerous ion was complexed with an excess (0.27 gram) of ferron, neutralized by addition of an excess of sodium hydroxide, and then cautious addition of nitric acid until the solution was at its maximum color. This solution was poured through an Amberlite column which had been conditioned in the sodium cycle. The column was washed with 100 ml. of water. The combined effluent and wash were fumed with sulfuric and nitric acids to destroy the organic matter. The residue was taken up in water and transferred to a platinum dish. To this was added hydrofluoric acid but no precipitate formed, showing that the lanthanum and cerous ions were not complexed and therefore were adsorbed on the column.

f. Active solutions. The above results indicated a separation of the rare earths from the plutonium. In order to test the value of the procedure

Table 10

Effect of Formic Acid on Plutonium Complex in Adsorption Column

Description of Sample	Plutonium	
	c/m	%
Column I Effluent	1410	78
Column II Effluent	1718	95.7
Column III Effluent	205	11.3

Column I - Column in which ferron was complexed.
Formic acid added.

Column II - Column in which ferron was complexed.
No formic acid added.

Column III - No ferron or formic acid.

under actual conditions an active solution was used in the column experiments. This solution, hereinafter designated as Boyd's solution, was obtained from Dr. G. E. Boyd of the University of Chicago and consisted of the sodium bisulfate eluate from an Amberlite column using a bombarded uranium sample as starting material. Table 11 shows the results of a systematic analysis for the different radioactive elements present.

Table 11

Analysis of Solution from Boyd's Column

Element	Date of Analysis	Half Life of Element	Activity*
Lanthanum** Yttrium	10/21/43	57 days	32.6
Barium	10/11/43	12.8 days	7
Strontium	10/11/43	55 days 30 years	35
Cerium	10/21/43	28 days 275 days	46.8
UX	10/21/43	24.1 days	11.2

* The activity is expressed as divisions per minute per two milliliter sample, measured on stage 5 of a Lauritsen electroscope.

** The lanthanum present was due to the 12.8 day barium.

A solution was prepared containing 0.060 grams of uranyl nitrate, 1800 counts per minute of plutonium, 2 ml. of Boyd's solution, 5 milligrams of cerous and 5 milligrams of lanthanum ion, complexed with 0.28 grams of fer-

ron, and made up to 300 ml. The solution was neutralized by the addition of sodium hydroxide to the disappearance of the deep red color of the uranyl ferron complex followed by the addition of two drops of concentrated nitric acid to reproduce the deep red color. The solution was poured through an Amberlite IR-1 column, which was then washed with 2.5 per cent sulfuric acid and eluted with 1.25 molar sodium bisulfate. Analyses of the various fractions showed that practically all of the plutonium appeared in the effluent. An alpha count of the eluate was not much above the background value. The effluent contained only 3.4 per cent of the original beta activity, thus giving a decontamination factor of 30.

g. **Elution with ferron.** An alternative procedure would be to selectively elute the plutonium. In order to see if ferron would act as a specific eluant, the following experiment was tried. A solution containing 0.075 grams of uranium as uranyl ion and 1500 counts per minute of plutonium was neutralized to a pH of 4 with sodium hydroxide and passed through an Amberlite column which had been prepared in the sodium form. The column was washed with 50 ml. of water, then with 150 ml. of 3 per cent sodium sulphate, and finally with 50 ml. of water. The column was then eluted with two 100 ml. portions of ferron solution. The various fractions were analyzed, giving the results shown in Table 12.

Table 12

Elution of Plutonium with Ferron

Description of Solution	Plutonium in Solution c/m	Plutonium in Solution %
Effluent	15	1.0
Ferron Solution I	157.5	10.5
Ferron Solution II	155	10.3

The results indicate that plutonium cannot be eluted satisfactorily with ferron if it has been adsorbed on a column.

b. *Recovery of plutonium using Amberlite column.* In order to obtain some plutonium for experiments and at the same time test the results on a complete two column procedure, a program was set up for recovery of plutonium from some uranium which had been bombarded at Argonne. Some of the uranium was dissolved in nitric acid by R. R. Sleight. One portion was diluted to 2 liters and poured through an Amberlite column having an internal diameter of 0.88 inches and a bed height of 24 inches. After the solution had gone through, the uranyl ion was washed out with one liter of 0.25 molar sulfuric acid and then the plutonium was eluted with 150 ml. of 1.25 molar sodium bisulfate. These were the solutions which had been recommended by Boyd (36) and his co-workers at that time. The elution was incomplete so it was eluted a second and third time with 150 ml. portions of 1.25 molar sodium bisulfate and finally with 500 ml. of 1.25 molar sodium bisulfate.

The solutions were analyzed for plutonium and fission products to give the results shown in Table 13.

Table 13

Analysis of Solutions from Adsorption Column Run

Solution	Total Volume in ml.	Volume Taken for Analysis ml.	Plutonium c/m total	Fission Products d/m on Stage 5
Effluent	790	10	350	---
Wash	550	10	250	---
Eluate I	100	1	1100	600
Eluate II	225	1	34560	22500
Eluate III	200	1	13400	8800
Eluate IV	250	2	3500	1500
Eluate V	450	5	8000	

The results were very unsatisfactory because of the incomplete elution of the plutonium. The plutonium was desorbed from the column only when a very large amount of bisulfate was used. It was concluded that sodium bisulfate of this strength is not a satisfactory eluant.

A portion of the eluate, designated as Eluate III in Table 13, was used as starting material for a column run with ferron as a complexing agent. After addition of 10 milligrams of lanthanum carrier, the solution was made alkaline with sodium hydroxide. The lanthanum hydroxide was centrifuged off, washed, and added to approximately 50 milligrams of sodium diuranate. The precipitates were dissolved in dilute nitric acid and made up to a volume of 15 ml. An analysis showed that this solution contained a total of 32,500 counts per minute of plutonium. To this solution were

added 5 milligrams of barium ion, 5 milligrams of cerous ion, and 0.5 gram of ferron. The solution was diluted to 300 ml., neutralized to the dark reddish brown color of the mixed ferric ferron and uranyl ferron complexes, and poured through a column, 0.8 square centimeter in cross section, filled with Amberlite IR-1 to a height of 40 centimeters. The column was washed with 50 ml. of water, then with 100 ml. of 0.25 molar sulfuric acid, and finally eluted with 100 ml. of 1.25 molar sodium bisulfate. The solutions were analyzed for fission products and plutonium, giving the results shown in Table 14.

Table 14

Analyses of Solutions from Adsorption Column Run Using
Complexed Eluate from the First Column as Feed Solution

Description of Solution	Fission Products d/m	%	Plutonium c/m	%
Effluent	1450	75	32420	100
Water Wash	10	0.5	38	0.12
Acid Wash	0	0	0	0
Eluate	100	5	73	0.23
Total	1560	80	32531	100

In this experiment the beta and gamma activity in the effluent was very high. This differed from all previous experiments but it could be explained by assuming that the beta and gamma activities were all attributable to UX. A measurement of the decay of the effluent activity over several weeks gave

a half life of 26 days, suggesting that all of the activity was UX_1 and UX_2. The results showed that thorium was complexed in the same manner as plutonium. In an actual run on a large scale this would not be a disadvantage since the total amount of activity due to UX would be very low and would cause no health hazard. In the present series of experiments, however, it was troublesome since it was difficult to determine the exact amount of total activity which was due to the UX and that which was due to the fission products. The decontamination factors were usually corrected for the UX present, but this correction depended upon a separation step which was not very satisfactory. The obvious method of overcoming this difficulty was to use starting materials of higher activity so that the beta activity due to UX would be less than 0.1 per cent of the total.

3. Experiments using active materials

a. Preparation of active solution. In order to test the procedure using active material, a solution of 1500 ml. of eluate from an Amberlite column was obtained from Mr. E. R. Russell of the University of Chicago. The solution had been prepared in the following manner. A slug, supposed to have been at half level of the Clinton pile, was taken from that pile on February 17, 1944. It was dissolved and run through an Amberlite column in Chicago by Russell on April 6, 1944. The plutonium and fission products were eluted from the column with a 15 per cent solution of sodium bisulfate on that date and shipped to Ames on April 7, 1944. In subsequent experiments it will be referred to as Russell's solution.

An analysis gave the following:

Beta and gamma activity - 340 d/m per ml. ($\cong$ 5 microcuries)

Plutonium - 700 c/m per ml.

b. __Adsorption experiment using complexed active solution as starting
material__. In the first run, a 25 ml. sample of Russell's solution was com-
plexed with ferron, neutralized with sodium hydroxide to a pH of 6, and di-
luted to 100 ml. To this solution were added 5 milligrams of lanthanum, 5
milligrams of cerous, and 5 milligrams of uranyl ion as carriers. This so-
lution was poured through a column, 0.8 centimeters in diameter, at a rate
of 3 to 4 ml. per minute. The column was washed with dilute sulfuric acid
and eluted with a 15 per cent solution of sodium bisulfate. The various
fractions were analyzed by the lanthanum fluoride procedure, giving the re-
sults shown in Table 15.

Table 15

Fractionation of Plutonium and Fission Products by an Amberlite Column

Solutions	Volumes Milliliters	Plutonium c/m	%	Fission Products d/m	%
Effluent	100	5360	75.6	2.12	0.21
Wash	30	829	11.7	0.5	0.05
Eluate	250	900	12.7	992	99.8

These results appeared promising since they showed that the fission
products were almost completely adsorbed while the greater part of the plu-
tonium remained in the complexed state and went on through.

c. Additional wash using dilute ferron solution. In this experiment 25ml. of Russell's solution were complexed, neutralized, and diluted to 125 ml. The procedure was exactly the same as in the previous experiment except that the column was washed twice, once with dilute ferron solution containing some uranyl carrier at a pH of 5 and then with dilute sulfuric acid. The analyses gave the following results.

Table 16

Fractionation of Fission Products and Plutonium Adsorption
Column Experiment Using Complexed Feed Solution and Ferron Wash

Solutions	Volume ml.	Plutonium c/m	%	Fission Products d/m	%
Effluent	125	6790	91.65	48	3.0
Ferron Wash	150	445	6.09	8.4	0.5
Acid Wash	200	14	0.19	22	1.35
Eluate I	30	42	0.57	114	7.0
Eluate II	370	110	1.50	420	25.9

The yield for the effluent and dilute ferron wash was nearly 98 per cent, 6 per cent appearing in the wash solution. These figures demonstrated the necessity of washing the column with water or other solution of pH about 7 in order to secure high yields of plutonium. As soon as dilute acid was poured through, the complex was destroyed and the plutonium was adsorbed on the column. Again the beta and gamma activities were low, being only about 3 per cent of the total, not corrected for UX.

d. *Adsorption and analyses, including thorium separation.* It now
seemed advisable to adjust the conditions very carefully and make a quan-
titative run in order to determine the best yield of plutonium obtainable
and the best decontamination factor. In order to determine the decontam-
ination factor some correction must be made for UX.

The procedure was the same as in the previous experiment, except that
a dilute ferron solution at a pH of 6 was used to condition the column.

The various fractions were caught separately and analyzed for fission
products and for plutonium. The total fission products in the effluent
were then brought into solution and thorium carrier was added. The tho-
rium was separated and the activity of the fission products free of UX
was measured. The results of the analyses are shown in Table 17.

Table 17

Plutonium and Fission Products in Various Solutions from Column Run

Solution	Plutonium		Fission Products No corr. for UX		Fission Products Corr. for UX	
	c/m	%	d/m	%	d/m	%
Effluent	19,270	105	148.6	1.48	7.3	0.07
Ferron Wash	167	0.9	6.0	0.06		
Acid Wash	95	0.5	17.0	0.17		
Eluate	874	4.8	-	-		

The plutonium analyses gave a total of 110 per cent of the original.
Using the ionization chamber and the linear amplifier, the results often

were in error to this extent. The best method of evaluation was to analyze the least active fraction and obtain the amount in the main fraction by subtracting these values from the total amount present. The thorium separation showed that practically all of the activity was due to UX. This was checked by several analyses in a similar experiment on a larger scale. The results, listed in Table 18, again show that from 95 to 97 per cent of the activity was due to UX.

Table 18

Separation of UX from Fission Products

Sample	Total Beta Activity d/m	Beta Activity After UX Separation d/m
I	80.4	1.3
II	53.8	1.6
III	76.0	2.0
IV	73.6	1.0
V	229.0	11.0

Since the fission product activity appearing in the effluent amounted to only 5 per cent of that of the UX, a considerable error was introduced at this point. This illustrated the need for very active samples if an accurate evaluation of the process was to be accomplished.

4. Large scale column work

The results on a small scale showed that it was possible to have a two step column procedure which would give a good yield of plutonium and a high decontamination factor. In order to check these results thoroughly, it was decided to build a pilot plant in which very active material could be processed on a scale of 1 kilogram of uranium per run.

a. Construction of "hot lab". In order to use active material in large quantities, it was necessary to build a laboratory to be used specifically for the processing of uranium and sufficiently shielded so that it would not be harmful to other persons on the outside. All operations must be carried on by remote control in order to safeguard the health of the operator.

One room was set aside for this work. It was completely refurnished and equipped for remote control operation. A hood was formed by blocking off one corner of the room with a concrete wall 14 inches thick, having a door, windows, and several openings for control rods. All active material was to be processed in this portion of the laboratory thus permitting an operator to work in the remainder of the laboratory with safety. In order to remove all fumes and accompanying radioactivity, a fan was connected with the hood and the fumes were led directly to a vent on the roof. This fan was kept on at all times during which there was any possibility of radioactivity appearing in the atmosphere inside the hood.

The uranium was dissolved in a 40 liter Glascote steam jacketed

kettle equipped with a stainless steel gate valve and stainless steel pipe to draw off waste solutions. The uranium solution was removed from the dissolver by means of a stainless steel pump and transferred to a 40 liter pyrex jar placed in a specially constructed stainless steel can. The uranium solution was neutralized and diluted by addition of water and dilute sodium hydroxide solutions added from the outside through glass and Saran tubes which led through the wall. Complete mixing of solutions was accomplished by bubbling with compressed air. The pH was measured with a Beckman Laboratory Model pH Meter equipped with 10 foot leads. The electrodes were mounted in a stainless steel pipe and placed about 2 feet below the level of the solution. The dilute uranyl nitrate solution at a pH of about 2.5 was transferred to a 40 liter pyrex reservoir by means of an air lift. From the reservoir it flowed by gravity through an Amberlite IR-1 column.

The column was of pyrex, 5.4 centimeters in diameter and 200 centimeters high, having a resin bed height of 120 centimeters. All solutions were introduced from outside and flow rates were controlled by means of specially constructed stainless steel screw clamps equipped with rods for remote control. The column is illustrated in Figure 2.

The effluent from the column was flowed through a pyrex line into a 50 liter steam jacketed Glascote evaporator, evaporated to about 6 liters, and then drained through a stainless steel pipe into a stainless steel reservoir tank which had been placed several feet underground in the court outside the room. This tank and several others like it served as storage

-54-

To manifold outside of
hood for introducing
solutions or for air
vent

To reservoir for
feed solution

To outside of hood for
leading or emptying
column with adsorbent

Liquid level

Adsorbent

Glass wool

To evaporator

To complexer

To drain or reser-
voir outside of
hood
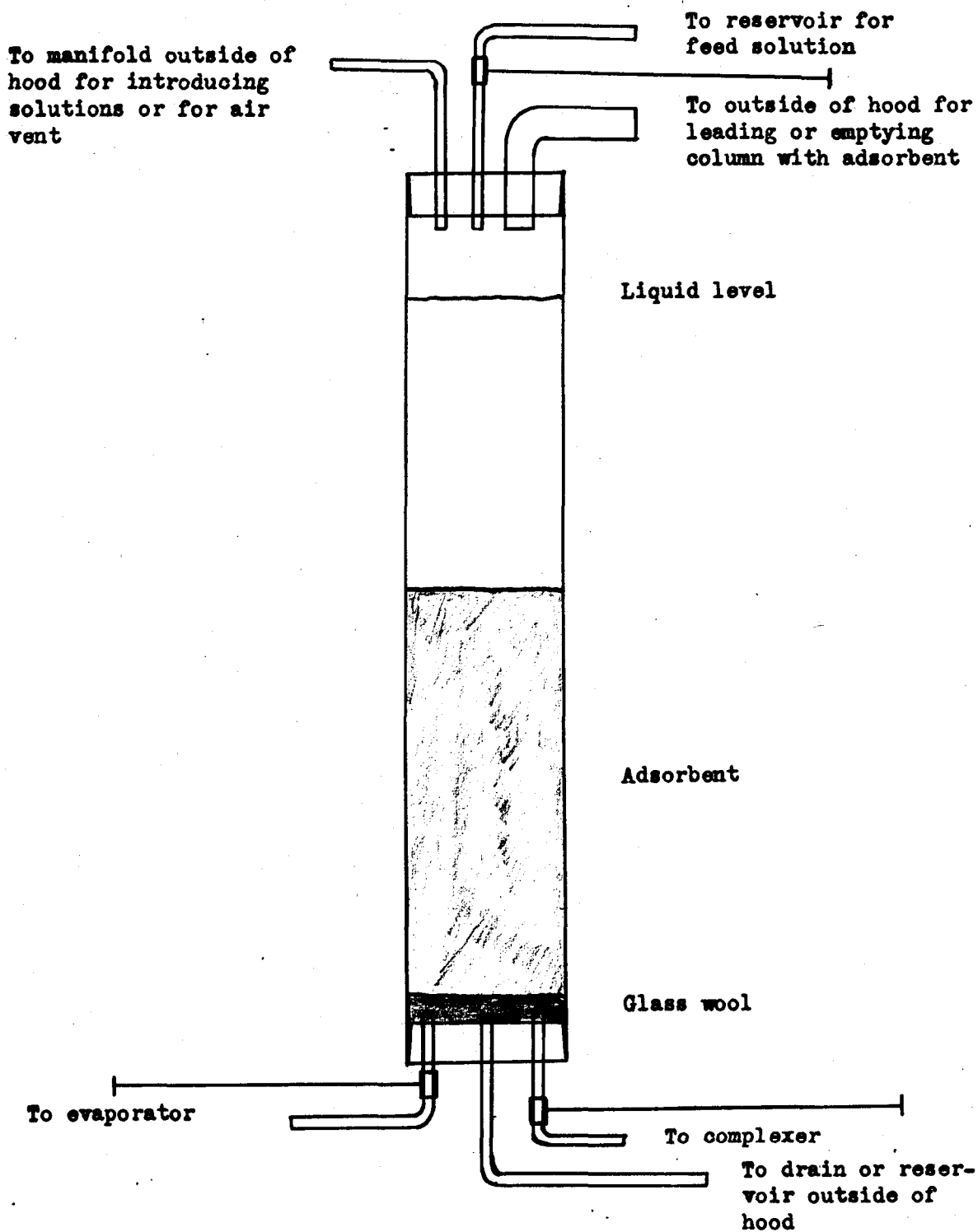
Figure 2. Column I (Separation Column).
Not Drawn to Scale

for active or valuable material. The first part of the wash solution was added to the effluent and the last part sent down the drain. The eluate was transferred to a 40 liter pyrex jar equipped with a compressed air agitator for mixing the solutions, pH electrodes, and various Saran lead-in pipes for introducing solutions. After suitable treatment, the solution was complexed and transferred to a 40 liter pyrex reservoir. From here it flowed by gravity through the second column, 8.2 centimeters in diameter and 200 centimeters high, having a resin bed height of 120 centimeters. The effluent from this column was sufficiently inactive even in the case of the hottest slugs that it could be handled safely outside the hood. The floor plan of the "hot lab" including the storage tanks is shown in Figure 3.

Since it was difficult to obtain the desired equipment immediately, the "hot lab" was fully equipped only after a long period of time. It was necessary, however, to start experiments immediately so makeshift materials were used for the first runs. The uranium was dissolved in a pyrex jar placed on a hot plate inside the hood. The waste solutions were stored in jars until the tanks were available. These makeshifts were not too much of a problem since the first slugs were extremely weak.

b. <u>Preliminary adsorption column run using Clinton slug</u>. The first experiments were carried out using very inactive material in order to test the mechanical aspects of the assembly. Some slugs obtained from the Clinton pile were tested October 2, 1944. Rough measurements showed that they contained from 5 to 10 millicuries of beta and gamma activity, and

D - Dissolver
E - Evaporator
N - Neutralizer
C - Complexer
Cl - Separation
        Column
C2 - Column 2
C3 - Column 3
        (Shielded)
S - Sink
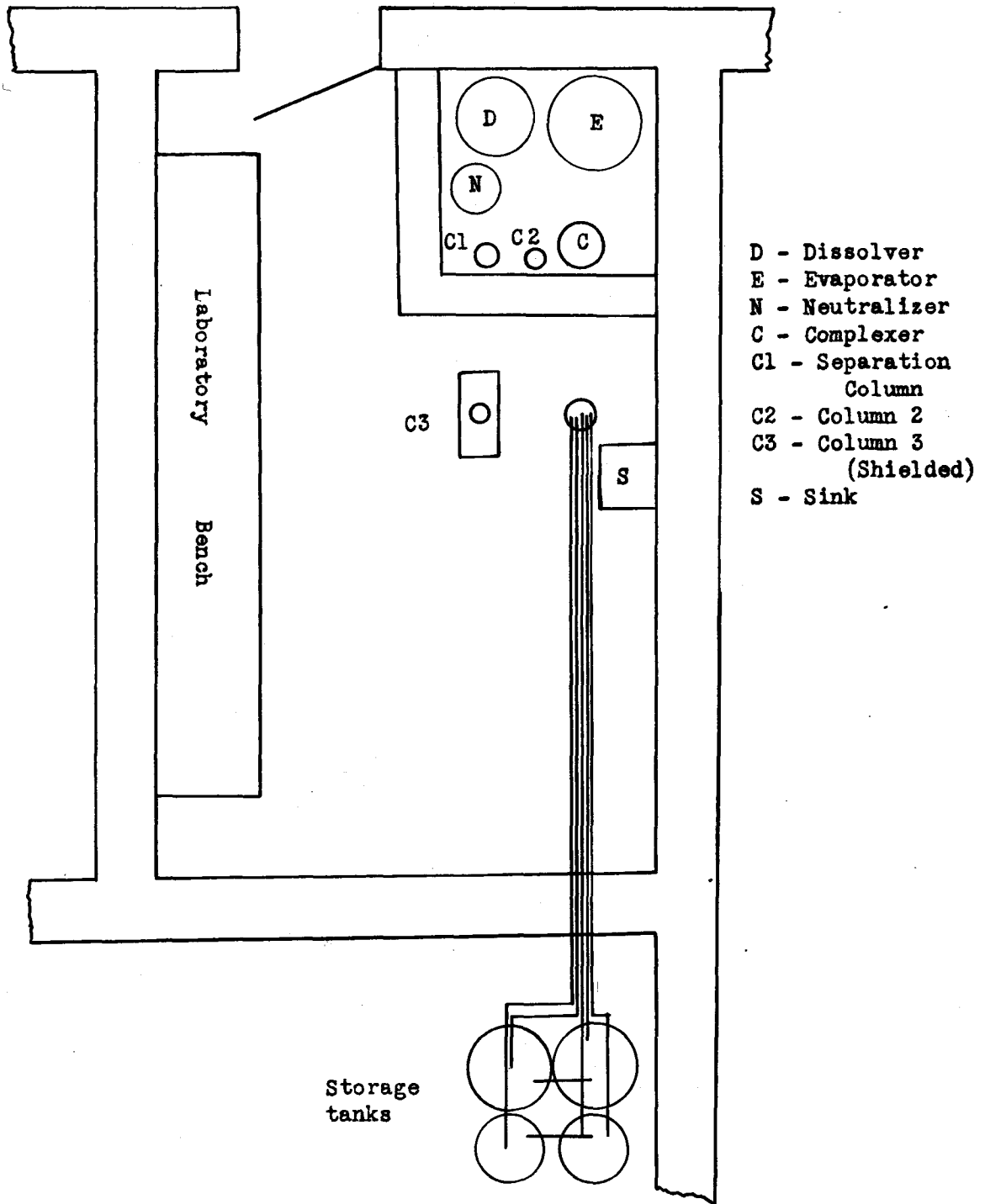
Figure 3. Floor Plan of "Hot Lab".
Connections to Storage
Tanks Not Shown

from 10 to 20 micrograms of plutonium. Slugs in this shipment were la-

beled CA-1, CA-2, CA-3, and CA-4.

The aluminum jacket was removed from slug CA-1 and the slug was dis-

solved in nitric acid. The solution was neutralized and run through the

first Amberlite column using the general procedure outlined above. The

uranium was precipitated as the diuranate and given to the analytical

group for recovery. The plutonium was eluted with sodium bisulfate and

given to another group for further experiments.

Some difficulty was encountered in dissolving the uranium since so

much nitric acid was lost by evaporation. The final figures showed that

it required 4 liters of concentrated nitric acid to dissolve 1 kilogram

of uranium, which is far above the theoretical amount needed. Since the

addition of nitric acid is by remote control and the amount needed varies

with many factors, there is usually a large excess of nitric acid present.

The elution of plutonium from the column was complete.

e. <u>Adsorption and precipitation step using Clinton slug</u>. Slug CA-2

was dissolved, neutralized, and run through the first Amberlite column.

The plutonium was eluted with sodium bisulfate and run into the complexer.

It was necessary at this stage to reduce the high concentration of sodium

salts in order to obtain complete adsorption of fission products on the

second Amberlite column.

This was accomplished by precipitating the plutonium as hydroxide,

removing the clear supernatant liquid, and then dissolving the plutonium

hydroxide in dilute acid. This solution was diluted, complexed, and then

run through the second Amberlite column. The effluent was analyzed and found to contain nearly all the plutonium and only a small portion of the fission products.

d. **Adsorption run through two columns using precipitation at a pH of 7.0.** At this point it was thought desirable to use one slug and carry the process through the various steps using rigid control and make a quantitative balance of the various activities. Slug CA-3 was dissolved in nitric acid; the solution was diluted and run through the first Amberlite column. The plutonium was eluted with sodium bisulfate and led into the complexer. The solution was brought to a pH of 7.0 with sodium hydroxide and allowed to stand until the hydroxide had settled to the bottom. The clear supernatant was removed and the residue was dissolved in dilute sulfuric acid. Carriers were added to the resulting solution which was then diluted, complexed, and allowed to flow through the second Amberlite column. The various fractions were analyzed and gave the following results, which can be seen in Table 19.

The results show a surprisingly low yield for plutonium, and reference to the table indicates that the loss occurred in the precipitation step. In all cases in which a large excess of sodium hydroxide was present, this loss did not occur. It should be noted that the beta decontamination was very efficient but the low yield of product made this method worthless.

Table 19

Fractionation of Plutonium and Fission Products in Two Column Procedure

Solution	Alpha %	Beta %	Gamma %
Original	100	100	100
Precipitate	86.5	20.2	43.1
Supernatant	10.8	42.3	5.0
Effluent, Col. II	83.9	1.2	-
Eluate, Col. II	2.6	11.5	-

e. Two column procedure using oxalic acid as eluant for the first
column. While these experiments were being carried out, Boyd and his
group had developed a new procedure (37) for separation and partial de-
contamination of plutonium using one column filled with Amberlite IR-1.
In this method the first steps were exactly like the original procedure
described in Section II,B of this paper. Before elution of the plutonium,
the column was washed with a dilute (0.04 molar) solution of oxalic acid.
This solution selectively elutes zirconium and columbium since these two
elements so readily form complexes with oxalic acid. The plutonium was
eluted with a concentrated (0.5 molar) solution of oxalic acid, and most
of the remaining fission products were eluted with an 18 per cent solution
of sodium bisulfate. This procedure gave a higher decontamination factor
than the previous one column method. Another advantage was the fact that
in this method at the end of the run the column was relatively inactive.

Previously, when only the elution with sodium bisulfate was used, the zir-
conium and columbium remained on the column. This created a problem since
these two isotopes had such a high gamma ray activity (Tables 1 and 2).
The oxalic acid elution gave a decontamination factor in the neighborhood
of 100.

An experimental run was carried through in order to check the two
column procedure using oxalic acid elution described above. Slug CA-4
was dissolved in nitric acid. The uranyl nitrate solution was neutralized,
diluted, and run through the Amberlite IR-1 column. The residual uranium
was washed from the column with dilute sulfuric acid as in all previous ex-
periments. The zirconium and columbium were then selectively eluted with
dilute (0.04 molar) oxalic acid. After this step the plutonium was eluted
with concentrated oxalic acid, giving a much higher decontamination factor
than was obtained using sodium bisulfate elution. The product eluate was
placed in a 26 liter pyrex jar equipped with a heating element, and the
oxalic acid was decomposed by heating with sulfuric acid to fumes of sulphur
trioxide. The residue was dissolved in water, diluted, transferred to the
reservoir, and allowed to flow through the second Amberlite column.

This procedure was time consuming because of the slow flow rate in the
elution of zirconium and columbium. Another disadvantage was the lower
yield of plutonium in the product solution as determined by difference.
The results are indicated in Table 20.

Table 20

Distribution of Product and Fission Products

Solution	Beta d/m X 10^{-6}	%	Gamma d/m X 10^{-2}	%	Plutonium Micrograms	%
Original	1.591	100	83.1	100	58	100
Dilute Oxalic	0.37	23.2	61.0	74.0	0.085	0.14
NaHSO$_4$ Eluate	0.686	43.1	6.3	7.5	1.0	1.72
Product Solution through Column II	-	-	-	-	56.0	96.5
Eluate	0.008	0.5	0.5	0.6	0.93	1.6

f. Receipt and measurement of new shipment of slugs from Clinton. The original fission product activity in the CA slugs was so low that only the strong fractions could be measured with any accuracy. Twelve new slugs having a higher activity were received from the Clinton pile on December 11, 1944. Rough dosage measurements of the gamma radiation gave the following results:

Weak slugs - at 2 meters distance the dosage measurement was 0.015 r per hour.

Strong slugs - at 6 meters distance the dosage measurement was 0.014 r per hour.

The weak slugs were labeled CB-1 to CB-6, and the strong slugs were labeled CC-1 to CC-6.

g. Decontamination study using dilution as a means of lowering the salt concentration. A simple method of lowering the salt concentration

would be to dilute the eluate to a suitable volume. Since all procedures

must be carried out by remote control any simplification is very desirable.

To test this method, Slug CB-1 was dissolved, and the resulting solution

was run through the first Amberlite column. The column was washed with

dilute sulfuric acid and eluted with 19 per cent sodium bisulfate. The

eluate was run into the complexer, diluted, and brought to a pH of 5.5.

After the addition of the usual carriers, the solution was complexed with

20 grams of ferron, brought to a volume of 28 liters, transferred to the

reservoir, and then allowed to flow through the second Amberlite column.

Incomplete measurements showed that this procedure was unsatisfactory. The

high salt concentration caused a loss of plutonium and a low decontamination

factor since the sodium ions had a tendency to wash the plutonium down the

column.

h. Use of additional column to remove ferron. The effluent from the

second column is a very dilute salt solution containing ferron complexes of

uranium, plutonium, zirconium, and other elements. The next step should be

one which would remove the ferron and effect a concentration. A column

procedure for accomplishing this was devised and tested in the following

manner.

One portion of the effluent from the second column was diluted from

22 liters to 30 liters. After acidification with 100 ml. of 10 normal sul-

furic acid, the solution was stirred thoroughly and then passed through a

column filled with Amberlite IR-1 in the hydrogen form. At intervals samples

were taken and analyzed for plutonium and for fission products. The results

are listed in Table 21.

This preliminary experiment was very promising since it showed that the ferron could be removed by adsorbing the plutonium on the column with loss of only about 2 per cent. At the same time there was effected a decontamination and a volume reduction. Most of the fission products went on through while a few remained on the column even after elution.

The activity of the column at various heights was measured during the course of elution. The measurements were taken with a Lauritsen electroscope mounted on an adjustable tripod. The measured activities as tabulated in Table 22 show that a considerable amount of the activity was located near the top of the column.

Table 22

Activity of Amberlite Column

Distance from Top of Column in Centimeters	After Washing	Activity in Divisions per Minute After Eluting with			
		0.1 liter	0.25 liter	0.6 liter	1.0 liter
0	308	445	300	387	286
20	272	334	344	247	300
40	143	146	177	94	92.5
60	118	114	114	111	512
80	81.6	92.4	91.6	226	52.5
90	81.6	84.0	-	235	63.5

An analysis of the eluate for fission products showed that the decon-

Table 21

Analysis of Samples of Various Fractions Coming Through Column III

| Liters Run Through | Plutonium | | Beta and Gamma |
	c/m per 10 ml.	% of total	d/m (St. 9) per 10 ml.
0	0	0	0
4	6	0	40
6	20	0.8	63
8	44	1.8	83
9	56	2.3	103
10	51	2.0	100
13	34	1.3	87.5
17	47	1.8	83
20	54	2.2	90.5
22	61	2.4	101
24	57	2.3	100
26	55	2.2	111
28	62	2.5	95
30	61	2.4	78
0.7	23	1.0	62.5
1.8	5	0.2	34.5
0.6	9	0.4	13.5
0.5	4	0.2	9.6
0.6	0	0	9
0.8	0	0	10
0.95	0	0	10
0.2	0	0	10
0.3	0	0	9
0.7	0	0	-
Eluate			
2.5	25,550	-	-
2.5	2,900	-	-
0.6	930	0.8	-
0.5	690	0.5	-
1.8	100	0.3	-

tamination factor in the third column was approximately 6.

1. **Comparison of ferron obtained from different sources.** During the first part of the investigation the ferron used as complexing agent for the plutonium was obtained from Eastman Kodak, but later when the experiments were on a much larger scale and it became necessary to use larger amounts of the reagent, a portion was obtained from G. D. Searles and Company of Chicago. The ferron obtained from Searles was much cheaper and it seemed to fit our purpose as well. One of the major purposes of the research was to devise a large scale procedure with a capacity of about one ton per day. Since the cost of materials is a major item in such a program it is always desirable to use a cheaper reagent. In order to see if there was any essential difference between the two samples of ferron, the following experiment was run using the two reagents under similar conditions.

Two small columns, 1.4 centimeters in diameter, were filled with Amberlite IR-1 to a height of approximately 50 centimeters. These columns were washed, conditioned, and classified; and then the following solutions were run through.

Column A

a. A conditioning solution of 250 ml. of dilute ferron (Eastman) solution at a pH of 5.3, containing uranyl, yttrium, cerium, lanthanum, and strontium carriers,

b. A solution having a total volume of 250 ml. at a pH of 6.3, and containing 25 ml. of column one eluate and the same carriers as the conditioning solution.

c. 200 ml. of dilute ferron solution as a wash,

d. Sodium bisulfate eluant,

Column B

The same solutions as through Column A except that the ferron was that obtained from Searles.

The solution coming through the columns was analyzed for plutonium and for fission products, and finally the Amberlite was destroyed and analyzed. The results are given in Table 23.

Table 23

Comparison of Yields and Decontamination Factors
Using Ferron Obtained from Different Sources

Solution	Plutonium c/m	%	Beta and Gamma d/m on Stage 5	%	Decontamination Factor
A. Eastman Ferron					
a. Effluent	45160	93.6	250	1.1	93
b. Eluate	2900	6.0	-		
c. Left on Column	175	0.36	-		
B. Searles Ferron					
a. Effluent	41040	92.3	330	1.4	70
b. Eluate	3000	6.8	-		
c. Left on Column	390	0.9	-		

The results were slightly better when the ferron obtained from Eastman was used, but the difference was not too great showing that either reagent could be used.

j. **Determination of loss in precipitation step.** In all the previous runs which had been carried out on a large scale the salt concentration was lowered by simple dilution to about 6 times the original volume. Although this gave satisfactory results on a small scale column, on a large column there was too much leakage of fission products. If the salt in the experiment from column one could be efficiently removed by some simple procedure the concentration of ions in the feed solution for column two would be very low. This would greatly increase the capacity of the second column and would give higher decontamination factors. Any procedure for lowering the salt concentration must be carried out by remote control and must result in low loss of plutonium. In order to devise such a procedure the following experiment was carried out.

To 1 liter of diluted eluate from column one were added lanthanum, yttrium, barium, cerium, strontium, and uranyl carriers, and the solution was made alkaline with sodium hydroxide. After standing 24 hours, the precipitate settled to a compact layer on the bottom, leaving a clear supernatant solution which was poured off and placed to one side. One liter of distilled water was added to the precipitate and this was thoroughly agitated and allowed to stand 24 hours. The clear supernatant was added to the first portion and the combined supernatant solutions were analyzed for plutonium. The results showed that less than 1 per cent of the plutonium was lost by this crude procedure.

The uranyl carrier was added in previous experiments as an indicator

ion. The progress of the plutonium ion could be followed by noting the deep red color of the complex at a pH of about 7. At a low pH, when the color of the uranyl ferron complex disappeared, the plutonium was no longer complexed. In this experiment the uranyl ion served another purpose. Since the diuranate is a dense precipitate it sinks rapidly and serves as an excellent carrier. The uranyl ion is very easily removed by a column procedure so it could be added without fear of contamination.

k. Column behaviour of complexed solutions low in salt concentration. The precipitate from the previous experiment was dissolved in dilute sulfuric acid, complexed with ferron, neutralized to a pH of 5.7, and diluted to 900 ml. A column, 1.4 centimeters in diameter, was filled with Amberlite IR-1 to a depth of 65 centimeters. After the Amberlite had been backwashed and conditioned the feed solution was run through at a rate of 5 to 6 ml. per minute. After washing the column with dilute ferron solution, then with water, and finally with a 1 per cent solution of oxalic acid, the plutonium was eluted with an 18 per cent solution of sodium bisulfate. The effluent, after the addition of carriers, was run through a second Amberlite column prepared in the same manner as the first. The effluent was acidified to a pH of 2.5 and poured through a third Amberlite column in the hydrogen form. The column was washed with dilute sulfuric acid and then eluted with sodium bisulfate. The results are shown in Table 24.

Table 24

Analyses of Various Fractions of Column Experiment

Solution	o/m	Beta and Gamma d/m Stage 5
Original	1.9×10^6	9.4×10^5
Column II		
Effluent	1.89×10^6	8.2×10^5
Adsorbent	5.2×10^5	
Column III		
Eluate I		
400 ml.	1.4×10^6	
Eluate II		
50 ml.	1×10^5	
Eluate III		
500 cc.	20,000	124
Adsorbent	5,000	

This experiment demonstrated the need of a better method of analyzing for plutonium. The lanthanum fluoride procedure used in this and all previous experiments was a long and rather inaccurate method involving several precipitations. The analysis was so time consuming that only a few fractions could be analyzed. In this experiment the most important result was the higher decontamination factor obtained in the second column. Without any correction for UX this factor was over 100. In order to determine the percentage of the total activity due to fission products either a thorium separation must be made or more active slugs must be used as starting material.

1. Precipitation procedure and column run. A smaller scale decontamination run was made using the precipitation method of lowering of salt concentration. One liter of eluate from the first column was diluted and the usual carriers were added. The solution was made 1 normal in sodium hydroxide and allowed to settle for 24 hours. At the end of this time the supernatant was decanted, the precipitate was slurried with water and allowed to settle, and the supernatant was decanted into the same beaker that held the first solution. The combined supernatant solutions were analyzed for plutonium and found to contain 8200 counts per minute or

$$\frac{8200 \times 100}{2 \times 10^6} \cong 0.4 \%$$

The precipitate was dissolved in dilute sulfuric acid, diluted, complexed, neutralized to a pH of 5.4, and run through an Amberlite IR-1 column in the sodium cycle. Additional carriers were added to the effluent which was then run through another Amberlite IR-1 column in the sodium cycle. The effluent was acidified to a pH of 2.4 and then run through an Amberlite IR-1 column in the hydrogen cycle. The last column was washed with dilute sulfuric acid and eluted with sodium bisulfate. The solutions were analyzed giving the results shown in Table 25. The decontamination factor was high but the yield was too low to be satisfactory.

Table 25

Yields and Decontamination Factors for
Multitple Column Procedures on Small Scale

Solution	Plutonium c/m	Beta and Gamma d/m Stage 5
Original (Complexed Solution from Column I)	2.8×10^6	7×10^5
Column II Effluent	2.8×10^6	14,000
Column IV Eluate I Eluate II Eluate III	2.14×10^6 88,200	1,976 540

m. <u>Effect of high pH</u>. An experiment was run in the same manner as the previous experiment except that the complexed feed solution was at a pH of 8.4. The recovery of plutonium was very good but the decontamination was unsatisfactory since at this high pH the ferron also complexes the rare earths.

n. <u>Installation of dissolver, evaporator, and storage tanks</u>. In the previous experiments the uranium slugs had been dissolved in a pyrex jar placed on a hot plate. A 10 gallon steam jacketed kettle to be used as a dissolver and a 12 gallon steam jacketed evaporator were installed and connected to the underground storage tanks.

Slug CB-2 was placed in the dissolver and heated with dilute nitric acid and mercuric nitrate until the aluminum coat was dissolved. The aluminum nitrate solution was pumped off and the uranium was dissolved in concentrated nitric acid. It was not possible to control the temperature and a large excess of nitric acid was required. The excess nitric acid was neutralized by the addition of 500 grams of sodium hydroxide. The uranyl nitrate solution was diluted and run through an Amberlite column. The column was washed with dilute sulfuric acid and eluted with sodium bisulfate. The figures, given in Table 26, show a high loss appearing in the effluent.

Table 26

Elution of Plutonium from Amberlite Column

Solution	Plutonium	
	Micrograms	% of Original
Original	208	100
Eluate	153	73.5
Effluent		26.5

c. Decontamination run using hot slugs. The apparatus had been tested thoroughly with inactive slugs. Because of the difficulty caused by UX (see Section IV.C), the use of weak slugs was unsatisfactory and in order to secure more accurate results some stronger slugs were used.

Slug CC-1 was dissolved and the uranyl nitrate solution after dilution and neutralization was run through an Amberlite column. The column was washed with dilute sulfuric acid and eluted with sodium bisulfate.

After addition of suitable carriers, the eluate was made alkaline with sodium hydroxide and allowed to stand until the hydroxides had settled. After decantation of the clear supernatant liquid the residue was dissolved in dilute acid and then diluted, neutralized, complexed, and run through a second Amberlite column. In order to remove the last traces of fission products which might have been washed through, the effluent was run through another Amberlite column. The effluent from this last column was acidified with sulfuric acid to a pH of 2.42 and passed through an Amberlite column in the hydrogen form. The column was washed with dilute sulfuric acid and eluted with sodium bisulfate in several fractions. The results are summarized in Table 27.

p. Dosage measurements. When very active slugs are used it is necessary to measure the amount of activity in various localities and thus determine the working period which will give a reasonable margin of safety. The instrument chosen to make these measurements was a Lauritsen electroscope which had been calibrated by the Medical Group at the University of Chicago Metallurgical Laboratory. According to their figures, approximately 0.01 r per hour gave 20 divisions per minute on the electroscope. This figure corresponded to the daily dose for a 10 hour day. The following measurements were taken prior to the first run:

Table 27

Analyses of Solutions from Run Using Slug CC-1

Solution	Plutonium Milligrams	Fission Product d/m
Original	4.36	6.8×10^{7}
Column I		
Eluate	3.45	2.97×10^{7}
Post Eluate	0.04	
Supernatant from Eluate	0.028	2×10^{5}
Column II		
Effluent	3.57	3.6×10^{5}
Wash	0.002	
Column III		
Effluent	2.59	
Wash	0.06	
Eluate	0.438	
Column IV		
Effluent	0.02	
Wash	0.075	
Eluate I	0.028	
Eluate II	2.46	1.5×10^{4}
Eluate III	0.07	
Eluate IV	0.02	

Background in center of laboratory before

slug was introduced into the hood   2 divisions per minute

Background after slug was introduced   3.5 divisions per minute

Background just outside door of hood   30 divisions per minute

Background just inside door of hood   120 divisions per minute

These measurements showed that the room was safe, except inside the

hood. Any place inside the hood itself was unsafe for periods longer

than two hours per day.

q. Adsorption column decontamination in which excess nitric acid is

destroyed. Slug CC-2 was dissolved and the procedure was carried through

the first column. A large portion of the plutonium appeared in the ef-

fluent with the uranium just as in the run with slug CC-1. The loss in

these cases probably occurred because the nitric acid was present in ex-

cess and required a large amount of sodium hydroxide for neutralization.

The sodium nitrate thus formed greatly increased the ionic concentration

and caused a leakage of the plutonium into the effluent. Another decon-

tamination run (using slug CC-3) was made exactly as in the run with CC-1,

except that the excess nitric acid was destroyed with formic acid at a

slightly elevated temperature. The results given in Table 27 to show the increased yield. The general

pared with those in Table 27 to show the increased yield. The general

effect is treated in detail under "Discussion".

The loss in the effluent was much lower in this run in which the

excess nitric acid was destroyed. The over-all yield was good in all

steps except in the very first column. The final yield in the combined

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Table 28

Distribution of Fission Products and Plutonium in Various Fractions of a Multiple Column Adsorption Run Using Formic Acid for Destruction of the Excess Nitric Acid.

Solution	Plutonium		Fission Products
	Micrograms	% of Total	
Original	5460	100	5.36×10^7
Column I			
Effluent	390	7.1	
Wash	15	0.27	
Eluate	5300	91.5	
Post Eluate	50	0.91	
Backwash	10	0.18	
Column II			
Effluent	5320*	91.7	
Wash			
Eluate	69	1.1	
Column III			
Effluent	5000	91.0	276000
Wash			
Eluate	69	1.1	
Column IV			
Effluent	40	0.72	21760
Eluate I	4560	83.5	
Eluate II	400	7.2	
Total Eluate	4960	90.7	

$$\text{Decontamination Factor} = \frac{5.36 \times 10^7}{2.17 \times 10^4} \cong 2000$$

* At this point a portion was removed for other experiments.

eluate from the last column was 4.96 milligrams or about 99 per cent of the amount in the eluate from the first column. In these experiments using the active slugs, the samples were counted using the proportional counter.

r. Elution of plutonium from third column using oxalic acid. The above procedure gave a method of utilizing several adsorption columns in a single integrated procedure. The decontamination factor was still too low to be of any great value. Since the single fission product responsible for the greatest activity at this stage was zirconium, it was decided to selectively elute the zirconium from the third column with dilute oxalic acid and then elute the plutonium with concentrated oxalic acid. The concentration of the oxalic acid solutions were the same as recommended by Boyd in his separation procedure (37). This procedure requires larger volumes and slower flow rates. For these reasons it was very time consuming when used on the first or separation column. The succeeding columns, however, are much smaller and a modification of this procedure could be used advantageously.

A portion of the effluent from the second column in one run was brought to a pH of 2.55 by the addition of concentrated sulfuric acid and diluted to about 19 liters. It was passed through a column, 3 centimeters in diameter, packed with Amberlite IR-1 in the hydrogen form to a depth of 120 centimeters. The column was washed with dilute sulfuric acid and eluted first with dilute oxalic acid and then with concentrated oxalic acid. The results of the analyses of various fractions

for plutonium and fission products are shown in Table 29. The experiment was not very successful since too much of the plutonium appeared in the by-product eluate.

An attempt was made to elute the plutonium with a solution, 10 per cent in acetic acid and 10 per cent in sodium acetate. The elution was incomplete even when a large amount of solution was used.

s. Four column procedure with oxalic acid elution. Oxalic acid elution had been tried previously with weak slugs but did not give conclusive results because of the relatively high concentration of UX activity. Another decontamination run was carried out using slug CC-4 as starting material.

The procedure for the first three columns was the same as in the previous runs. The fourth column, however, was eluted first with dilute oxalic acid, then with concentrated oxalic acid, and finally with sodium bisulfate.

The dilute oxalic acid was prepared by adding 10.46 grams of $H_2C_2O_4 \cdot 2 H_2O$ for each liter of water. The concentrated oxalic acid was a 4 per cent solution. These strengths were those recommended by other workers for elution of plutonium from the first column and should have been satisfactory in this case.

The dilute oxalic acid was started at 6:45 A.M. and continued until 11:30 P.M. After draining to a level slightly above the bed, the column was filled with concentrated oxalic acid. At 12:15 A.M. the concentrated oxalic acid first appeared in the eluate.

The data for the run are given in Table 30. An elution curve is

Table 29

Plutonium and Fission Products in Solutions from Column

Sample	Volume	Plutonium		Fission Products	
		c/m per ml.	% of feed	d/m per ml.	%
Effluent					
I	1	12	6.0	20.5	80
II	10	13	6.5	21.1	80
III	19	22	11.0	20.5	80
Acid Wash					
I	1	2	0	0.95	
II	7	0	0	1.10	
III	18	1	0	1.40	
Dil. Oxalic					
I	0.3	24	0.2	77.0	
II	1.7	90	2.6	2.25	
III	3.5	203	10.0	0.55	
IV	5.0	181	18.0	0.5	
V	7.5	200	31.0	0.43	
Conc. Oxalic					
I*	At start	285			
II	After 1.23 l.	522			
III	After 1.76 l.	231	40		
IV	After 2.26 l.	141			
V	Final	63			

* Ten ml. samples were taken for analyses after a certain volume of eluate had flowed through.

plotted in Figure 4. The results show that a large percentage of the plutonium was lost in the dilute oxalic acid wash probably because the concentration of the oxalic acid was too high. On the other hand, the elution of the plutonium was very slow and only partially complete. The decontamination factor for that plutonium which did appear in the proper place was very high.

Table 30

Analysis of Main Fraction of Concentrated Oxalic Acid Eluate

Element	Micrograms	Divisions per Minute	Specific Decontamination Factor
Plutonium	2.30		
Zirconium		143	8.0×10^5
UX		23	1.4×10^5
Cerium		7	2.3×10^6
Yttrium		1	2.2×10^6

The decontamination factor for the total beta activity, not including UX, may be calculated as

$$\frac{5 \times 10^7}{150} = 3.33 \times 10^5$$

This is satisfactory indicating that further work should be done on this procedure in order to increase the yield.
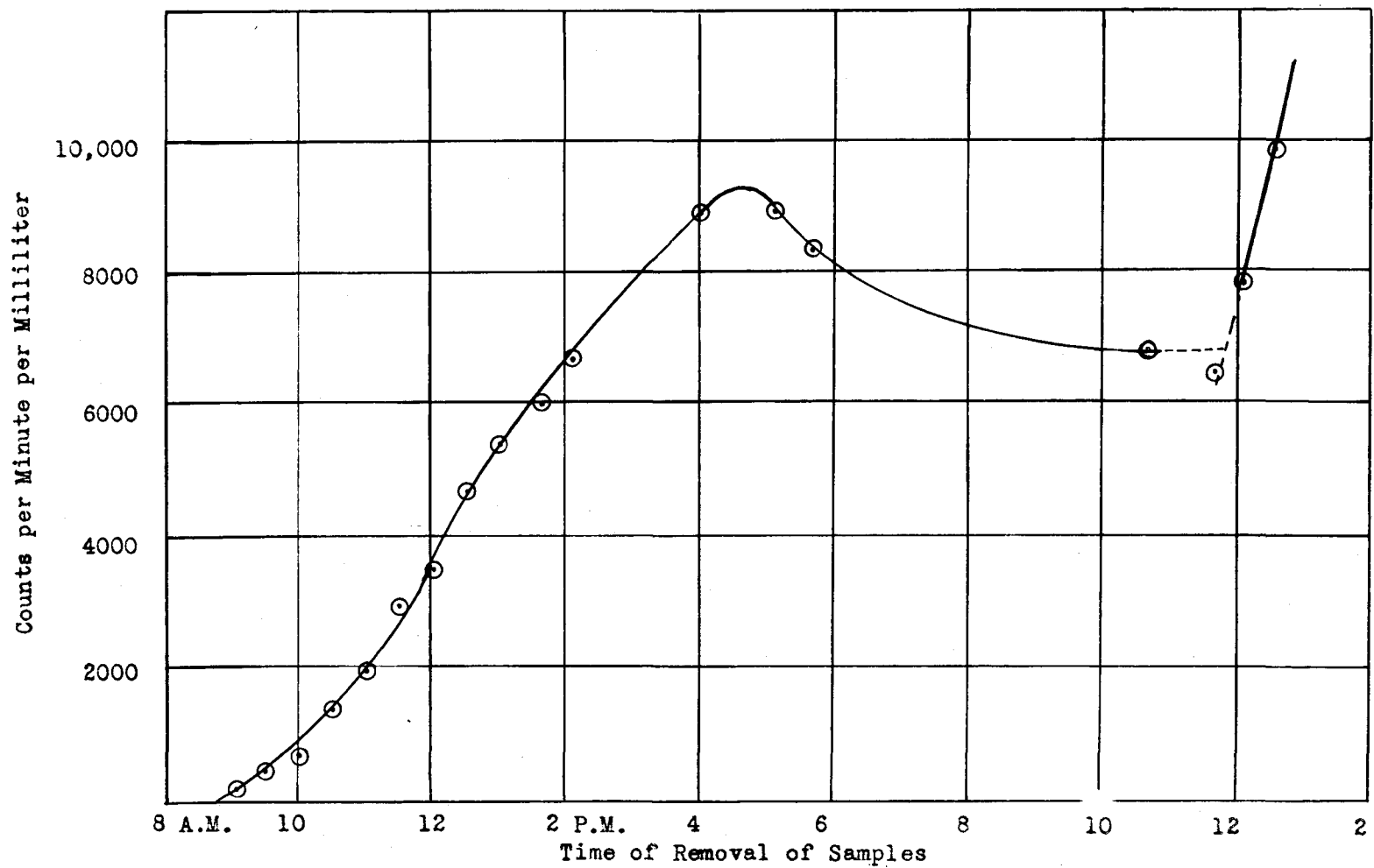
Figure 4. Schumann Curve for Oxalic Acid Procedure on Small Scale.

From the preceding experiments it was concluded that the best pro-
cedure was one using three columns, the first or separation column filled
with Amberlite in the hydrogen form, the second filled with Amberlite in
the sodium form, and the third filled with Amberlite in the hydrogen form.
The second column served to remove most of the rare earth fission products
and the third column removed the zirconium, complexing agent, iron, and
other impurities. This column also gave a volume reduction. The use of
four columns was discontinued since it lowered the yield of plutonium and
did not increase the decontamination factor to any great extent.

5. Development of oxalic acid procedure using small columns

a. Oxalic acid wash and eluant. In these experiments a more dilute
oxalic acid solution (0.045 molar) was used as a by-product eluant to
remove the zirconium and columbium. In order to effect a faster and more
complete elution of plutonium, a saturated (approximately 8 per cent)
solution of oxalic acid was used to elute the plutonium.

The first fraction of the eluate from the fourth column as described
in Table 28 served as the starting material to prepare the feed solution
for these experiments. Ten ml. of this material having no other anion
besides sulfate was diluted to 1 liter, acidified to a pH of 2.5, and
poured through an Amberlite IR-1 column, 1.4 centimeters in diameter and
60 centimeters high. The column was washed with dilute sulfuric acid
and then eluted first with dilute oxalic acid, then with concentrated ox-
alic acid, and finally with sodium bisulfate. A detailed summary of anal-

yses of various fractions of the different solutions is shown in
Table 31.

Table 31

Analyses of Solutions From Trial Run Using Oxalic Acid Eluants

Description of Solutions	Volumes in ml.	Flow Rates ml/min.	Plutonium		Fission Products Total d/m
			Micro-grams	% of Total	
Effluent	1000	10.5	0	0	2000
H$_2$SO$_4$ Wash	250	10.5	.01	0	
Dilute Oxalic					
I	300	3.1	.04	0.1	
II	150	3.1	.04	0.1	
III	400	3.1	1.8	0.45	
IV	195	3.1	3.5	0.9	
V	20	3.1	0.7	0.2	
Conc. Oxalic					
I	165	3.1	400	95.85	17.1
II	260	3.1	9.7	2.4	
III	30	3.1	1.7	0.4	
NaHSO$_4$		6.2			512

These results are shown graphically as curve "a" in Figure 5.
From the table and the graph it is seen that virtually no loss occurs in
the dilute oxalic acid eluate until after a volume of approximately 500
ml. have passed through. At this point the concentration of plutonium
in the eluate increases sharply and keeps increasing steadily. Therefore
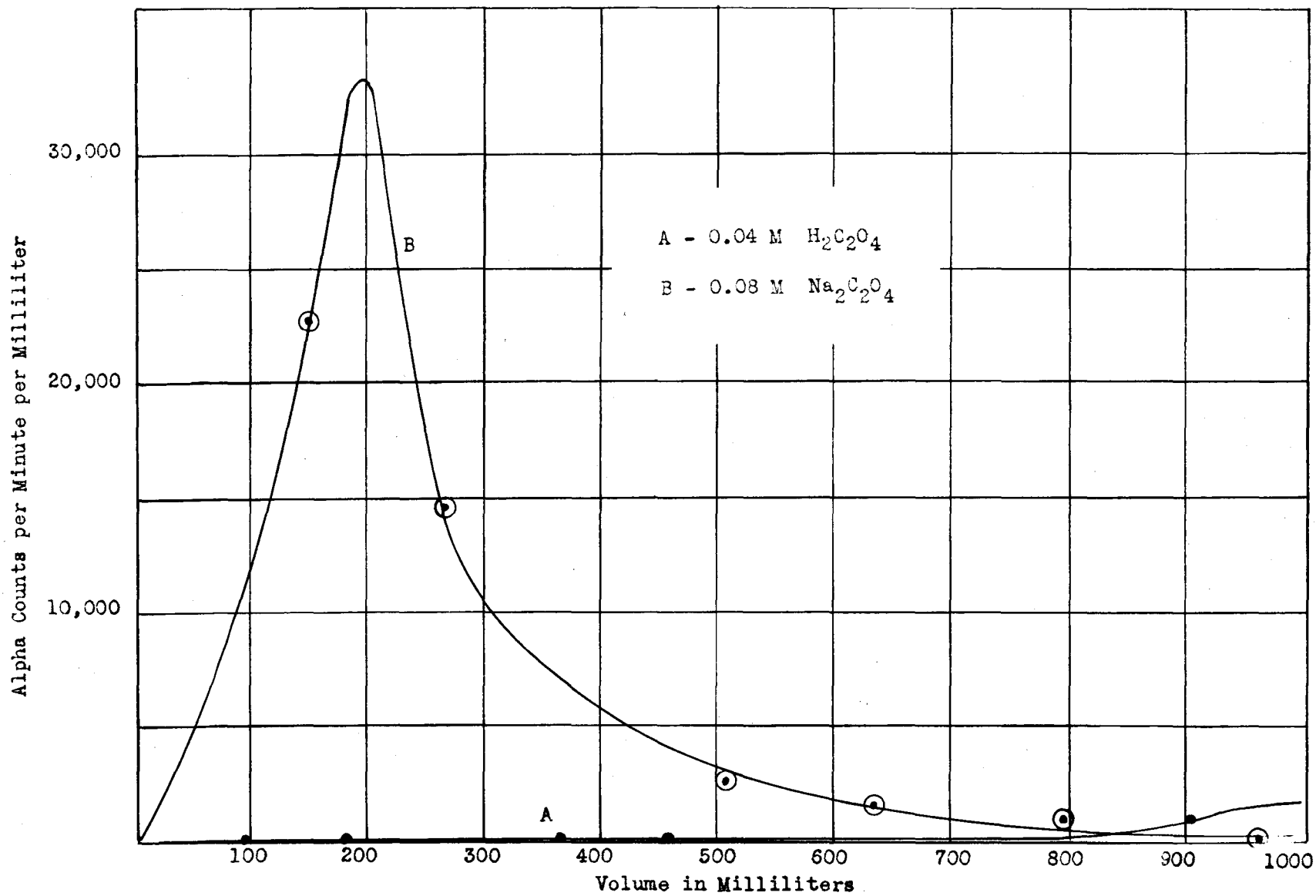
Figure 5.   Schumann Curves for Wash Solutions.

if less than 500 ml. of dilute oxalic acid solution are used the loss will be negligible. Approximately 96 per cent of the plutonium appeared in the first fraction of the concentrated oxalic acid eluate.

Another fact of importance which will be referred to later is the fact that use of an additional column using oxalic acid elution gives an additional decontamination factor, in this case about a factor of 100. This experiment was repeated with essentially the same results.

b. Sodium oxalate wash. A similar experiment was performed using 0.08 molar sodium oxalate as by-product eluant instead of 0.04 molar oxalic acid. The results are shown in Table 32.

Table 32

Plutonium Appearing in Fractions of Dilute Sodium Oxalate Eluant

Time of Analysis	Volume of Eluate	Plutonium c/m per ml.
1:00 P.M.	150	22,400
1:40	270	14,200
3:00	510	2,700
3:40	630	210
4:35	795	160
5:10	935	
6:25	1,125	10
7:20	1,290	220

These results are shown graphically in curve "b", Figure 5. The shape of the elution curve is very different from that for the dilute oxalic

acid. The above figures show that sodium oxalate is entirely unsatis-

factory as a by-product eluant since there is too great a loss of

plutonium. The best by-product eluant as shown by the preceding ex-

periments was 0.04 molar oxalic acid. An excess of the by-product

eluant must be avoided, in order to prevent a large loss of plutonium.

6. Specific decontamination factors

In order to evaluate and further improve the process it was neces-

sary to determine the specific activities in the various fractions dur-

ing an adsorption run, preferably on a large scale.

A hot slug was dissolved and run through the first two columns using

the same procedure as described in the previous experiments. An analysis

of the effluent from the second column was made periodically in order

to determine if there was any increase in the fission product activity.

The analyses as given in Table 53 show that the effluent is homogeneous.

This effluent was acidified to a pH of 2.5 and run through the third

column containing Amberlite IR-1 in the hydrogen form. The column was

washed with dilute sulfuric acid, and then eluted with the following so-

lutions:

    a. Dilute (0.04 M) oxalic acid solution,

    b. Saturated oxalic acid solution,

    c. Sodium bisulfate solution.

The solutions were analyzed for plutonium and fission products. The re-

sults are shown in Table 34. The discrepancy in the analyses of plu-

Table 33

Analyses of Portions of Effluent from Second Column

Time of Removal of Sample	Volume in Liters	Plutonium c/m per ml.	Fission Products	
			Total d/m per ml.	Fluoride Insol. c/m per ml.
2:00 P.M.	8.0	8,170	6.7	5.2
4:00	11.6	7,060	6.75	5.0
7:30	18.0	7,390	6.85	4.85
9:00	20.7	7,450	7.1	4.92
11:00	24.3	7,600	6.85	5.1
1:40 A.M.	29.0	7,750	6.50	5.0

Table 34

Analysis of Solutions for Plutonium and Fission Products

Solution	Plutonium Milligrams	Fission Products Total	Fluoride Insoluble
Original	4.46	3.5×10^7	2.74×10^7
Column I			
Effluent	0.240		
Wash	0.092		
Post Eluate	none		
Column II			
Effluent	3.95	216000	144000
Wash	0.0027		
Column III			
Effluent			
Wash			
Dilute Oxalic Eluate			
Concentrated Oxalic			
Eluate I	3.47	3714	2907
Eluate II	0.22		
Eluate III	0.06		4000

tonium arises partially from the difficulty of estimating the total volume. The volumes of all but the final solution were estimated by noting the height of liquid in a pyrex jar. In this run there was still considerable loss of plutonium in the effluent from the first column.

In Table 35 are listed the specific decontamination factors. The decontamination factors for the rare earths are especially satisfactory. An adsorption curve of the activity appearing in the dilute oxalic acid eluate of the third column showed that practically all of the activity was due to the 65 day zirconium-35 day columbium chain.

7. **Final adsorption column run**

a. **Arrival of very active slugs.** The previous experiments had demonstrated that the adsorption column decontamination procedure was capable of securing a high decontamination factor and a satisfactory yield. In most of the runs, however, only certain factors were studied in detail. In order to test out the procedure it was decided that a test run should be made, in which every step of the procedure should be carefully examined and all yields and decontamination factors should be thoroughly checked.

Since the decontamination factors were extremely high, of the order of 10^6, it was necessary to start with very active material. Consequently some very active slugs were requested from Clinton. On December 13, 1945, these slugs were received. They were measured, using a Landswerk

Table 35

Specific Activities of Various Solutions

Solution	Total	Zr(+ Cb)	Ce	Y	UX
Original Effluent	5.5×10^7	0.67×10^7	2.16×10^7	0.43×10^7	0.18×10^7
Column II Product Eluate	2.16×10^5	1.2×10^5	0.08×10^5	0.013×10^5	0.16×10^5
Column III	3714	807	15.5	1.5	15.5
Decontamination Factor	10000	8000	1.4×10^6	2.9×10^6	10^5

pocket electroscope, to give the following results at a distance of one foot:

Through 1.5 inches of lead - 0.6 r per hour

Without lead - 0.9 r per minute.

These figures mean that without any shielding, the maximum safe working time at a distance of one foot is less than eight seconds.

The data sheet accompanying the slugs gave the following information:

Date charged   August 6, 1945

Date discharged September 5, 1945

Accumulated kilowatt hours on pile during exposure = 2.5 X 10^6

The slugs were labeled CD-1, CD-2, and CD-3.

b. First column. The procedure has been described in the previous experiments, but in this run it will be repeated in detail since in the final procedure all the best features were incorporated.

Slug CD-1 was dissolved in 6.5 liters of nitric acid. After the excess nitric acid had been carefully destroyed by heating it with 225 ml. of formic acid the solution was pumped over to the neutralizer. The pH was about 2.8, which was too high since the neutral point of uranyl nitrate solution of this concentration is 2.45. Enough nitric acid (45 ml.) was added to bring the pH to this value, and the solution was pumped to a reservoir and then allowed to flow through a column filled with amberlite IR-1 in the hydrogen form. The column was washed with dilute sulfuric acid and eluted with sodium bisulfate. The eluate was placed

in the complexer and the following carriers were added:

5.5 grams uranyl ion,

0.070 gram yttrium ion,

0.140 gram cerium ion,

0.140 gram lanthanum ion,

0.070 gram strontium ion,

0.070 gram barium ion.

The solution was made 1 normal in sodium hydroxide, mixed thoroughly, and allowed to stand one day. The dense precipitate settled and the clear supernatant was siphoned off. The residue was slurried with water and allowed to stand one day. The clear supernatant was again siphoned off and the residue was dissolved in 70 ml. of 10 normal sulfuric acid. This solution was diluted, complexed with 25 grams of ferron, diluted to 26 liters, and neutralized with sodium hydroxide to a pH of 5.8.

c. Second column. The complexed eluate was poured through a column filled with Amberlite IR-1 in the sodium cycle. The column was washed with dilute sulfuric acid and eluted with sodium bisulfate.

d. Third column. This column was carefully prepared using classified Amberlite IR-1 in the hydrogen form as adsorbent and de-ionized distilled water for all solutions. The column was conditioned carefully and backwashed thoroughly.

The feed solution was the effluent from the previous column after it had been acidified to a pH of 2.5. The column was washed with dilute sulfuric acid and then successively eluted with dilute oxalic acid, concen-

trated oxalic acid, and sodium bisulfate. The concentration and flow rates of the various solutions are shown in the flow sheets (Figure 6).

c. **Analyses of plutonium and fission products.** The analyses of the various fractions for plutonium are given in Table 36. The total loss was less than one per cent. On a large scale this would not be a loss since the solutions could be re-processed separately. A possible method of doing this is outlined in the complete flow sheets (Figure 6). The only loss of any importance occurs in the effluent from the first and third columns. The other solutions could be discarded unless it was desired to recover the fission products.

The solutions were analysed for fission products giving the results shown in Table 37. All activities have been corrected to December 13, 1945, the date of the analysis of the original solution.

The decontamination factors for the individual fission products are shown in Table 38. The factors are listed for each column and then for the over-all or total decontamination factor.

From this table it can be seen that the different columns may be used in series to give a high decontamination factor. In the first column the mono- and bi-valent ions were removed. Ruthenium and tellurium were also removed, probably as a complex anion. The rare earths were removed in the second and third columns and zirconium was removed in the third column. Each column performed a special purpose to give a good over-all yield.

The dangerous activities were removed early in the procedure. The greater part of the gamma ray activity was removed in the first column.

UNH FEED	DILUTE ACID WASH	FISSION PRODUCT ELUANT	POST ELUANT	OXALIC ACID WASH	RINSE AND BACKWASH
10% UNH	0.25 M H_2SO_4	18% $NaHSO_4$	18% $NaHSO_4$	0.8% Oxalic	Distilled Water
30 liters	20 liters	7.6 liters	3 liters	26 liters	12 liters
100 gal/ft²/hr	100 gal/ft²/hr	60 gal/ft²/hr	60 gal/ft²/hr	30 gal/ft²/hr	100 gal/ft²/hr

COLUMN I
ADSORBENT BED

AMBERLITE IR-I
H^+ FORM

1100 grams
120 cm high
5.2 cm diameter
22.6 cm cross section

SECRET

PRE-EFFLUENT	UNH EFFLUENT	H_2SO_4 WASTE	ELUATE I	ELUATE 2	OXALIC ACID ELUATE
10 liters	32 liters	8 liters	7.6 liters	3.6 liters	26 liters
no Pu	0.5% Pu	no Pu	98.7% Pu	0.75% Pu	no Pu
	35% β	2% β	50% β	~1% β	12% β
	30% γ	2% γ	30% γ	~1% γ	35% γ
0.5% U	99% U	0.5% U	no U		

Discard | Adjust pH to 2.5, and then, if desired, to additional column for greater recovery of plutonium. (COLUMN Ia) | Discard, or recover by-products. | Carrier added. | To be used in making up eluant for next run. | To storage or separation.

NaOH to I N
Let settle, and
decant supernatant.

PRECIPITATE
Dissolve in dilute H_2SO_4
Dilute to 30 liters.
Add Ferron
Adjust pH to 5.5

To COLUMN 2

SUPERNATANT

Discard

Figure 6.   Flow Sheet for Decontamination Pro-
cedure Using Ion Exchange Columns.

FEED SOLUTION

Complexed Ferron solution
from eluate of Column I

30 liters

100 gal/ft²/hr

WASH

2.5% H_2SO_4

6 liters

100 gal/ft²/hr

BY-PRODUCT ELUANT

18% $NaHSO_4$

4 liters

60 gal/ft²/hr

COLUMN 2
ADSORBENT BED

AMBERLITE IR-I
Na^+ FORM

120 cm high
3.2 cm diameter
8.1 cm² cross section

EFFLUENT
25 liters
98.7% Pu
6% Zr
1% rare earths
No other β or γ

WASH
6 liters
0% Pu
<1% β and γ

BY-PRODUCT ELUATE

Ba, Sr, Ce, La, Y, other
rare earth fission
products, some Cs, Te,
Zr, and UX.

Figure 6. (Continued)

FEED SOLUTION

Complexed effluent from column 2 after pH has been adjusted to 2.5

100 gal/ft²/hr

FIRST WASH

Dilute sulfuric acid (0.25%)

8 liters

100 gal/ft²/hr

OXALIC WASH

Dilute oxalic acid 0.04% $H_2C_2O_4$

8 liters

30 gal/ft²/hr

PRODUCT ELUATE

Saturated oxalic acid

1.6 liters

30 gal/ft²/hr

RINSE

Distilled water

5 liters

100 gal/ft²/hr

COLUMN 3
ADSORBENT BED
AMBERLITE IR-I
H^+ FORM

120 cm high
3.2 cm diameter
8.1 cm cross section

EFFLUENT
25 liters
Te activity
0.2% Pu

NaOH to I N

H_2SO_4 WASH
8 liters
~0% β, γ
~0% Pu

$H_2C_2O_4$ WASH
8 liters
6% Zr - Cb

PRODUCT ELUATE
1.6 liters
98.5% Pu
DCF Ce 4.6 X 10⁶
Y 9.0 X 10⁵
Zr -Cb 3.1 X 10³
No other appreciable activity

RINSE

Figure 6. (Continued)

COLUMN FOR RECOVERY OF PLUTONIUM FROM EFFLUENT

EFFLUENT FROM COLUMN 3
Make alkaline with NaOH (I N)
Allow to settle
Decant supernatant

RESIDUE
Dissolve in H_2SO_4
Adjust pH to 2.5

SUPERNATANT
↓
Discard

FEED SOLUTION	WASH	ELUANT
5 liters	0.25 M H_2SO_4	18% $NaHSO_4$
100 gal/ft²/hr	2 liters	I liter
	100 gal/ft²/hr	60 gal/ft²/hr

AMBERLITE COLUMN
AMBERLITE IR-I (H⁺ FORM)
1.6 cm² cross section
60 cm high

EFFLUENT AND WASH	ELUATE	POST-ELUATE AND RINSE
8 liters	0.6 liters	I liter
Inactive solution	18% $NaHSO_4$	
	0.2% Pu	

DISCARD   UNITE WITH Ib or Ic   DISCARD

Figure 6. (Continued)

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COLUMN Ia

RECOVERY OF PLUTONIUM FROM EFFLUENT OF COLUMN I

```
┌─────────────────┐  ┌─────────────────┐  ┌─────────────────┐  ┌─────────────────┐
│      FEED       │  │   ACID  WASH    │  │     ELUANT      │  │     RINSE       │
│   32 liters     │  │    20 liters    │  │   7.6 liters    │  │    5 liters     │
│Effluent of Column I│ │  0.25 M H₂SO₄  │  │   18% NaHSO₄    │  │ Distilled Water │
│    pH = 2.5     │  │                 │  │                 │  │                 │
│    0.5% Pu      │  │                 │  │                 │  │                 │
│    35% β        │  │                 │  │                 │  │                 │
│    30% γ        │  │                 │  │                 │  │                 │
│    99% U        │  │                 │  │                 │  │                 │
│ 100 gal/ft²/hr  │  │ 100 gal/ft²/hr  │  │ 60 gal/ft²/hr   │  │ 100 gal/ft²/hr  │
└─────────────────┘  └─────────────────┘  └─────────────────┘  └─────────────────┘
```

ADSORPTION COLUMN
AMBERLITE IR-I (H⁺ FORM)
1100 grams
120 cm high
5.4 cm diameter
22.6 cm² cross section

```
┌─────────────────┐  ┌──────────────────┐  ┌─────────────────┐  ┌───────────────────────┐
│ PRE-EFFLUENT    │  │ EFFLUENT AND WASH│  │    ELUATE       │  │  BACKWASH AND RINSE   │
│   10 liters     │  │    33  liters    │  │   7.6 liters    │  │                       │
│                 │  │     0% Pu        │  │    0.5% Pu      │  │ Essentially distilled water│
│                 │  │     99% U        │  │  Some β and γ   │  │                       │
│                 │  │    β and γ       │  │                 │  │                       │
└─────────────────┘  └──────────────────┘  └─────────────────┘  └───────────────────────┘
    DISCARD          TO URANIUM RECOVERY      RECOVERY OF Pu           DISCARD
```
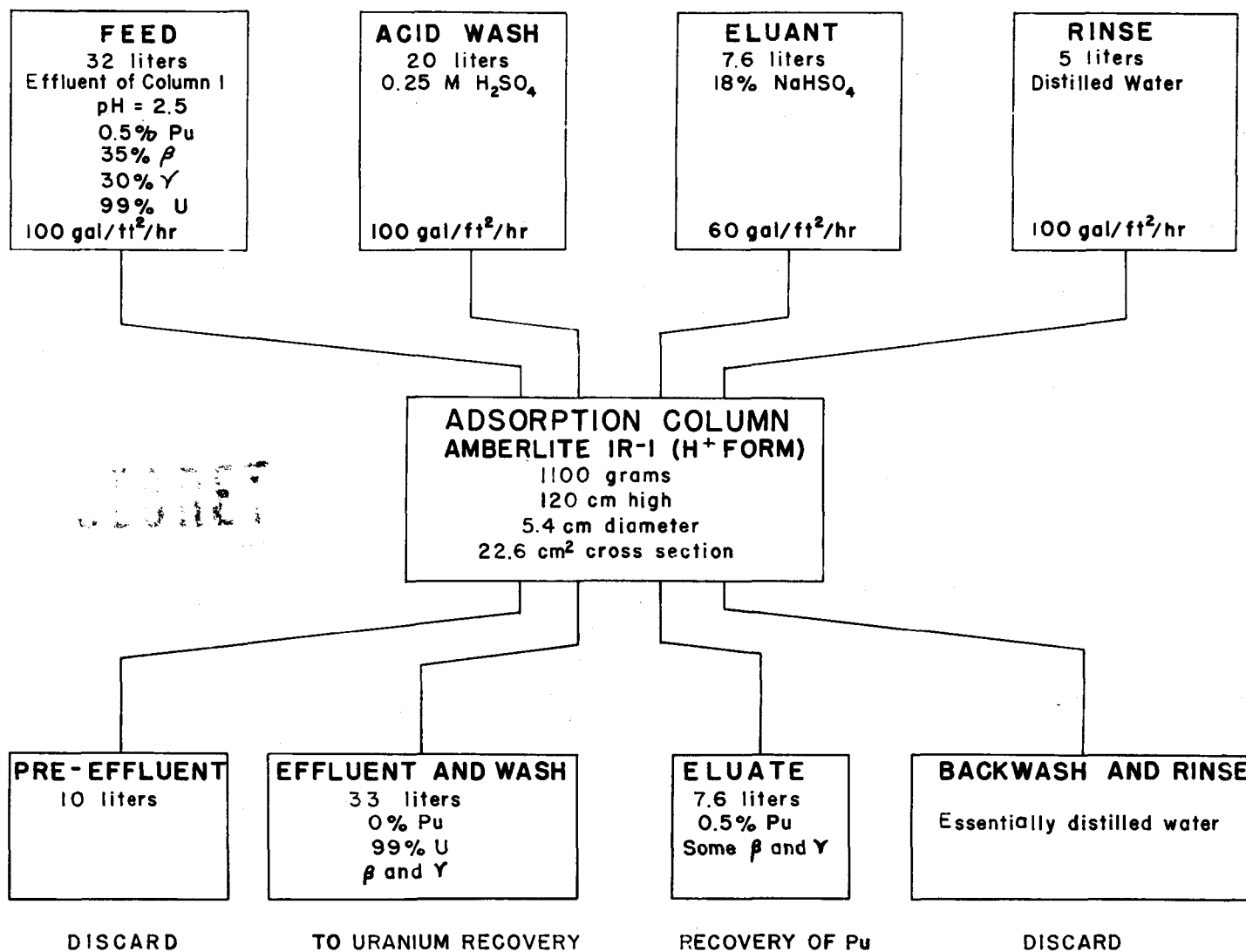
Figure 6. (Continued)

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Table 36

Analyses of Fractions for Plutonium

Descriptions of Solutions	Plutonium Milligrams	% Loss
Original	4.82	
Column I		
Effluent and Wash	0.027	0.55
Post Eluate	0.035	
Backwash	none	
Column II		
Acid Wash	none	
Column III		
Effluent	0.0097	0.2
Sulfuric Acid Wash	none	
Dilute $H_2C_2O_4$	0.002	0.05
Concentrated $H_2C_2O_4$		
Eluate I	4.93	
Eluate II	0.0336	
Eluate III	not analyzed	
NaHSO$_4$ Eluate	0.002	0.05

Table 37

Specific Activities of the Fission Products in the Different Solutions. Adsorption Column Run Using Very Hot Slug

Fission Products	Original Solution d/m X 10⁻⁷	Column I Effluent d/m X 10⁻⁷	Column I Eluate d/m X 10⁻⁷	Column II Effluent d/m X 10⁻⁵	Column III Product Eluate d/m
300 day Cerium } 28 day Cerium }	9.28	1.67	7.44	6.86	20
57 day Yttrium } 13.5 day Praseodymium }	5.6	1.89	3.6	0.25	60
55 day Strontium } 30 year Strontium }	5.93	1.44	0.25	0.84	Negligible
68 day Zirconium } 35 day Columbium }	4.85	0.624	1.28	30.06	15800
42 day Ruthenium } 330 day Ruthenium }	1.42	0.858	0.01₈	0.05	Negligible
90 day Tellurium } 32 day Tellurium }	0.185	0.118	----	2.77	Negligible
Total Activity	27.3	6.6	12.6	43.13	21520*

* The additional activity in the product eluate from Column III is due to UX_1.

Table 38

Decontamination Factor for the Columns

Element	D. F. for Col. I	D. F. for Col. II (First Column Through Second Column)	D. F. for Col. III (Second Column Through Third Column)	Total Decontamination Factor
Ce	1.25	84	44300	4.64×10^6
Y	1.55	1440	400	9.0×10^5
Sr	23.7	29.8	*	$> 10^7$
Zr and Cb	3.8	4.27	190	3.1×10^3
Ru	78.8	36	†	$> 10^7$
Te	*	*	*	$> 10^7$
Total	2.17	29.2	272	1.73×10^4

* Too weak to measure.

and the cerium with the hard beta ray was removed in the second column.

From Table 37, it should be noted that even in this last experiment about 25 per cent of the final activity was due to UX. This activity from UX was over 60 times as strong as that from the total rare earths. The activities of the various fractions were measured over a sufficient period of time to obtain an accurate value for the half life. This was necessary in the case of the rare earths to show that the activity was not due to a contamination by UX.

V. DISCUSSION

A. Effect of Excess Nitric Acid on Yield

As it has been stated previously, the loss of plutonium in the first column is highly dependent upon the total salt concentration of the original solution. This can be observed very easily from Table 39.

Table 39

Loss of Plutonium in the First Column Effluent

Slug No.	Table No.	NaOH Grams	Plutonium in Original. Milligrams	Plutonium Loss in Effluent Milligrams	%
CC-1	27	750	4.36	0.91	20.8
CC-2		1100	5.2	3.36	64.7
CC-3	28	200	5.4	0.39	7.2
CC-4		105	4.74	0.293	6.2
CC-5	34	57	4.46	0.24	5.4
CD-1	36	0	4.32	0.027	0.56

In the third column is listed the amount of sodium hydroxide added to the uranyl nitrate in the neutralizer in order to bring the pH to 2.4. To bring out more clearly the dependence of the loss upon the salt concentration, the values are plotted graphically in Figure 7.
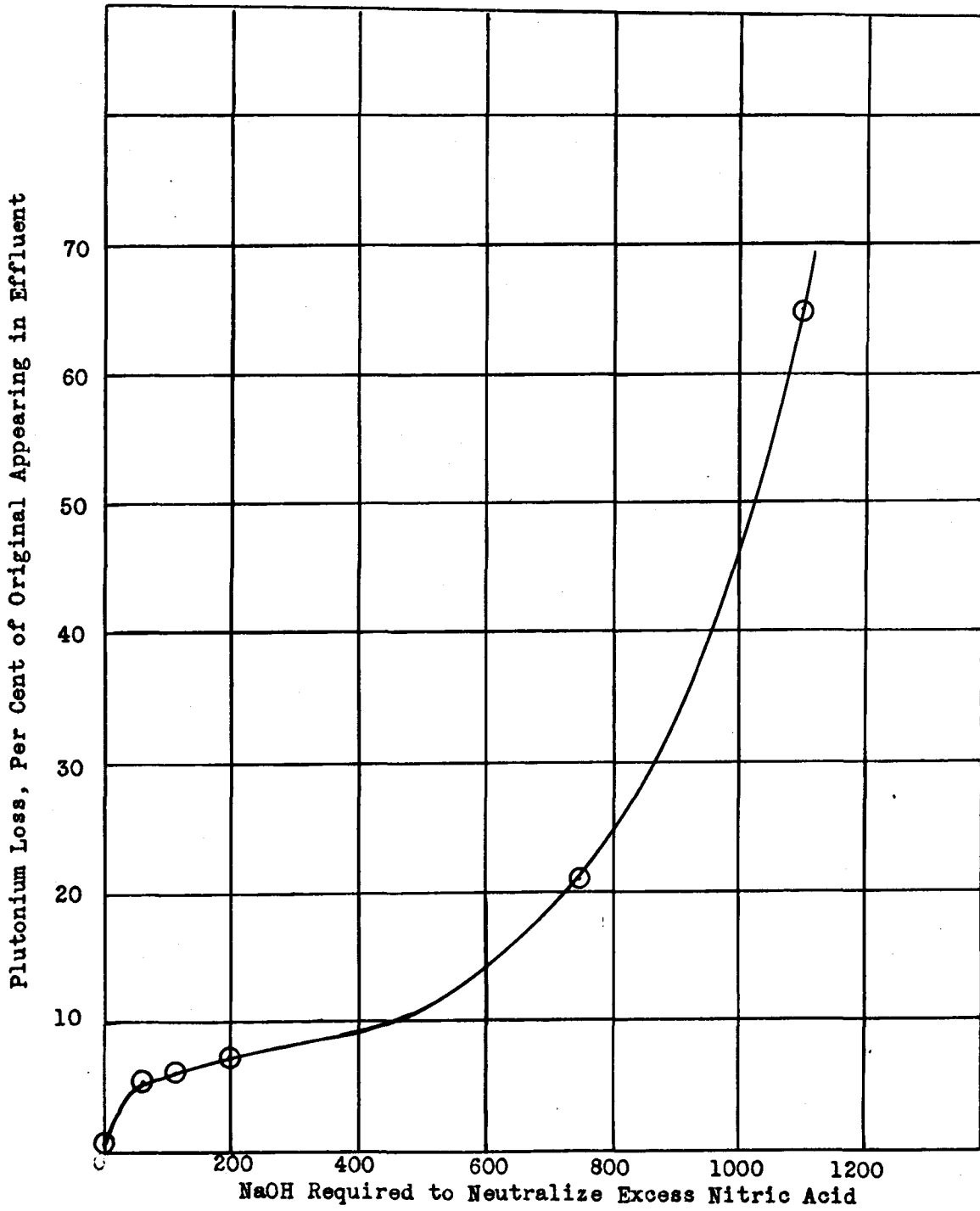
Figure 7. Relation of Salt Concentration to Plutonium Loss.

B. Further Decontamination

As is evident from Table 37 and Table 38, the principal contaminant in the eluate of the third column is zirconium. It should be possible to greatly increase the decontamination factor by removing zirconium by some specific method. There are a number of such methods which have been worked out in detail. One is the fluoride precipitation which is efficient and would give a very good decontamination, but which has several obvious disadvantages. A much more attractive procedure would be the use of another adsorption column, similar to column one but much smaller in size. The plutonium in the eluate from the third column could be separated by the precipitation step as outlined above, or by evaporation and decomposition of the oxalic acid with sulfuric acid. The plutonium would be dissolved by dilute acid. The resulting solution, after dilution to a suitable volume would serve as the feed for an additional or fourth column. The specific decontamination factor for zirconium in this column is in the order of one hundred, and this method would then give an overall decontamination factor of 10^6 to 10^7, using adsorption columns exclusively. The details of this additional column have been worked out on a laboratory scale, and the results were presented in an earlier section of this paper (IV,E,5,b). Up to this point there have been no centrifugations, filtrations, or other steps likely to cause trouble when remote control methods are used exclusively. The eluate from the fourth column would be safe to handle without excessive precautions because of the high decontamination factor.

C. Adaptation to a Larger Scale

No difficulties were observed in this laboratory in changing from small columns to a pilot plant scale using one slug per run. The only difference was in the application of technique suitable for operation on a larger scale. Since adsorption column technique has already been developed in industry as, for example, in the de-ionisation of water, there should be no difficulty on this score. In fact, it was found that as larger and larger columns were used the recovery was better, thus indicating that on a plant scale the recovery would be even more satisfactory.

In the pilot plant the second column was much larger than necessary since it was an experimental column and was used for many modifications of the procedure. As finally outlined, the feed solution for the second column would contain very few ions other than plutonium and the fission products. The theoretical size of the second column would then depend upon the total amounts of these ions in solution and upon the resistance of the adsorbent to the radiation. Taking these considerations into account, some data are given below on the amounts of solution and size of apparatus which would be necessary for processing one ton batches:

Amount of original uranyl nitrate solution	25,000 liters
Amount of feed for second column	250 liters
Amount of feed for third column	250 liters
Amount of feed for fourth column	30 liters

Using these figures, a person was able to calculate the size and number of the columns required for each step. The results are presented in Table 40.

Table 40

Size and Number of Columns Required for One Ton of Uranium

	Number of Columns	Diameter of Column in Inches	Bed Height in Feet
Column I	5	12	8
Column II	1	8	4
Column III	1	3	4
Column IV	1	2	4

D. Recovery of Fission Products

It may be desirable to recover some of the fission products in a relatively pure form. This recovery is simplified by the adsorption process. Zirconium and columbium may be obtained from the first column by an oxalic acid elution following the removal of plutonium. Barium, strontium, cerium, and yttrium may be separately eluted from the second column by fractionation with citric acid using procedures already well developed (38). Tellurium is concentrated in the effluent from the third column (39). Cerium, ruthenium, rhodium, and tellurium are completely or largely in the effluent of the first column together with all of the uranium.

SUMMARY

This dissertation presents the status of the adsorption column procedure for separation and decontamination of plutonium as it was developed at Iowa State College.

Starting with a single column for the separation of plutonium from uranium, the method was developed to a three column procedure giving, in addition, specific decontamination factors of 10^4 to 10^6 with yields of over 99 per cent. This procedure consists of the following steps:

a. The uranium from the pile is dissolved in nitric acid, neutralized, and poured through a column filled with Amberlite IR-1 in the hydrogen form. After the column has been washed with dilute sulfuric acid to remove the uranium the plutonium is eluted with an 18 per cent sodium bisulfate solution.

b. The eluate from the first column is made 1 normal in sodium hydroxide, agitated, and allowed to stand for a sufficient time for the hydroxides to settle. The supernatant is decanted off and the hydroxides are dissolved in dilute acid. The resulting solution is diluted, complexed, and neutralized to a pH of 5.5. This solution is poured through a second column filled with Amberlite IR-1 in the sodium form.

c. The effluent from the second column is acidified to a pH of 2.5 at which point the complex is destroyed. This acidified solution is poured through a column filled with Amberlite IR-1 in the hydrogen form. In this step the plutonium, no longer in the complexed state, is adsorbed on the column.

d. The column is washed with dilute sulfuric acid to remove any

mono- or bivalent ions, and then washed with dilute oxalic acid in order to

remove zirconium and columbium in a complexed form. Finally, the plutonium

is eluted with concentrated oxalic acid. This solution is then ready for

additional decontamination.

A method is outlined whereby the decontamination factor can be in-

creased to any desired figure by the use of additional columns, and flow

sheets incorporating this method are included.

A "hot lab" suitable for large scale experiments with material of mod-

erately high radioactivity was designed and built. Materials having an ac-

tivity up to five curies were processed in this laboratory. Since the room

was designed for samples having a total activity of approximately one curie,

it would be inadvisable to process any highly active material there. For

this reason the laboratory at Iowa State College is not the proper place

for further studies along this line. Using only relatively weak starting

materials, such as the Clinton slugs containing about five curies, it is im-

possible to develop the method any further then its present state unless it

is desired to resort to invalid assumptions or extrapolations. Synthetic

starting materials will give results of doubtful value since it is possible

that some isotope present in the original material to an extremely small

amount might account for a considerable percentage of the final activity.

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