

Combination of Unit Processes for Isolating Plutonium

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The various laboratory and industrial methods used in the isolation of plutonium from neutron irradiated uranium can be divided into a few unit processes, from which a relatively small number of simple flow-sheets can be derived. Some of these unit processes and flow-sheets are discussed.

When uranium has been irradiated for some time with slow neutrons it contains a certain amount of fission products, and a roughly equivalent amount (by weight) of plutonium. It is a difficult chemical problem to isolate this plutonium in the form of some pure compound and also to recover the uranium, whether this is done in the laboratory or on an industrial scale, since the plutonium and the uranium have to be separated from the fission products, which consist of about 30 different elements spread out over all groups in the periodic system. In addition, the fission products cause great health hazards because of their penetrating radiation, and should be removed almost completely from the plutonium and the uranium.

1. SURVEY OF COMBINED PROCESSES

Excellent reviews have been given of the chemistry of plutonium ¹⁻³ as well as methods for its isolation from neutron irradiated uranium ⁴⁻⁶. The aim of this paper is to point out how all these processes, published or unpublished, can be regarded in principle as composed of a number of unit processes, namely:

Reduction-oxidation processes, which we shall denote by (V for valency)

V66, giving Pu(VI) and U(VI),
V46, giving Pu(IV) and U(VI),
V36, giving Pu(III) and U(VI),
V34, giving Pu(III) and U(IV).

Table 1. Examples of media and treatments that will give plutonium and uranium in the valency states indicated. All time refers to plutonium concentrations $\leq 10^{-3}$ M.

Unit process V66: oxidation to Pu(VI)* and U(VI).
a. 70 % HClO_4 , 195° C, 15 min ²⁴ . b. 0.1 M $\text{S}_2\text{O}_8^{2-}$, 1 M H^+ , 20° C, Ag^+ catalyst, 5 min. c. 0.1 M $\text{Cr}_2\text{O}_7^{2-}$, 1 M H^+ , Co^{3+} catalyst, 90° C, 10 min. d. 0.2 M BrO_3^- , 1 M H^+ , 95° C, 30 min. e. NaBiO_3 , 5 M H^+ , 20° C, 5 min.
Unit process V46: transformation to Pu(IV)* and U(VI).
a. ≥ 8 M HNO_3 , 90° C, 30 min. b. conc. H_2SO_4 , several hours fuming. c. ≥ 8 M HClO_4 , 90° C, 30 min.
Unit process V36: reduction to Pu(III)*, U(VI).
a. pass in SO_2 , 1 M H^+ , 20° C, 15 min. b. 0.05 M N_2H_4 , 2 M H^+ , Fe^{2+} catalyst, 20° C, 20 min.
Unit process V34: reduction to Pu(III)* and U(IV).
a. Fe-powder, 1 M HCl , 20° C, 5 min. b. Zn or Zn-Hg, $\text{pH} \leq 1$, 20° C, 1 min. c. electrolysis, 1 M H^+ , 20° C <i>cf.</i> ²⁵ . d. dissolving of metal in conc. HCl , F^- catalyst. Note: After reduction a short aeration may be necessary to oxidize U(III) to U(IV).

* Mainly according to Ref.¹

Separation processes, denoted by

- S6, when Pu(VI) and U(VI) are collected together in a separate phase,
 S46, when Pu(VI) or Pu(IV) and U(VI), or U(IV), are collected together in a separate phase,
 S4, when Pu(IV) or U(IV) is collected in a separate phase,
 S34, when Pu(III) and U(IV), or Pu(IV), are collected together in a separate phase,
 S3, when Pu(III) is collected in a separate phase.

Tables 1 and 2 give examples of the principal reduction-oxidation and separation unit processes. They are also discussed in the following sections 2 and 3.

In each of the separation processes, some of the fission products will follow the actinides: the fission products accompanying the hexavalent, tetravalent and trivalent actinides will be denoted by FP^6 , FP^4 and FP^3 , respectively. The remaining fission products are denoted by FP^x .

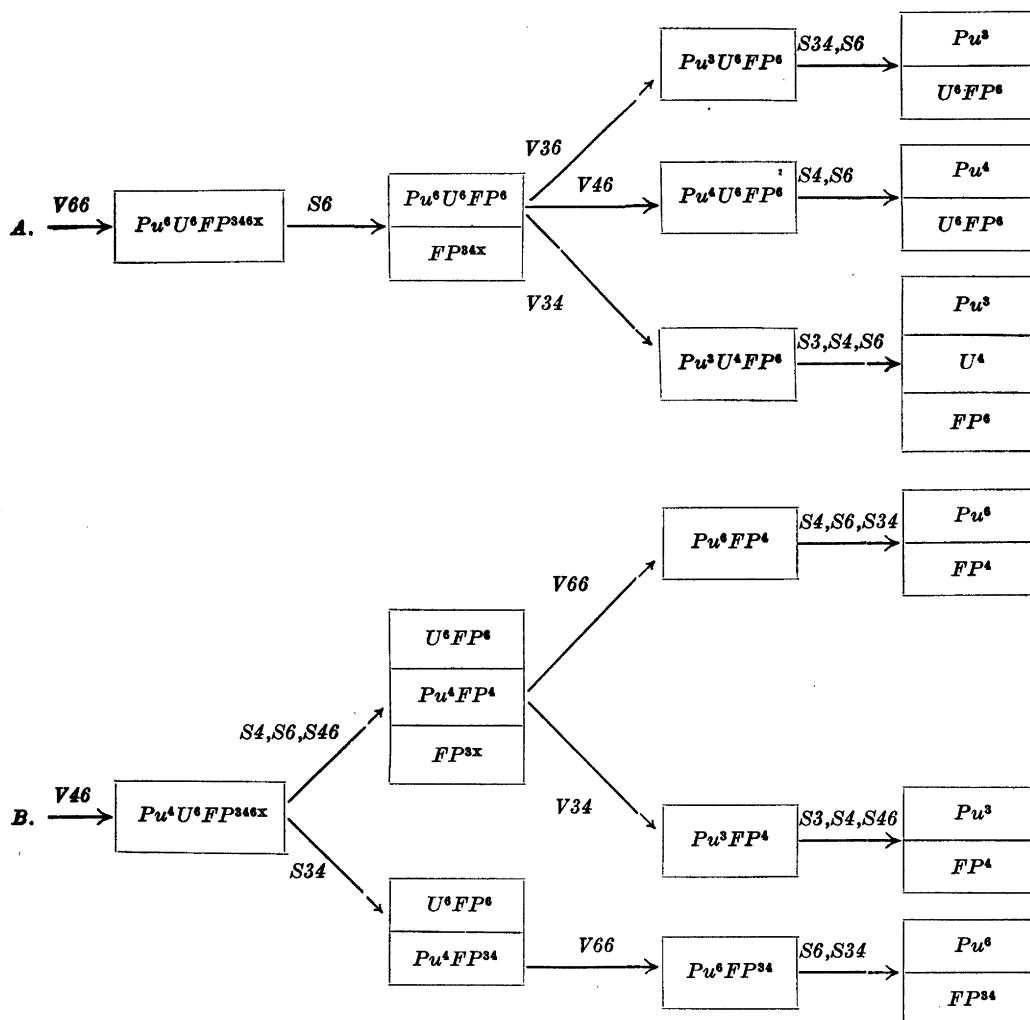
Table 2. Examples of processes for the separation of actinides.

Unit process S6: separation of hexavalent actinides.
a. 0.5 M HNO_3 , 2 M $\text{Mg}(\text{NO}_3)_2$, extraction with diethyl ether ⁴ b. 0.1 M HNO_3 , 3 M $\text{Ca}(\text{NO}_3)_2$, extraction with hexone ²⁷ c. pH 1.5, extraction with 3 M acetylacetone in hexone ²⁸ d. precipitation with 1 M CH_3COOH , 0.5 M CH_3COONa , 5 M NaNO_3 , U(VI) carrier ⁴
Unit process S46: joint separation of tetravalent and hexavalent actinides.
a. 8 M HNO_3 , extraction with diethyl ether ²⁹ b. 1 M HNO_3 , 4 M $\text{Ca}(\text{NO}_3)_2$, extraction with hexone ²⁷ c. pH 4, extraction with 3 M acetylacetone in CHCl_3 ²⁸ d. 2 M HNO_3 , extraction with tributyl phosphate ⁷ e. precipitation with excess of H_2O_2 , pH ~ 1 ³⁰
Unit process S4: separation of tetravalent actinides.
a. pH 1.0, extraction with 1.5 M cupferron in CHCl_3 ³¹ b. pH 1.0, extraction with 0.1 M thenoyltrifluoroacetone (TTA) in C_6H_6 ^{32,33} c. pH 2.0, extraction with 2 M acetylacetone in C_6H_6 (only U(IV), Pu(IV)) ²⁸ d. precipitation with 0.2 M IO_3^- , 3 M H^+ , Ce(IV) or Zr(IV) carrier ^{3,4,30} e. precipitation with 0.3 M H_2PO_4 , 3 M H^+ , Zr(IV) or Bi(III) carr. ^{3,4,13,30} f. precipitation with <i>m</i> -nitrobenzoic acid, pH ~ 3 , Th(IV) carrier ³⁰
Unit process S34: joint separation of trivalent and tetravalent actinides.
a. precipitation with 1–3 M HF , 1 M H^+ , La(III) carrier ^{3,4,30} b. precipitation with 0.1 M $\text{H}_2\text{C}_2\text{O}_4$, 1 M H^+ , Ce(IV) or Th(IV) carrier ^{3,4,30} c. sorption on cation exchange resin, elution with complexing agent <i>e.g.</i> ¹⁰
Unit process S3: separation of trivalent actinides.
No good process for a selective separation of trivalent actinides has been described. The best approximation to an S3 process may be an S34 process followed by an S4 or S46 process.

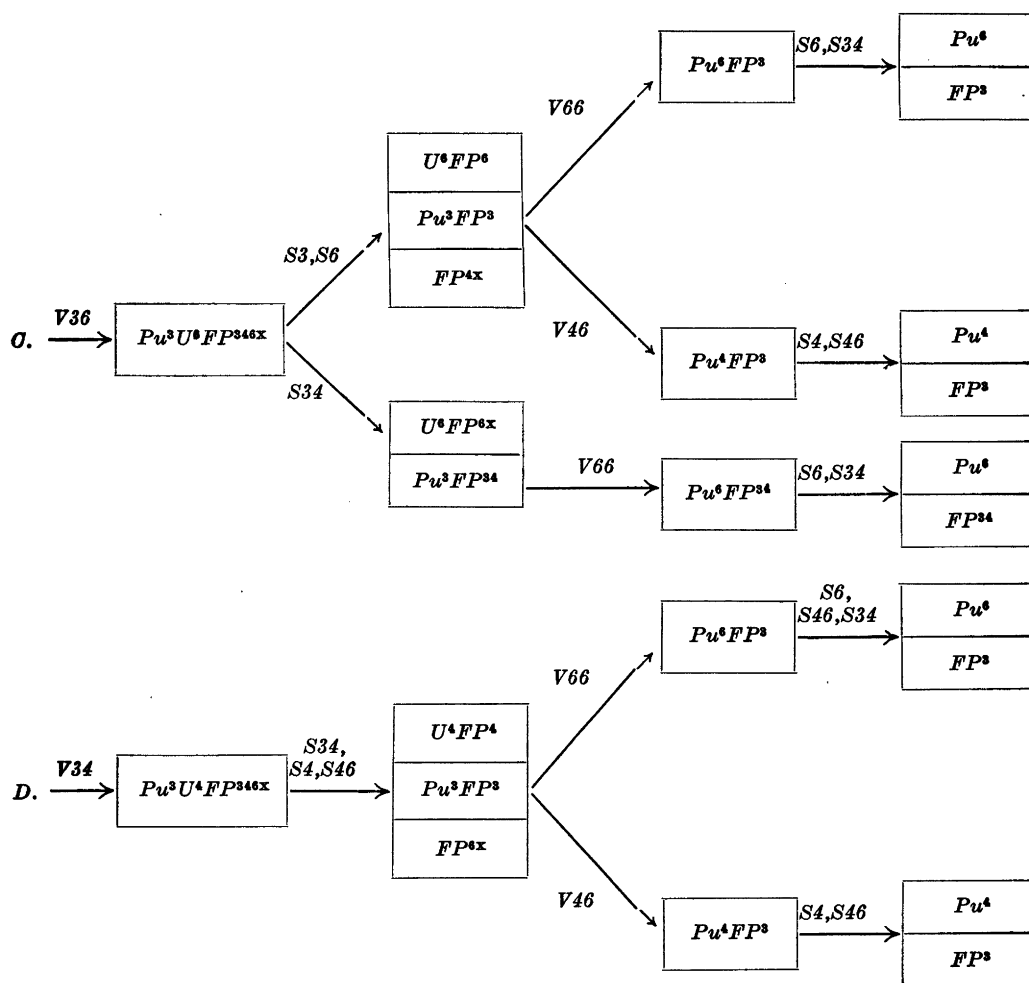
Table 3 gives a survey of the simplest combinations of the unit processes. The main interest has been in the isolation of plutonium. Most of the processes lead to uranium mixed with some fission products, generally FP ⁶. This mixture can be separated by applying a suitable combination of unit processes, although this will not be discussed here.

It has been assumed in Table 3 that the fission products normally keep their oxidation numbers constant in the different processes. This is generally true, although important exceptions exist, which have to be considered in a more detailed discussion. Although most of the fission products may be removed by processes given in the diagrams, it may be necessary to add some extra operation for removing some particular fission products.

Table 3. Some possible combinations of unit processes for the isolation of plutonium from neutron irradiated uranium. The superscripts indicate valency states; the letter-figure combinations on the arrows refer to unit processes in Tables 1 and 2. See text for significance of single, double or triple rectangles.



The diagrams in Table 3 are self-explanatory. A single rectangle with its preceding arrow indicates the redox-process through which the different valency states are obtained. Two adjacent rectangles with the preceding arrow indicates a process in which the elements have been separated into two different phases (e. g. aqueous phase, precipitate, ion exchanger, organic solvent); any process on the arrow can be used. Three adjacent rectangles with the preceding arrow indicate the separation of the elements into at least three phases,

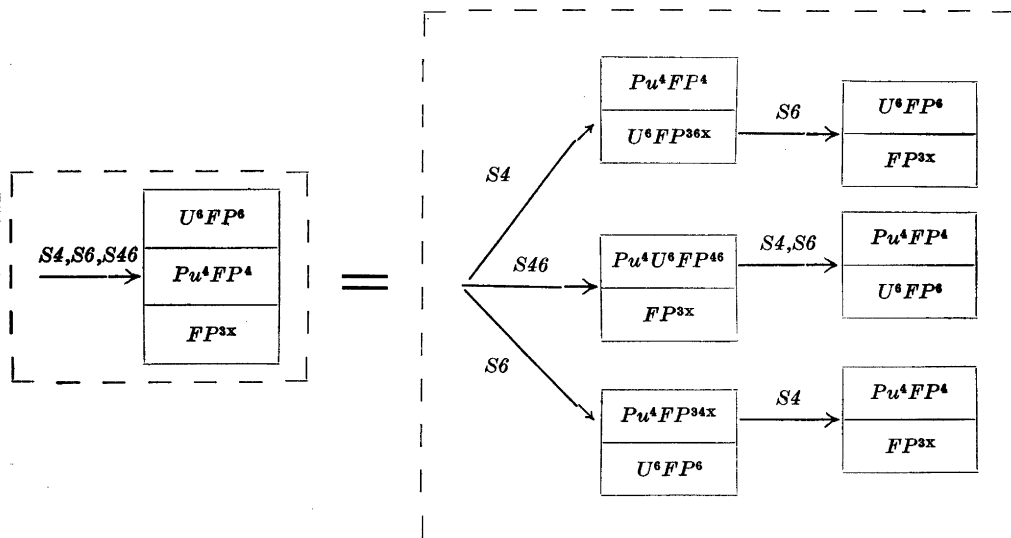


by two subsequent separation processes, which can be applied in an arbitrary order; at least two of the processes on the arrow have to be used. As an example of the last case, the second upper step of diagram B in Table 3 has been fully expanded in Table 4.

2. REDUCTION-OXIDATION PROCESSES

When irradiated uranium metal is dissolved in non-oxidizing agents, one will generally find the oxidation states Pu(III) and U(IV). When dissolved in hot HNO_3 the final products are mainly Pu(IV) and U(VI). A very large number of reduction-oxidation processes can be used to convert plutonium and uranium into other valency states.

Table 4. The possible combinations of a "three adjacent rectangles" unit process. Any combination of processes S4, S46 and S6 will yield the same result: Pu^4FP^4 , U^6FP^6 and FP^{3x} in three different phases after two separation processes. The example is taken from diagram B in Table 3, the second step of the upper flow-sheet.



The time and temperature for a conversion $>90\%$ for some processes in non-complexing media are given in Table 1. The processes are usually faster at lower H^+ concentrations.

In some of the V36-processes, U(VI) is also reduced, but the latter reduction is so slow, that it can be neglected during the time of reduction of plutonium (*e. g.* the reduction with SO_2 in V36a). Since the equilibrium between Pu(IV) and Pu(V, VI) is often attained very slowly, the reaction has to be catalysed.

Although tracer amounts of plutonium can be kept for quite a long time as Pu(VI) in non-reducing solutions, or as Pu(III) in non-oxidizing solutions, Pu(IV) disproportionates rapidly into Pu(III) and Pu(VI) at low acidities. Considerable amounts of Pu(V) may also be formed. However, the disproportionation is less than 1 % per hour at $pH < 1$, and almost negligible at hydrogen ion concentrations above 5 M.

The presence of a complexing agent may stabilize a certain valency state. *E. g.*, if H_2SO_4 is used for adjusting pH, the Pu(IV) valency state will be stabilized, and the oxidation to Pu(VI) or reduction to Pu(III) will proceed much slower, if at all.

It must be stressed that when the oxidation states of plutonium or uranium are changed, some fission products also change their valency state. *E. g.*, when Pu(IV) is oxidized to Pu(VI), Ce(III) is oxidized to Ce(IV), which accompanies Pu(VI) in an S46 process. Thus in diagram C of Table 3, the final step of the upper process will lead to Pu(VI) contaminated with Ce(IV), if an S46 process is chosen instead of the S6 or S34 process. Other similar cases may

be distinguished. This may necessitate more steps than are indicated in Table 3, and is of importance in the selection of a certain unit process.

3. SEPARATION PROCESSES

For the processes given in Table 2, it has generally been assumed that the anions present are non-complexing (*i. e.* ClO_4^- , or perhaps NO_3^-), except for the anions of the reagents. The concentration given for a reagent is the "free concentration", *i. e.* the reagent concentration in excess over the amount complexed by metals present. This is especially important to keep in mind when large amounts of uranium are present.

A large number of methods can be used to precipitate the +3, +4 and +6 oxidation states of the actinides. However, only some familiar methods with a certain degree of specificity are given in Table 2. To obtain complete separation from impurities, several repeated precipitations usually have to be carried out. Dissolving the precipitates constitutes a special problem; the most common methods are digestion with strong acid or alkali (in the latter case followed by an acid treatment), or treatment with a substance that forms a soluble complex with the anion or cation of the precipitate.

In Table 2 only few of many possible extraction processes are given. The decontamination factor from the individual fission products is in most cases better than 100. In some cases (*e. g.* S6b and S46b), however, repeated extractions (3 to 5) must be carried out in order to obtain a yield >99 % in the organic phase, if equal phase volumes are used. In other cases it may be necessary to wash the extract to obtain a good decontamination, *e. g.* in case S46d, where the distribution ratios of some metals are ⁷: Pu(IV) 100, Pu(VI) ~3, U(VI) 30, Th 10, Zr, Nb, La and others ≤0.1.

The solubility of the metal complexes formed with organic ligands (S6c, S46c, S4abc) is usually low; the metal complex concentration should therefore possibly not exceed 0.001 M. However, if this concentration is considerably exceeded, so that a precipitate is formed, it may be dissolved by increasing the volume of the organic solvent. In extractions with organic ligands, the distribution ratio of a metal is very sensitive to a change in pH or ligand concentration; the relation between these variables must be understood when such separation processes are used ⁸.

The solubility and distribution constants vary somewhat for actinides in the same valency state. The precipitation and especially adsorption and liquid-liquid extraction methods can therefore be used for fractionating ions of same valency state. These possibilities have not been indicated in Tables 2 and 3.

Some of the reagents in Table 2 (*e. g.* strong HNO_3 , IO_3^- , $\text{H}_2\text{C}_2\text{O}_4$) may effect the redox-potential of the solution, and may make them unsuitable in certain combinations.

The fission products FP^3 (mainly the trivalent rare earths) and FP^4 (mainly Ce(IV) and Zr(IV)) will generally closely accompany the trivalent and tetravalent actinides. The FP^6 fission products include some elements, which follow U(VI). These elements can usually be removed without changing the valency state of uranium, if several repeated separation cycles (*e. g.*, a column extraction) are carried out. After a cooling time of >2 months for the fission pro-

ducts the main part of the FP^x fission products constitutes alkali (Rb, Cs), alkaline earth (Sr, Ba) and noble gas (Kr, Xe) elements. All these elements are removed by most of the separation procedures in Table 2.

Many other processes can be devised for the separation of groups of elements, or to remove troublesome fission products (*e. g.*, sorption processes). A number of such processes have been described in connection with the isolation of actinide elements^{4,8,9-13}. The general procedure is only indicated here, and will subsequently be denoted by Sx.

4. GENERAL CONSIDERATIONS ON THE ISOLATION OF PLUTONIUM

When plutonium is isolated on the laboratory scale, the radiation from the fission products may be so low that ordinary chemical operations can be used. The selection between different separation schemes will then only depend on which process is the best from a purely chemical standpoint. In order to obtain a good yield of plutonium, the adsorption of low concentrations of Pu(IV) on glass surfaces must be considered^{14,15}. This adsorption is most pronounced in the region where Pu(IV) hydrolyses, *i. e.* at pH > 1. When the Pu(IV) concentration is >10⁻⁴ M, the adsorption on glass vessels can be neglected. However, in precipitation experiments, the general principles with carriers and hold-back carriers^{4,8,16} must be followed, if not considerable amounts of plutonium should be lost.

When plutonium is isolated on an industrial scale, the radiation from large amounts of fission products necessitate chemical operations by remote control^{4,8,17}. Some processes, which have been found useful in the laboratory, may then be less practical; for example liquid-liquid extraction processes may be preferred to precipitation processes¹⁸. Since radiation can decompose chemical compounds^{4,8,19}, it may be important to remove most of the highly radioactive elements as soon as possible, and also to use compounds, which are less sensitive to radiation decomposition, or which limit the action of the radiation. Several other important questions must also be considered, *e. g.* corrosion problems²⁰, maintenance of equipment²¹, cost of chemicals, *etc.*, which all influence the selection of a separation or redox process. These questions, which mainly are of technological importance, will not in general be considered in the following discussion of the flow-sheets in Table 3.

5. DISCUSSION OF THE COMBINATIONS OF UNIT PROCESSES

Only the simplest combinations of unit processes are given in Table 3. Simpler combinations can in general be devised only at the expense of the purity of some products, *e. g.* the uranium. More complicated combinations involving more steps can of course also be given. However, the complicity of a flow-sheet is not necessarily described by the number of steps in the diagram, where it has been assumed that the separations are practically complete in each process. Since this is generally not true, each of the separation processes has to be repeated several times. A few extra processes may also have to be added.

In most instances, the redox process given can be combined with the previous or subsequent separation process, so as to constitute only one process. For example, in the upper flow-sheet of diagram A in Table 3, the last two processes may be combined so that plutonium is extracted as Pu^3 from an organic solvent containing the $\text{Pu}^6\text{U}^6\text{FP}^6$ mixture into an aqueous solution containing a reducing agent (V36, S^6), thus leaving U^6FP^6 in the organic phase. Such combinations are in general more suitable for liquid-liquid extraction and ion exchange processes than for precipitation processes.

The different combinations of unit processes given in Table 3 will be discussed below in the light of the redox and separation processes presented in Tables 1 and 2.

To obtain $\text{Pu}(\text{VI})$ and $\text{U}(\text{VI})$ in diagram A, the metal has to be dissolved and treated with a strong oxidizing agent (process V66). Most of the fission products are removed in the first separation step (S^6). Of the three following possibilities, the one involving a V34 process is somewhat more complicated, but has the advantage of giving purer uranium. The two other ways are of approximately equal simplicity. In both cases the redox process may be combined with the separation process in the manner described above.

A slight variation of the upper flow-sheet in diagram A of Table 3 may be made, if an S34 process is used instead of the S^6 process in the first step. This process will lead to equally pure plutonium¹³, but less pure uranium (U^6FP^{6*}).

To obtain $\text{Pu}(\text{IV})$ and $\text{U}(\text{VI})$ (diagram B, Table 3), the metal is suitably dissolved in HNO_3 , or a mixture of HNO_3 and H_2SO_4 . By applying an S46 process plutonium and uranium are separated from the bulk of the fission products. Pu^4FP^4 and U^6FP^6 can be separated from each other by an S4 or S^6 process. The combination of S46, and S4 or S^6 processes can be made in a simple manner; *e. g.* if process S46b is combined with S^6b (see Table 2), Pu^4 and U^6 will first be extracted together into the organic (hexone) phase, from which Pu^4 is then washed out when the organic phase is equilibrated with a less acid aqueous phase. The conditions for a process of this kind can of course be chosen much better than happens to be the case in the examples S^6b and S46b. The subsequent separation of Pu^4FP^4 can be made in two ways of approximately equal simplicity.

As pointed out previously, a redox and a separation process can be combined into one process. Such a combination in diagram B may be S46, V34, *i. e.* from the mixture of $\text{Pu}^4\text{U}^6\text{FP}^{46}$ obtained in an organic solvent after an S46 process, plutonium is washed out into an aqueous phase with some reducing substance.

The lower flow-sheet in diagram B, which in practice is equivalent to the lower flow-sheet of diagram C, represents the "lanthanum fluoride cycle"²². Several repeated cycles of S34, V66, S34, V34 processes have to be carried out to obtain pure plutonium²³.

Processes of the kind shown in diagram A or B seem to be used in practice on a large scale^{6,20*}.

* Added in proof: At the Geneva Conference on the Peaceful Application of Atomic Energy, August 8–20, 1955, a number of papers describing large scale processes of this type have been declassified (see *e. g.* *Nucleonics*, September, 1955).

The flow-sheets starting with Pu(III) and U(VI) in diagram C seem to offer no advantage over the flow-sheets previously described. Besides the difficulties, which may be encountered in preparing the Pu^3U^6 solution, all flow-sheets start with a precipitation or sorption step (no S3 or S34 liquid-liquid extraction process has been described), and the bulk of the fission products (FP^3) are not removed until the last separation process.

To obtain Pu(III) and U(IV) in diagram D, the metal has either to be dissolved in a non-oxidizing acid, *e. g.* HCl with some F^- as catalyst (V34d), or to be dissolved in an oxidizing acid and the solution then reduced in an V34 process. The former process constitutes a serious corrosion problem, since stainless steel, and perhaps glass, cannot be used. The latter process involves considerable amounts of reducing agents, since all U(VI) has to be reduced to U(IV). From the solution obtained by either method, $\text{Pu}^3\text{U}^4\text{FP}^{34}$ are removed by a precipitation process. Plutonium is not separated from the bulk of the fission products (FP^3) until the last step. The separation of U^4 from FP^4 can easily be effected by an S4 or S6 process after the oxidation of uranium to U^6 .

Of the combinations given in the Table 3, those named A and B seem to be the simplest and most attractive, especially perhaps for large scale work.

The number of chemical methods one might use for each unit process is already considerable, and a great number of other methods could certainly be invented. The number of ways in which a certain scheme such as A or B in Table 3 may be realized is thus great indeed.

However, for each specific combination, one would also have to find out how a number of the minor elements present will behave. Elements with constant oxidation number (like most lanthanides) will cause little trouble, but some transition elements, like Mo and Ru, may change oxidation state in the red-ox processes and then appear at unwanted places. Such elements might need a special separation step. However, considering the very great number of methods possible, it seems probable that combinations could be found that contain no more unit process than do A or B in Table 3.

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* N.N.E.S. = *National Nuclear Energy Series*, published by McGraw-Hill Book Company, New York.

** Roman numerals refer to papers in the series "Studies on the Extraction of Metal Complexes".

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