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Studies on the Extraction of Metal Complexes

XXVII. The Distribution of Some Actinides and Fission Products between Methyl *Iso*butyl Ketone and Aqueous Solutions of HNO_3 and $Ca(NO_3)_2$

JAN RYDBERG and BRITA BERNSTRÖM

Research Institute of National Defence, Dept. 1, Sundbyberg 4, Sweden

The distribution ratios of U(VI), Pu(VI), Pu(IV), Th(IV), Zr(IV), La(III), Ca(II), Na(I) and HNO_3 between methyl *iso*butyl ketone (hexone) and aqueous solutions of varying HNO_3 and $Ca(NO_3)_2$ concentrations have been determined and are given in Figs. 2—10. Some possible methods of separating uranium and plutonium from certain fission products are discussed.

Recently, a considerable number of papers [1] have been released on the separation of uranium, plutonium and mixed fission products from each other by means of different liquid-liquid extraction methods. The two most used organic solvents seem to be hexone (methyl *iso*butyl ketone) and TBP (tributyl phosphate), both of which are used for the extraction of the metal nitrates.

The present work * deals with the extraction of U(VI), Pu(VI), Pu(IV), Th(IV), Zr(IV), La(III), Ca(II), and Na(I) nitrates from aqueous solutions with various concentrations of HNO_3 and $Ca(NO_3)_2$ as salting-out agents. The elements studied represent about 90 % of the β- and γ-activity from the fission products of natural uranium ** which has been irradiated in a pile for several months and cooled for about the same time; the rest of the radioactivity is mainly due to Ru-Rh, which elements are not considered here.

In the present study, distribution experiments were run with each metal separately. The metal concentration of each phase was determined after equilibration. The ratio of the metal concentration in the organic phase to that in the aqueous phase gives the distribution ratio q of the metal. It was

* Based on Report FOA1, No. H 1149—8509, 1954.

** Cs and Rb are assumed to accompany Na, Sr and Ba to accompany Ca while all the rare earths resemble La. Nb is assumed to follow Zr.

generally found that q increases with the HNO_3 or $Ca(NO_3)_2$ concentration of the aqueous phase. Since very little $Ca(NO_3)_2$ dissolves in the organic phase, the variation of q with increasing HNO_3 concentration has been determined at a constant $Ca(NO_3)_2$ concentration in the aqueous phase. In the following, q_{Ca}, q_{La}, etc. will be used as abbreviations for the distribution ratios of the metals given by the subscripts.

EXPERIMENTAL

Chemicals. Hexone (methyl *iso*butyl ketone, $C_4H_9COCH_3$) of technical quality was purchased from the Svenska Shell AB; after filtration it was washed with $NaHCO_3$ and water to remove acid and water-soluble impurities and to saturate it with water.

^{234}Th was prepared according to Dyrssen [4].

^{140}La was obtained as the neutron-irradiated oxide, which was dissolved in HNO_3.

U(VI) solutions were prepared by dissolving UO_3 of high purity in HNO_3.

Zirconium nitrate of puriss. quality was dissolved in 1 M HNO_3. The solution was filtered and standardized by weighing the ignited oxide.

$Ca(NO_3)_2$ and $NaNO_3$ were of analytical grade.

General procedure. All distribution experiments were carried out at room temperature (20 ± 2° C). The metal nitrate and $Ca(NO_3)_2$ were mixed with varying amounts of HNO_3 and shaken with an equal volume of hexone. In all systems, equilibrium was established within 5 min. At high HNO_3 concentrations, the phases were found to undergo large volume changes. This is due to an appreciable extraction of HNO_3 into hexone whereas only negligible amounts of $Ca(NO_3)_2$ are extracted. In order to maintain the $Ca(NO_3)_2$ concentration of the aqueous phase constant throughout a series of distribution experiments, distilled water was added with repeated shaking up to the original volume of the aqueous phase. The two phases were then separated by centrifuging and samples were withdrawn for metal analysis and the titration of nitric acid.

Solubility of $Ca(NO_3)_2$ in HNO_3—H_2O. The addition of HNO_3 to concentrated $Ca(NO_3)_2$ solutions causes $Ca(NO_3)_2$ to crystallize out because its solubility product is exceeded. Solutions of varying HNO_3 content were saturated with $Ca(NO_3)_2$ and allowed to stand for a couple of days to attain equilibrium. Calcium was determined by weighing the ignited oxide after careful evaporation of a definite volume. The acid concentration was determined by titration. Fig. 1 shows the solubility of $Ca(NO_3)_2$ in water solutions as a function of the HNO_3 concentration. As a consequence, the distribution experiments are limited to a smaller acid concentration range at high $Ca(NO_3)_2$ concentrations.

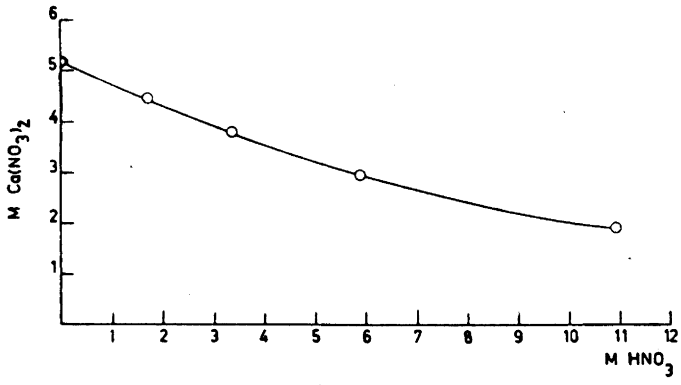

Fig. 1. The solubility of $Ca(NO_3)_2$ in HNO_3 solutions.

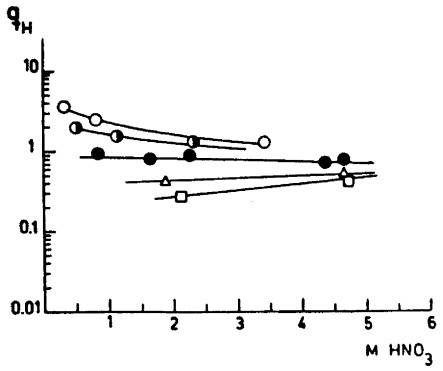

Fig. 2. The distribution ratio q_H of HNO_3 as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentrations of $Ca(NO_3)_2$: ○ 4—3.8 M*, ◑ 3 M, ● 2 M, △ 1 M, □ no $Ca(NO_3)_2$ present.

The molal solubility of $Ca(NO_3)_2$ in solutions of varying HNO_3 content has been investigated by Basset and Taylor [5]. By determining the density of the aqueous solutions, a check was made that our results were in agreement with those obtained by Basset and Taylor.

The distribution ratio of HNO_3, q_H. The distribution ratio q_H of HNO_3 between the organic and aqueous phases was determined by titration of the acid in each phase with NaOH. In Fig. 2, q_H is plotted against the equilibrium concentration of HNO_3 in the aqueous phase for different $Ca(NO_3)_2$ concentrations *.

The distribution ratio of sodium, q_{Na}. A gravimetrical determination of the distribution of $NaNO_3$ gave an upper limit of $q_{Na} \leqq 10^{-3}$.

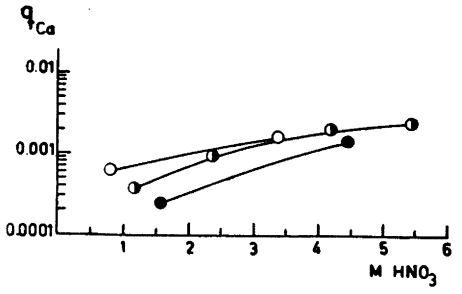

Fig. 3. The distribution ratio q_{Ca} of calcium as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Total concentrations of $Ca(NO_3)_2$: ○ 4—3.8 M*, ◑ 3 M, ● 2 M.

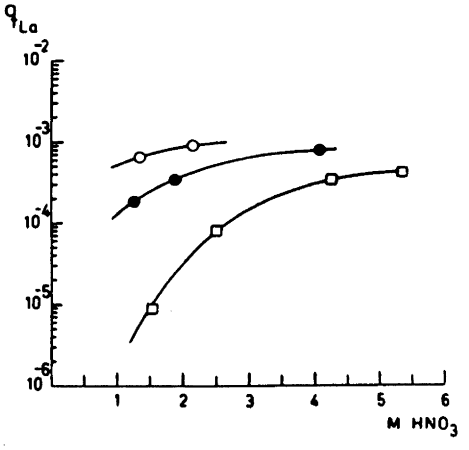

Fig. 4. The distribution ratio q_{La} of lanthanum as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentrations of $Ca(NO_3)_2$: ○ 4—3.8 M*, ● 2 M, □ no $Ca(NO_3)_2$ present.

* The $Ca(NO_3)_2$ concentration can be kept constant at 4 M only for acid concentrations $\leqq$ 1 M. To obtain a higher acidity one is forced to start the distribution experiment with an initially acid hexone phase. After equilibrium the aqueous phase has increased in volume due to the distribution of HNO_3, thus causing a decrease of the $Ca(NO_3)_2$ concentration.

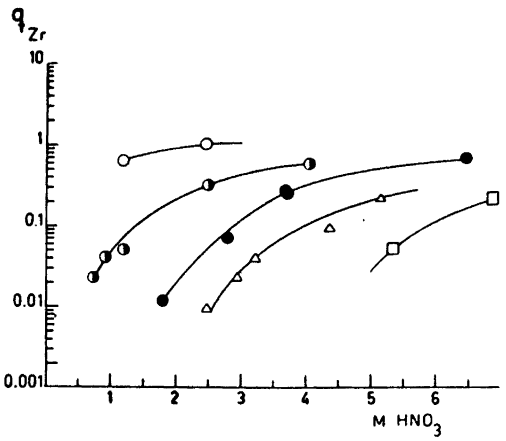

Fig. 5. The distribution ratio q_{Zr} of zirconium as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentrations of $Ca(NO_3)_2$: ○ 4—3.7 M*, ◑ 3 M, ◉ 2 M, △ 1 M, □ no $Ca(NO_3)_2$ present.

The distribution ratio of calcium, q_{Ca}. The distribution ratio of Ca between hexone and water is very low. In order to determine the Ca concentration of the hexone phase, a known volume of the phase was taken and evaporated to dryness, whereupon the residue was dissolved in distilled water. Ca was determined by a substitution titration with EDTA (ethylenediamine tetraacetic acid) at pH = 10 using Eriochrome Black T as indicator [6,7]. Blanks were run in the same way. The distribution data obtained are plotted in Fig. 3.

The distribution ratio of lanthanum, q_{La}. The distribution was followed by means of ^{140}La as a tracer. Dry samples of each phase were counted. The La solution used was of very high specific activity, which made it possible to count the aqueous phase after a 100-fold dilution thus avoiding vitiating salt residues of $Ca(NO_3)_2$. In Fig. 4, q_{La} is plotted versus the equilibrium HNO_3 concentration of the aqueous phase.

The distribution ratio of zirconium, q_{Zr}. With an original zirconium concentration of 0.1 M in the aqueous phase, it was possible to determine the distribution of zirconium by gravimetrical analysis. Since $Ca(NO_3)_2$ was present in the aqueous phase, only samples of the hexone phase were weighed after the evaporation and ignition to the oxide. The weights were corrected for the small amounts of calcium coextracted into the hexone phase according to Fig. 3. The phase volumes were measured after equilibrium so that the zirconium content of the aqueous phase could be calculated from the difference between the total amount of zirconium added and that found in the organic phase. The data are given in Fig. 5.

The distribution ratio of thorium, q_{Th}. By means of ^{234}Th (UX_1), the distribution of thorium was followed radiometrically. The thorium concentration in these experiments was $\leq 10^{-5}$.

Liquid counting was used, which involved corrections due to the different absorptions of the radiation in the hexone phase and in the aqueous phases of varying $Ca(NO_3)_2$ concentrations. Using the same liquid counter, these corrections were measured experimentally in the following manner:

a) the counting rate of a definite amount of ^{234}Th was measured in 1 M HNO_3 and in 1 M HNO_3 solutions containing 1, 2, 3 and 4 M $Ca(NO_3)_2$.

b) the counting rate of the same amount of ^{234}Th was measured in hexone after an extraction with 0.2 M TTA (thenoyltrifluoroacetone) in hexone from a 0.05 M $HClO_4$ phase; in this case $q_{Th} > 500$.

The results for q_{Th} are plotted in Fig. 6.

The distribution ratio of hexavalent uranium, q_U, *at* U *concentrations* ≤ 0.1 *M*. After equilibration, samples were withdrawn and evaporated to dryness whereupon the residues were dissolved in 0.1 M $HClO_4$. The uranium content was determined colorimetrically by means of the thiocyanate method [8]. The residues sometimes contained appreciable amounts of Ca but it was found that this did not interfere with the method.

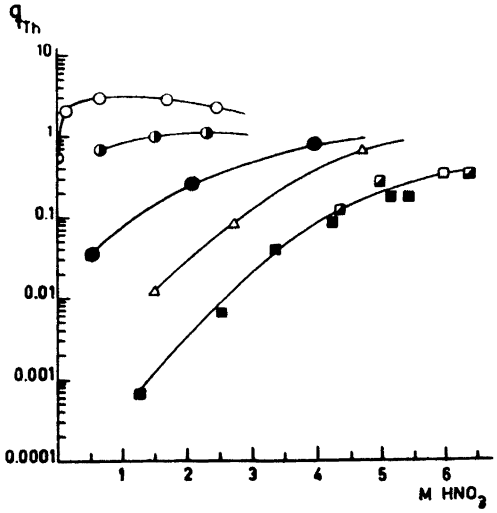

Fig. 6. The distribution ratio q_{Th} of thorium as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Initial concentration of Th $\leq 10^{-5}$ M, except for ◪ where Th concentration is 0.1 M. Concentrations of $Ca(NO_3)_2$: ○ 4—3.7 M*, ◑ 3 M, ● 2 M, △ 1 M, □ ◪ ■ no $Ca(NO_3)_2$ present. (□ radiometrical, ◪ gravimetrical, ■ radiometrical with 0.1 M U present).

The titration of HNO_3 was carried out with methyl orange as indicator in order to avoid titration errors due to the uranium present. The curves for different $Ca(NO_3)_2$ concentrations are found in Fig. 7.

The distribution ratio of thorium and hexavalent uranium at U *concentrations between 0.1 and 1 M.* The experiments were carried out with uranium (UI) in radioactive equilibrium with ^{234}Th (UX_1). It was then possible to determine the distribution of the two

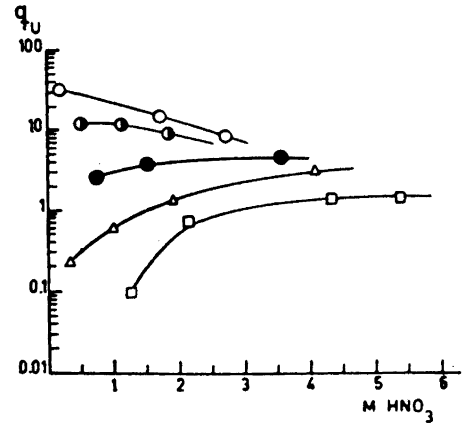

Fig. 7. The distribution ratio q_U of hexavalent uranium as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentration of $Ca(NO_3)_2$: ○ 4—3.6 M*, ◑ 3 M, ● 2 M, △ 1 M, □ no $Ca(NO_3)_2$ present.

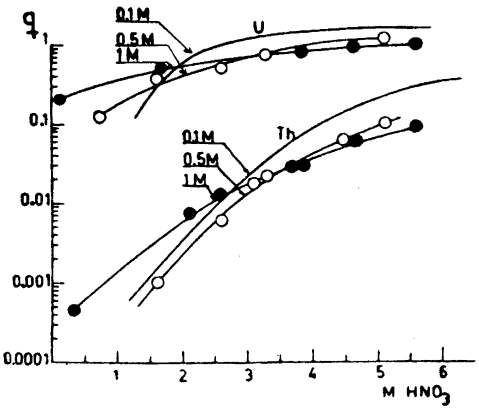

Fig. 8. The distribution ratios q_U of hexavalent uranium and q_{Th} of thorium as functions of the equilibrium concentration of HNO_3 in the aqueous phase. No $Ca(NO_3)_2$ added. Total concentration of U(VI): ● 1 M, ○ 0.5 M. For comparison the curves for 0.1 M U are drawn.

* See footnote, p. 88.

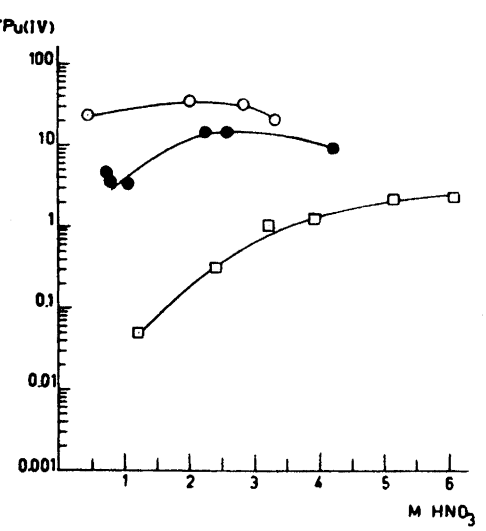

Fig. 9. The distribution ratio $q_{Pu(IV)}$ of Pu(IV) as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentrations of $Ca(NO_3)_2$: ○ 4—3.5 M*, ● 2 M, □ no $Ca(NO_3)_2$ present.

metals separately in the solutions using the same analytical procedures as before. The HNO_3 concentration of the aqueous phase was determined by a NaOH titration after removing the uranyl ions by running the sample through the hydrogen form of a cation exchange column (Dowex 50). It is noted that for each UO_2^{2+} that is adsorbed 2 H^+ are removed and must be subtracted in the NaOH titration. The data are given in Fig. 8 where q_U and q_{Th} have been plotted against the HNO_3 concentration of the aqueous phase at equilibrium.

The distribution of tetravalent plutonium, $q_{Pu(IV)}$. A solution of Pu(IV) in 10 M HNO_3 (3×10^{-3} mg Pu/ml) was available. A TTA extraction was employed to confirm the tetrapositive state of plutonium [13].

In the distribution experiments with Pu(IV), 1 ml of this solution was added to a 4 ml aqueous phase of varying HNO_3 content and the resulting solution was then mixed with an equal volume of hexone. After the separation of the phases by centrifugation, samples of 0.1 ml were taken from the two phases and evaporated on Pt-dishes. The pipets were rinsed with 1 M HNO_3 solutions and the washings were also added to the dishes. The dry samples were measured internally in an argon-methane proportional counter. With $Ca(NO_3)_2$ present in the aqueous phase, direct radiochemical analysis of the aqueous phase was not possible. The procedure used was therefore to extract plutonium from the $Ca(NO_3)_2$ solution with a 0.05 M solution of dibutyl phosphate in $CHCl_3$. Tests were made to show that plutonium(IV) was extracted quantitatively under the conditions in question, *i. e.* from acid solutions of 2 M and 4 M $Ca(NO_3)_2$. The results are plotted in Fig. 9.

The distribution of hexavalent plutonium, $q_{Pu(VI)}$. To obtain Pu(VI), different oxidizing agents can be used, *cf.* Refs.[2,11]. The symbols in Fig. 10 represent the following procedures:

◑. A plutonium solution kept in 5 M HNO_3 was treated for 5 min with solid $NaBiO_3$; the excess bismuthate was removed by centrifugation. The oxidized plutonium solution was then immediately used in distribution experiments with hexone, pretreated only as described under "Chemicals".

□. The plutonium solution was treated with 0.001 M $Cr_2O_7^{2-}$ in 1 M HNO_3 with Co^{2+} as catalyst for 10 min at 90° C. The hexone used in the distribution experiments was pretreated with dichromate solutions in the same way but at room temperature. Dry, thin samples could not be obtained in the distribution experiments when more concentrated dichromate solutions were used.

* See footnote, p. 88.

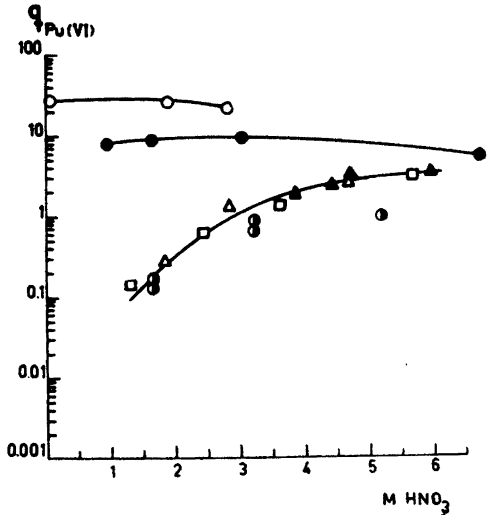

Fig. 10. The distribution ratio $q_{Pu(VI)}$ of Pu(VI) as a function of the equilibrium concentration of HNO_3 in the aqueous phase. Concentrations of $Ca(NO_3)_2$: O 4—3.6 M *, ● 2 M, □ ◑ △ ▲ no $Ca(NO_3)_2$ present (for explanation of symbols see text).

▲. The plutonium solution was made 10 M in HNO_3 and 0.67 M in $KBrO_3$; the hexone was shaken immediately before the distribution experiments with an equal volume of 10 M HNO_3 and 0.1 M $KBrO_3$.

△. The plutonium solution was made 1 M in HNO_3 and 0.2 M in $KBrO_3$ and kept at 95° C for 30 min; the hexone was pretreated with 0.1 M $Cr_2O_7^{=}$ in 1 M HNO_3 followed by washing with sodium hydroxide and finally steam distilliaton of the hexone (*cf.* Ref.[1] Paper 541, Vol. 9).

For the curves with 2 M (symbol ●) and 4 M (symbol O) $Ca(NO_3)_2$, 0.2 M $KBrO_3$ was used as oxidant. The plutonium analysis of the two phases was performed in the following manner: a) a dry, thin sample of the hexone phase could be obtained directly by evaporation, b) when no $Ca(NO_3)_2$ was present, 0.1 ml of the aqueous phase was evaporated and counted; when $Ca(NO_3)_2$ was present, 3 ml of the aqueous phase was adjusted to approximately 0.05 M in H^+ by adding concentrated NH_3 and then shaken with 2 ml hexone 0.05 M in dibutyl phosphate; preliminary tests showed that plutonium(VI) is extracted quantitatively under these conditions. The results are found in Fig. 10.

DISCUSSION OF RESULTS

The results obtained above are collected in Figs. 11—15, from which it is possible to choose conditions for separating the different metals from each other.

When uranium and plutonium are dissolved in hot, concentrated HNO_3, one gets mainly U(VI), Pu(IV) and Pu(VI). Now it can be seen from Figs. 11, 13 and 15 that the distribution ratios of these species are close together, which makes it difficult to separate them from each other. If it is desired to separate uranium from plutonium, one should make use of the facts that plutonium can be reduced to Pu(III) without the reduction of U(VI) [1,2] and that Pu(III) behaves much similar to La(III) [3], which is easily separated from U(VI) [1,2].

The following discussion will only deal with the separation of uranium together with plutonium from the other metals, which represent most of the

* See footnote, p. 88.

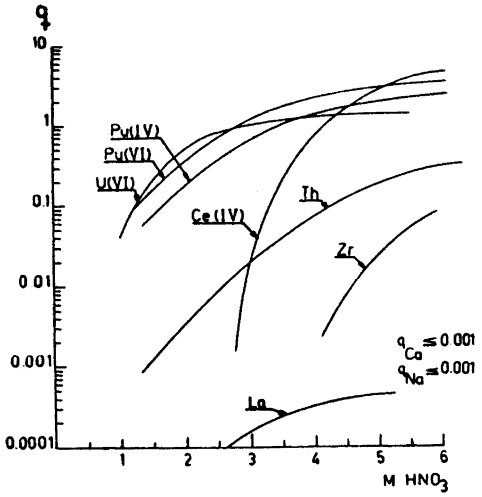

Fig. 11. The distribution ratios of U, Pu(IV) and Pu(VI), Th, Zr, Ce(IV) and La as functions of the equilibrium concentration of HNO_3 in the aqueous phase. No $Ca(NO_3)_2$ added. The Ce(IV) curve is taken from Glendenin *et al.*[12].

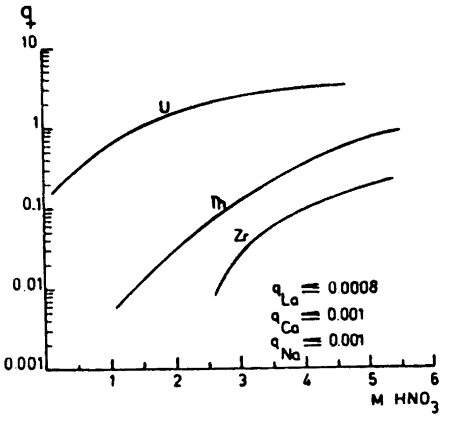

Fig. 12. The distribution ratios of U, Th and Zr as functions of the equilibrium concentration of HNO_3 in the aqueous phase. Concentration of $Ca(NO_3)_2$ 1 M.

undesired impurities in pile irradiated uranium. In order to avoid complications due to hydrolyses of some of the metals, the discussion will be limited to acidities ≤ 1 M in H^+.

Extraction formulas and definition of the decontamination factor

For batchwise extractions of a single (stationary) aqueous phase with fresh organic solvent (also called "multiple extraction"), the equation

$$P = 100 \cdot q \cdot r_v \sum_{1}^{n} (1 + q \cdot r_v)^{-n} \qquad (1)$$

gives the percentage P of the metal obtained in the combined organic phases after n extractions when the ratio between the volumes of the organic and aqueous phases is r_v. It is seen that the larger $q \cdot r_v$ is, the more complete will the extraction be.

For counter-current extractions (batchwise or continuous) with n extracting and m stripping stages and introduction of the feed at the stage $m = n = 1$, the ratio R of the amount of the metal leaving in the organic phase to that leaving in the aqueous phase is given by

$$R = \frac{E^m(E^n - 1)}{E^m - 1} \qquad (2)$$

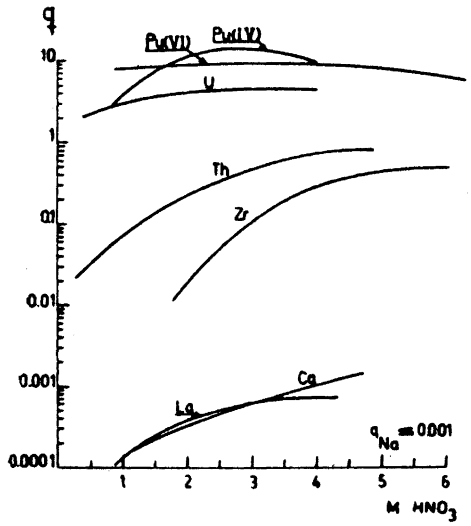

Fig. 13. The distribution ratios of U, Pu(IV) and Pu(VI), Th, Zr, La and Ca as functions of the equilibrium concentration of HNO_3 in the aqueous phase. Concentration of $Ca(NO_3)_2$ 2 M.

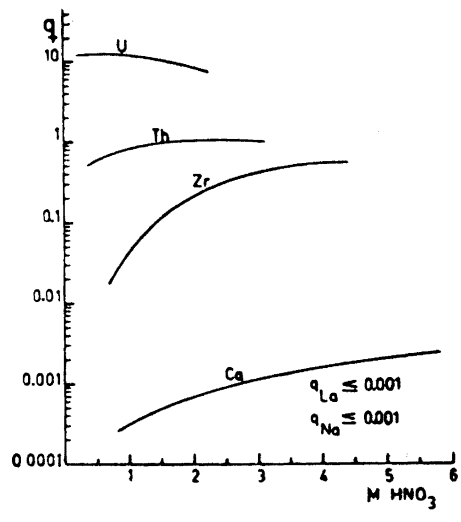

Fig. 14. The distribution ratios of U, Th, Zr and Ca as functions of the equilibrium concentration of HNO_3 in the aqueous phase. Concentration of $Ca(NO_3)_2$ 3 M.

where $E = q \cdot r_v$ (E is called extraction factor). Eqn. 2 is valid provided r_v is constant throughout all stages, which implies that the volume of the feed is negligible. Convenient graphs of this equation have been given by Bartels and Kleiman [9].

The decontamination factor (*D. F.*) is here defined as the ratio of the desired product (A) to the contaminants (B) in the organic phase at the n:th stage divided by the corresponding ratio in the original aqueous phase (= feed),

$$D.\,F. = \frac{(A)_n/(B)_n}{(A)_0/(B)_0} \qquad (3)$$

The extraction of uranium and plutonium into hexone without the addition of $Ca(NO_3)_2$

In Fig. 11, the distribution ratios q of the different metals are compared for the case where no $Ca(NO_3)_2$ is added. Since the distribution ratios are fairly low for uranium and plutonium, the ratio r_v of the volume of the organic phase to that of the aqueous phase must be considerably greater than 1 in order that a good yield of these ions shall be obtained in the combined organic phases for a reasonably small number of extraction stages.

As an example, a multiple extraction using a HNO_3 equilibrium concentration of 2 M, where the decontamination factor is large, will be described. (*Cf.* Fig. 16 which illustrates how the separation factor between U and Th (*i.e.* q_U/q_{Th}) varies with the HNO_3 and $Ca(NO_3)_2$ concentration). Let us assume according to Fig. 11 that $q_{Pu(IV)} \approx q_{Pu(VI)} \approx q_{U(VI)} \geq 0.2$ at 2 M HNO_3. If $r_v = 5$, then

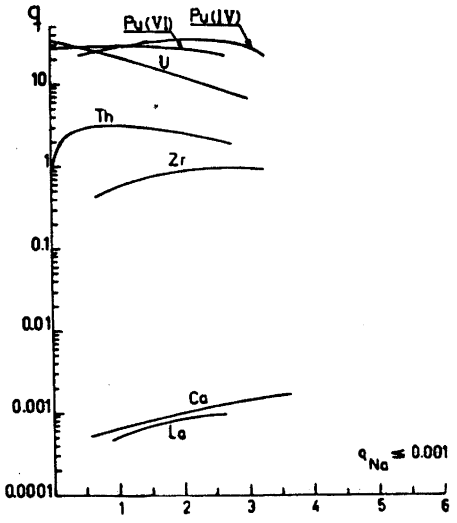

Fig. 15. The distribution ratios of U, Pu(IV) and Pu(VI), Th, Zr, La and Ca as functions of the equilibrium concentration of HNO_3 in the aqueous phase. Concentration of $Ca(NO_3)_2$ 4—3.5 M *.

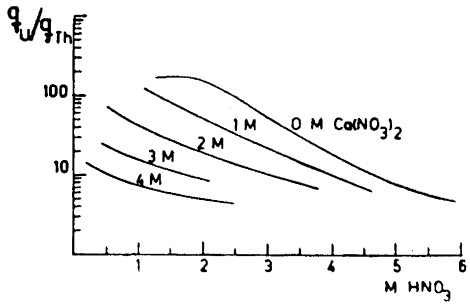

Fig. 16. The separation factor q_U/q_{Th} as a function of the equilibrium concentration of HNO_3 in the aqueous phase at varying $Ca(NO_3)_2$ concentrations.

eqn. 1 indicates that, with 6 extractions ($n = 6$), more than 98 % of U(VI), Pu(IV) and Pu(VI) is extracted. The decontamination factor will be > 8 with respect to thorium and $> 10^3$ with respect to La and probably also to the other elements in Fig. 11 (Ce, Zr, Ca and Na).

In a counter-current extraction, E in eqn. 2 must be > 1 in order to get any appreciable extraction of an element. Thus either q or r_v must be increased compared to the multiple extraction above. Since $r_v = 5$ is about the practical upper limit with hexone, q must be increased, which is possible by going to higher HNO_3-concentrations. Let us assume that $q_{U(VI)} \approx q_{Pu(IV)} \approx q_{Pu(VI)} \geq 0.6$ in 3 M HNO_3 while, for the other elements in Fig. 11, $q \leq 0.02$. For $n = 4$ and $m = 3$ (*i. e.* 6 stages altogether since $m = 1$ and $n = 1$ is the feed stage) and $r_v = 5$, it is found that more than 99 % of U(VI), Pu(IV) and Pu(VI) will be extracted with a decontamination factor $> 10^3$.

This shows that with a counter-current technique it is feasible to get a good separation of uranium and plutonium from fission products. However, a drawback of these extractions is the large volumes of organic solvent needed.

The extraction of uranium and plutonium into hexone from $Ca(NO_3)_2$ solution

By comparing Figs. 12—15, where 1, 2, 3 and 4 M $Ca(NO_3)_2$ was present in the aqueous phase, it is seen that the distribution ratios of all metals increase with the $Ca(NO_3)_2$ concentration. This makes it possible to use $r_v \approx 1$ at high

* See footnote, p. 88.

$Ca(NO_3)_2$ concentrations. It is also noted that the curves for the different metals become closer to each other which means that the separation between the elements becomes less efficient (*cf.* Fig. 16). For the separation of U(VI), Pu(IV) and Pu(VI) from the fission products, it is necessary to consider primarily the decontamination due to zirconium.

Let us assume that a multiple extraction is carried out at 1.5 M HNO_3 and with 3 M $Ca(NO_3)_2$, where we estimate from Figs. 13 and 15 that $q_{Pu(IV)} \approx \approx q_{Pu(VI)} > q_{U(VI)} = 10$ (Fig. 14). It can be calculated from eqn. 1 with $r_v = 1$ that 3 multiple extractions will yield 99.9 % U(VI), Pu(IV) and Pu(VI) in the hexone phase. However, at the same time about 25 % of the zirconium present will go into the hexone phase ($q_{Zr} = 0.1$).

If the extractions instead are carried out in a counter-current manner with $n = 3$, $m = 3$, one can calculate, using eqn. 2, that > 99 % of U(VI), Pu(IV) and Pu(VI) will be extracted with < 1 % zirconium.

The advantage of using high salt concentrations is that the ratio r_v of the volume of the organic phase to that of the aqueous phase can be kept ≈ 1. An easier separation of the hexone and aqueous phase with high salt concentration is also obtained due to the increased density of the aqueous phase. A drawback of the method is that more difficulties are in general encountered in taking care of salt-rich radioactive wastes.

The extraction of uranium and thorium at higher uranium concentrations

In most practical separation processes, one has to start with a high concentration of uranium. Since uranium nitrate will act as a salting-out agent and increase the distribution ratios, a separate investigation was made in which the initial uranium concentration was increased to 1 M and q_U and q_{Th} were determined (Fig. 8). In agreement with the results obtained with $Ca(NO_3)_2$, an increased uranium concentration increases the distribution ratios most at HNO_3 concentrations < 1 M. At high acidities, the distribution ratios q_U and q_{Th} show a tendency to decrease with increasing uranium concentration.

However, for the case discussed above where the extraction is made from a $Ca(NO_3)_2$-free solution at 3 M HNO_3, one can assume that the same separation of uranium and plutonium from the bulk of the fission products will be obtained when starting with higher initial uranium concentrations.

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