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SOLVENT EXTRACTION RECOVERY OF PLUTONIUM FROM RAFFINATE CONCENTRATES IN THE PUREX PROCESS

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Abstract: Raffinate concentrates which are produced in purification cycles of the Purex process contain plutonium(IV,VI), uranium(VI), both lyophilic and hydrophilic decomposition products of tributyl phosphate, large amounts of nitric acid and, eventually, ammonium nitrate and neptunium(IV,V,VI). Conditions were sought for the recovery of plutonium from the concentrates by the extraction of plutonium(IV) and plutonyl nitrates with 30 vol.% tributyl phosphate in an alkane diluent. The feed preparation for the plutonium recovery, the distribution behaviour of plutonium(IV,VI) during the phase contacting in a mixer-settler, and some disturbing phenomena like crud formation were investigated and flowsheets were elaborated for the extraction of plutonium from both neptunium free and neptunium containing concentrates.

Wiedergewinnung von Plutonium aus Raffinatkonzentraten im Purex-Verfahren

Zusammenfassung: Raffinatkonzentrate, die in Reinigungszyklen des Purex-Verfahrens anfallen, enthalten Plutonium(IV,VI), Uran(VI), lyophile sowie hydrophile Zersetzungsprodukte des Tributylphosphats, große Mengen von Salpetersäure und, gegebenfalls, Ammoniumnitrat und Neptunium (IV,V,VI). Bedingungen wurden gesucht, unter denen das Plutonium aus den Konzentraten durch Extraktion mit 30 Vol.% Tributylphosphat in einem Alkanengemisch zurückgewonnen werden kann. Die Herstellung einer Einsatzlösung, das Verteilungsverhalten von Plutonium(IV,VI) und einige Störerscheinungen wie z.B. Crudbildung wurden untersucht und Fließschemata für die Extraktion von Plutonium aus neptuniumfreien und neptuniumhaltigen Konzentraten wurden ausgearbeitet.

INTRODUCTION

Among other waste liquids, raffinate concentrates are originated in the solvent extraction purification of uranium and plutonium in the Purex process. The concentrates are intermediately contaminated with fission products and typically contain large amounts of nitric acid as well as small to moderate amounts of uranium, plutonium and, eventually, neptunium. Also present in the concentrates are different organic and inorganic impurities, the amount of which can vary in a broad range. The amount of plutonium in the concentrates represents a minute fraction only (<1%) of the total plutonium inventory in the whole process, but the discarding of the concentrates would undesirably produce alpha contaminated radioactive waste. Neither direct recycling of the concentrates into the Purex process is satisfactory, because it would introduce potentially interferring impurities into process solutions.

Thus, it appeared desirable to elaborate a method for recovering plutonium selectively from the concentrates and gaining it in the form of a solution which could be recycled into the process. Necessary requirements were a good recovery yield, i.e. ≥95% (the concentrates should be decontaminated from plutonium as effectively as possible), and separation of the recovered plutonium from at least weakly extractable impurities present in the concentrates. Not primarilly important was separation from fission products because recovered plutonium, if it is not sufficiently decontaminated, can be recycled into a highly radioactive part of the Purex process. We chose for the plutonium recovery an operation on which the whole Purex process is based, namely the extraction with tributyl phosphate (henceforth TBP) in an alkane diluent. The main pecularities of the plutonium extraction from solutions as complex as the concentrates can be are:

1) the presence of organic and inorganic impurities which are formed by the decomposition of TBP residues and are able to complex plutonium(IV) in the aqueous or the organic phases,

2) the presence of ammonium nitrate which is formed from hydrazine nitrate used in the Purex process as a protecting reductant for uranium(IV),

3) the existence of a fraction of the plutonium in a hexavalent form,

and

4) possible presence of neptunium which is not desirable to be contained in the plutonium recovered or to be recycled with it into the Purex process.

In our work we investigated important problems of the plutonium recovery from raffinate concentrates, like the feed preparation (dissolution of solids, valence adjustment of plutonium etc.), counter-current extraction of plutonium with 30 vol.% TBP in an alkane diluent, and further treatment of the plutonium extracted.

EXPERIMENTAL

Common chemicals (uranyl nitrate, nitric acid etc., most of them reagent grade) were used as received. Plutonium(IV) nitrate, recovered in this institute from spent nuclear fuel and provided in the form of an aqueous 0.8M solution containing 6M nitric acid, was also used as received. A 30 vol.% solution of TBP in a mixed n-alkane diluent (C_{10} to C_{13}) was washed before use with a sodium carbonate solution and with a dilute nitric acid solution. Simulated raffinates were used in preliminary work, but true raffinate concentrates from cold pilot plant experiments were mostly taken for extraction studies. The pilot plant experiments were performed in this institute in a pulsed column facility with the aim to study the performance of an electrochemical separation of plutonium from uranium. Before concentrating the true raffinates by evaporation, the TBP content in them was reduced to a level of ≤10 mg/l either by extracting TBP into kerosene or by adsorbing it on a polystyrene divinylbenzene resin [1].

Counter-current extraction experiments were performed in 16-stages laboratory mixer-settlers with a stage efficiency of 80 to 90%. Components of single streams were determined in the analytical department of the author's institute. The methods used in the inorganic analysis were x-ray fluorescence for the determination of macro amounts of uranium and plutonium, spectrophotometry for the determination of small amounts of uranium, alpha and gamma spectrometry for the determination of trace plutonium and neptunium respectively, and alkalimetric titration after masking heavy metals with oxalate and fluoride ions for the determination of nitric acid [2]. TBP and dibutyl phosphoric acid were determined by gas chromatography [3], while a ion chromatographic method was used for the determination of monobutyl phosphoric acid and phosphoric acid [4].

Concentration profiles in a mixer-settler were calculated for a stage efficiency of 85% with the program VISCO [5], developed and commonly used in this institute.

RESULTS AND DISCUSSION

Products of TBP Decomposition Present in Raffinate Concentrates

All common hydrolysis products of TBP are present in the concentrates, i.e. phosphoric acid as well as its monobutyl and dibutyl esters. The absolute concentrations of the products are dependent on the quality of the TBP removal from raffinates and on the degree to which the raffinates are concentrated by evaporation. Relative concentrations of single hydrolysis products of TBP are functions of the temperature and duration of the evaporation. A part of TBP can co-distil with nitric acid during the evaporation, and the decomposition of the retained part of TBP to phosphoric acid is not complete even after a very long evaporation time. To give an example, after 100 and 200 h evaporation at ~80°C as little as 4 an 2% respectively of the retained TBP amount remained undecomposed, 30 and 12% respectively decomposed to dibutyl phosphoric acid, 33% decomposed in both cases to monobutyl phosphoric acid, and 33 and 53% respectively decomposed to phosphoric acid. Even in experiments with extremely highly evaporated concentrates we never observed precipitation of plutonium(IV) phosphate or plutonium(IV) butylphosphates. Colloidal solids might have been present in such concentrates, but they did not appear to interfere with the extraction of plutonium(IV).

Presence of Ammonium Nitrate in Raffinate Concentrates

Ammonium nitrate can cause the formation of a crystalline solid, which most probably is a mixture of ammonium hexanitratoplutonate(IV) and ammonium trinitratodioxouranate(VI). The solid is well soluble both in water and in a 30 vol.% kerosene solution of TBP. It is interesting that it dissolves in the TBP solvent in the form of ammonium salts, without leaving any undissolved residue of ammonium nitrate. The solubility of plutonium(IV) nitrate in the raffinate concentrates is a complex function of the concentrations of nitric acid and ammonium nitrate. An extreme example can be given: saturation plutonium(IV) and uranium(VI) concentrations of 2.3 and 50 g/l respectively were found in a concentrate which contained 12M nitric acid and 4.5M ammonium nitrate. The presence of the crystalline solid does not represent any problem, because the concentrates are diluted with water before the plutonium extraction and this leads to dissolution of the solid.

Valence Adjustment of Plutonium

The concentrates contain plutonium as a mixture of Pu(IV) and Pu(VI). The content of Pu(VI) did not exceed 20% of total plutonium in our experiments and was a function of the conditions of the raffinate evaporation. As it is demonstrated below, no valence adjustment to exclusively Pu(IV) is needed before the extraction. If the valence adjustment is necessary in a particular case, it can easily be made by adding an amount of uranium(IV) which represents a slight excess with respect to Pu(VI) but is substoichiometric with respect to Pu(IV). Even at ~10M nitric acid the uranium(IV) produces in a fast reaction a mixture of Pu(IV) and Pu(III), and the plutonium(III) is reoxidized at the high acid concentration spontaneously to Pu(IV) during 18 h. Hydrazine nitrate, added to a concentration of 0.2M, reduced Pu(VI) during 24 h completely to Pu(IV) without any detectable further reduction to Pu(III). It need not be pointed out that the use of hydrazine at a high nitric acid concentration (10M) is only acceptable in a laboratory experiment.

Recovery of Plutonium from Neptunium Free Solutions

Two neptunium free true raffinate concentrates from pilot plant investigations were available for the study of the plutonium recovery. Flush out solutions were also added to one of the raffinates, which then exhibited an increased plutonium content. The concentrates strongly differed in the degree to which they had been concentrated by evaporation. Plutonium was present in the concentrates as a mixture of

Pu(IV) and Pu(VI), and it was not attempted to adjust its oxidation state to exclusively Pu(IV). The extraction of plutonium from the concentrates was performed at room temperature. A feed solution was prepared from each raffinate by dilution with water shortly or immediately before the extraction, in order to reduce the concentration of nitric acid to a value suitable for the extraction of plutonium. The feed solution, the barren solvent and a scrub solution (1.0M HNO_3) were introduced into the 8th, first and 16th stages of the extractor respectively. The scrubbing of the loaded solvent was in our experiments desirable for partial removal of nitric acid, which would have interferred with eventual subsequent separation of plutonium from uranium. If the plutonium recovery is applied in a Purex plant without any subsequent separation of plutonium from uranium, the scrubbing can be omitted. However, we recommend not to omit the scrubbing, because it removes coextracted phosphoric acid from the loaded solvent. The conditions of the extraction experiments can be characterized as follows:

Experiment		A	B
Raffinate concentrated by a factor of		16	200
Concentrate diluted to feed by a factor of		1.3	1.7
Feed composition:	Pu(IV,VI)	39.4 g/l	2.93 g/l
	U(VI)	52.9 g/l	34.9 g/l
	nitric acid	5.14M	5.73M
Pu fraction existing as Pu(VI)		17%	5%
Flows:	feed	340 ml/h	680 ml/h
	scrub	140 ml/h	90 ml/h
	solvent	470 ml/h	440 ml/h

The loaded solvent was transferred into a further mixer-settler, where plutonium was separated from uranium by a conventional method (reduction of bulk Pu(IV) with hydroxylamine nitrate and completion of the reduction by adding a small amount of uranium(IV), both at 35°C). Uranium(VI) was then stripped at room temperature with initially 0.05M nitric acid in a third mixer-settler.

Concentration profiles of plutonium(IV,VI), uranium(VI) and nitric acid in the extraction mixer-settler were measured after running the experiment for >10 h. In Figs. 1 and 2 the measured profiles of total plutonium are shown and compared with calculated profiles of plutonium(IV). Also compared are measured distribution ratios of total plutonium and calculated distribution ratios of plutonium(IV) in single stages of the extractor. Following features of the experiments should be pointed out:

1) In the extraction section of the extractor (stages 1 to 8) the measured concentrations of plutonium are systematically higher than the calculated values. This can be ascribed to the presence of plutonium(VI) in the feed solution and to complexing of plutonium in the aqueous phase with hydrophilic decomposition products of TBP, mainly phosphoric acid. The highly evaporated concentrate taken for the run B must of course contain markedly more phosphoric acid than the moderately evaporated concentrate taken for the run A. In agreement with this the deviation of the experimental concentration profiles from the calculated ones, and also the difference between the experimental and calculated distribution ratios of Pu, is visibly greater in the run B (Fig. 2) than in the run A (Fig. 1). In the scrub section of the extractor (stages 9 to 16), the calculated concentration profiles and distribution ratios of plutonium fit the experimental values quite well.

2) The loading of the solvent with heavy metals had in both runs to be kept rather low, due to the lowered extraction efficiency of plutonium. In the run A, moreover, at the increased plutonium content in the feed solution it was necessary to prevent the formation of a second organic phase. To do this, we kept the plutonium concentration in the solvent below 40 g/l [6]. As it is seen in Fig. 1, the highest concentration of plutonium was in the run A reached in the 10th stage of the extractor and amounted 34.5 g/l.

3) At the necessarily moderate loading of the solvent with heavy metals, namely with 60 to 65 g (U+Pu)/l, the plutonium loss in the run A varied during the experiment between 0.1 and 0.3% and fell down to 0.04% before the run was stopped. The loss of uranium was unmeasurably low (<0.1%). In the run B, at a solvent loading of ~60 g (U+Pu)/l, the plutonium and uranium losses were as high as 3% and 1% respectively. A suppression of the solvent flow by 10% enhanced the solvent loading to

a still moderate value of ~66 g (U+Pu)/l, but increased the plutonium loss to 5%.

An experiment was also made before which the oxidation state of plutonium in the feed solution was adjusted with hydrazine nitrate to Pu(IV). The raffinate was for this experiment concentrated by evaporation by a factor of 30. Otherwise the experiment was similar to the run A. In spite of the absence of Pu(VI) in the feed, the plutonium loss was ~1%. It appears that the degree of concentrating the raffinate by evaporation, i.e. the concentration of phosphoric acid in the concentrate plays a more important role than the presence of Pu(VI). It is also possible that the lower extractability of Pu(VI) in comparison with Pu(IV) is compensated by a weaker complex formation with phosphoric acid in the aqueous phase.

Recovery of Plutonium from Neptunium Containing Solutions

If neptunium is to be left in the aqueous phase during the extraction of plutonium, it would have to be kept in the pentavalent state. Due to the disproportionation of neptunium(V), this is hardly possible at high nitric acid concentrations in the feed solution as they were accepted in the above described experiments. An adjustment of the acid concentration to a value of <1M would be needed [7]. However, a sufficient dilution of the concentrate would represent an undesirable volume enlargement and a denitration of the concentrate would be an undesirable additional operation. Thus we decided to recover plutonium from a neptunium containing concentrate in two steps: first we reduced Pu(IV,VI) to Pu(III) and Np(V,VI) to Np(IV) with uranium(IV) nitrate, and extracted U(IV,VI) together with Np(IV) in the first extraction step in leaving Pu(III) in the aqueous phase. Then we reoxidized Pu(III) electrochemically to Pu(IV) [8] and extracted it subsequently in the second extraction step.

Since no true neptunium containing raffinate was available, a simulated raffinate was prepared and concentrated by evaporation. The feed solution was in both extraction steps introduced into the 12th stage of the mixer-settler and a 5M solution of nitric acid was used for scrubbing in the first extraction step (see below). The conditions of the run were:

Raffinate concentrated by a factor of		60
Concentrate diluted to feed by a factor of		1.8
Feed composition in the 1st step:	Pu(III)	0.93 g/l
	U(VI)	18.8 g/l
	U(IV)	8.54 g/l
	Np(IV)	0.23 g/l
	nitric acid	5.37M
Feed composition in the 2nd step:	Pu(IV)	0.81 g/l
	nitric acid	4.80M
Flows in the 1st step:	feed	940 ml/h
	scrub (5M HNO_3)	100 ml/h
	solvent	480 ml/h
Flows in the 2nd step:	feed	1200 ml/h
	scrub (1M HNO_3)	25 ml/h
	solvent	100 ml/h

Experimental and calculated concentration profiles are shown in Figs. 3 to 5. The concentration profile of Np(IV) was only measured in the solvent phase in the 1st extraction step and is not shown here, because its shape is very similar to the shape of the corresponding uranium profile. The results can be summarized as follows:

1) The concentration profiles of total uranium (Fig. 3) indicate that a considerable amount of uranium(IV) remained unoxidized during the first extraction step. About 1% of total uranium accompanied plutonium(III) in the aqueous output, exclusively in the form of the rather weakly extractable U(IV). The amount of Np(IV) carried together with Pu(III) was as low as <0.7% and this degree of separation was fully satisfactory.

2) Not satisfactory was the yield of plutonium in the aqueous output in the first extraction step. As Fig. 4 shows it, the experimental plutonium concentration in the solvent in the extraction section of the extractor was much higher than the calculated concentration. This indicates that either a fraction of plutonium(III) was reoxidized in the extractor or plutonium(IV) was not reduced completely in the feed solution. As much as ~5% of total plutonium was lost into the solvent

and left the extractor together with uranium(IV,VI) and neptunium(IV). 3) In the second extraction step, the experimental concentration profiles deviated positively from the calculation in the first to 7th stage of the extractor (Fig. 5). Like in the above described runs A and B, the deviation can be ascribed to the presence of phosphoric acid and plutonium(VI) in the feed solution. Nevertheless, in spite of this and of the rather low organic to aqueous flow ratio the loss of plutonium into the aqueous waste stream was sufficiently low, namely ~0.8%.

Further Treatment of Extracted Plutonium

The plutonium extracted can be separated from uranium (if present in the solvent) and gained in the form of an aqueous solution in the common way, i.e. by reduction to the very weakly extractable plutonium(III). Uranium(IV) formed internally in an electrolytical mixer-settler or added externally to an aqueous stream, hydroxylamine nitrate or any other common reductant can be used for converting plutonium(IV,VI) to plutonium(III) and transferring so the whole plutonium amount into an aqueous stream. Such an operation is optimally performed at about 1M nitric acid in the aqueous phase and is not disturbed by side phenomena. On the other hand, there occurs a severe crud formation if the plutonium(IV,VI) is attempted to be reextracted with <0.1M nitric acid. The crud consists of mainly a bright solid, which most probably is plutonium(IV) monobutyl phosphate, plutonium(IV) dibutyl phosphate or a mixture of them. The crud formation is partially suppressed by an addition of excess uranium(IV) nitrate. It should be noted that a considerable amount of crud is also formed if a solvent loaded with uranium(VI) alone is contacted with <0.1 nitric acid. The extent of the crud formation increases with the degree to which the raffinate taken for the feed preparation has been concentrated by evaporation. Since monobutyl and dibutyl phosphoric acids are at least partly extracted with 30% TBP, the reextraction of plutonium(IV,VI) with a very dilute solution of nitric acid is disturbed not only by the crud formation, but also by a considerable retention of plutonium in the solvent.

To study the distrubing phenomena more in detail, we made a series of batch distribution experiments. The starting solution was a simulated raffinate, which was concentrated by evaporation by a factor as high as 450. TBP was decomposed during the evaporation mainly to phosphoric and monobutyl phosphoric acids. A considerable part (~75%) of the small amount of dibutyl phosphoric acid present in the concentrate existed as a course colloid (probably plutonium dibutyl phosphate) filterable with a paper filter (blue ribbon). Plutonium(IV,VI) was first extracted from the concentrate at a high nitric acid concentration (~5M), and subsequently attempted to be reextracted with 0.01M nitric acid. The tendency to the crud formation was markedly less pronounced, if the concentrate was filtered before the solvent was loaded with plutonium(IV,VI) from it. Thus, colloid impurities brought into the loaded solvent from the starting concentrate seem to support physically the crud formation. The amount of plutonium retained in the solvent corresponded at a 1:1 stoichiometry to the sum of the analytical concentration of monobutyl and dibutyl phosphoric acids in the concentrate.

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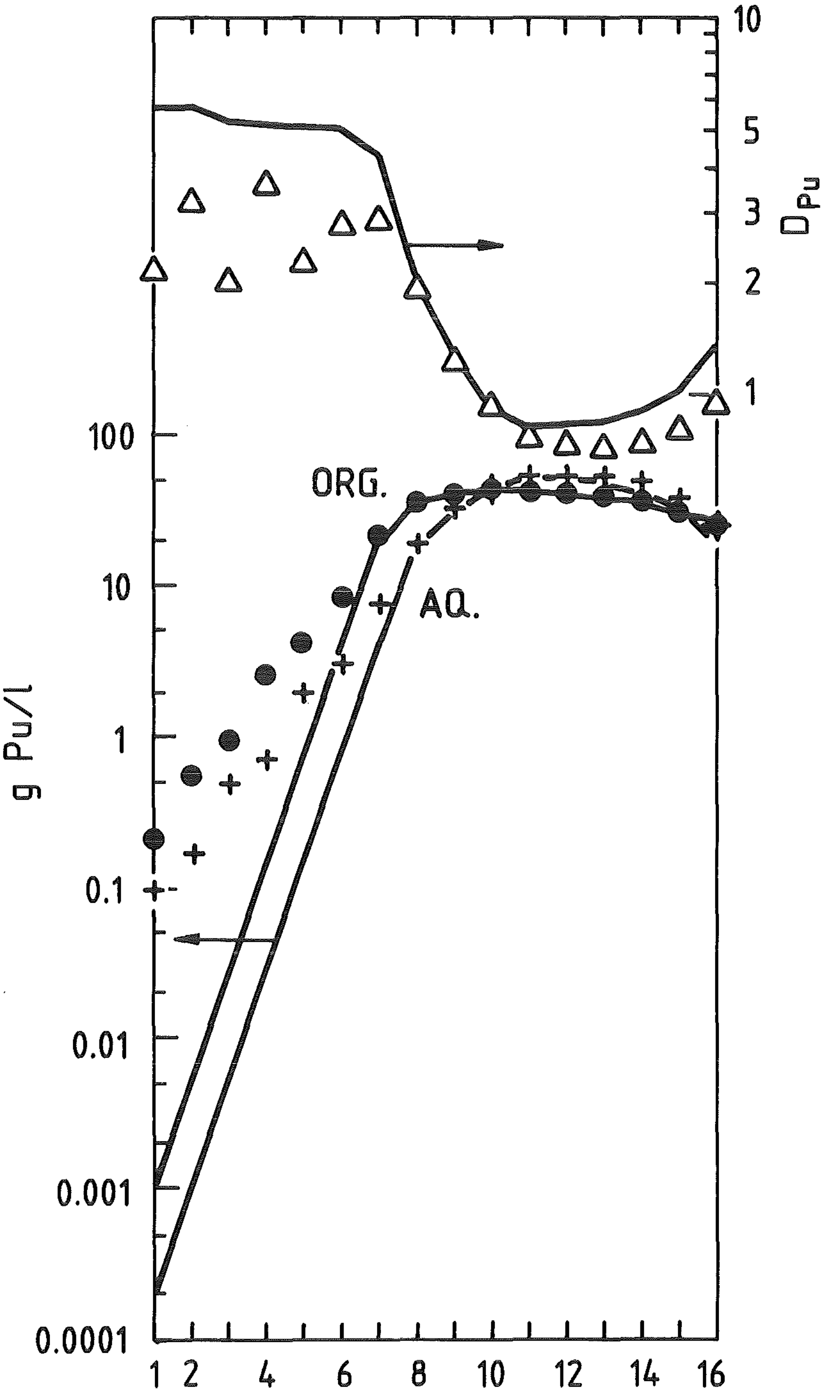

FIG. 1
Profiles of the concentrations and of the distribution ratio of Pu(IV,VI) in the extraction from a neptunium free raffinate concentrate in a mixer-settler (run A). Points: experimental concentrations and distribution ratios of total Pu; solid lines: calculated profiles of Pu(IV). For conditions of the run see the text.

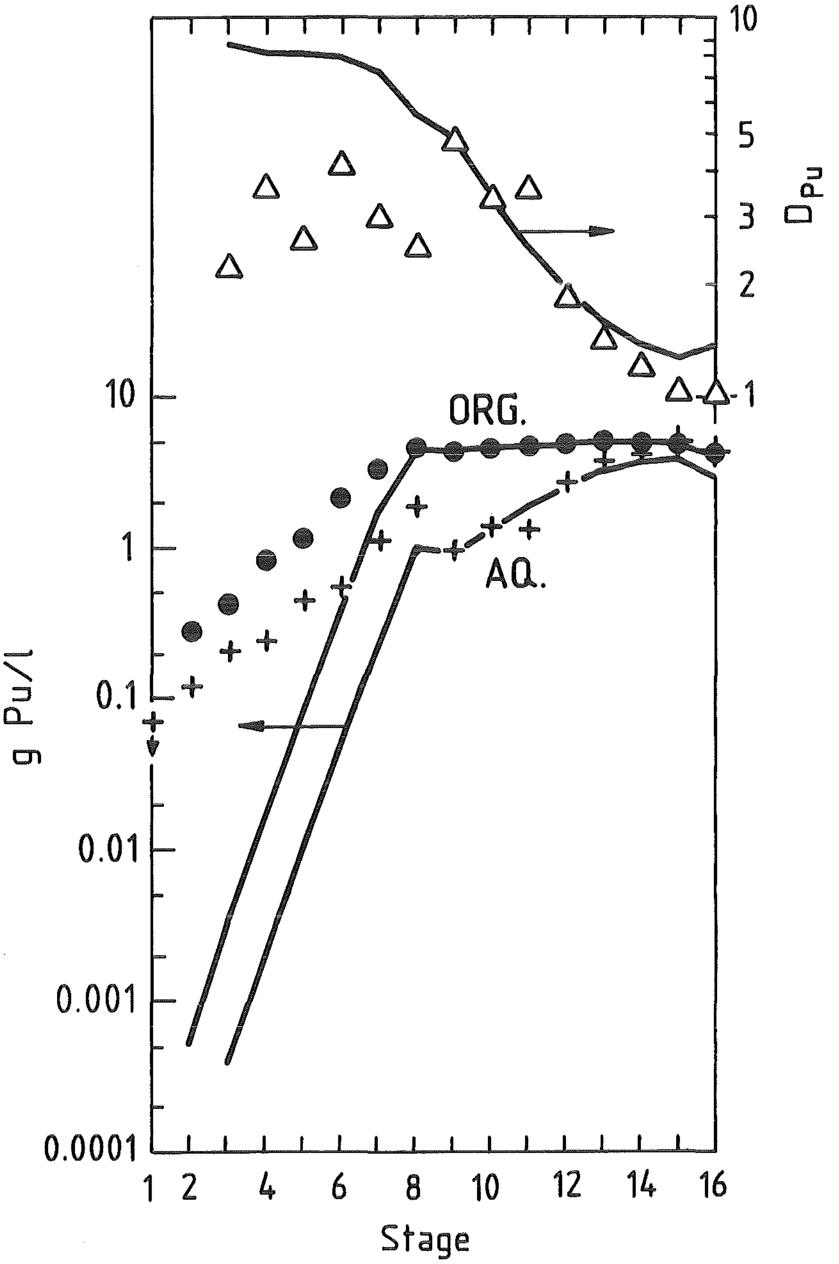

FIG. 2
Profiles of the concentrations and of the distribution ratio of Pu(IV,VI) in the extraction from a neptunium free raffinate concentrate in a mixer-settler (run B). Points: experimental concentrations and distribution ratios of total Pu; solid lines: calculated profiles of Pu(IV). For conditions of the run see the text.

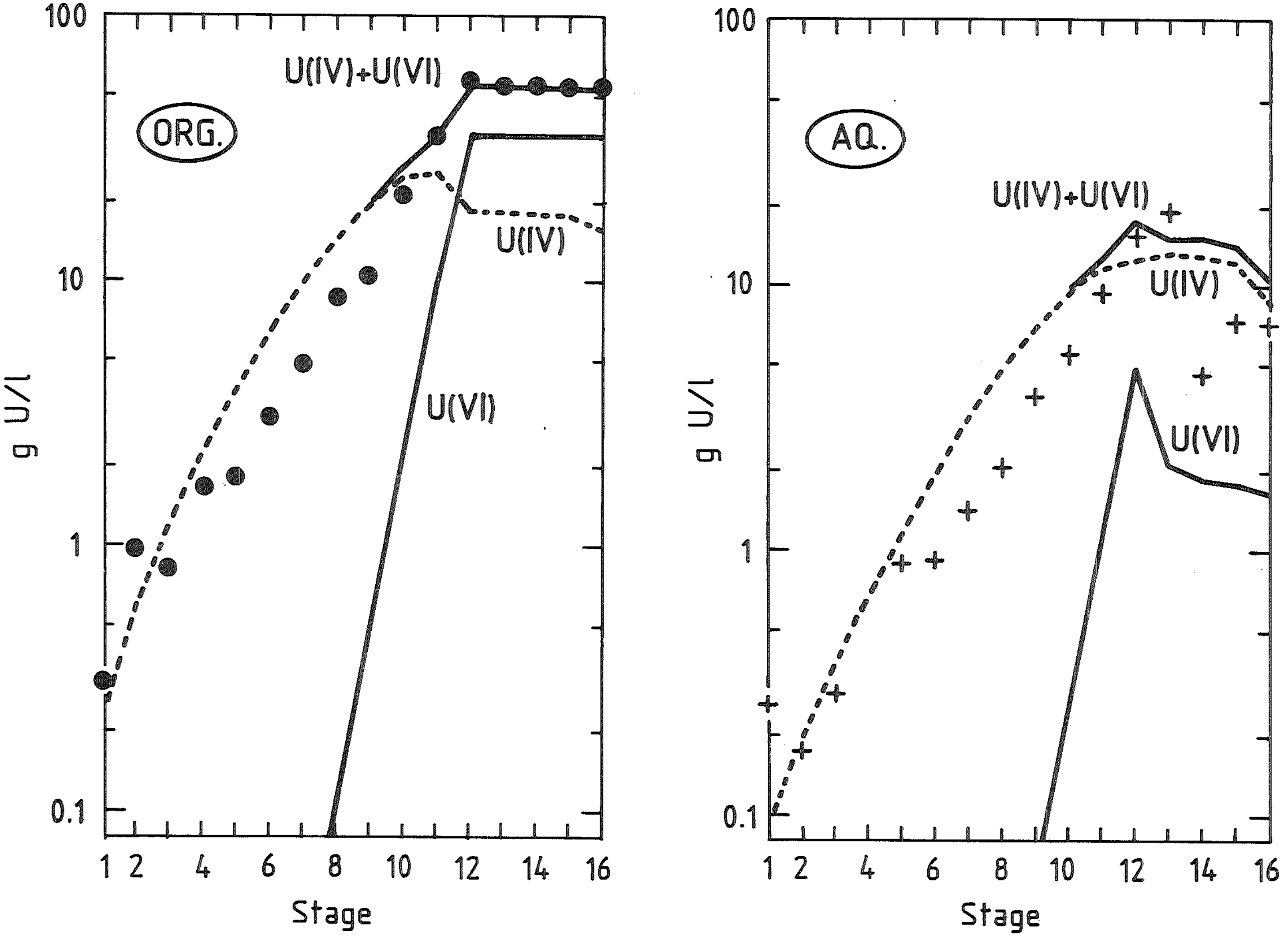

FIG. 3
Concentration profiles of U(IV,VI) in the first extraction step from a neptunium containing raffinate concentrate in a mixer-settler. Points: experimental concentrations of total U; solid lines: calculated profiles of U(IV), U(VI) and total U. For conditions of the run see the text.

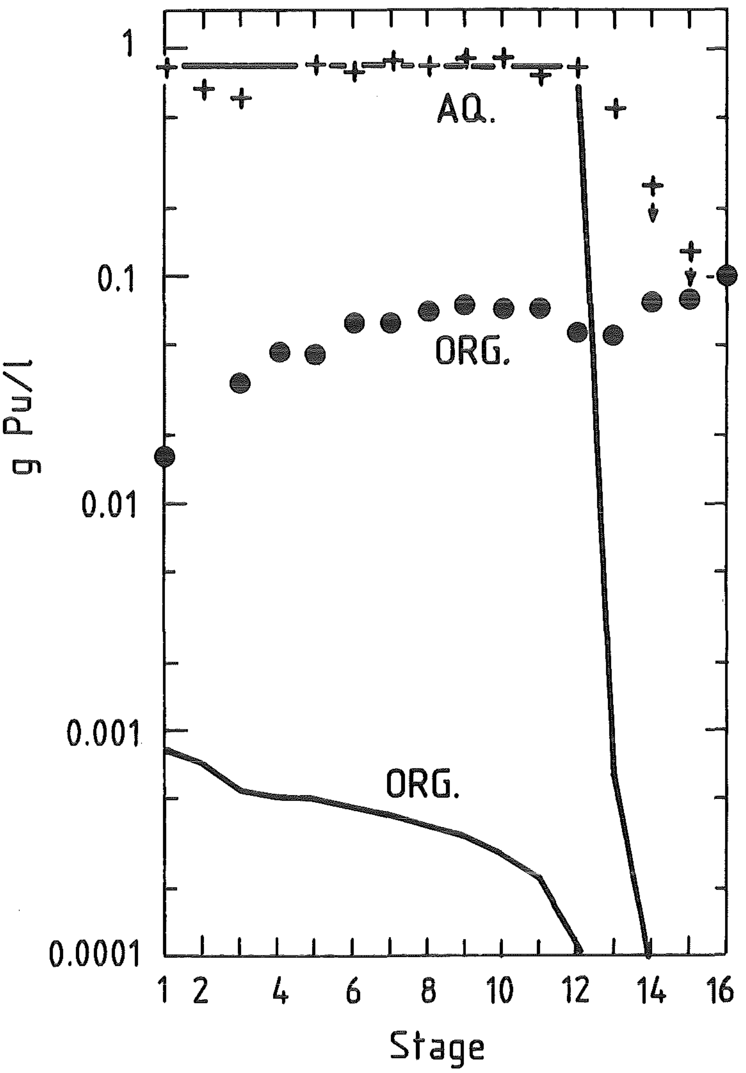

FIG. 4
Concentration profiles of Pu(III,IV) in the first extraction step from a neptunium containing raffinate concentrate in a mixer-settler. Points: experimental concentrations of total Pu; solid lines: calculated profiles of Pu(III). For conditions of the run see the text.

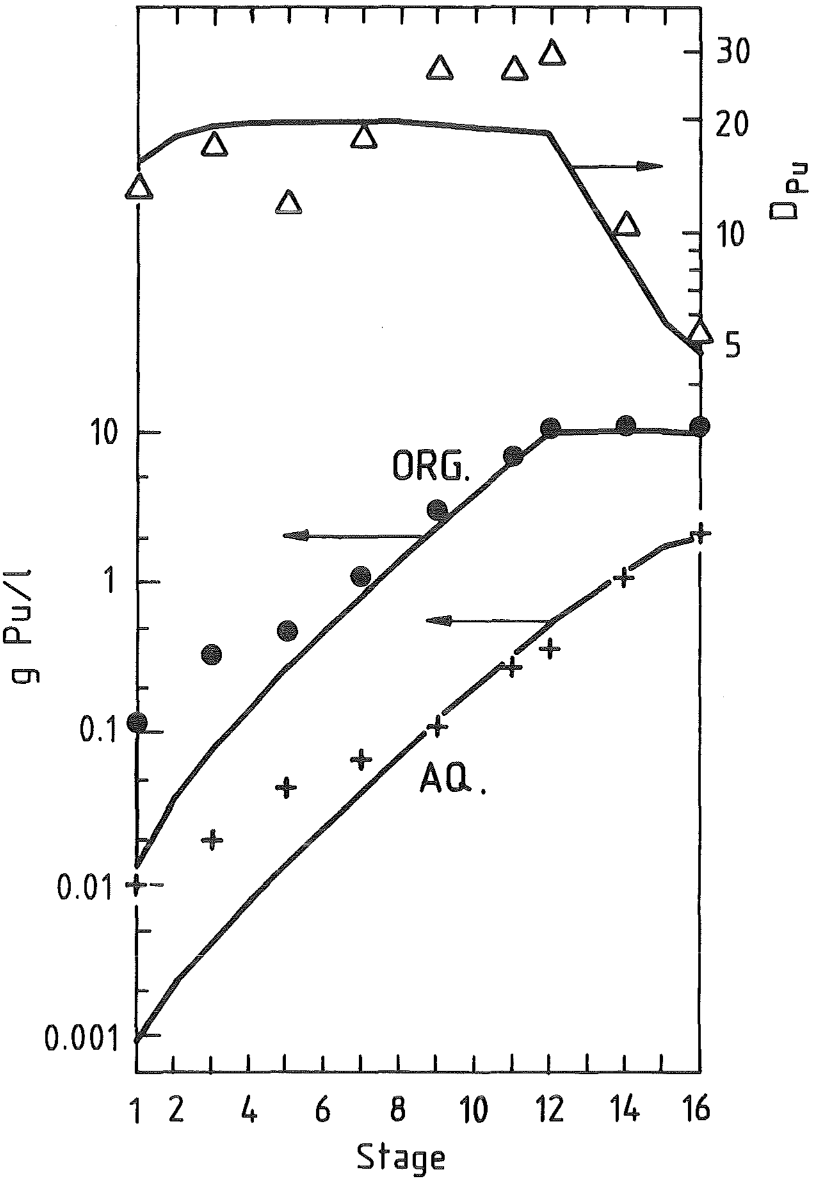

FIG. 5
Profiles of the concentrations and of the distribution ratio of Pu(IV,VI) in the second extraction step from an initially neptunium containing raffinate concentrate in a mixer-settler. Points: experimental concentrations and distribution ratios of total Pu; solid lines: calculated profiles of Pu(IV). For conditions of the run see the text.