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Flowsheet Studies on Processing of Plutonium Fuels by Solvent Extraction[x)]

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One of the problems arising in the processing of power reactor fuels lies in the fact that plutonium is considered as the fissile material in a number of advanced reactor designs. In particular, fast breeder reactors (with plutonium enrichments of about 15 - 20 % in the original core and of the order of 5 % in a final core-plus-blanket mixture) and thermal plutonium-recycle reactors (with original plutonium enrichments of the order of 1 - 3 %) will provide fuels with rather high plutonium concentrations. The chemical flowsheets used in the processing of these fuels must be adapted to this fact. A number of studies has been carried out in Karlsruhe, of which results on solvent extraction flowsheets are summarized in this report.

I. Reprocessing of Fast Breeder Reactor Fuels

Purex-type processes are usually used in modern reprocessing plants and will perhaps remain in use for a rather long period of time because of economic, reliability, and know-how reasons. The German reprocessing prototype plant WAK[1)], which is near to completion at Karlsruhe, will use a 30 vol.% TBP flowsheet to recover uranium and plutonium from slightly enriched uranium. A study made in the frame of a long-range development program commonly executed by Gesellschaft für Kernforschung (owner of WAK) and Gesellschaft zur Wiederaufarbeitung von Kernbrennstoffen (operator of WAK), led to the conclusion that adaptation of this plant to reprocessing of fast breeder fuel elements will be possible if, among other things, a common core-blanket management is done and a "dilute" extraction flowsheet is applied.

1. Interdependence of Uranium and Plutonium Distribution Coefficients

As a basis for flowsheet optimization, the distribution of uranium(VI) and plutonium(IV) between aqueous nitric acid and 20 vol.%

TBP/n-dodecane was studied for the single metals[2] as well as for mixtures of the two metals[3]. The dependence of the distribution of plutonium on the organic uranium loading at a total nitric acid concentration of 3.25 M is presented in fig. 1, while fig. 2 shows the distribution of uranium as a function of the organic plutonium loading for the same system. Empirical functions were derived from such data which allow for the calculation of the distribution coefficients in these multicomponent systems. In order to do this, the apparent equilibrium constants K_{app} of the equilibria

$$(1)\quad M^{m+} + mNO_3^- + n\ TBP \rightleftharpoons M(NO_3)_m(TBP)_n$$

$$(2)\quad K_{app}(M^{m+}) = \frac{(M(NO_3)_m(TBP)_n)}{(M^{m+})\ (NO_3^-)^m\ (TBP)^n}$$

where ( ) = concentration,
M^{m+} = UO_2^{2+}, Pu^{4+}, or H^+

were expressed as functions of the total ionic strength J of the aqueous phase:

$$(3)\quad K_{app}(Pu^{4+}) = 12.163 - 9.033\ J + 2.230\ J^2 - 0.163\ J^3$$

$$(4)\quad K_{app}(UO_2^{2+}) = 8.791 + 6.071\ J - 6.176\ J^2 + 1.579\ J^3$$

while a similar expression (equ. 5) from Jury and Whatley[4] was used for the extraction of nitric acid.

$$(5)\quad K_{app}(H^+) = 0.385 - 0.155\ J + 0.024\ J^2$$

These equations are valid in the concentration ranges 20 - 30 vol.% TBP, 0.1-0.6 M U(VI), 0.01 - 0.2 M Pu(IV), and 0.6-3 M HNO_3.

Finally, the distribution coefficients of the different components can then be expressed in terms of the concentrations and of the apparant equilibrium constants of all the components of the system. Work is now under way to develop a computer program for the calculation and optimization of counter-current flowsheets.

2. Counter-Current Studies of the HA Contactor

It is a well-known fact that extraction of plutonium nitrate by TBP is lower than that of uranyl nitrate. In other words, plutonium is more easily displaced from the organic phase by uranium than vice versa (cf. figs. 1 and 2). If a high metal loading of the organic phase is maintained, this effect will lead to an accumulation of the plutonium in the middle stages of the HA contactor due to excessive recycling. It is only after this plutonium accumulation has reached a sufficiently high value that the plutonium is finally "pushed" into the organic product solution. Such a "recycle" flowsheet[5,6] is shown in fig. 3. If the loading of the organic phase is lowered, the plutonium accumulation becomes less important, as is shown in the "coextraction" flowsheet of fig. 4[5,6]. High loading of the organic phase is desirable since this leads to good decontamination of the plutonium and uranium from fission products. On the other hand, it is obvious from fig. 3 that such a "recycle" flowsheet cannot be used in existing plants with geometrically not safe equipment, since supercritical plutonium concentrations will build up in the middle part of the HA contactor. Nevertheless, such flowsheets might be considered if separate fast breeder reprocessing plants using geometric criticality control would be built in the future. Even the "coextraction" flowsheet of fig. 4 is not fully concentration safe, so that "dilute" flowsheets of the type shown in fig. 5[6] may be chosen for existing plants.

3. Uranium-Plutonium Partitioning in the 1B Contactor Using Uranium(IV) as the Reductant

In the WAK[1], the partitioning (1B) bank is included into the first extraction cycle. Uranium(IV) nitrate will be used to

reduce plutonium to plutonium(III). A number of laboratory counter-current runs was performed[6] in which the acidity, the excess of uranium(IV), the point of introducing the uranium(IV) solution (1BX), the flow ratios, and the residence time were varied. As an example, fig. 6 presents the results of a flowsheet with a maximum acidity of 1.7 M HNO_3; the organic phase (1BF) introduced into the 1B contactor was in this case identical with the organic product solution (HAP) of the "dilute" flowsheet run shown in fig. 5. The plutonium product (1BP) contained 1 % of uranium, corresponding to a decontamination factor of ca. 10^4. The plutonium content in the uranium product stream (1BU) was 0.04 % of the total plutonium which corresponds to a decontamination factor of ca. $5 \cdot 10^3$.

From a number of similar experiments, the following general conclusions could be drawn: A 3 - 4.5 fold excess of U(IV) was not sufficient to obtain plutonium losses of less than 0.2 % in the 1BU solution, while a 7 fold excess was sufficient, provided the acidity was below 2.4 M. A lowering of the residence time per stage from 4.7 min to 3.0 min did not make a difference. Splitting of the U(IV) into two streams - one introduced as usual with the 1BX solution in a middle stage of the mixer-settler and one introduced with the 1BXS solution at the uranium product exit stage - likewise did not give a major effect. As to be expected, uranium decontamination of the 1BP plutonium product stream was best with high-acidity flowsheets.

II. Direct Electrolytic Reduction of Plutonium in the 1B Contactor

Large amounts of reductant are required in the 1B contactor if fuels with a high plutonium content are processed. This will perhaps prevent the use of ferrous sulfamate in the reprocessing of, e.g., fast breeder reactor fuels, and is at least not convenient even if uranium(IV) nitrate is used as the reductant. Thus a study was carried out to develop a direct electrolytic in-line reduction of the plutonium in the mixed-phase system of the 1B contactor[7].

One condition for such a process is that the Pu(IV)/(III) reduction rate is sufficiently high. In particular, the influence of the cathode potential applied and of the solution partners on the reduction rate was of interest. Nitric acid in concentrations of 0.3 - 1.5 M did not influence the reduction rate. Hydrazine, which would be added as a scavanger for nitrous acid, lowered the time necessary for quantitative reduction. The dependence of the reduction rate on the uranium(VI) concentration and on the cathode potential applied can be seen from fig. 7 which presents a potential - current diagram. In the potential range of the Pu(IV)/(III) limiting current, i.e. between ca. + 400 and -100 mV versus SCE, the reduction rate is proportional to the Pu(IV) concentration. If the reduction is carried out in the potential range of the U(VI)/(IV) stage, i.e. between ca. -100 and -500 mV versus SCE, uranium(IV) is formed in addition to the directly formed Pu(III). This U(IV) reduces, in its turn, immediately any Pu(IV) present, so that the total Pu(IV)/(III) reduction rate is raised by this "indirect" reduction via U(IV). This offers the possibility of regulating, by varying the potential applied, the reduction rate in a counter-current system.

Counter-current runs were carried out using a 16-stage plexiglass laboratory mixer-settler equipped with gold cathodes in 8 mixer chambers and platinized titanium anodes in the corresponding settler chambers. The organic uranium-plutonium feed solution (1BF) was introduced into stage No. 8, while the aqueous phase (1BX, nitric acid + hydrazine) was introduced into stage No. 1 and the organic scrub solution (1BS) into stage No. 16. Table 1 shows the flowsheet conditions of three runs, one of them (No.1) having a plutonium:uranium ratio typical of fast breeder fuels and two of them (No.2 and 3) having plutonium:uranium ratios typical of light-water reactor fuels. In runs No. 1 and 2, the anodes in the mixer-settler were shielded by clay diaphragms in order to prevent re-oxidation of the plutonium and any degradation of the solvent, while in run No. 3 the diaphragms were removed. The uranium-plutonium separations attained in these runs were equivalent to those experienced with uranium(IV) re-

duction. As an example, concentration profiles for run No. 2 are shown in fig. 8. Engineering studies are now under way for a pilot mixer-settler unit for plant use.

Table 1. Flowsheet conditions for three runs of an electrolytic 1B mixer-settler.

Run No.	1 BF	1 BU	1 BP
1	240 ml/h 4,5 g Pu/l 48,2 g U/l	350 ml/h 0,002 g Pu/l 38,0 g U/l	66 ml/h 21,2 g Pu/l <0,01 g U/l
2	480 ml/h 0,34 g Pu/l 77,0 g U/l	551 ml/h 0,004 g Pu/l 69,1 g U/l	44 ml/h 3,74 g Pu/l 0,01 g U/l
3	400 ml/h 0,5 g Pu/l 73,4 g U/l	471 ml/h <0,002 g Pu/l 61,5 g U/l	44 ml/h 3,4 g Pu/ 0,006 g U/l

III. Recovery of Plutonium from Non-Irradiated Fuel Fabrication Scrap

A process has been developed for the recovery of plutonium from the scrap which arises during the fabrication of power reactor fuels enriched in plutonium[8]. Such fuels usually consist of a UO_2-PuO_2-mixture. Anion exchange is often used for recovery of the plutonium from this scrap. However, the capacity of the anion exchange resin for plutonium is lowered in the presence of uranium, which is of particular importance in the case of the low-enriched thermal plutonium-recycle fuels where uranium is present in a large excess. Thus a solvent extraction process was developed which, as a major requirement, was to use a non-inflammable solvent. A 15 vol.% trilaurylamine (TLA) solution in carbon tetrachloride was selected as the solvent, based on the good Pu(IV)/U(VI) separation factor of the TLA extractant and on the non-inflammability of the CCl_4 diluent.

After dissolution of the scrap, the aqueous feed solution is adjusted to ca. 2 M nitric acid. Valency adjustment of the plutonium to the +4 state is necessary if any Pu(VI) should have been formed during dissolution. Extraction isothermes for the extraction of plutonium(IV) by 15 vol.% (ca. 0.24 M) TLA/CCl_4 from 2 M nitric acid as a function of the uranium concentration are shown in fig. 9, while fig.10 presents the extraction of uranium under the same conditions as a function of the plutonium concentration. It can be seen from these figures that the plutonium distribution coefficients and the plutonium-uranium separation factors remain high enough even at high uranium concentrations to guarantee a good separation of the two metals with a few counter-current stages.

It is a well-known fact that backwash of plutonium from organic tertiary amine phases offers some difficulties. In order to avoid contamination of the plutonium product by unwanted elements, backwash by solutions based on acetic acid was considered, which is however known to be a slow reaction (cf.[9]).

The kinetics of backwash of plutonium(IV) by 1 M acetic/0.05 M nitric acid from 15 vol.% TLA/CCl_4 is shown in curve 1 of fig. 11. Good recovery of plutonium may be possible even in a single-stage contactor provided that the residence time of the solutions is of the order of several minutes. Still better (lower) distribution coefficients and faster kinetics can be reached by the addition of ascorbic acid as a reductant for plutonium, as is demonstrated by curve 2 of fig.11. The latter solution was adopted for practical use.

On the basis of the above results, a counter-current flowsheet consisting of 6 extraction, 4 scrub, and 1 backwash stages was developed. A geometrically safe test facility using centrifugal contactors in extraction and scrub and a one-stage mixer-settler with long residence time for backwash is now under construction[10].

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10. B. Roth and R. Beutner, unpublished.

Fig. 1. Plutonium (IV) extraction isothermes for various organic uranium loadings. 20 vol.% TBP/n-dodecane, 3.25 M total HNO_3, T = 25°C.

Fig. 2. Uranium (VI) extraction isothermes for various organic plutonium loadings. 20 vol.% TBP/n-dodecane, 3.25 M total HNO_3, T = 25°C.

Fig. 3. "Plutonium recycle" flowsheet with >90 % saturation of the organic phase.

Fig. 4. "Plutonium coextraction" flowsheet with ca. 80 % saturation of the organic phase.

Fig. 5. "Dilute" flowsheet with ca. 50 % saturation of the organic phase.

Fig. 6. Partitioning flowsheet, using as feed (1 BF) the organic product (HAP) of fig. 5.

Fig. 7. Potential- current diagram for the electrolytic reduction of Pu (IV) in the presence of uranyl nitrate.

Fig. 8. Concentration profiles for direct electrolytic reduction of plutonium in the 1 B mixer-settler, run No. 2 (cf. table 1).

Fig. 9. Extraction of tetravalent plutonium by 15 vol.% TLA/CCl_4 from 2 M HNO_3 as a function of the uranium concentration. T = 25°C.

Fig. 10. Extraction of hexavalent uranium by 15 vol.% TLA/CCl_4 from 2 M HNO_3 as a function of the plutonium concentration. T = 25°C.

Fig. 11. Kinetics of backwash of ca. 5 g/l plutonium (IV) from 15 vol.% TLA/CCl_4 (equilibrated with 2 M aqueous nitric acid). Curve 1: 2 M acetic/0.05 M nitric acid. Curve 2: 2 M acetic/0.05 M nitric/0.03 M ascorbic acid.

Fig. 1

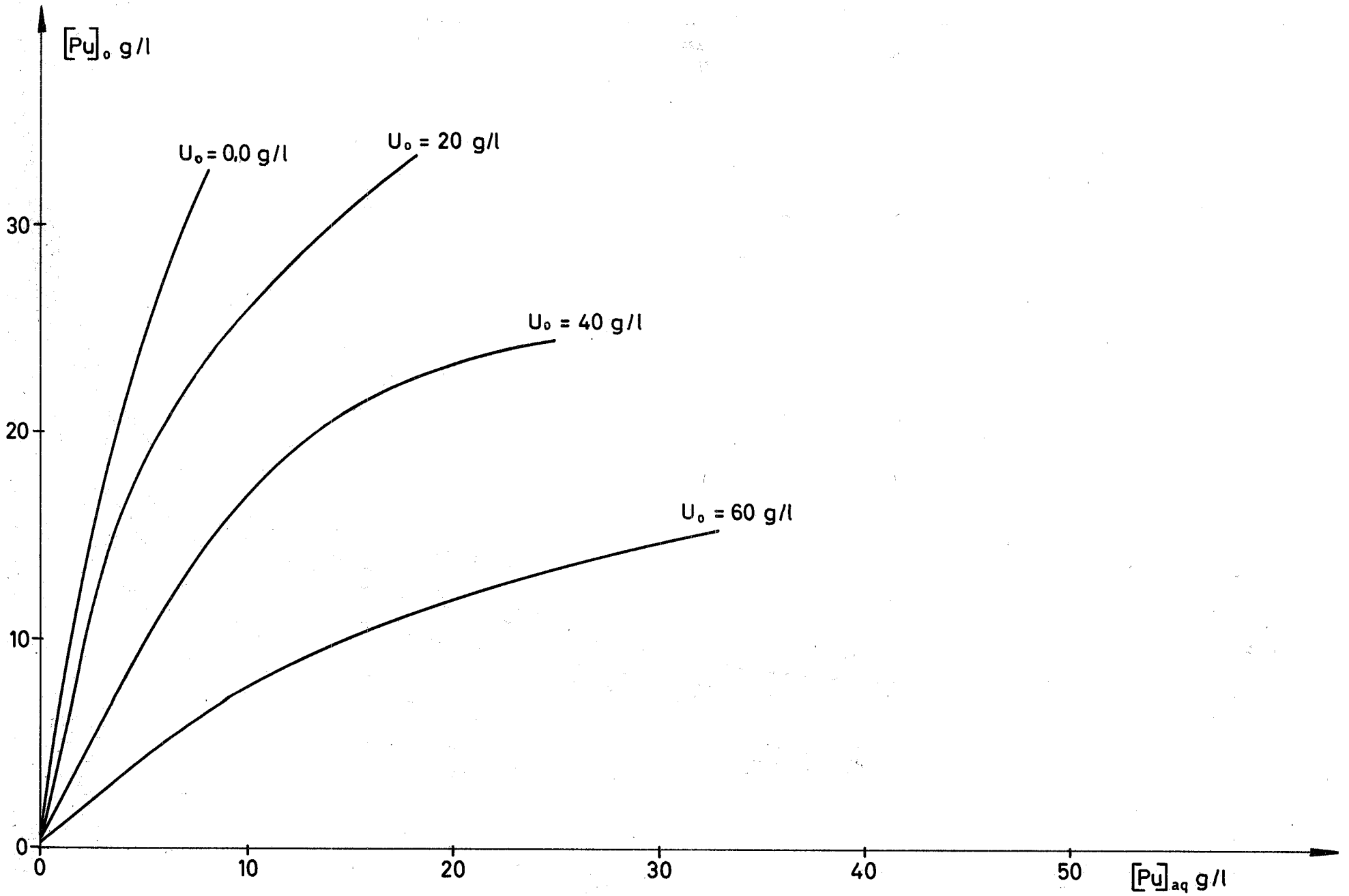

[Pu]o g/l
Uo = 0.0 g/l
Uo = 20 g/l
Uo = 40 g/l
Uo = 60 g/l
0
10
20
30
0
10
20
30
40
50
[Pu]aq g/l

Fig. 2

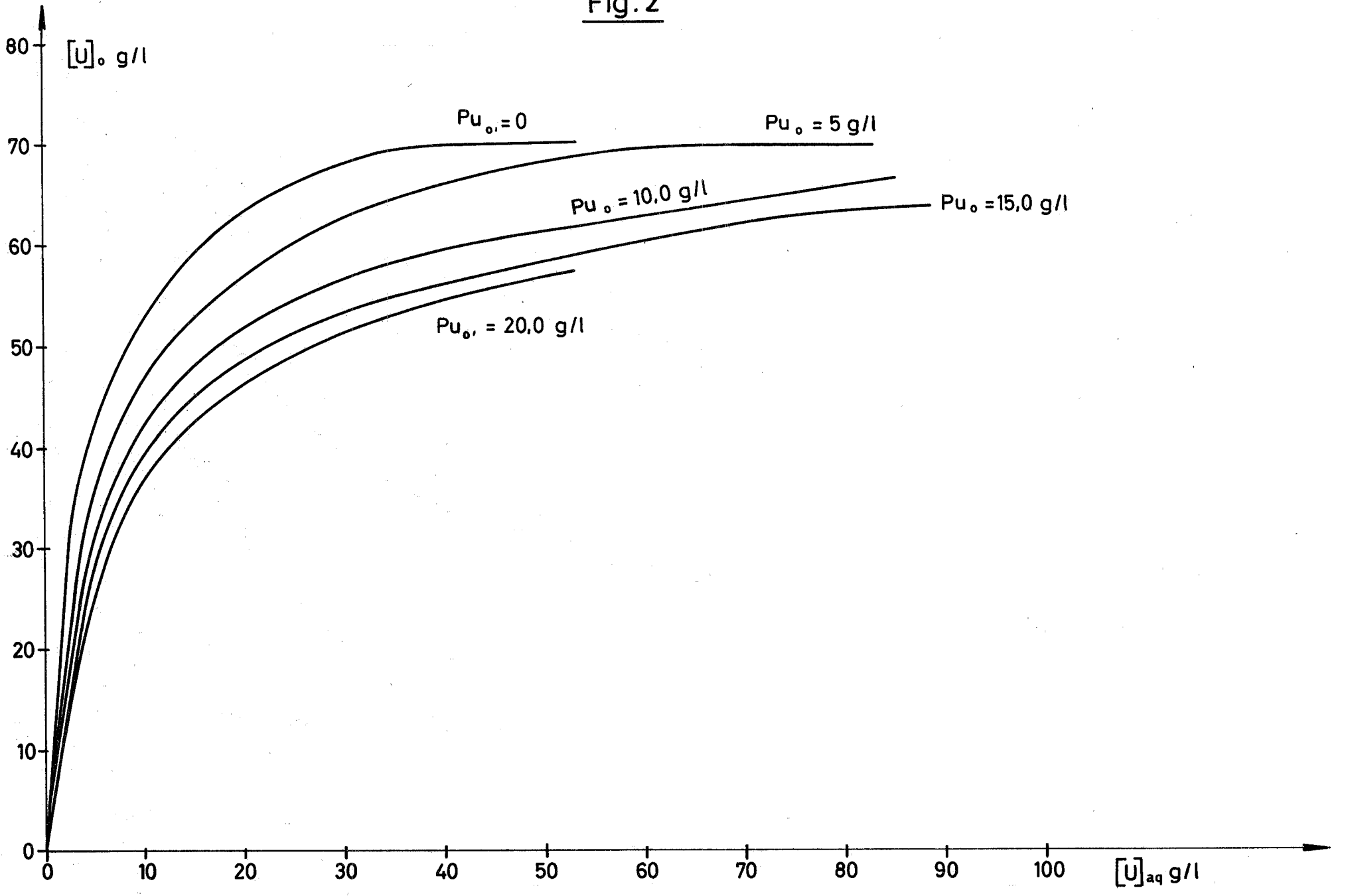

[U]o g/l
Pu o = 0
Pu o = 5 g/l
Pu o = 10,0 g/l
Pu o = 15,0 g/l
Pu o = 20,0 g/l
0
10
20
30
40
50
60
70
80
90
100
[U]aq g/l

Fig. 3

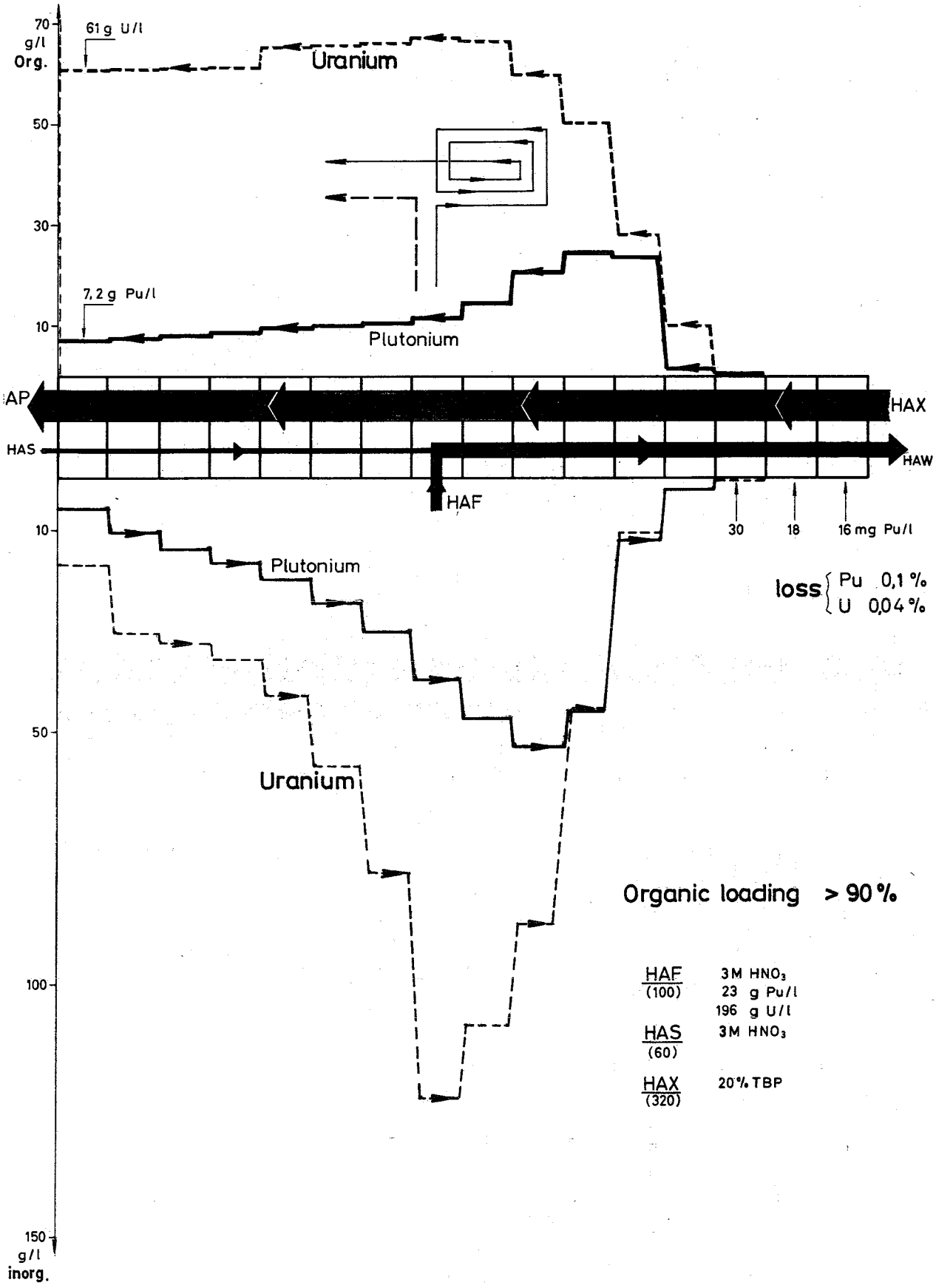

70
g/l
Org.
61 g U/l
Uranium
50
30
7,2 g Pu/l
10
Plutonium
AP
HAX
HAS
HAW
HAF
10
30
18
16 mg Pu/l
Plutonium
loss { Pu 0,1 %
U 0,04 %
50
Uranium
Organic loading > 90 %
100
HAF (100) 3M HNO3
23 g Pu/l
196 g U/l
HAS (60) 3M HNO3
HAX (320) 20% TBP
150
g/l
inorg.

Fig. 4

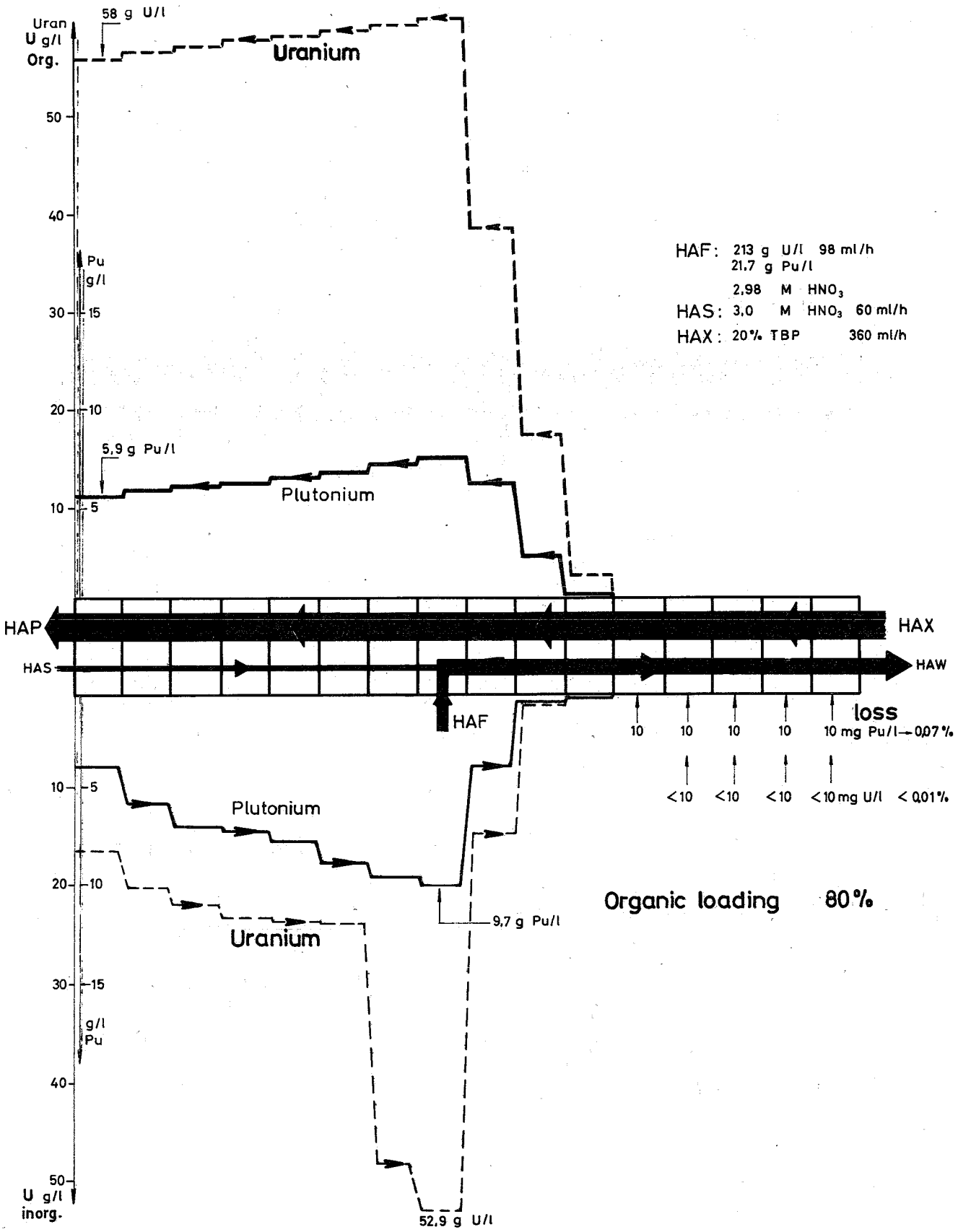

Uran
U g/l
Org.
58 g U/l
Uranium
50
40
Pu
g/l
30
15
20
10
5,9 g Pu/l
Plutonium
10
5
HAF: 213 g U/l 98 ml/h
21,7 g Pu/l
2,98 M HNO3
HAS: 3,0 M HNO3 60 ml/h
HAX: 20% TBP 360 ml/h
HAP
HAX
HAS
HAW
HAF
loss
10 10 10 10 10 mg Pu/l — 0,07%
< 10 < 10 < 10 < 10 mg U/l < 0,01%
10
5
Plutonium
20
10
Uranium
9,7 g Pu/l
Organic loading 80%
30
15
g/l
Pu
40
50
U g/l
inorg.
52,9 g U/l

Fig. 5

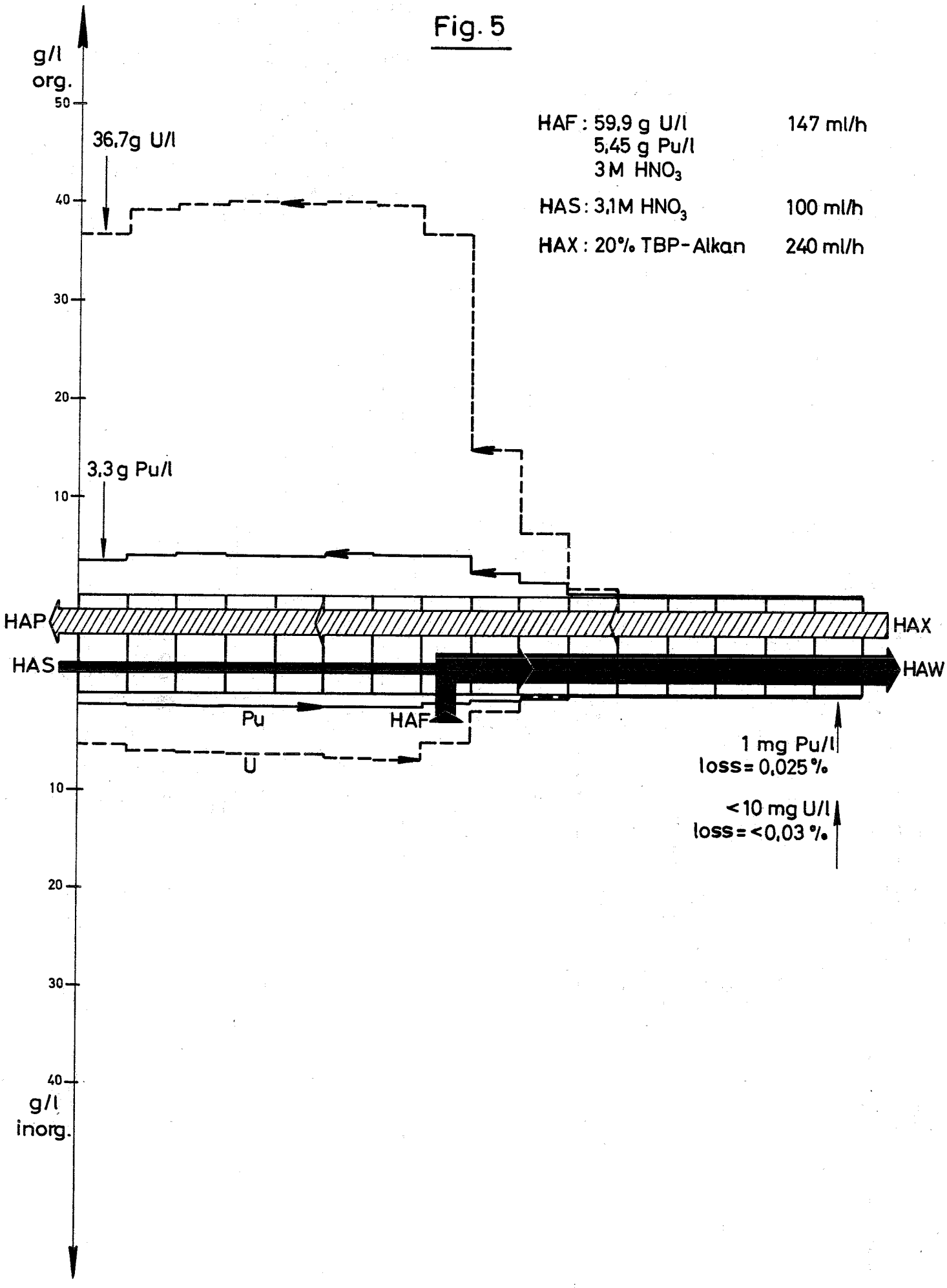

g/l org.
50
40
30
20
10
36,7g U/l
3,3 g Pu/l
HAP
HAS
HAX
HAW
Pu
HAF
U
10
20
30
40
g/l inorg.
HAF : 59,9 g U/l 147 ml/h
5,45 g Pu/l
3 M HNO3
HAS : 3,1 M HNO3 100 ml/h
HAX : 20% TBP-Alkan 240 ml/h
1 mg Pu/l
loss = 0,025 %
< 10 mg U/l
loss = < 0,03 %

Fig. 6

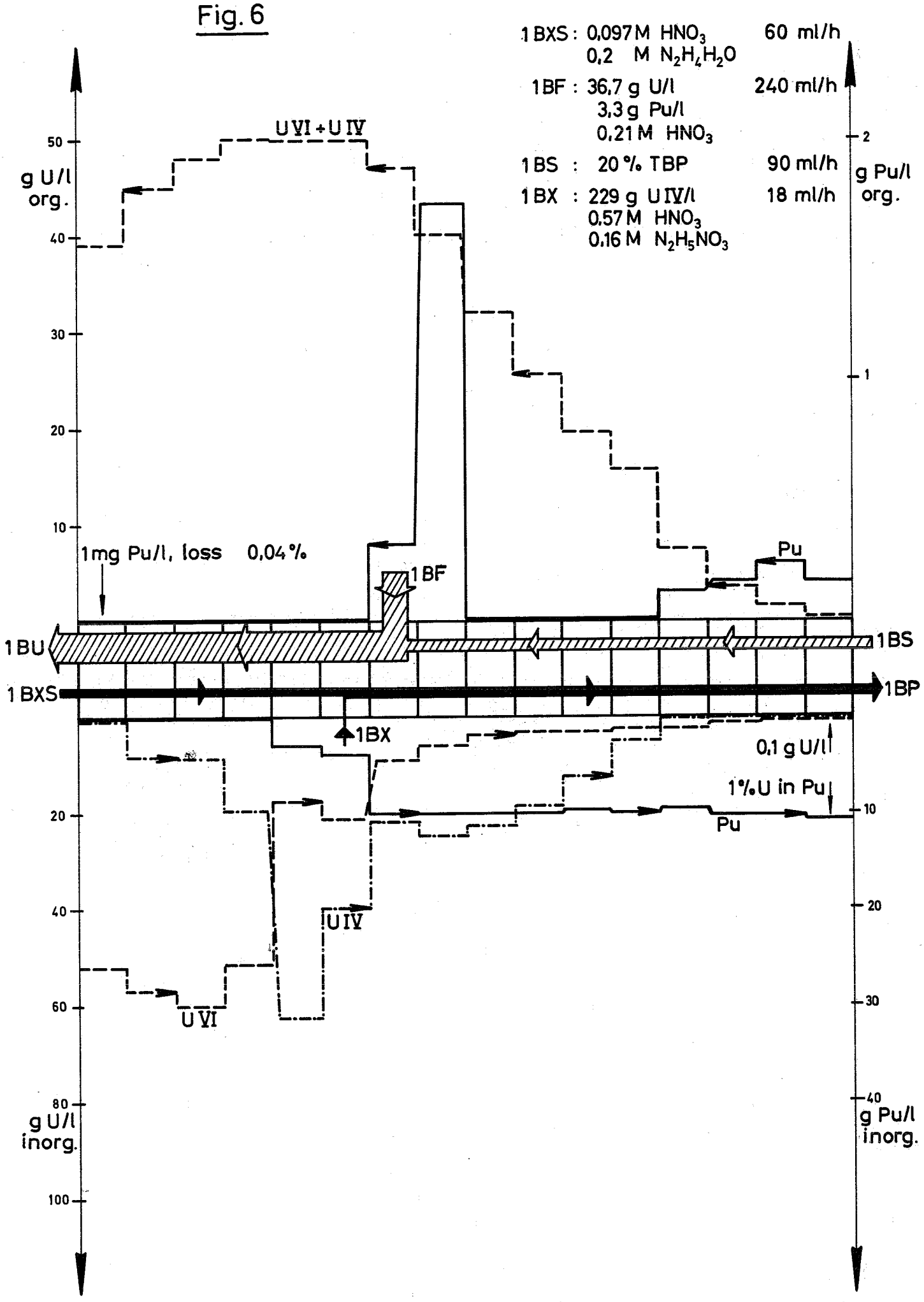

1 BXS : 0,097 M HNO_3 60 ml/h
0,2 M $N_2H_4H_2O$
1 BF : 36,7 g U/l 240 ml/h
3,3 g Pu/l
0,21 M HNO_3
1 BS : 20 % TBP 90 ml/h
1 BX : 229 g U IV/l 18 ml/h
0,57 M HNO_3
0,16 M $N_2H_5NO_3$
U VI + U IV
g U/l org.
g Pu/l org.
1mg Pu/l, loss 0,04 %
1 BF
Pu
1 BU
1 BS
1 BXS
1 BP
1 BX
0,1 g U/l
1 % U in Pu
Pu
U IV
U VI
g U/l inorg.
g Pu/l inorg.

Fig. 7

Potential-current curve of a solution of
0,08 M Pu(IV) 0,1 M U(VI) 0,4 M HNO_3 0,01 M N_2H_5OH
at the gold cathode

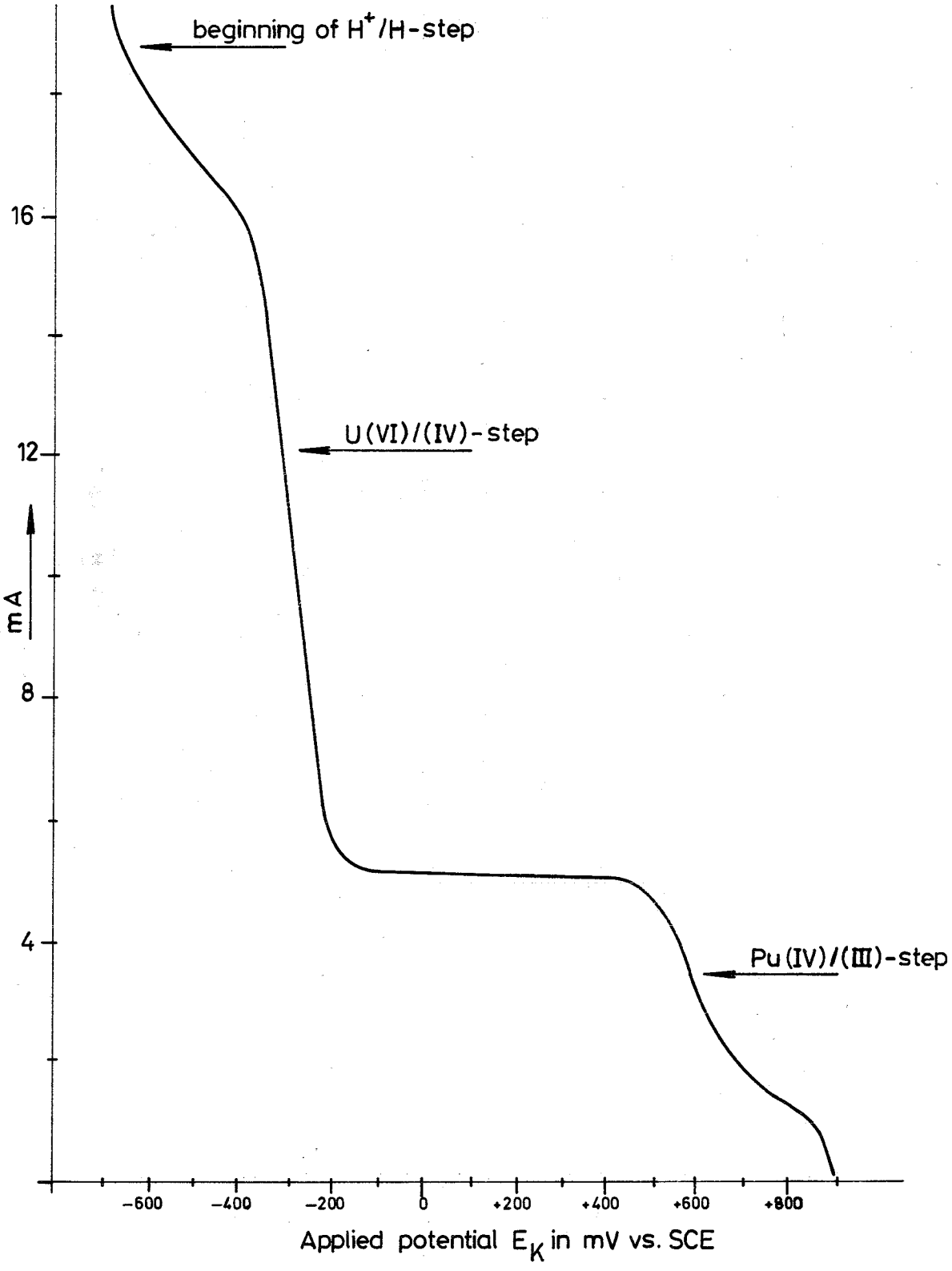
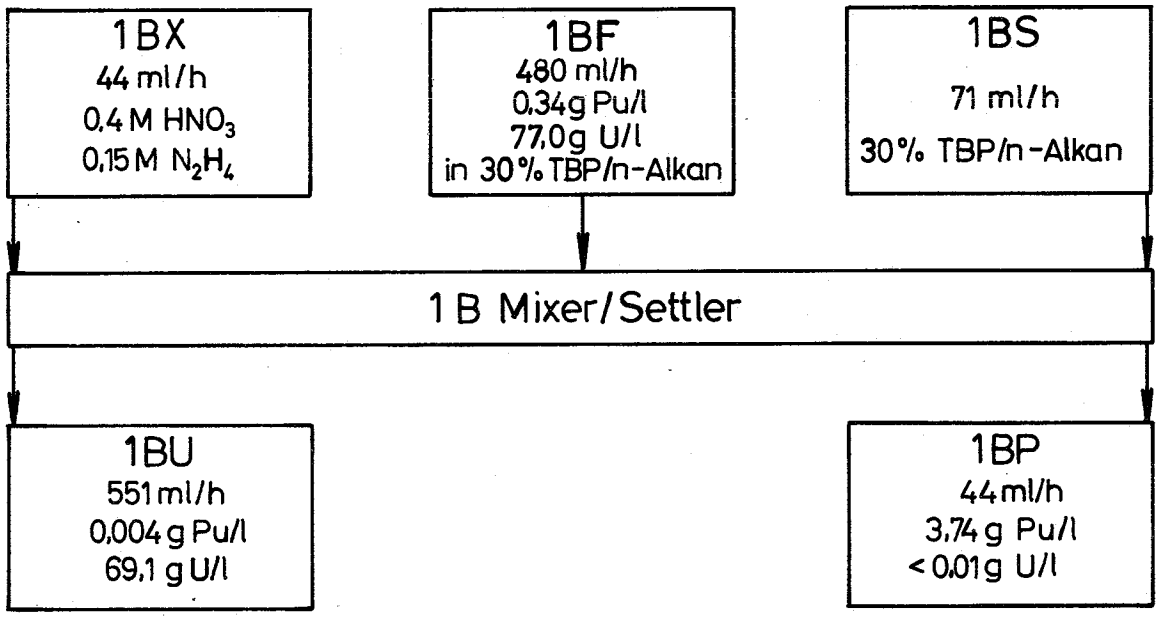


Fig.8

Process 2



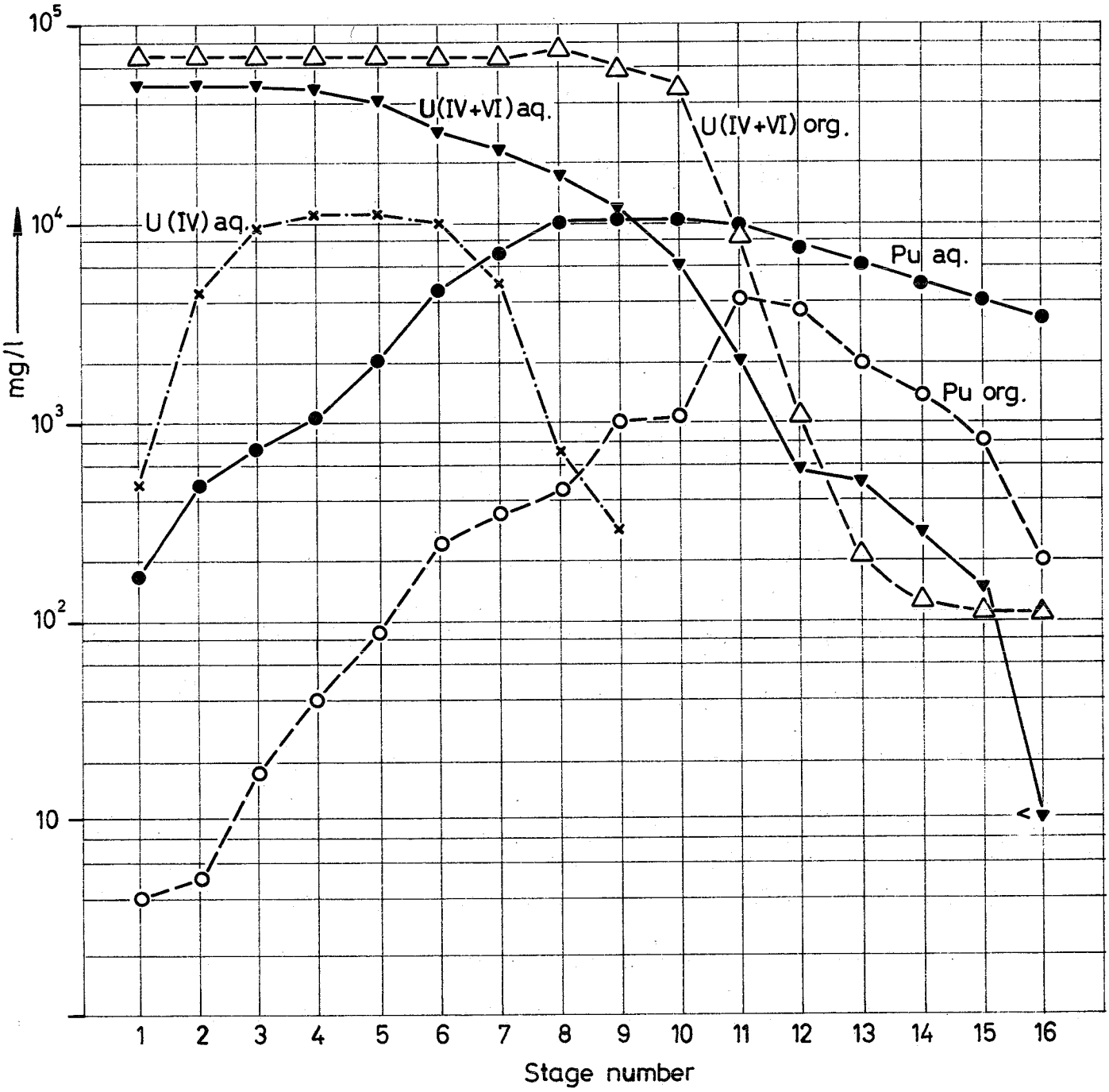


Fig. 9

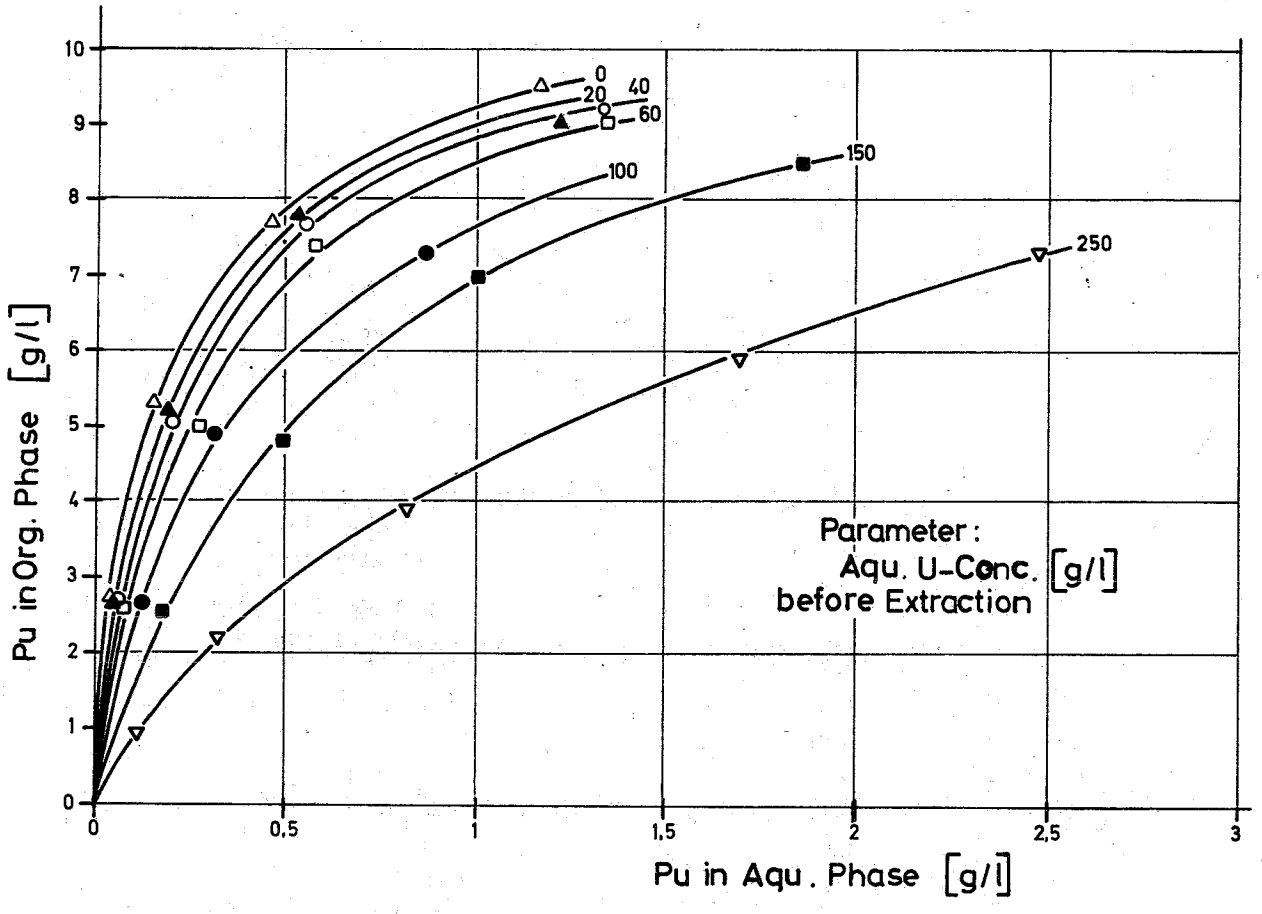

Pu in Org. Phase [g/l]
Pu in Aqu. Phase [g/l]
0
20
40
60
100
150
250
Parameter:
Aqu. U-Conc. [g/l]
before Extraction
0
0,5
1
1,5
2
2,5
3
1
2
3
4
5
6
7
8
9
10

Fig.10

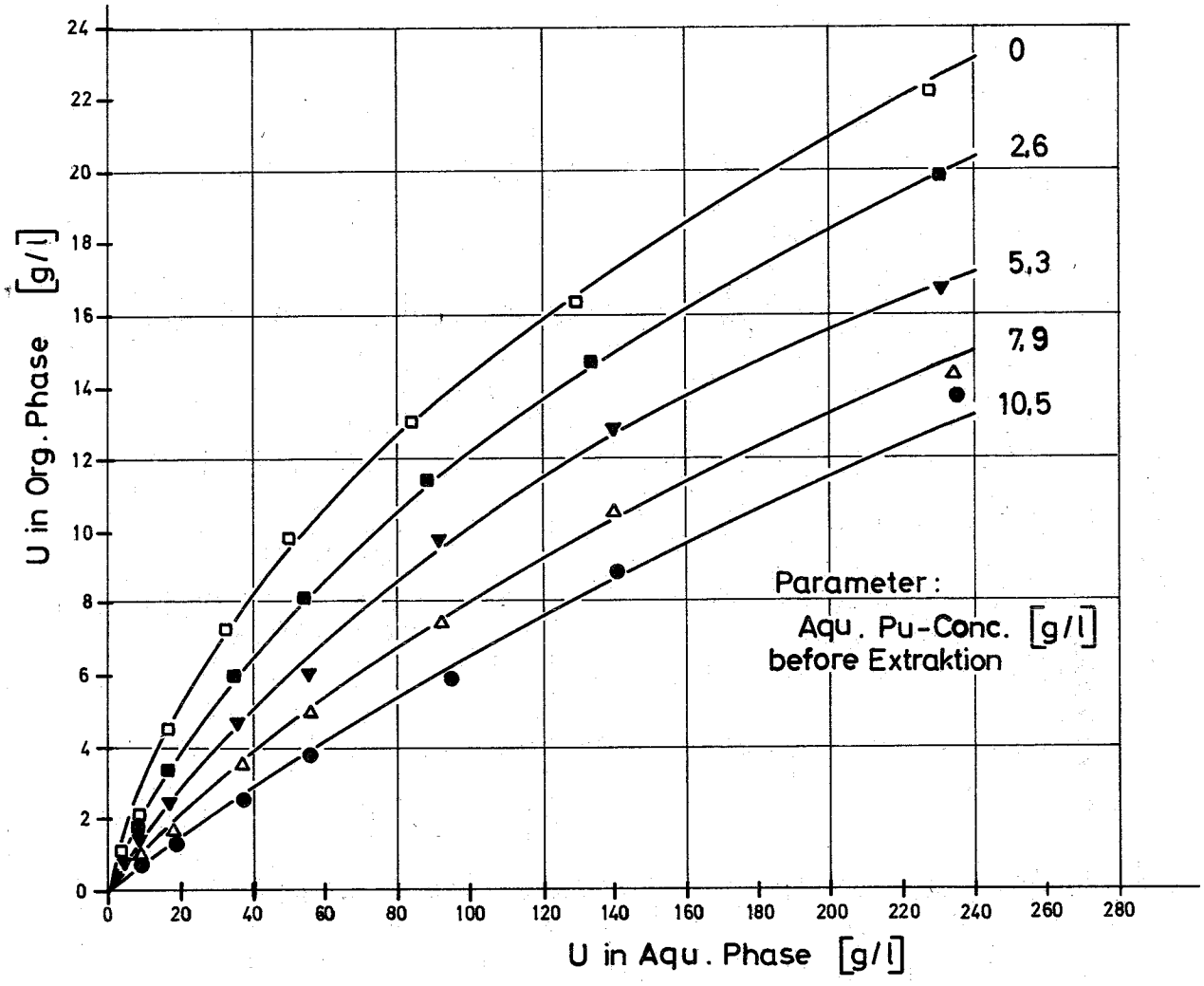

U in Org. Phase [g/l]
U in Aqu. Phase [g/l]
0
2,6
5,3
7,9
10,5
Parameter :
Aqu. Pu-Conc. [g/l]
before Extraktion

Fig. 11