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H.-J. Bleyl, D. Ertel, G. Koch
Institut für Heiße Chemie
Projekt Wiederaufarbeitung und Abfallbehandlung

Kernforschungszentrum Karlsruhe

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Gesellschaft für Kernforschung m.b.H., Karlsruhe

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Abstract

This paper summarizes the results of recent reprocessing studies made in the experimental facility MILLI at Karlsruhe. MILLI is a highly shielded, critically eversafe, laboratory-scale solvent extraction facility with a nominal throughput of 1 kg U+Pu per day. Processing of three types of fuel is reported: (1) LWR fuels burned up to 37000 MWd/t and cooled between 240 days and 2 years, (2) LWR plutonium recycle fuels burned up to 21000 MWd/t and cooled between 1 and 2 years, and (3) FBR-UO_2/PuO_2 fuel burned to 61000 MWd/t and cooled for 8 years. Particular attention is given to fuel dissolution, first-cycle PUREX solvent extraction, and neptunium behaviour during solvent extraction.

Zusammenfassung

Erfahrungsbericht über die Wiederaufarbeitung von LWR-, Plutoniumrezyklierungs- und Schnellbrüter-Brennstoffe in der MILLI-Anlage

In diesem Bericht werden neue Versuchsergebnisse zur Wiederaufarbeitung von Kernbrennstoffen in der Karlsruher Experimentieranlage MILLI zusammenfassend dargestellt. MILLI ist eine hochabgeschirmte, geometrisch kritikalitätssichere Labor-Extraktionsanlage mit einer Nominalkapazität von 1 kg U+Pu pro Tag. Es wird über die Aufarbeitung von drei Brennstofftypen berichtet, (1) LWR-Brennstoffe mit mittleren Abbränden bis zu 37000 MWd/t und Kühlzeiten zwischen 240 Tagen und 2 Jahren, (2) LWR-Plutoniumrezyklierungsbrennstoffe mit mittleren Abbränden bis zu 21000 MWd/t und Kühlzeiten zwischen 1 und 2 Jahren, und (3) Schnellbrüter-UO_2/PuO_2-Brennstoff mit einem Abbrand von 61000 MWd/t und einer Kühlzeit von 8 Jahren. Insbesondere wird das Auflösungsverhalten der Brennstoffe, das Extraktionsverhalten im 1. PUREX-Zyklus sowie das Verhalten des Neptuniums bei der Lösungsmittelextraktion diskutiert.

1. Introduction

Experiments on the extraction of high-burned fast breeder fuels are reported from Dounreay[1], Windscale[2], Fontenay aux Roses, La Hague[4] and Karlsruhe[3]. In Oak Ridge the dissolution of irradiated ceramic fuels has been studied for a number of years[5].

Recently, studies on dissolution and solvent extraction of high-burnup LWR fuels have been reported from Karlsruhe[6] and Oak Ridge[7]. The present paper describes the results of several reprocessing campaigns on LWR, Pu-recycle, and FBR fuels of high burn-up which have been performed in the MILLI facility at Karlsruhe. Characteristic data of the fuels are presented in Table 1. One of the goals of these campaigns was to demonstrate the applicability of the PUREX process to the processing of power reactor fuels with high burn-up levels and short cooling times. Another goal was to demonstrate and test the chemical flowsheet proposed for large-scale reprocessing of LWR fuels, as discussed in the preceding paper[8].

2. The MILLI Facility

The miniature pilot plant MILLI is a partly shielded, critically eversafe, laboratory-scale facility designed for dissolution and extraction of highly irradiated fast breeder fuels[9]. The layout capacity is 1 kg fuel per day and per cycle, or 1 milliton, from where the name MILLI is derived. The facility is in hot operation since 1971. One dissolver and filter, the first "co-decontamination" and the second partitioning cycle are located in two hot cells (Fig. 1). The HC and the 1A mixer-settlers can be circumvented so that flowsheets with first-cycle separation can also be performed (Fig. 2). The third extraction cycle is contained in a

slightly shielded gas-tight glove-box. The extractor used are slab-type mixer-settlers, critically safe by geometry. The installed slab tanks and other equipment are also critically safe by geometry. Over a period of six years different experiments with highly active materials have been achieved in MILLI.

3. Fuel Dissolution

The fuel pins were cut into pieces of about 5 cm length, and were leached with boiling nitric acid. The dissolver solution was filtered over sintered metal filters of <14 µm or <1 µm pore size, and the residues collected, weighed, and analized for fissile materials content.

Uranium oxide LWR fuels from the Obrigheim (KWO) and Kahl (VAK) power stations were dissolved in 6 molar HNO_3 within 2 to 4 hours. Undissolved residues amounted to 0.2 to 0.3 wt-% of the fuel, with 0.2 to 0.36 % Pu-content, corresponding to 0.05 to 0.1 % of total Pu.

The UO_2-PuO_2 fuel irradiated in the Dounreay Fast Reactor (DFR) was of the "coprecipitated" type, i.e. the fuel had been manufactured by coprecipitation of U and Pu with subsequent calcination[10]. The fuel was essentially completely dissolved with 8 to 10 molar nitric acid within 2 to 3 hours[3]. Undissolved residues amounted to 0.3 to 0.7 % of the fuel, and were mainly composed of fission products and of products from the stainless steel cladding, in the following sequence of decreasing quantities: Mo, Ru, Fe, Ni, Rh, Tc, Pd, Sn, Zr. The fissile materials content of the insolubles was very low, i.e. U, 0.04 % of total U; Pu, 0.04 % of total Pu. The Pu/(Pu+U) ratios in the residues were 0.13 to 0.18, i.e. in the same order as in the fuel (0.15). An accumulation of PuO_2 in the insolubles was not observed. Throughout the whole dissolution process the Pu/U ratio was constant. There was no evidence

for a preferred dissolution of the more easily soluble uranium oxide. We consider the dissolution behaviour of this fuel as very satisfactory.

For analysis the stainless steel cladding was completely dissolved and its plutonium and uranium content determined. The content of plutonium and uranium in the hulls was between 0.02 to 0.04 % of the fuel. The Pu/(Pu+U) ratio was 0.13 to 0.16, again corresponding to the fuel composition.

In experiments with small samples of FBR fuel fabricated by mechanical blending of UO_2 and PuO_2, burn-up 100000 MWd/t, about 1,5 % of the total Pu remained undissolved after 6 h leaching in 10 molar nitric acid. We consider this result as not satisfactory.

Additional dissolution experiments were done with unirradiated and irradiated UO_2-PuO_2 plutonium recycle fuels. The fuels were of the "mixed-oxide" type, i.e. they had been manufactured by mechanical blending of UO_2 and PuO_2 powders. Material with different grain size was investigated. Some samples had been fabricated without pretreatment, the others with an additional pretreatment. The fuel contained about 2 % and 3 % plutonium respectively. Irradiation was performed in the Obrigheim power station.

Dissolution was achieved in boiling nitric acid of different concentrations. When dissolved in boiling 10 molar nitric acid, unirradiated material fabricated without pretreatment resulted in a not negligible amount of undissolved plutonium. With fuel of at least 25000 MWd/t burn-up, the amount of insoluble Pu was reduced to ca. 2 % of the total Pu, but even this result cannot be considered as satisfactory. The insoluble residues could be completely dissolved with 10 molar nitric acid containing 0.1 moles/l hydrofluoric acid. However, due to the well-known problems inherent with HF, we do not recommend to use HNO_3-HF as a dissolution reagent in a large-scale reprocessing plant.

Dissolution experiments with unirradiated samples of another UO_2-PuO_2 fuel type, which had been fabricated with an additional pretreatment, showed a much better dissolution behaviour. In this case, <2.5 % of the fuel remained undissolved with 10 molar nitric acid. Since the experiments reported above, and other published data[5], indicate that the dissolution behaviour of UO_2-PuO_2 fuels is improved by irradiation, we believe that this result can be considered as encouraging.

4. First Extraction Cycle

Particular attention was given to the examination of the highly-active first extraction cycle since difficulties with this cycle have been reported when high-burnup fuels were processed. A major cause for the reported difficulties is the formation of interfacial "cruds", i.e. insoluble, slimy materials which may lead to irregular extraction behaviour or even to plugging of extraction equipment. The cruds are composed primarily from fission product zirconium and from the TBP radiolysis products, dibutyl and monobutyl phosphoric acids (HDBP and H_2MBP). Moreover solid fine particles which have not been removed from the feed solution tend to accumulate with the cruds. In the French AT-1 pilot plant at La Hague, which is equipped with mixer-settlers, crud formation in the first contactor was observed during reprocessing of FBR fuels; as stated by Boudry and Miquel[11], "the processing of oxides, irradiated to more than 50000 MWd/t, in mixer-settlers without eliminating or complexing the zirconium, is quite out of the question". Tc counteract this effect, complexation of the zirconium by fluoride ion is successfully applied in the AT-1 plant[11]. In the German WAK pilot plant at Karlsruhe, which is likewise equipped with mixer-settlers, processing of LWR fuels with 15000 to 20000 MWd/t burn-up caused severe problems due to the accumulation of cruds in the first mixer-settler, which finally was plugged so that shut-down of operation became

necessary[12]. The problems could be much reduced by a reconstruction of the mixer-settler[13]. Nevertheless, from the much better performance of pulsed columns in the processing of high-burnup fuels which is reported from the Eurochemic plant at Mol, Belgium[14], it has been concluded [15] that pulsed columns are superior to mixer-settlers in the processing of highly radioactive solutions.

In the MILLI, which due to its small throughput is also equipped with mixer-settlers, similar deleterious effects could be observed with high-burnup fuels. This experience, together with the experience from other plants reported above, motivated us to seek for a simple chemical solution of the crud problem, but avoiding use of strongly corrosive reagents like fluoride. When DFR fuel of 61000 MWd/t burn-up was processed in 1974 using a flowsheet with low organic loading, plugging of the HA contactor occurred which forced to shut down the operation[3]. However, using a "high-load" flowsheet, the campaign could be finished without any further operational inconvenience[3]. The principle of this flowsheet is to use a high loading of the organic phase, in excess of 75 % at the HA product outlet, and a high acidity of at least 3 moles/l HNO_3, in the HA contactor.

Parallel to the development of the new flowsheet, a study was undertaken on the solubility and formation of zirconium dibutyl-phosphate compounds[16]. As has long been known, zirconium distribution is enhanced by HDBP, but the enhancement by HDBP is decreased when uranium is added; zirconium distribution coefficients from 3 molar HNO_3 as a function of the HDBP concentration in the 30 % TBP/n-alkane solvent are presented in Table 2.

The distribution of HDBP between 3 molar HNO_3 and 30 % TBP/n-alkane (Table 3) is strongly increased by the presence of zirconium, and less strongly by the presence of uranium. In the presence of both Zr and a large excess of U, the HDBP distribution coefficients are suppressed to approximately the level which is found with uranium alone.

The zirconium dibutylphosphate precipitate which is formed in HNO_3-$UO_2(NO_3)_2$-TBP-n-alkane two-phase systems, has a composition between $Zr(NO_3)_2(DBP)_2$ and $Zr(OH)(NO_3)(DBP)_2$. The solubility of this precipitate in aqueous solutions (Table 4) is low but increases with increasing acidity and, more pronounced, with increasing uranium concentration. In the organic phase (Table 5), the solubility of the precipitate is higher than in aqueous solutions by a factor of 20 to 100, and depends on the HNO_3 concentration while the influence of the uranium concentration is not pronounced. The present solubility data are in good agreement with those reported by Davis and Carmichael[17].

The formation rate of the precipitate in a two-phase system is low. Fig. 3 presents a picture of the amount and rate of precipitation for different HNO_3 concentrations. The Zr:HDBP ratio used in these experiments was 40 % in excess of the "stoichiometric" 1:2 ratio. Both the amount and the rate of formation of the precipitate decrease with increasing nitric acid concentration.

Fig. 4 shows the influence of uranium on the amount and rate of precipitate formation from a 3 M HNO_3 - 30 % TBP/n-alkane two-phase system. In the presence of 220 g U/l both the amount and rate of precipitate formation is low while in the absence of uranium a much greater part of the zirconium is precipitated. Since HDBP is consumed by the precipitation, the distribution coefficient of the dissolved zirconium is decreased during precipitate formation.

"Cold" counter-current experiments with synthetic solutions in laboratory-scale mixer-settlers were performed with feed solutions containing 240 g U/l and 0.7 g Zr/l at different acidities, and with 30 % TBP/n-alkane extractant containing 200 mg HDBP and H_2MBP/l. Cruds were formed with low acidities and with low uranium loadings of the organic phase, but could be suppressed when the aqueous acidity was kept at 3 to 4 moles HNO_3/l, keeping at the same time the organic uranium loading

high. A high acidity is also favourable with regard to low plutonium losses. The upper limit of solvent loading is set by possible plutonium losses. It was found that a loading of 100 g uranium per liter organic phase (ca. 80 % saturation of the TBP) is still tolerable. With higher loadings, internal build-up of plutonium in the extractor starts to become significant, which if the loading is further increased, finally leads to plutonium losses with the aqueous raffinate.

For the LWR fuel flowsheet discussed in the preceding paper[8], we have therefore fixed the solvent loading to <100 g U+Pu/l at the HA product outlet (HAP solution).

The first test of this flowsheet with a true high-burnup fuel was performed in 1974 with FBR fuel of 60000 MWd/t burn-up and ca. 8 years cooling time, see "DFR(I)" campaign in Table 1 [3]. In this campaign a first-cycle codecontamination flowsheet was applied (HA-HC contactors). In order to demonstrate the benefits of the new flowsheet, two different conditions were tested for the first cycle:

(a) "low load" flowsheet: 52 g/l U+Pu in HAP (42.6 g/l U, 9.3 g/l Pu), aqueous acidity over the HA contactor 2 to 3 moles HNO_3/l;

(b) "high-load" flowsheet: 110 g/l U+Pu in HAP (91.4 g/l U, 18.8 g/l Pu), aqueous acidity over the HA contactor 3 to 4 moles HNO_3/l.

With flowsheet (a), severe crud formation was observed in the extraction (HA) and in particular in the back-extraction (HC) mixer-settlers which caused hydraulic disturbances and finally a plugging of the equipment; after 30 hours the mixer-settlers could no longer be operated, and the plant had to be shut down. As expected, the decontamination achieved was poor, see Table 6.

The operation was resumed after thorough cleaning of the plugged equipment with the "high-load" flowsheet (b). No further interferences by crud or other problems were observed over the whole campaign. The concentration profile (Fig. 5) shows an increase of the U and Pu concentrations near to the feed stage, demonstrating a slight build-up at this high loading. Nevertheless the relatively high plutonium loss of ca. 0.4 % in the aqueous raffinate appears to be not a consequence of the high loading, because the low distribution coefficients of <1 in the last three extraction stages point to the presence of some inextractable Pu species as the cause for these losses.

Subsequent demonstration tests of the flowsheet have been made with LWR fuels, see Table 1. In these cases, the first cycle was run with U/Pu partitioning (HA-1AS-1B-1C mixer-settlers). The campaigns were run with fuel charges of 10 to 15 kg, with operation times of the first cycle up to 10 days. In all cases, crud accumulation in the mixer-settlers remained low, and did not cause interference of the operation. As an example, a concentration profile is shown for the "KWO(II)" campaign in Fig. 6. With 105 g/l U+Pu in the HAP, no evidence for Pu accumulation in the extraction part of the HA mixer-settler is found. The plutonium loss with the aqueous raffinate (HAW) is 0.04 %. The overall decontamination factors obtained for the different campaigns are listed in Table 7.

5. Behaviour of Neptunium

The path of the neptunium has been followed during the KWO campaigns.

The calculated Np content was 440 to 460 mg Np per kg fuel. In the KWO(I) and KWO(II) campaigns after dissolution 410 to 430 mg Np/kg fuel were found (Table 8), which is in good agreement with the calculated value.

Ten years ago we studied the quantitative recovery of the neptunium[18], because of the predicted applications of neptunium as a raw material for Pu-238 production. However, no demand exists at present for neptunium as a valuable product. In contrast, there is nowadays the demand for quantitative removal of neptunium, in order to meet the specifications of the products uranium and plutonium. These specifications are

<1 ppm Np in uranium
$<10^3$ ppm Np in plutonium.

The Np decontamination factors (DF) needed are

>500 in uranium
>50 in plutonium.

There is a great incertitude about the behaviour of neptunium in a specific reprocessing plant, due to the complicated process behaviour of this element[19]. During the dissolution of the fuel, due to the presence of NO_2^- neptunium is mainly in the pentavalent state. Prolonged boiling of the solution leeds to removal of NO_2^-, and to oxidation of Np-V to the well extractable Np-VI. Depending on the dissolution conditions the ratio Np-VI : Np-V varies. At the high acidity applied in our first extraction cycle (Table 9) only about 10 % of the neptunium is removed with the aqueous raffinate (HAW) while ca. 90 % is extracted with the products. In the organic extractant concentrations of $<3 \cdot 10^{-3}$ moles/l nitrous acid were measured. At concentrations of this size, nitrous acid promotes the formation of extractable Np-VI[20].

The distribution behaviour of neptunium in the U/Pu partitioning step, which in the MILLI normally is performed with U-IV nitrate, is not uniform. It is known that the reduction with U-IV of Np-VI to Np-V is fast, while the Np-V $\longrightarrow$ Np-IV step is slow. In "cold" counter-current laboratory tests with synthetic solutions about 70 % of the neptunium was in the uranium and

30 % in the plutonium stream after partitioning with U-IV. In the tests with highly irradiated KWO fuel, between 50 and 85 % of the extracted neptunium was found in the uranium stream (Table 9). The neptunium values given in this and the following tables are overall values of one campaign on the basis of analysis from tank inventories.

The second uranium cycle serves primarily for the removal of plutonium from uranium[8]. Plutonium is reduced with hydrazine-stabilized U-IV nitrate; up to 99.9 % of the plutonium present in the 2D feed solution are removed with the aqueous raffinate. Simultaneously Np-VI is reduced to lower valencies. Depending on the organic to aqueous flow rates, varying proportions of the neptunium are removed (Table 10) with the aqueous waste. With the "dilute" flowsheet which we propose for the second uranium cycle[8] overall DF values between 100 and 200 were obtained, while with a "concentrated" second cycle flowsheet a DF of about 10 for neptunium was measured[21].

Fig. 7 presents the concentration profiles of neptunium, plutonium, uranium, and nitric acid in the second uranium purification cycle of the KWO(II) campaign. The neptunium DF was 130 in this case, while the DF for plutonium was 150. An amelioration of these results was achieved by changing the acid concentrations in the extractor.

Removal of residual neptunium must be performed in the third uranium cycle. This can be achieved by the introduction of sufficient nitrous acid to produce inextractable Np-V.

With concentrations of HNO_2 in the TBP between 0.04 and 0.1 moles/l decontamination factors up to 10^3 for neptunium were achieved, see Table 11.

Addition of nitrous acid to the plutonium purification cycles yields adequate DF values for neptunium already in one cycle, see Table 12, KWO(II) campaign.

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Table 1: Data of fuels processed in MILLI

Reactor	VAK	KWO	KWO	KWO	KWO	DFR
Location	Kahl	Obrigheim	Obrigheim	Obrigheim	Obrigheim	Dounreay
Type[1]	BWR	PWR	PWR	PWR	PWR	FBR
Campaign	VAK(I)	KWO(I)	KWO(II)	KWO(III)	KWO(PuI)	DFR(I)
Year	1974	1975	1975	1976	1977	1974
Fuel type	UO_2	UO_2	UO_2	UO_2	UO_2-PuO_2	UO_2-PuO_2
Burn-up, MWd/t	18000	31000	37000	33000	max. 21000	max. 61000
Cooling time, years	2.5	1.8	2.1	0.68	1 - 2	8
% ^{235}U, initial	2.5	3.1	3.1	3.1	0.72	60
% ^{235}U, final					~0.5	~40
% Pu, initial[2]	0	0	0	0	2.5 and 4.1	15.0
% Pu, final[2]	0.5	1	1	1	1.9 and 3.1	15.1
Cladding[3]	Zry	Zry	Zry	Zry	Zry	SS

[1] PWR = pressurized water reactor, BWR = boiling water reactor, FBR = fast breeder reactor

[2] Percent of total metal U+Pu

[3] Zry = Zircaloy, SS = stainless steel

Table 2: Distribution coefficients of Zr(D_{Zr}) as a function of the HDBP concentration with 30 % TBP/alkane

$V_o : V_a = 1 : 1$

Aqueous sol.	HDBP mg per liter organic					
	0	10	100	200	1000	2000
0.6 g Zr/l 3 M HNO_3	0.006	0.018	0.038	0.071	0.58	2.0
0.6 g Zr/l 220 g U/l 3 M HNO_3	0.0003	0.0003	0.0006	0.001	0.005	0.01

Table 3: HDBP distribution coefficients

30 % TBP-alkane / 3 M HNO_3

$V_o : V_a = 1 : 1$

Aqueous phase		Organic phase mg HDBP/l			
U g/l	Zr g/l	20	200	1000	2000
0	0	17	17	17	17
0	0,6	120	130	400	precipitate
220	0	26	40	40	60
220	0,6	30	50	100	100 precipitate

Table 4: Solubility of zirconium dibutylphosphate in aqueous solutions at 20°C

M HNO_3	$Zr(OH)(NO_3)(DBP)_2$ mg/l	M HNO_3	U g/l	$Zr(OH)(NO_3)(DBP)$ mg/l
0	1.8	0	11	10.6
0.1	4.4	0	110	94
1	12.3	0	220	160
3	25.6	3	11	37
4	31.6	3	110	142
6	57.2	3	220	344

Table 5: Solubility of zirconium dibutylphosphate in 30 % TBP/alkane

M HNO_3	U g/l TBP	$Zr(OH)(NO_3)(DBP)_2$ mg/l
0	3	5340
0	93	8180
0.025	0	7150
0.02	114	6780
0.59	0	2100
0.60	0.6	2610

Table 6: Decontamination factors obtained in the HA mixer-settler with low and high organic loading, DFR(I) campaign

	Saturation of the 30 % TBP	
	low	high
U g/l	42.6	91.4
Pu g/l	9.26	18.8
	Decontamination factors	
Cs^{137}	3630	11400
Ce^{144}	100	>33000
Ru^{106}	3.5	500
Zr^{95}	10	310
γgross	700	$5.8 \cdot 10^3$

Table 7: Decontamination factors of the 1st cycle

Fuel (campaign) Feed activ.[x] (Ci/l)	VAK ca. 50	KWO(I) ca. 150	KWO(II) ca. 120	KWO(III) ca. 230
U product				
Zr-95	8×10^3	$3,5 \times 10^3$	7×10^3	4×10^3
Ru-106	$1,3 \times 10^3$	$2,0 \times 10^3$	$0,8 \times 10^3$	$0,6 \times 10^3$
Ce-144	3×10^5	_xx)	_xx)	_xx)
Cs-134/7	$1,5 \times 10^5$	$2,5 \times 10^5$	$1,5 \times 10^5$	$0,4 \times 10^5$
Total γ (Eγ ≥ 100 keV)	$1,6 \times 10^4$	$1,5 \times 10^4$	$1,0 \times 10^4$	$0,3 \times 10^4$
Pu product				
Zr-95	$0,9 \times 10^3$	$0,4 \times 10^3$	9×10^3	$0,3 \times 10^3$
Ru-106	$0,6 \times 10^3$	$1,5 \times 10^3$	$0,9 \times 10^3$	$0,8 \times 10^3$
Ce-144	$1,0 \times 10^5$	$0,6 \times 10^5$	_xx)	_xx)
Cs-134/7	$0,3 \times 10^5$	5×10^5	3×10^6	$1,3 \times 10^5$
Total γ (Eγ ≥ 100 keV)	$0,6 \times 10^4$	$1,0 \times 10^4$	$1,1 \times 10^4$	$0,1 \times 10^4$

x) Feed inventory of the fission products listed in the table

xx) Below limit of detection

Table 8: Analysis of Np in LWR fuels

Experiment	KWO(II)	KWO(III)
Burn-up (MWd/kg)	37	33
Np found (mg/kg fuel)	410	430
Np calculated (mg/kg fuel)	440-460	

Table 9: Np distribution (%) in the 1st partitioning cycle

Experiment	KWO(I)	KWO(II)	KWO(III)
Raffinate (HAW)	0.4 %	14 %	9 %
U product (1CP)	76 %	51 %	35 %
Pu product (1BP)	14 %	28 %	38 %

Table 10: 2nd uranium cycle
Np removal by U(IV)

Experiment	KWO(II)	KWO(III)	
	dil	dil.	conc.
Feed, U g/l	50	47	293
Extraction, V_o/V_{aq}	0.6	0.6	2
Scrub, V_o/V_{aq}	4.5 - 5.2	6	6
Scrub, U(IV) g/l	1.3 - 5	0.2 - 0.4	0.5 - 1
DF(Np), overall	125	200	10

Table 11: Np removal by nitrous acid
3rd uranium cycle

Experiment	KWO(I)	KWO(II)
U in org. phase, g/l	75	69
HNO_2 " , mmol/l	0.1 - 0.4	40 - 100
DF(Np), overall	70	10^3

Table 12: Np removal by nitrous acid
2nd plutonium cycle

Experiment	KWO(I)	KWO(II)	KWO(III) x)
HNO_2 in org., mmol/l	15 - 50	40 - 70	20 - 80
HNO_3 in aqu., mol/l	3	1.9	2
DF(Np), overall	7 - 14	330	30

x) disturbance by HDBP

List of figures

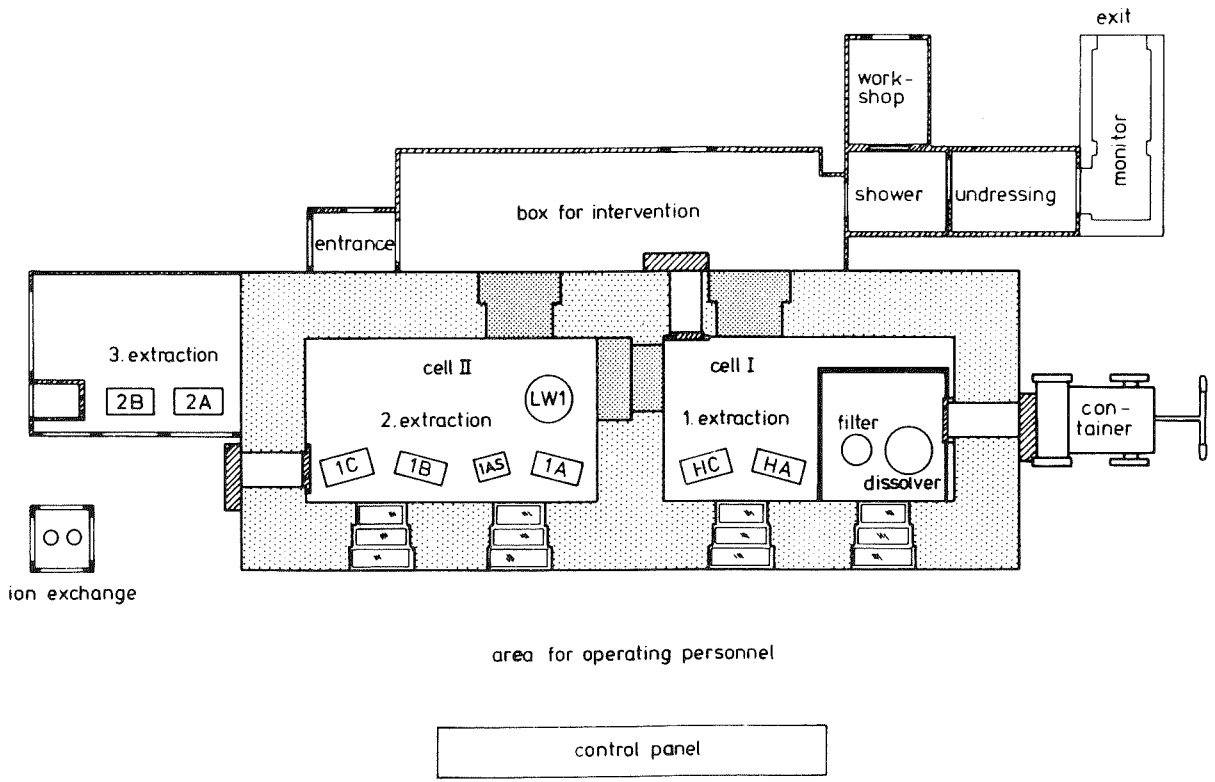

Fig.1 Outline of the MILLI facility

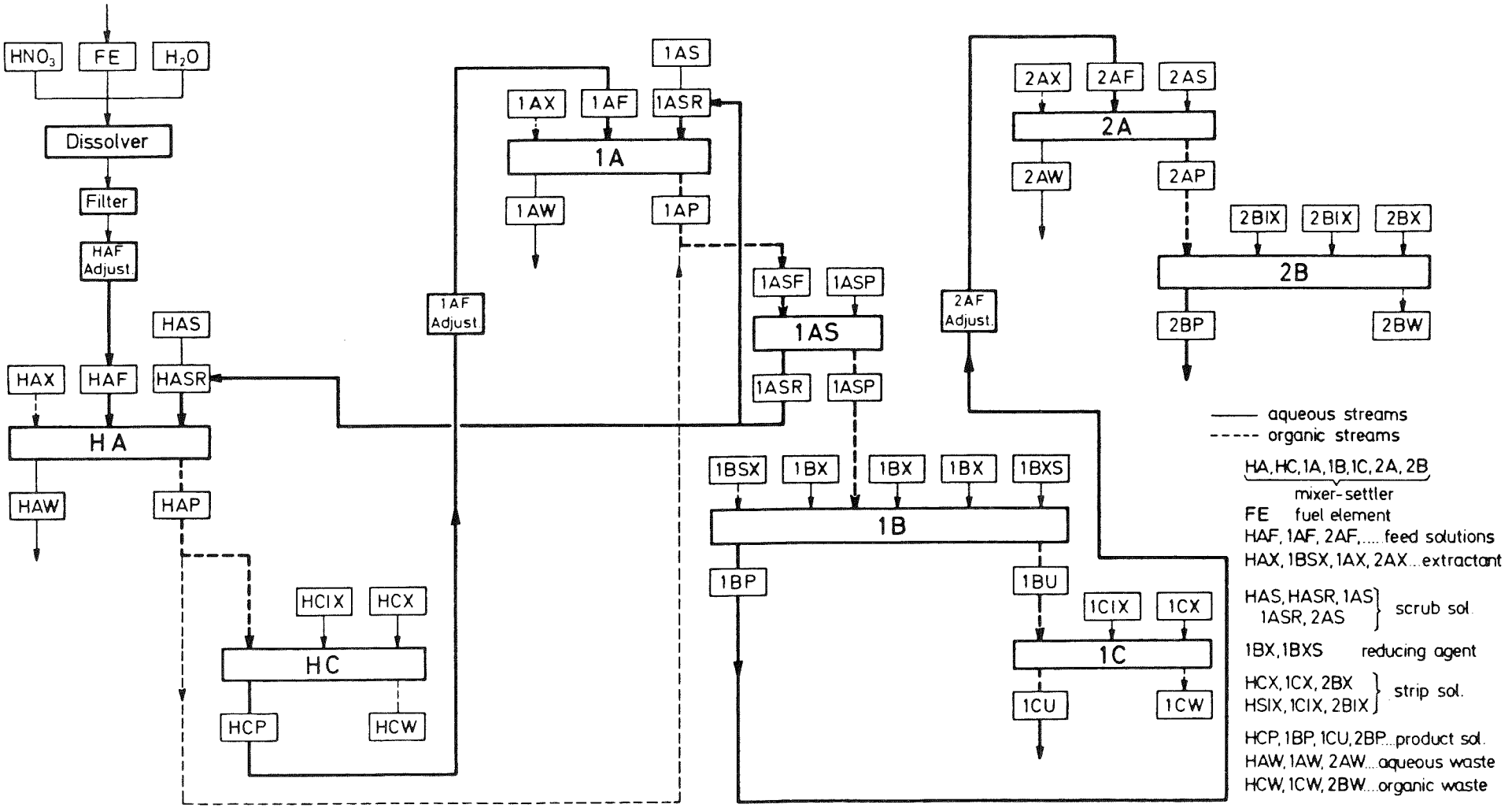

Fig. 2 Basic flowsheet of MILLI

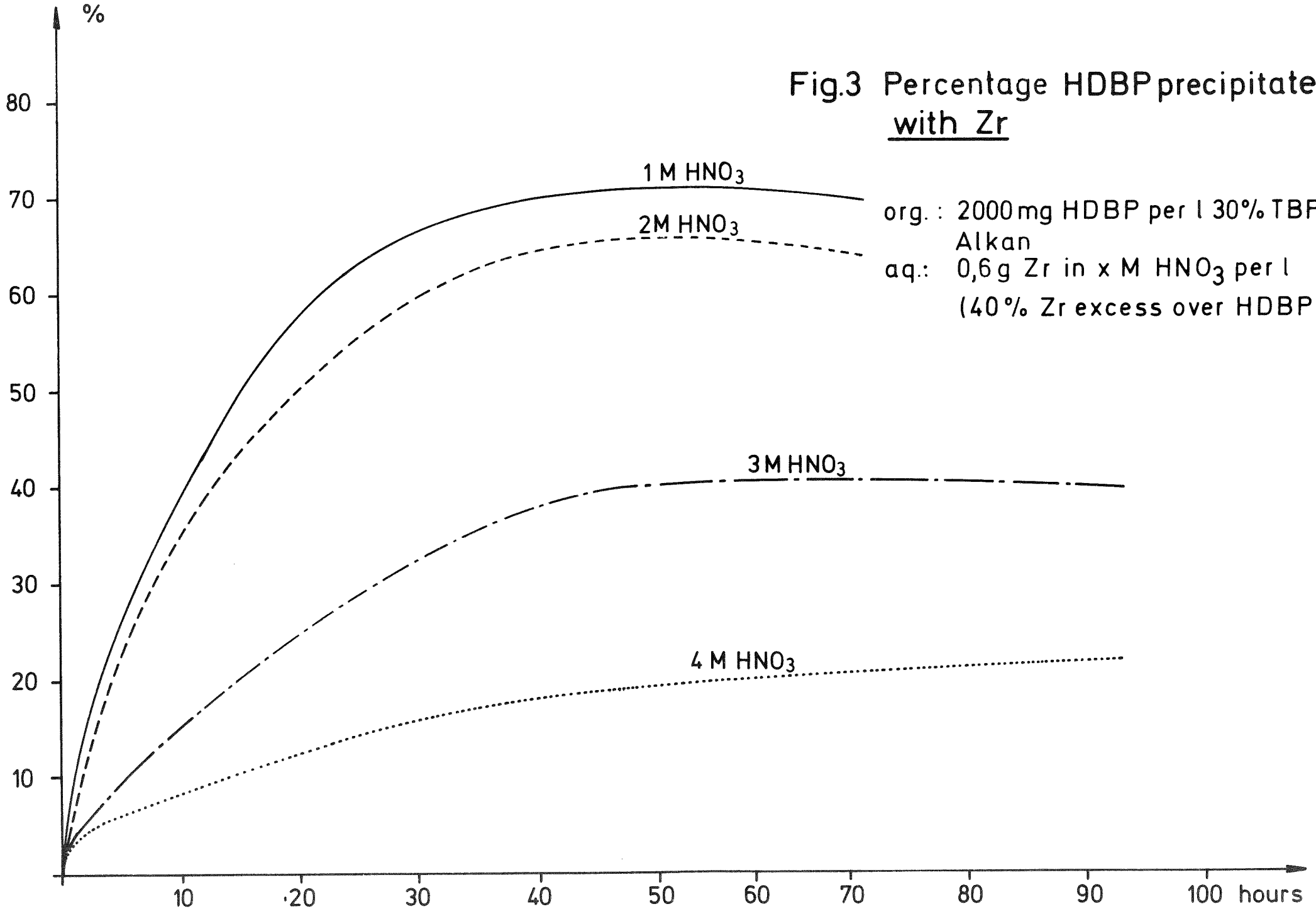

Fig.3 Percentage HDBP precipitated with Zr

org.: 2000 mg HDBP per l 30% TBP/ Alkan

aq.: 0,6 g Zr in x M HNO_3 per l (40% Zr excess over HDBP)

Fig.4 Precipitation of Zr with HDBP

aqueous phases

No.1 220 g U/l
0,6 g Zr/l
3 M HNO_3

No.2 0,6 g Zr/l
3 M HNO_3

$V_o : V_a = 1:1$

organic : 2000 mg HDBP per l 30 % TBP/Alkan

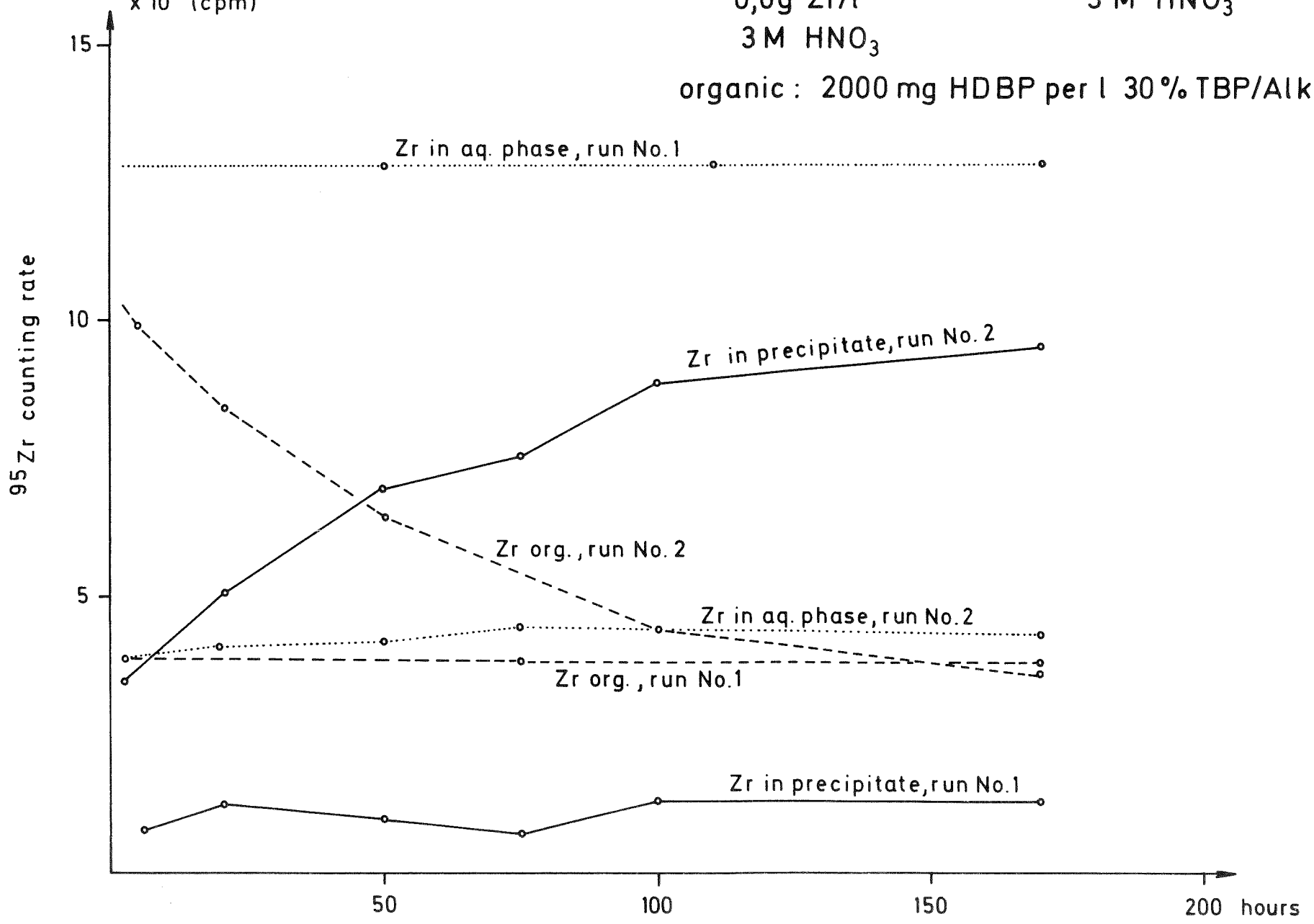

Fig.5 1st Extraction Cycle

Codecontamination (HA)

Fuel: Dounreay(~ 61000 MWd/t)

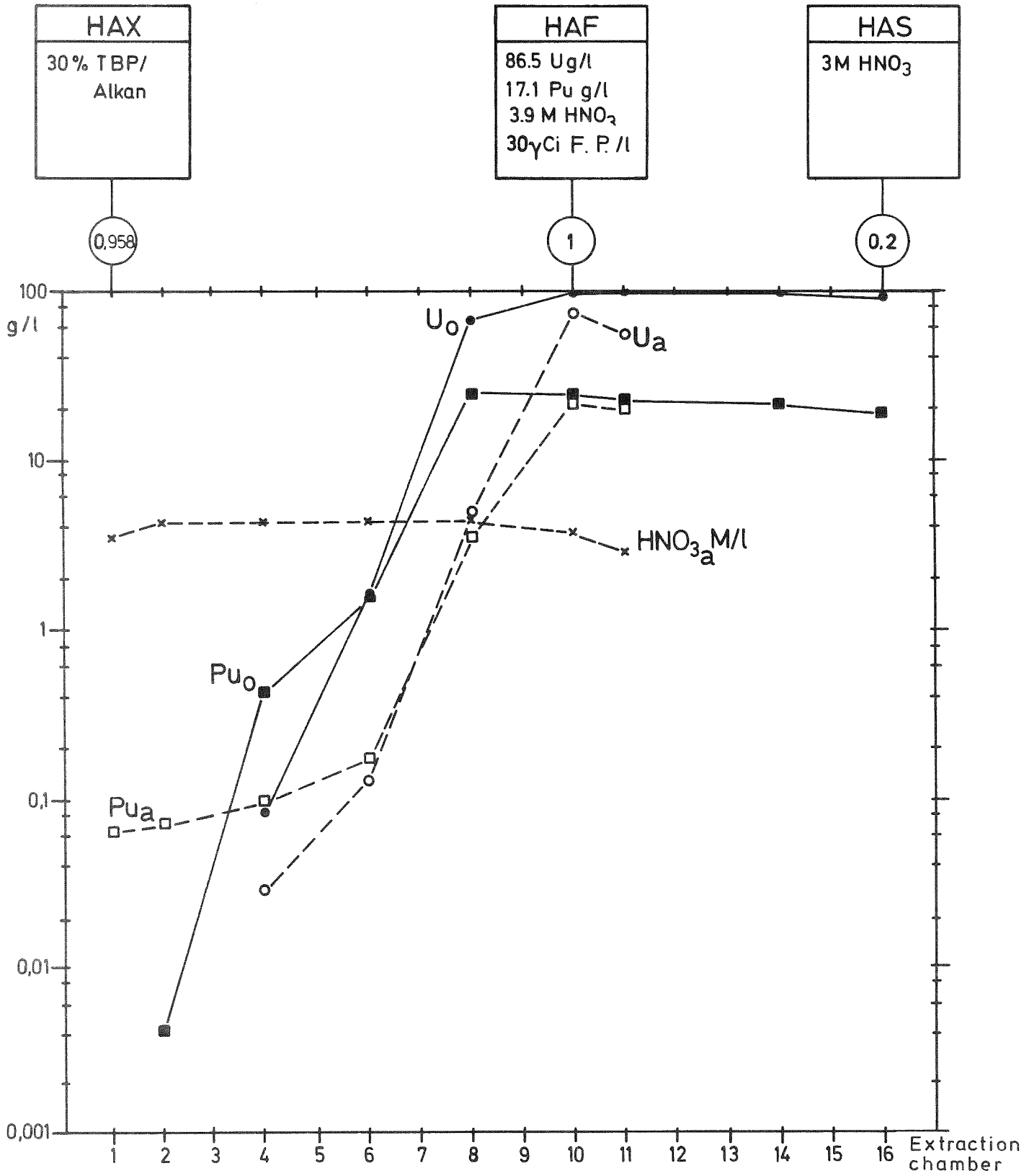

Fig. 6 1st Extraction Cycle

KWO II fuel, 37 MWd/kg

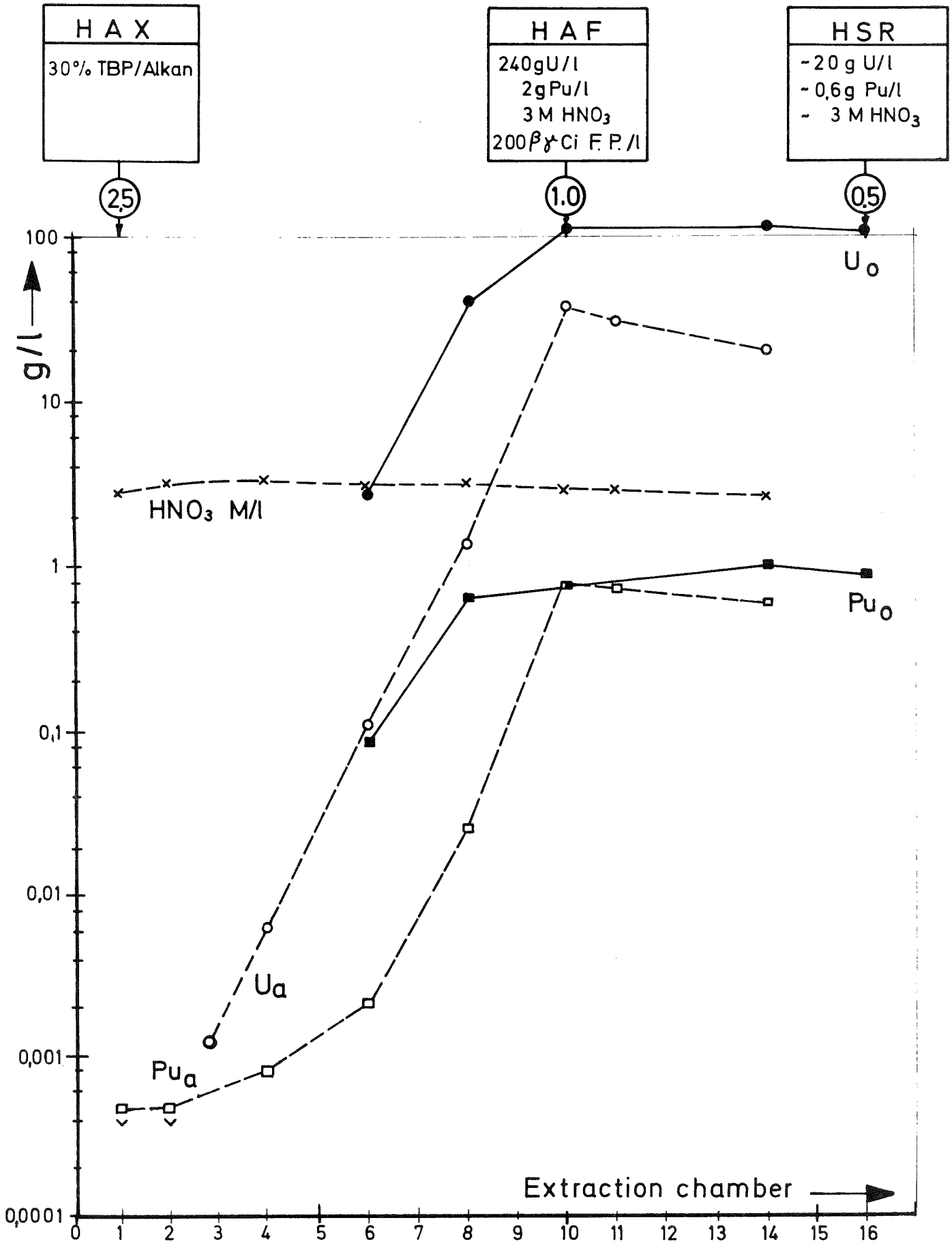

Fig. 7 2nd Uranium Cycle extraction and scrubing