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OPERATING EXPERIENCE WITH MINKA: U-PU SEPARATION IN THE PRESENCE OF TECHNETIUM WITH AN ORGANIC CONTINUOUS PULSED COLUMN

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ABSTRACT

In the MINKA pulsed column system installed at the Institut für Heiße Chemie U-Pu separation in an organic continuous BX column was investigated. This is a report about operating experience accumulated with this partitioning system and about the influence of technetium on the U-Pu separation efficiency. Moreover, this is a report about hydrazine degradation in aqueous Tc-bearing process solutions and the formation of the hydrazine daughter products ammonium and hydrazoic acid.

INTRODUCTION

Since 1985 flowsheet studies on the PUREX process have been performed at the Institut für Heiße Chemie of the Karlsruhe Nuclear Research Center in a miniature pulsed column system (MINKA).

During the period from 1985 until 1987 the extraction behavior of U, Pu and HNO_3 in the extraction and scrub columns was investigated in a first series of experiments conducted under off-normal process conditions, especially with a view to plutonium accumulation (1-6).

Since 1987 a second test series has been devoted to U-Pu separation in an organic continuous partitioning column with external

U(IV) feed (7). According to investigations in the United Kingdom (8), this mode of operation of the partitioning column exhibits an improved operating behavior and hence a higher separation efficiency than U-Pu separation in the aqueous continuous mode of operation as previously practiced in industrial scale reprocessing plants (9).

It is the purpose of the experiments to allow an intercomparison of the processes based both on the aqueous continuous mode of operation and on the electrochemical U-Pu separation process developed at the Institut für Heiße Chemie (10-13) and in this way to make selection of the optimum process variant more convenient to the users.

This paper is a report about operating experience accumulated with the organic continuous U-Pu separation column with external U(IV) feed and in the presence of technetium. The investigations concentrated on the examination of the influence exerted by technetium on the effectivity of U-Pu separation, the degradation with time passage of hydrazine, and the formation of hydrazoic acid and ammonium as daughter products of hydrazine.

EXPERIMENTAL

Interconnected Columns

Four pulsed columns were interconnected in MINKA to form a closed extraction cycle with a view to studying U-Pu separation under the conditions applicable to the first cycle. The process flowsheet is evident from Fig. 1. P11, P15, etc. designate the metering pumps for organic and aqueous process streams, respectively. Mass flowmeters (MM) or volume flowmeters (VM) and balances, respectively, are used as flowmeters. The transfer tanks are denoted B16, B36, etc.

MINKA is coupled to the other two experimental facilities of the Institute, MILLI (15) and PUTE (16), by fixed pipework for supply and discharge.

All columns of MINKA have an extraction length of 3.5 m. Along the column height temperature measurement and sampling systems for the organic and aqueous phases are installed at eight locations. Moreover, further process solutions can be fed into the columns at these locations (Fig. 1: column levels 1, 3, 7, etc.). It appears from Fig. 1 that column A is divided into a 3 m long extraction section and an 0.5 m long scrubbing section. The A column and the BX partitioning column are operated in the organic continuous mode, whereas the Pu scrubbing column (BS) and the U backextraction column (IC) operate in the aqueous continuous mode. Other data pertaining to the columns have been compiled in Tab. 1.

The MINKA extraction cycle comprises two two-stage Hollymott

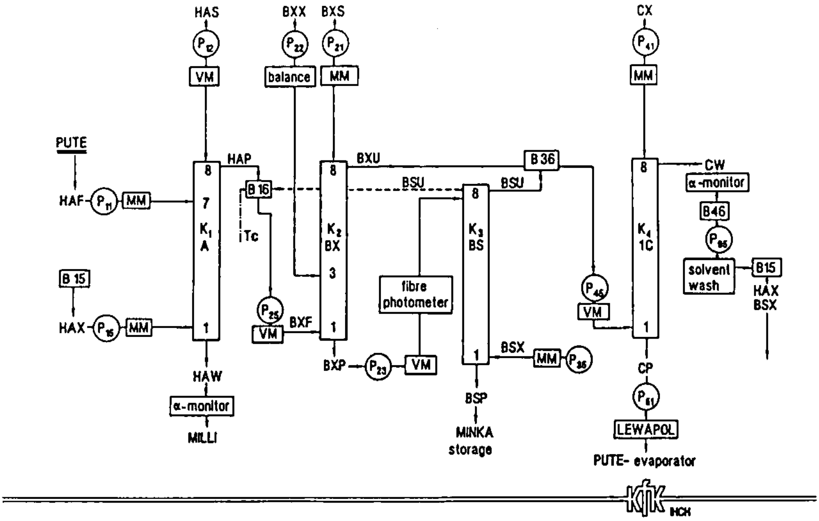

Fig. 1 MINKA

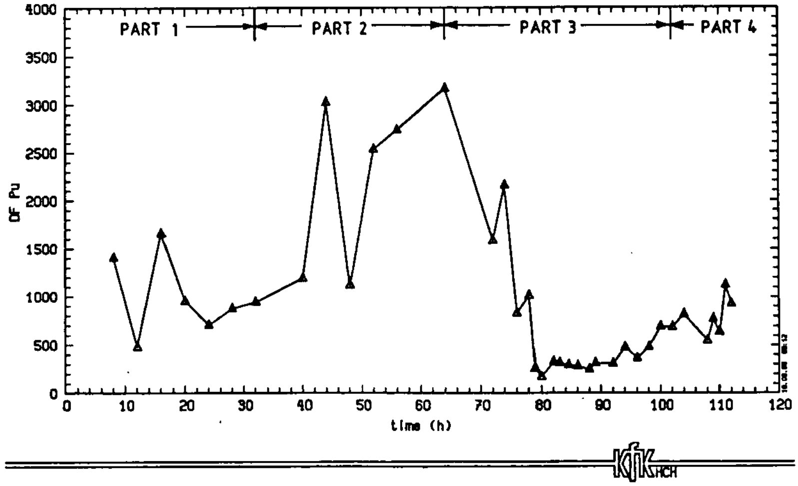

FIG.2 DFpu BX-COLUMN

Table 1 Design of MINKA columns

Column	A	BX	BS	IC
Function	(a) extraction (b) scrub	separation	Pu-scrub	U-strip
Cont. phase	organic	organic	aqueous	aqueous
Height (m)	(a) 3.0 (b) 0.5	3.5	3.5	3.5
Diameter (cm)	2.6	2.6	3.3	3.5
Sieve plates:				
Holes (mm)	1.5	1.5	3.0 nozzle	3.0
Space (mm)	30	30	50	50
Pulsation				
Frequency (min^{-1})	70	90	70	60
Amplitude (mm)	15	15	15	25

Table 2 Flowsheet conditions of U-Pu separation

Process Stream	Relative Flow Rate	Composition of the Solution					
		HNO_3 (M)	N_2H_4 (M)	U (g/l)	Pu (g/l)	Tc (g/l)	TBP (%)
BXF	1	0.01	-	80	0.8	0.08	30
BXS	0.14	0.1	0.2	-	-	-	-
BXX	0.03	1.0	0.2	140	> 70%U(IV)	-	-
BSX	0.17	<0.01	-	$<10^{-3}$	$<10^{-4}$	-	30
CX	~ 1.5	0.1	-	-	-	-	-

mixer-settlers for solvent cleanup where the solvent is scrubbed with sodium carbonate and subsequently with diluted acid.

The uranium product and later on also the plutonium product are freed from entrained extractant before they are concentrated in the evaporator of PUTE using sorption resins (Lewapol) (14).

Flowsheet Conditions

The composition of the organic feed solution to be supplied into the U-Pu partitioning column (Fig. 1: BXF) and the operating parameters of the BX column have been adapted to the conventional design for LWR fuel; see Tab. 2.

The A column of MINKA had to be operated under conditions not typical of PUREX in order to achieve the BXF concentrations. Moreover, Tc-separation during extraction and scrub in the A column were completely dispensed with. It was intended to record in this way the influence exerted by technetium on U-Pu separation under most adverse conditions. Therefore, technetium in the form of aqueous Tc(VII) stock solution was metered continuously into the organic product of the A column (Fig. 1: HAP) in the experiment. In the feed stream of the BX column (Fig. 1: BXF) a Tc concentration of 60-70 mg/l was established.

The U(IV) solution from BXX was metered into the BX column at one single feed point. Experiments on plutonium accumulation (6) had shown that under the conditions prevailing in the BX column, in the absence of U(IV), the maximum of Pu concentration occurs in the bottom part of the column. Therefore, the feed point for the BXX solution in the partitioning experiment was fixed at 1 m above the organic BXF feed (Fig. 1: BX column, level 3).

The experiments on U-Pu separation in the organic continuous BX column were performed in three parts. They differ from each other by the return of the organic phase from the Pu scrub column (Fig. 1: BSU) either into the organic feed stream of the BX column or into the C column and, moreover, by interconnection with the BS column.

The aqueous Pu product of the BX partitioning column (Fig. 1: BXP) was fed into the BS column during parts 1-3 of the experiment in order to separate more uranium. In the final part of the experiments the BXP feed into the BS column was discontinued and reoxidation in the quiescent aqueous phase of the BS column was observed in its temporal development. The individual parts of the experiment, the corresponding durations, and the respective process variant have been compiled in Tab. 3.

Flood Point of the BX Column

The flood points for the organic continuous BX column were determined in the 30% TBP-80 g U/l and 0.1 M HNO_3-0.2 M $N_2H_5NO_3$ systems. For the O/A = 7.2 phase ratio and a pulsation amplitude of

Table 3 Parts of the MINKA experiment

Part	Time (h)	Mode of operation	
1	33	BX, BS	as single columns, BXP transfer into the BS column without BSU recycling into BXF
2	31	BX + BS	columns interconnected, BXP transfer into the BS column and BSU recycling into BXF
3	39	Part 2	plus Tc
4	7	BX, BS	as single columns, no BXP transfer into the BS column and no BSU recycling into BXF

Table 4 Formation and consumption of N-compounds in the BX-BS columns in the presence of Tc

	BX column	BS column	BX + BS
Consumption			
N_2H_4/Pu	6.5 - 10 avg. 8.2	4.0 - 8.4 avg. 7.6	avg. 15.8
Formation			
HN_3/Pu	1.8 - 4.1 avg. 2.6	1.3 - 1.8 avg. 1.6	avg. 4.3
NH_4/Pu	2.0 - 4.8 avg. 3.7	1.7 - 2.6 avg. 2.2	avg. 5.9
HN_3/N_2H_4	0.21 - 0.37 avg. 0.28		
NH_4/N_2H_4	0.26 - 0.41 avg. 0.32		

15 mm specific throughputs of 160 and 120 l/dm^2h were achieved at 80 and 90 l/min pulsation frequencies, respectively (7).

To achieve a satisfactory U-Pu separation efficiency of the organic continuous BX column, fast and uniform dispersion of the aqueous BXX-U(IV) solution supplied is of primary importance. This was achieved in the MINKA-BX column at high pulsation frequency and high throughput (~ 90% of the flooding capacity) during a long period of testing.

These operating conditions of the BX column cannot be transferred to technical scale columns where as early as at the design stage suitable measures (dispersion promoters) must be taken which ensure prompt and uniform dispersion of the BXX reduction solution on a technical scale.

RESULTS AND DISCUSSION

Effectivity of U-Pu Separation

To evaluate the separation efficiency in the organic continuous system the decontamination factor (DF) for plutonium was referred to (31). The development versus time of this value is evident from Fig. 2. The decontamination factors measured in the first part of the experiment (0-32 hours, without BSU return into BXF) agree well with previous results (7). The decontamination factor was markedly improved by application of the BX-BS interconnected system and by BSU return into BXF. The Pu content in BXU diminishes from 0.8 mg Pu/l on the average in the first part of the experiment to 0.2-0.5 mg Pu/l BXU in the second part of the experiment.

It is evident from Fig. 2 that the decontamination factors for plutonium in these two parts of the experiment undergo abrupt changes. They may be caused by temporary, insufficient U(IV) dispersion whose cause, however, cannot be explained.

From the 64th hour on technetium was fed into the BX-BS system. As early as 2-3 hours after the onset of technetium feed very violent gas evolution started in the BX column which continued until the end of the experiment. At the same time, a clear reduction in the U-Pu separation efficiency was observed. The lowest decontamination factors for plutonium were measured 15-17 hours after the onset of Tc feed, namely DF = 200-250. The corresponding Pu content in BXU was 2-3 mg Pu/l. In the subsequent test interval (80-96 hours), a plutonium concentration of 1.5-1.7 mg/l was established in BXU which corresponds to a DF = 300-350. In the subsequent course of the experiment (96-104 hours) the plutonium content in BXU decreased from about 0.8 mg/l which can be seen from the rise in the decontamination factor for plutonium to values of 400-700.

In the final part of the experiment (104-113 hours) the BS column was decoupled from the interconnected system in order to observe reoxidation of the quiescent aqueous phase. This measure had no influence on the separation efficiency of the BX column. The plutonium content in BXU varied at that point in time between 0.7 and 1 mg/l corresponding to a DF of 900-400.

Degradation of Hydrazine

The development versus time of the hydrazine concentration in the aqueous product streams of the BX and BS columns has been plotted in Fig. 3. The reduction in hydrazine concentration with the onset of Tc feed (as from the 64th hour) is clearly visible. This elevated degradation of hydrazine results from the oxidation of hydrazine with technetium as the catalyst (18-20).

In the BX column about 50% of the hydrazine supplied degrade with a holdup time of the aqueous phase of about 8 min. The aqueous phase (BXP) had the following composition: ~ 1 M HNO_3, 3.5-4 g Pu/l, 15-20 g U/l, and 0.4-0.5 g Tc/l.

In the BS column the holdup time of the aqueous phase is 5-6 hours. In that column hydrazine continues to undergo slow degradation to a residual concentration of 5×10^{-3} mole/l while no noticeable plutonium reoxidation takes place by this degradation.

The development of hydrazine degradation depends on the initial concentration of hydrazine, the technetium content of the solution, its HNO_3 concentration, and the temperature (17-19).

The influence of the Tc concentration on the degradation of hydrazine at room temperature has been represented in Fig. 4 for two process samples collected from MINKA.

Sample 1 was taken from the bottom part of the BX column and sample 2 from the top part of the BS column. Sample 3 is a simulated solution (21). At the beginning of hydrazine degradation the samples had the following compositions:

Sample	M HNO_3	M N_2H_4	g Pu/l	g U/l	g Tc/l
1	1.07	0.123	3.9	17.7	0.43
2	1.07	0.116	4.5	1.2	0.24
3	1.43	0.116	0.7	6.2	0.33

It is evident from Fig. 4 that the degradation of hydrazine in the samples does not obey a simple equation describing the rate of degradation.

Within the range of concentrations up to about 2×10^{-2} mole/l the initial degradation in the presence of 430 mg Tc/l can be estimated formally to take $t_{1/2}$ = 80 min, and in the presence of 240 mg Tc/l it should last $t_{1/2}$ = 160 min. Further degradation of hydrazine then proceeds at a much faster rate.

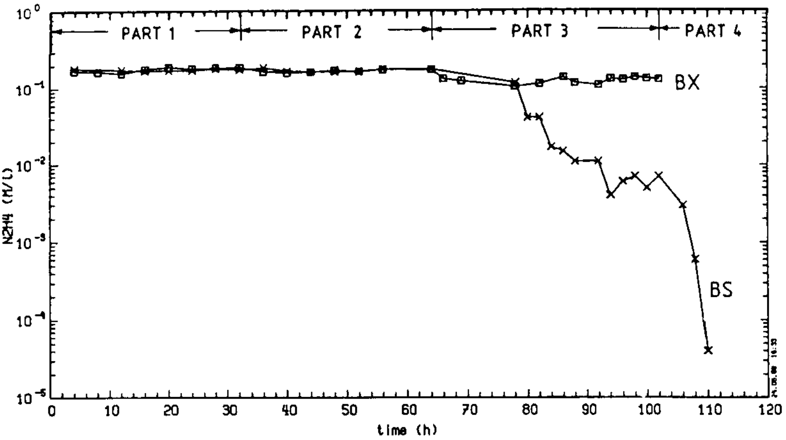

FIG.3 AQUEOUS CONCENTRATIONS OF N2H4 IN THE BX-BS COLUMNS

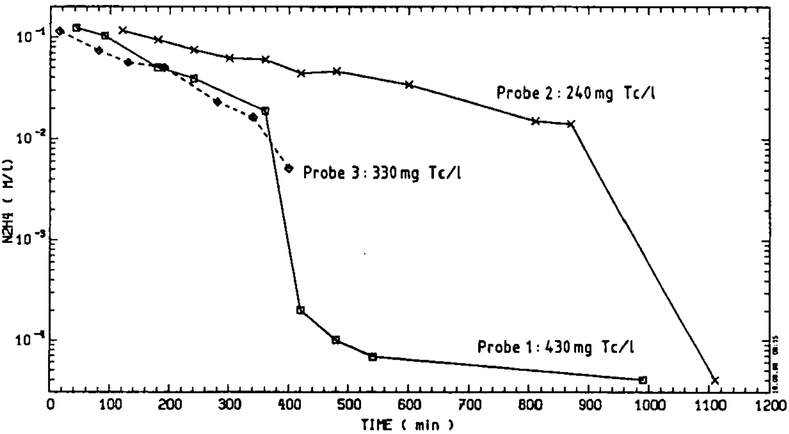

FIG.4 DESTRUCTION OF N2H4 IN BXP SOLUTIONS

From information contained in (17) the values calculated for the system are e.g. 1.2 M HNO_3, 0.1 M N_2H_4, 10 g/l U(IV), and 0.16 g Tc/l, half-life about 110 min as regards the initial degradation.

The degradation of hydrazine in the simulated solution containing 330 mg Tc/l is initially analogous to the values valid for the MINKA sample 1.

Besides the degradation of hydrazine, also the extraction behavior of Tc and Pu in the presence of 30% TBP/kerosene was investigated in that sample (21).

It is a striking finding that in that sample and with a U(IV)/Pu ratio of 8.2 and 1.4 M HNO_3 as well as 0.11 M N_2H_4, the reduction of plutonium proceeds at a slower rate and less independently than in the absence of Tc (22-26). Only after 30 min holdup of the sample the minimum distribution coefficients had been achieved for the two elements: $D = 0.04$ for plutonium and $D = 0.01$ for technetium. These values are higher than the comparable individual coefficients of distribution. For Pu(III) the values indicated for D in the literature are $D \leq 0.02$ (27-29) and for Tc(IV) $D < 10^{-3}$ (19). We suppose that the slower reduction of plutonium in the presence of technetium is the main cause of the poorer U-Pu separation efficiency in the BX column.

Reoxidation of plutonium and technetium must be expected to occur in the aqueous plutonium product solutions with progressing degradation of hydrazine. As shown in Fig. 3, the hydrazine concentration in the aqueous plutonium product solution during the approximately 5 hours of holdup of the solution in the BS column is reduced in the presence of technetium (part 3 of the experiment) from 0.15 M in BSP to $5\text{-}10 \times 10^{-3}$ M in BSP. On the other hand, the plutonium content in the organic scrub stream of the BS column (BSU) remained nearly constant during the 38 hours of the experiment (part 3), i.e. at 120-140 mg Pu/l. The corresponding BSP solutions contained 3.7-4.2 g Pu/l in addition to ~ 1 M HNO_3, $\leq$ 1 g U/l and ~ 0.4 g Tc/l as well as $< 10^{-2}$ M N_2H_4.

With the plutonium content of the BSU stream remaining constant in the third part of the experiment it is evident that under the conditions prevailing in the MINKA BS column no reoxidation of plutonium took place.

Only after the BS column had been decoupled in part 4 of the experiment, the plutonium content of the BSU stream increased substantially after 8 hours to attain 0.2 g Pu/l. The N_2H_4 concentration in BSP had dropped during that period to 5×10^{-5} M. After another 3 hours the plutonium content in BSU exceeded the value of 2 g/l.

Formation of Ammonium and Hydrazoic Acid

During catalytic degradation of hydrazine by nitric acid in the presence of technetium the reaction products formed are ammonium (NH_4^+) and hydrazoic acid (HN_3) (17-20).

Therefore, within the framework of the MINKA experiments, also the development of their concentrations versus time in the aqueous product solutions of the BX and BS columns has been analyzed.

In Figs. 5 and 6 the results have been plotted for NH_4^+ and HN_3, respectively.

With the onset of technetium feed (starting in the 64th hour) the NH_4^+ and HN_3 concentrations, respectively, in both product streams increase by almost one order of magnitude.

The partly abrupt changes in the development of concentrations and above all the decrease of the NH_4^+ values in the samples after 100 hours duration of the experiment cannot yet be explained for the time being.

In Tab. 4 specific values have been entered for the N_2H_4 degradation measured in MINKA and the formation of NH_4^+ and HN_3 associated to it.

For comparison with other variants of U-Pu separation (9-13) the degradation of N_2H_4 was related to the plutonium throughput and, moreover, the formation of the reaction products was related to the degraded amount of N_2H_4 and the plutonium throughput.

In the absence of technetium about 2 mole N_2H_4/Pu are consumed in the interconnected BX-BS column system. The formation of HN_3 attains a comparable order of magnitude.

In the presence of technetium 15.8 mole N_2H_4/Pu are consumed and 4.3 mole HN_3/Pu and 5.9 mole NH_4^+/Pu, respectively, are formed. On the average, 167 mmole/h N_2H_4 are fed into the BX column which give rise to the formation of 0.32 mole NH_4^+/N_2H_4 and 0.28 mole HN_3/N_2H_4.

The values indicated in the literature for the 1.2 M HNO_3, 0.1 M $N_2H_5NO_3$, 160 mg Tc/l system as the mole ratios of formation are 0.15 HN_3/N_2H_4 and 0.24 NH_4^+/N_2H_4, respectively (18). In plutonium bearing solutions with 1.5 M HNO_3, 0.6 M $N_2H_5NO_3$, 200 mg Tc/l and 2.5 g Pu/l no formation of HN_3 was detected, and for ammonium a mole ratio of formation of 0.5 NH_4^+/N_2H_4 was determined (20).

In further experiments performed in MINKA in the framework of the studies on the IMPUREX process (30) U-Pu separation in the organic continuous BX system will be studied with partial and substantial separations, respectively, of technetium.

Acknowledgement

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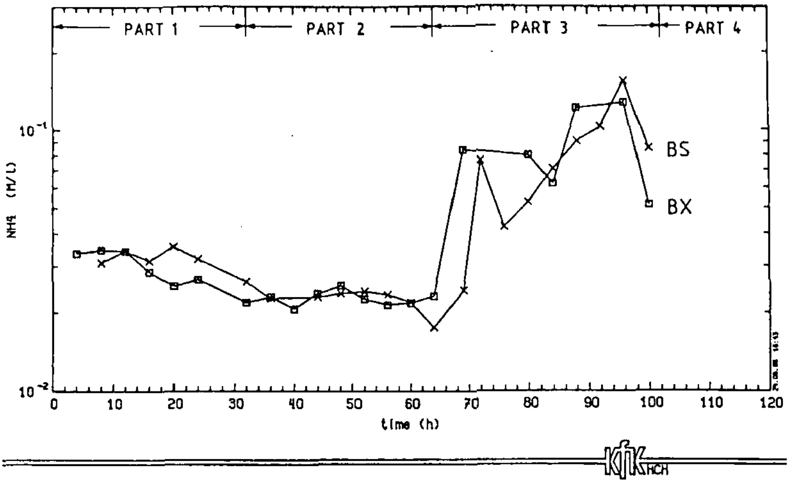

FIG.5 AQUEOUS CONCENTRATIONS OF NH4 IN THE BX-BS COLUMNS

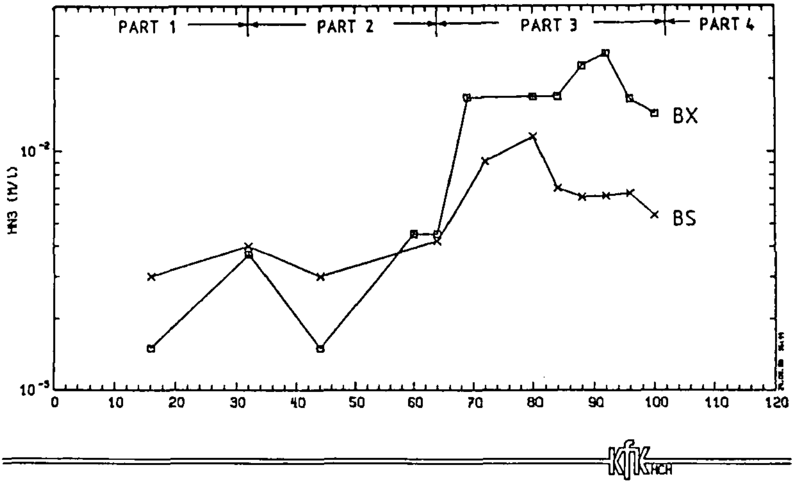

FIG.6 AQUEOUS CONCENTRATIONS OF HN3 IN THE BX-BS COLUMNS

tem and likewise the operators of the MINKA and PUTE team for their excellent work done in the conduct of the experiments. They would like to thank also Dr. D. Ertel and Dr. L. Stieglitz and their coworkers for the fast and exact analyses of the many samples collected from the process.

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