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Neptunium Decontamination in a Uranium Purification Cycle of a Spent Fuel Reprocessing Plant

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ABSTRACT

Recent trends in reprocessing of spent LWR-fuel necessitate improved neptunium decontamination in uranium purification cycles.

For the uranium purification cycles of the WAK plant and the EUROCHEMIC plant, respectively, the time dependent performance of the 2D-extractors has been calculated using the VISCO program for the mathematical modelling of solvent extraction processes. Results have been validated using data acquired in laboratory-scale extraction facilities and in the plant.

Intercycle evaporation and thus high uranium concentration in the aqueous feed solution results in a high organic-to-aqueous flow ratio within the extraction part of the 2D-extractor. The required neptunium decontamination is achieved by allowing a considerable amount of uranium to leave the extractor with the aqueous raffinate rather than with the organic product stream. Thereby an increased amount of process control is required.

As an alternative, neptunium can be sent directly to the aqueous raffinate stream by feeding diluted uranium solutions, received from the preceeding backextraction step, to the 2D-extractor. Then the uranium yield of the extraction step is high, while the amount of process control required is low.

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1. INTRODUCTION

For several reasons we expect that reprocessing of spent LWR-fuel necessitates improved neptunium decontamination in uranium purification cycles.

First, there is obviously an economic incentive to increase the burnup of spent fuel. Since in a power reactor, neptunium chiefly arises from β-decay of uranium-237 which itself is either bred by two sucsessive (n,γ)-reactions from uranium-235 or by a (n,2n)-reaction from uranium-238, the neptunium content of spent fuel will increase with increasing burnup to a power of about 1.5.

Second, recycling of uranium gained by reprocessing of spent fuel will contaminate the fuel cycle with additional uranium-236, a parent of neptunium. Thereby the neptunium content of spent fuel will still be increased. On the other hand by thermal recycling of plutonium as mixed oxide fuel the neptunium content of spent fuel would be somewhat decreased, since the neptunium parent nuclide uranium-235 would be partially substituted by plutonium.

A third and very important reason is the current practice of reducing losses of fissile and fertile material in reprocessing of spent fuel by recycling the raffinates of the purification cycles to the feed of the first cycle.

Since the first cycle extraction conditions are very strict, i.e. high decontamination of fission products and low losses of fissile material, neptunium has been shown to follow mainly the uranium product (1). Thus neptunium decontamination has to be achieved in the uranium purification cycles. The raffinate recycle will accumulate neptunium along this path until the losses to the highly active raffinate of the first cycle will balance the amount of neptunium fed with the spent fuel solution.

Both principal ways to achieve the required neptunium decontamination in a uranium purification cycle have been described (2). Either the uranium received from the preceeding back-extraction step is concentrated in an intercycle evaporator prior to being fed to the purification cycle - concentrated flowsheet - or it is fed directly, with due adjustment of acid concentration - diluted flowsheet.

We would like to discuss some dynamical aspects of these flowsheet alternatives. Throughout the discussion we rely on mathematical simulation of the extraction processes. The method has been validated with laboratory and plant data.

2. METHODS

The VISCO-Code for mathematical modelling of the PUREX-process

In a recent paper the present status of the VISCO-code for mathematical modelling of the PUREX-process has been reported (3).

We list the input data which will be required by the program:

- chemical composition of the extractor feeds,
- volume flow of the feeds,
- mixing chamber volume of the extractor,
- settling chamber volume of the extractor,
- average drop size of the dispersed phase in the mixing chamber,
- operating temperature.

If oxidation/reduction reactions were to be included, additional information would have to be supplied to the program.

We confined our study to dynamical aspects of uranium extraction, trace amounts of plutonium and redox-reactions have been omitted. For neptunium the worst case has been taken into account, that in the presence of reducing agents the oxidation state is + 4.

The neptunium concentration will always be low enough, so that its influence on the distribution coefficients of uranium and nitric acid can be neglected.

The program will then calculate the dynamical behaviour of the extracting species, i.e. the concentration changes of uranium, neptunium, and nitric acid in the mixing and settling stages will be displayed on a real time scale.

However, work is in progress to extend the program to neptunium reduction/oxidation kinetics as well as to macro amounts of the species.

3. RESULTS AND DISCUSSION

3.1 Analysis of the concentrated flowsheet

3.1.1 Flowsheet of the Karlsruhe Reprocessing Plant (WAK)

In the second uranium cycle of the WAK-plant trace amounts of plutonium and fission products as well as a significant amount of neptunium are to be separated from uranium since the only additionally applied purification step, filtration on a silicagel column, will provide a significant decontamination factor only for zirconium/niobium. A suitable flowsheet for that purpose has been published (4). It has been shown in laboratory experiments (2), that under flowsheet conditions neptunium is kept in the aqueous phase by loading the organic phase with uranium down to the first extraction stage (where the organic extractant enters and the aqueous raffinate leaves the extractor). With these conditions one has to allow for a five to ten percent loss of uranium to the raffinate stream.

Any attempts to reduce the uranium losses, for instance by a small increase of the extractant flow, would create extractive conditions for neptunium(IV). The species would accumulate in the extractor and cause an increasing contamination of the uranium product. The neptunium could be flushed from the extractor by provoking a uranium break through to the raffinate, for instance by a small decrease of the extractant flow. This behaviour of neptunium is shown in fig. 1 using WAK plant data where spent PWR-fuel, with a burnup of about 30 GWd/t, was processed.

We plot uranium concentration of the aqueous raffinate batches and neptunium concentration of the uranium product batches (after backextraction and product concentration) versus operating time in days.

Analysing the concentrated flowsheet by making use of mathematical simulation, one easily recognizes one of the problems with

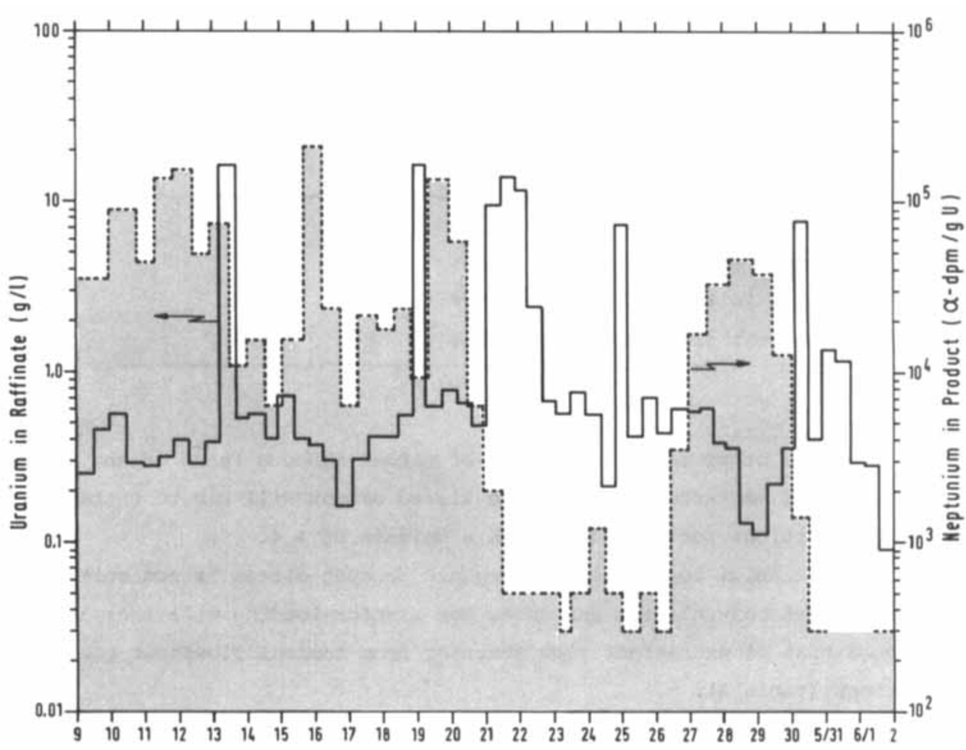


FIGURE 1. Second uranium cycle of WAK during a spent-LWR-fuel campaign:
uranium concentration (g/l) of the aqueous raffinate batches and neptunium concentration of the uranium product batches (decays per minute and gram uranium) versus time (date)

this flowsheet which is, keeping stable conditions for neptunium decontamination.

In table 1 we list the increased uranium losses to the raffinate upon slight changes of the feeds, which are either increase of aqueous feeds or decrease of organic feed respectively. We also list the time it takes until uranium leaves the extractor in the amount quoted. Obviously trouble with the scrub at the product side of the extractor will take the longest time to propagate to the raffinate side.

TABLE 1

Sensitivity of the Concentrated Flowsheet

deviation of feeds	uranium losses to raffinate	propagation time (h)
nominal flowsheet	5 %	-
uranium feed + 5 %	10 %	3
scrub + 10 %	8.5 %	6
extractant flow - 5 %	12 %	1.5

On the other hand, a decrease of either aqueous feeds or an increase of extractant flow by the listed amount will create extractive conditions for neptunium with a valence of + 4.

The uranium loading of the organic product stream is not suited for process control: for instance, the uranium loading will increase upon a rise of extractant flow starting from nominal flowsheet conditions (table 2).

As one would expect, the uranium concentration also depends on scrub flow as well as on scrub acid concentration (table 3).

However, the uranium concentration in either the organic or the aqueous phase of one of the lower extraction stages, which are close to the raffinate exit, is well suited for process control.

A second problem of the concentrated flowsheet is connected with processing of uranium feed batches which are out of specification limits, e.g. the uranium concentration being too low or the acid concentration too high, without disturbing the conditions for neptunium decontamination. In this case the ratios of organic to aqueous feed and scrub respectively have to be carefully selected.

Another problem will be the recovery of uranium (and plutonium) from the raffinate without reintroducing neptunium into the process.

3.1.2 Flowsheet of the Reprocessing Plant at Mol, Belgium (EUROCHEMIC)

The task of the second uranium cycle of the EUROCHEMIC plant corresponds to the one of the WAK plant, as does the chosen process

TABLE 2

Sensitivity of the Concentrated Flowsheet

extractant flow	uranium loading of organic product (g/l)
- 10 %	74
- 5 %	75
nominal flow	77
+ 4 %	78
+ 10 %	74

TABLE 3

Sensitivity of the Concentrated Flowsheet

deviation of scrub		uranium loading of organic product (g/l)
flow	+ 10 %	74
flow	- 10 %	80
acid concentration		
	+ 50 %	78
	- 50 %	76

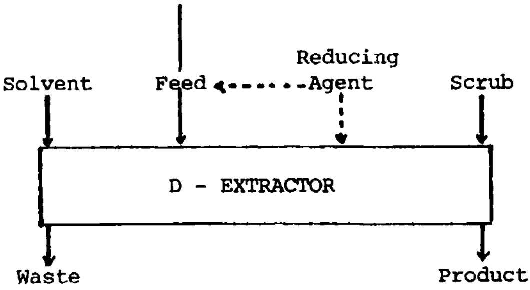
and the chemical flowsheet (5). However, there are some minor differences in the characteristic flowsheet data, which we compare in table 4.

Due to the slightly higher organic to aqueous flow ratio used in the extraction section of the EUROCHEMIC extractor, the uranium losses to the raffinate are significantly reduced as compared to the WAK plant flowsheet. However, conditions favorable for extracting neptunium(IV) are obtained. The differences in acid concentration of either feed or scrub are of minor importance. Moreover, high scrub acid concentration of the EUROCHEMIC flowsheet will extend the start-up procedure, since with good extraction conditions for uranium in the scrub section it will take a much longer time to

TABLE 4

Comparison of Characteristic Flowsheet Data of the Uranium Purification Cycles of the EUROCHEMIC and the WAK Plant, respectively

		EUROCHEMIC	WAK
flow ratio organic/ aqueous in section	extraction	2.7	2.1
	scrub I	} 6.5	3.6
	scrub II		5.1
acid concentration (mol/l)	feed	0.5	0.9
	scrub	1.0	0.1
addition of reductant to		feed	scrub
uranium concentration (g/l)	product	87	77
	raffinate	< 0.5	10



accumulate the equilibrium uranium hold-up than with low scrub acid concentration. We deduce this from mathematical simulation of the flowsheet.

The predictions for the EUROCHEMIC uranium cycle flowsheet were checked in a lab-scale mixer-settler experiment. In fig. 2 calculated concentration profiles are plotted for uranium, nitric acid, and neptunium, i.e. uranium concentrations in g/l, neptunium concentrations in percent of feed concentration, and acid concentrations in mol/l are plotted versus stage number. Measured organic and aqueous concentrations are given where available.

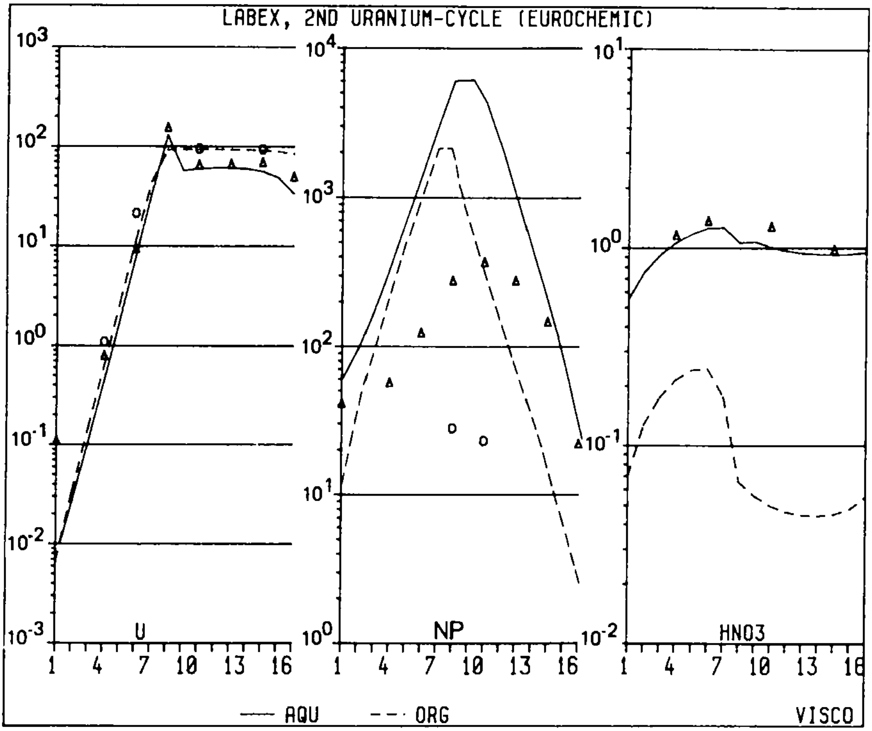


FIGURE 2. Second uranium cycle of EUROCHEMIC: lab-scale experimental check of mathematically simulated extraction profiles, i.e. calculated aqueous and organic phase concentrations of uranium (g/l), neptunium (percent of feed concentration), and nitric acid (mol/l) versus stage numbers. Measured organic (circles) and aqueous (triangles) concentrations are given where available.

Flowsheet:

stage 1:	solvent:	flow	1000 ml/h
stage 8:	U-feed :	flow	200 ml/h
		uranium	420 g/l
		HNO_3	0.5 mol/l
		U(IV)	1 g/l
		N_2H_4	0.1 mol/l
stage 16:	scrub :	flow	135 ml/h
		HNO_3	1.0 mol/l

Uranium and acid profiles:

Experiment is in close agreement with prediction.

Neptunium profile:

Calculation predicts a huge accumulation of neptunium and a decontamination factor of about 10 for the uranium product. In the experiment the neptunium contamination of the uranium feed happened to be very low which turned up some analytical difficulties. In the organic phase neptunium could only be found in those stages, where calculation had predicted the highest neptunium concentration. The decontamination factor varied between 2 and 5. However, the experimental aqueous profile is good evidence of the neptunium accumulation, in particular, at the end of the experiment, when sampling took place, there is still more neptunium fed to the extractor then is found in the exit streams. Thus neptunium accumulation had not yet ended.

Only the small difference between the amounts of neptunium being fed to and actually leaving the extractor, which can be recognized from stage 1 concentrations (fig. 2), will further increase the neptunium inventory of the extractor. Obviously, it will take a long time to reach equilibrium.

In addition, we have found, that adding a reducing agent to the uranium feed (EUROCHEMIC) rather than to a scrub stream (WAK) will seemingly reduce neptunium to a valence state of + 4, thus one cannot profit from the higher decontamination factor, one would anticipate for slow reduction kinetics of the reaction neptunium(V) → neptunium(IV).

3.2 Analysis of the Diluted Flowsheet

With the diluted flowsheet one will feed the uranium product of the preceeding back extraction step directly to the following extractor, after due acid adjustment. Thus with the high aqueous flow the ratio of organic to aqueous flow will be close to or less than 1. Under these conditions neptunium(IV) will no longer be accumulated significantly but sent to the raffinate while uranium may be extracted with high yield. However, addition of reducing agent (e.g. uranium(IV)) is recommended to reduce and hence decontaminate trace amounts of plutonium and of neptunium(VI). The results of lab scale demonstration runs have been reported (6).

In one of these runs, uranium was purified in a second cycle. Spent LWR-fuel with a high burnup has been processed through a first cycle. The first cycle uranium product without intercycle evaporation made up the feed solution for the experiment.

In figure 3 we compare experimental and calculated results. Again we plot calculated concentration profiles, i.e. uranium concentrations in g/l, neptunium concentrations in percent of feed concentration, and acid concentrations in mol/l are plotted versus stage number. Measured organic and aqueous concentrations are given where available.

Uranium and acid profiles:

Again experiment is in close agreement with prediction.

Neptunium profile:

In the extraction section, the calculated neptunium profile shows an accumulation to about 200 percent of feed concentration. This is caused by the rather high scrub acid concentration, chosen for the second cycle experiment. We calculate a neptunium decontamination factor for the uranium product of about 50.

Neptunium decontamination experimentally turned out to be much higher. The experimental aqueous neptunium profile even is qualitatively different from the calculated one. We attribute the finding to a rather large amount of neptunium(V). However, the experimental organic neptunium profile qualitively agrees with the one calculated for neptunium(IV).

Sensitivity analysis of the diluted flowsheet is nearly insignificant. Table 5 shows what will happen if one changes the extractor feeds.

Obviously the organic phase provides sufficient capacity to compensate for the deviation of feeds. The uranium yield of the ex-

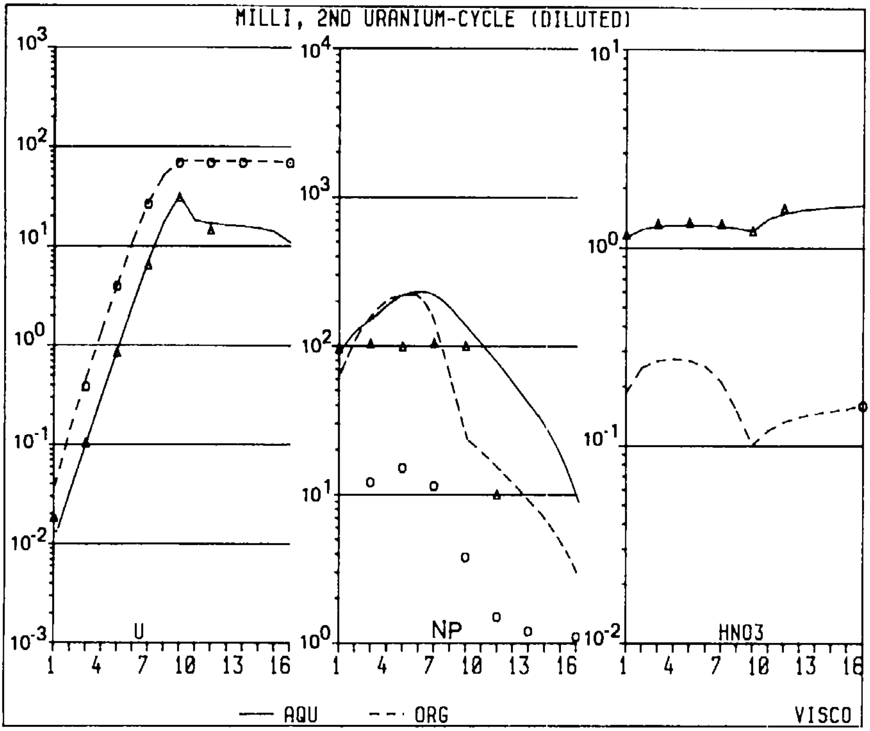


FIGURE 3. Second uranium cycle, diluted flowsheet: lab-scale experiment in a shielded facility with spent LWR-fuel (6) and mathematical simulation, i.e. calculated aqueous and organic phase concentrations of uranium (g/l), neptunium (percent of feed concentration), and nitric acid (mol/l) versus stage numbers. Measured organic (circles) and aqueous (triangles) concentrations are given where available.

Flowsheet:

stage 1:	solvent:	flow	0.73
stage 9:	U-feed :	flow	1.0
		U	50 g/l
		HNO_3	1.15 mol/l
stage 16:	scrub :	flow	0.16
		U(IV)	1.3 g/l
		N_2H_4	0.2 mol/l
		HNO_3	1.68 mol/l

TABLE 5

Sensitivity of the Diluted Flowsheet

deviation of feeds		uranium loading of organic product (g/l)
nominal flowsheet		74
uranium feed	+ 10 %	81
scrub	+ 15 %	74
solvent flow	- 10 %	82

traction remains 100 percent. An increase of scrub flow will give rise to a slight increase of uranium inventory in the extractor. Uranium/neptunium separation is not endangered by a deviation of feeds in the listed amount to either side of nominal conditions.

Therefore, with a correctly designed diluted flowsheet, the amount of process control is appropriately low.

4. CONCLUSIONS

It has already been shown - and operational experience with commercial reprocessing plants prove - that the required high neptunium decontamination in uranium purification cycles may be achieved by two different processes. They differ in that the uranium product of the preceeding cycle is either concentrated in an intercycle evaporator or it is not.

The concentrated variant requires an increased amount of process control to maintain stable conditions for neptunium decontamination. The methods to do that are well established. The actual challenge is to recover amounts of uranium (and plutonium) from the raffinates without returning neptunium back into the process (clearly the task has different aspects for the different flowsheets), or even more elegantly, to improve neptunium decontamination in the first highly active cycle of a reprocessing plant.

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