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Recovery of By-Product Actinides from Power Reactor Fuels

G. Koch

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Introduction

The principal task of the Institut für Heisse Chemie at Karls-
ruhe has been for some years, and will be for some more years,
to study the reprocessing of power reactor fuels, in particular
with respect to fast breeder reactors. In other words, the larger
part of the work of this institute has to do with the recovery
of uranium and plutonium from nuclear fuels. Now, although
plutonium is certainly a transuranium element, and certainly
a very important one, it is not intended to report on plutonium
recovery since it is understood to be outside the scope of this
symposium. However, we are also doing some research on different
aspects of transuranium element chemistry, one of them being
the recovery of by-product actinides from power reactor fuels,
which is covered in this report, and a second one being the
chemistry of metal-organic actinide compounds, which will be
discussed by Basil Kanellakopulos[1].

Actinide Production in Power Reactors

It is a well-known fact that rather large amounts of long-lived
neptunium, americium, and curium isotopes are formed during
reactor operation, particularly if the fuel receives a high
burn-up, as in modern light-water reactors and in future fast
breeder reactors. Table 1 shows a few examples of actinide
concentrations in fuels from two light-water reactors[2,3] and
from a projected sodium-cooled fast breeder reactor[4]. Future
production rates will of course much depend on the nuclear
power growth and on the reactor strategy followed in a parti-
cular country. Detailed calculations have for instance been
carried out in the United States for different assumptions
regarding the power growth and the reactor strategies[5].

Table 1: Neptunium, americium, and curium isotope contents
(grams per ton) in high burn-up fuels from two
light-water reactors (Yankee PWR, Vallecitos BWR)
and a projected sodium-cooled fast breeder reactor
(Karlsruhe Na-1 design study)[1-3]

Isotope	Isotope content (g/t) in fuel from				
	Yankee PWR[a]		Vallecitos BWR[b]		Na-1 FBR[c]
	burn-up 22,400 MWd/t calc.[2]	burn-up 24,300 MWd/t analyzed[3]	burn-up 16,070 MWd/t calc.[2]	burn-up 17,400 MWd/t analyzed[3]	core, burn-up ca. 86,000 MWd/t calc.[4]
^{237}Np	460	455	123	140	420
^{241}Am	122	119	43	45	606
^{243}Am	39	d)	d)	d)	133
^{242}Cm	1.2	1.0	0.29	0.39	24
^{244}Cm	7.6	7.9	0.12	0.48	15

a) 691 days after reactor shutdown
b) 476 days after reactor shutdown
c) At reactor shutdown
d) Not calculated or analyzed, respectively

However, due to the uncertainties inherent to these assumptions, even the most detailed calculations can, at present, give only the order of magnitude of the isotope amounts to be expected. A much simpler, and certainly less exact, order-of-magnitude estimate for the case of the Federal Republic of Germany is shown in table 2. The figures in this table have simply been calculated by making the following assumptions:

1. The nuclear power growth is as predicted by the pessimistic figures of the forecast report KFK-566[6], which are identical to the optimistic figures of the earlier report KFK-366[7].

2. The nuclear power production is done by advanced pressurized-water reactors fuelled with slightly enriched uranium without fuel recycle.

3. The thermal efficiency of the power plants is 32 %, the plant capacity factors are 0.7.

4. The fuel burn-up is 25.000 MWd/t, the isotope content is that calculated[2] for the 22.400 MWd/t Yankee PWR fuel (cf. table 1).

5. "Year of production" means, that the material is produced in the reactor. Before the isotopes become available, the fuel must be unloaded, cooled, and processed.

Although table 2 is indeed a very rough approximation only, it gives at least the impression that surprisingly large amounts of these actinides will be produced in the near future during normal power reactor operation. In fact, it appears that power reactor fuels will provide by far the most important source

Table 2: Estimated production (kg per year) of neptunium-237, americium-241/243, and curium-244 in power reactors in the Federal Republic of Germany

	Isotope production, kg/a			
Year	^{237}Np	^{241}Am	^{243}Am	^{244}Cm
1970	39	7.7	2.5	0.5
1975	120	31	9.8	2.0
1980	390	77	25	4.8
1990	910	240	77	15
2000	2,000	510	160	32

for transuranium elements up to curium. Considering the possible uses of these isotopes in technical and in scientific applications[8-10], it is certainly justified to study recovery processes for these by-products during or after fuel reprocessing.

Neptunium
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Neptunium is different from the two transplutonium elements in that it easily forms valency states which are extractable in Purex reprocessing systems. This means that neptunium may either be coextracted with the uranium and the plutonium, or may be

sent to waste and recovered from this source. Although experience in a number of plants shows that coextraction of neptunium in a Purex first cycle is far from being complete[11,12], this approach is attractive since it does not afford severe changes or additions to the plant equipment.

The first German reprocessing plant, called WAK[13], is now near to completion at Karlsruhe. This WAK is a prototype Purex plant with a capacity of 40 tons of Uranium oxide per year. Originally no provisions had been included for the recovery of neptunium. Later, in the frame of a long-range program commonly executed by Gesellschaft für Kernforschung (owner of WAK) and Gesellschaft zur Wiederaufarbeitung von Kernbrennstoffen (operator of WAK), it was decided to add a neptunium recovery unit based on a coextraction approach. Thus, a study on the behaviour of neptunium under WAK flowsheet conditions was undertaken by Werner Bähr[14], while counter-current runs were performed in cooperation with Wilhelm Ochsenfeld[15].

The first question was, what is the chemical state of the neptunium during fuel dissolution? The most conclusive results were obtained by spectrophotometric studies[14]. They showed that during dissolution of uranium dioxide and of uranium metal in nitric acid, all the neptunium is present in the pentavalent state. This may perhaps be due, at least in part, to the presence of large amounts of nitrous oxides during dissolution. However, if the dissolver solution is boiled for some time after complete dissolution, and the nitrous oxides are allowed to escape from the dissolver, oxidation to neptunium(VI) takes place, and is complete within a few hours.

Next, the extraction behaviour of neptunium(VI) in the presence of uranium was studied[14]. The results shown in fig.1 lead to the conclusion that under the flowsheet conditions of the WAK -

ca. 1.5 M nitric acid in the aqueous phase, ca. 60 % organic
loading in the scrub section, flow ratios organic by aqueous
of 2 by 1 in the extraction section and 6 by 1 in the scrub
section - essentially all of the neptunium(VI) will be extract-
ed. However, a cold laboratory counter-current run resulted
in a neptunium yield of only 54 % in the organic product,
although all the neptunium had originally been present as
neptunium(VI) in the feed solution[15]. Apparently some reducing
agent, presumably nitrous acid, is formed during extraction,
or is introduced with the process chemicals.

On the other hand, nitrous acid is used in the Hanford Purex
Plant to catalyze the oxidation of neptunium(V) to (VI) by
nitric acid[11]. Thus, the influence of varying concentrations
of nitrous acid and of uranium on the neptunium extraction
was studied[14], and was found to correspond to the results
obtained by Sidall and Dukes[16] in the absence of uranium.
As an example, fig. 2 shows the change of the neptunium
distribution coefficient with time at various nitrous acid
concentrations, starting with neptunium(V), at a constant organic
uranium loading of ca. 75 % and a constant aqueous nitric acid
concentration of 1.5 molar. In fact, the equilibrium distribu-
tion coefficients finally reached could well be correlated with
the equilibrium data given for uranium-free systems by Sidall
and Dukes.

In an attempt to raise the neptunium yield, the influence of
some oxidizing agents was studied[17]. In order to avoid the
oxidation of plutonium(IV) to (VI) and to suppress the oxida-
tion of fission products like cerium, the oxidant was intro-
duced into a lower stage of the HA mixer-settler, i.e. near
to the raffinate exit. Chromium(VI) and cerium(IV) both oxidize
neptunium(V) rapidly to (VI), and a counter-current run starting

with neptunium(V) in the feed, and introducing chromate into
the third-to-last settler chamber of the 16-stage mini-mixer-
settler, resulted in a neptunium yield of ca. 98 % in the HA
product. However, both oxidants have severe disadvantages, since
fission product cerium is rapidly oxidized to cerium(IV) by
chromate, which would lead to insufficient decontamination,
while cerium(IV) as the oxidant, because of its good extract-
ability, would move up to higher stages of the extractor and,
besides, would also exchange to some extent with fission product
cerium(III). Now, Dukes had found in 1959 that neptunium(V)
is also oxidized rather rapidly by pentavalent vanadium[18], and
in fact a number of counter-current tests introducing this
oxidant into the fourth settler chamber led to neptunium recoveries
of between 87 and 97 % in the HA product, even though all the
neptunium in the feed solution had been present in the penta-
valent state[17].

Next, the behaviour of neptunium in the 1B partition bank was
studied. In the WAK flowsheet, uranium(IV) nitrate is used
as the reductant for plutonium. Reduction of neptunium(VI) by
uranium(IV) is rapid only to the pentavalent neptunium[19],
while further reduction to neptunium(IV) is rather slow[20].
As a result, some of the neptunium will be present as non-ex-
tractable neptunium(V) in the 1B bank and thus will accompany
the plutonium, while some will be present as neptunium(IV) and
may accompany the uranium, in amounts which depend on the parti-
cular flowsheet conditions like acid concentration, flow ratios,
organic phase loading, temperature,and residence time. These
predictions were confirmed by counter-current runs in which
between 30 and 93 % of the neptunium went with the uranium while
between 7 and 70 % accompanied the plutonium. Nevertheless, we
feel that in the case of the WAK this is not so bad as it may

look at a first glance, since this plant accidentally involves
a rather fortunate flowsheet feature. The aqueous waste streams
of the second uranium and plutonium cycles of this plant are
combined in a common low-level waste evaporator, called 3W. This
means that in order to recover all the neptunium which went to
the 1B bank, both the uranium and the plutonium second cycle
have simply to be run in such a way that the neptunium goes to
the aqueous raffinate. Thus only minor changes in the second
cycle flowsheets will be necessary in order to direct the nep-
tunium to the 3W evaporator, from the bottoms of which the
element may then be recovered by anion exchange.

In conclusion, recovery of a considerable part of the neptunium
should be possible in the WAK, with only moderate changes to
the plan itself.

Americium and Curium
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In contrast to neptunium, these two elements are unavoidably
directed to the high-level waste during Purex reprocessing.
Recovery will thus have to start from this material, which means
that separate facilities will be necessary in order to do the
job. Up to now there are no plans in Germany for a commercial
recovery facility of this type. Our work on recovery processes
for these isotopes should thus be regarded as a pure development
work, the economic success of which is still questionable.
However, we are planning to build a facility called LISA in
which such separation processes can be demonstrated.

There is a different source of americium-241 which can provide
limited amounts of this isotope, that is the americium-241
formed during storage of plutonium. Normally, it will certainly

not be economic to process the stored plutonium just for the recovery of this americium, but there is one point in the plutonium fuel cycle where at least a minor part of this actinide can be recovered, that is from the scrap which arises during the fabrication of plutonium fuels. This scrap must be processed in order to recover the valuable plutonium, and here an americium recovery step can be provided. One way to recover the plutonium from the scrap is to dissolve the material (usually uranium-plutonium oxide) and to isolate the plutonium by anion exchange. The first portion of the ion exchange column effluent contains most of the americium, but only little uranium and plutonium. Thus a process has been devised for the recovery of the americium from this solution[21] which consists of the following steps:

The americium-rich part of the raffinate from the ion exchange column is evaporated to about 0.5 to 5 g/l americium. Uranium and plutonium are extracted away from the strongly acidic solution by 0.5 M tricapryl methyl ammonium nitrate (TCMAN) in an aromatic diluent, like Solvesso[22]. After removal of uranium and plutonium, the aqueous solution is adjusted to about 7 M ammonium nitrate and a pH of about 1.5 by the addition of ammonia and of solid ammonium nitrate. Americium is well extracted from this highly salted solution by 0.5 M TCMAN[23-25]. After scrubbing the organic phase with 7 M ammonium nitrate (pH ca. 2) to remove impurities, americium is stripped with dilute nitric acid. Finally, americium oxalate is precipitated and calcined to the oxide. Batch tests of this flowsheet with a minimum of multistage steps resulted in americium recoveries of more than 98 %, with a total impurity content of less than 1 %.

Returning now to the recovery of americium and curium from Purex high-level wastes, one major difficulty with this material is that a separation of trivalent actinides from lanthanides must

be accomplished. There is only a limited number of processes which do this job, some of them using highly corrosive reagents and high salting strengths, like the Tramex Process developed in Oak Ridge[26,27]. Moreover, a previous separation of the actinide/lanthanide group from the bulk of the impurities is usually necessary. At Hanford, where a recent campaign was carried out to recover americium and curium from the Shippingport blanket processing waste[28], this pre-separation of the actinide/lanthanide group was done by extraction with 50 % TBP from the highly salted Redox high -level waste, followed by a HDEHP extraction for further purification of this group. The isolation of americium and curium was then achieved by a modification of the Hanford ion exchange process. We feel that processes needing high salting and highly corrosive reagents will perhaps not be applied to economic routine processing facilities. Thus we were looking for some different approach.

Some years ago, Weaver and Kappelmann at Oak Ridge had developed an actinide/lanthanide separation process which they called Talspeak[29-31] and which seemed rather attractive, needing no corrosive materials nor any salting. This process is based on the preferential extraction of the lanthanides over the actinides by acidic organophosphorous compounds like di(2-ethylhexyl) phosphoric acid (HDEHP) from a solution containing a carboxylic acid, like lactic acid, and a polyamino polyacetic acid, like diethylene triamine pentaacetic acid (DTPA). Although a pre-separation of the actinide/lanthanide group was still involved, we felt that this step could be eliminated by using the flowsheet which is shown in fig. 3[32]. In this flowsheet, americium and curium are extracted in the 1A bank by HDEHP along with the rare earths from the high-level waste concentrate complexed by a complexant like citric acid. This is a conventional step which has successfully been applied in Oak Ridge[33] and in Hanford[34,35]. In the 1B bank, the actinides are partitioned away from the lanthanides by preferential backwashing of the actinides with a Talspeak-type solution (lactic acid plus DTPA, pH ca. 3). Finally, the rare earths are backwashed by nitric acid and sent to promethium recovery or to waste.

Judging from equilibrium data one could predict that the process should work, provided that there was no adverse kinetic effect, since slow extraction kinetics had been observed with some of the systems involved[29-31]. Thus we did some preliminary kinetic studies[32] which showed that the trivalent actinides and lanthanides reached equilibrium fast enough that essentially no kinetic inhibition of the process was to be expected. With other fission and corrosion products, slow extraction kinetics were found in some cases, but fortunately this will even aid in the decontamination of the americium/curium fraction. Let us take, as an example, the corrosion product iron. On the basis of equilibrium distribution coefficients, trivalent iron should follow the actinides in the extraction as well as in the partition step. However, since both the extraction of iron by HDEHP from citrate-complexed solution and its backwash by lactic acid - DTPA are slow, good decontamination from this metal is obtained.

The flowsheet has been tested in a number of counter-current runs which were performed with cold synthetic solutions. In table 3 the flowsheet conditions are shown under which the extraction and partition mixer-settlers were run. Fig. 4 presents the behaviour of the actinides and the lanthanides: coextraction in the 1A bank, and good separation in the 1B bank with americium and curium yields of about 99 %. In fig. 5, the behaviour of zirconium/niobium-95, ruthenium-106, and iron is shown. Decontamination factors obtained ranged from 400 for ruthenium, 500 for europium, 700 for iron up to more than 1000 for zirconium/niobium and cerium.

In conclusion, it seems that a one-cycle flowsheet of the type discussed may be a quite reasonable basis for a commercial recovery of americium and curium from high-level wastes.

Table 3: Flowsheet conditions for counter-current runs (R.E. = mixed light rare earths).

	Runs No.1 (Am), 2(Eu), 3(Ce)	Runs No.4 (Zr/Nb) 5(Fe), 6(Ru)	Run No. 7 (Cm)
1AF	0.05 M R.E. nitrates 0.25 M $NaNO_3$ 0.35 M Na citrate pH = 2.5 flow 120 ml/h	0.05 M R.E. nitrates 0.02 M $Fe(NO_3)_3$ 0.02 M $Al(NO_3)_3$ 0.25 M $NaNO_3$ 0.35 M Na citrate pH = 2.5 flow = 120 ml/h	0.025 M R.E. nitrates 0.01 M $Fe(NO_3)_3$ 0.01 M $Al(NO_3)_3$ 0.125 M $NaNO_3$ 0.25 M Na citrate pH = 2.5 flow = 180 ml/h
1AS	0.35 M Na citrate, pH = 2.5 flow 40 ml/h		0.25 M Na citrate pH = 2.5 flow 40 ml/h
1AX	0.3 M HDEHP, 0.15 M TBP, Shellsol-T, flow 180 ml/h		
1BX	1 M lactic acid, 0.05 M Na_5DTPA, pH = 3.0, flow 72 ml/h		
1BS	0.3 M HDEHP, 0.15 M TBP, Shellsol-T, flow 64 ml/h		

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Fig. 1 Extraction of Neptunium(VI) as a function of the uranium loading of the organic phase and of the nitric acid concentration. $5 \cdot 10^{-4}$ M Np, $5 \cdot 10^{-3}$ M CrO_4^{2-}, 25°C.

Fig. 2 Dependence of the neptunium distribution on the contact time and on the nitrous acid concentration in the presence of 0.6 M total uranium (ca. 75 % loading of the organic phase), starting with Np(V)

Fig. 3 Principle flowsheet for Am/Cm recovery from high-level waste.

Fig. 4 Concentration profiles of counter-current experiments (cf. table 3):
Run No. 1 (Am). Run No. 7 (Cm).   Run No. 2 (Eu).
Run No. 3 (Ce).

Fig. 5 Concentration profiles of counter-current experiments (cf. table 3):
Run No. 4 (Zr/Nb).   Run No. 5 (Fe).   Run No. 6 (Ru).

Fig.1

Temp. = 25°C
$N_p = 5 \cdot 10^{-4} M$
$Cr O_4^{--} = 5 \cdot 10^{-3} M$
30 vol.% TBP / n–Alkane C_{10}–C_{13}

D
$N_p VI$

10

3M HNO_3

2M HNO_3

1,5 M HNO_3

1M HNO_3

1

0,5 M HNO_3

0,2 M HNO_3

0,1

10   20   30   40   50   60   70   80   90

Uranium Loading of the Organic Phase

Fig. 2

without NO$_2^-$
0,0001 M NO$_2^-$
0,0005 M NO$_2^-$
0,001 M NO$_2^-$
0,005 M NO$_2^-$
0,01 M NO$_2^-$
0,05 M NO$_2^-$

HNO$_3$ = 1,5 M
N$_P$ = 5·10^{-4} M
Temp = 25°C
Org. U Loading ca. 75%
30 vol.% TBP / n-Alkane C$_{10}$-C$_{13}$

Mixing Time, min

Fig. 3

Fig. 4

Fig. 5

1A Bank — Relative Pulse Rates vs Stage No.

Curves labeled: Ru aqu., Zr/Nb aqu., Fe aqu., Fe org., Zr/Nb org., Ru org.

1B Bank — Relative Pulse Rates vs Stage No.

Curves labeled: Fe org., Ru org., Zr/Nb org., Ru aqu., Fe aqu., Zr/Nb aqu.