

# THEORETICALLY AND EXPERIMENTALLY DERIVED CRITERIA FOR PARTITIONING AND TRANSMUTATION OF RADIONUCLIDES IN EXISTING REACTORS

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## Abstract

In international co-operation partitioning schemes have been experimentally compared and minor actinides containing targets and fuels have been developed for transmutation purposes. In order to set targets values to what extent radioactive nuclides have to be partitioned and what should be the specification of fuels and targets for the transmutation, the most likely strategies of recycling minor actinides and technetium from existing reactors have been compared to the direct disposal concept of spent PWR fuels.

For a given reduction of the radiotoxicity by a factor of hundred, the research needs and the impact on the existing fuel cycle have been evaluated:

- basic data needed to design fuels
- simulation experiments to assess the radiation behaviour
- planning and execution of radiation experiments
- assessing the additional radiation doses of the new fuels
- decontamination factors for lanthanides
- separation yields in partitioning required for the given radiotoxicity reduction

The resulting target values for partitioning and specification for targets and fuels have been achieved to a large extent by experimental data.

## Scope of Partitioning

The transmutation of a radiotoxic nuclide cannot be carried to such a sufficiently high yield in a single irradiation, that the radiotoxicity is significantly (e.g. by a factor of 100) reduced. This is because the structure material of the target degrades as well during irradiation. Hence a recycling of the remaining radiotoxic nuclides becomes necessary. In case of a homogeneous, self generated recycling [1], the same partitioning process can be applied as used for the "first" separation from the waste.

Presently, there is no common agreement on the ranking of the radiotoxic nuclides, which pose a hazard, when eventually migrating out from a geophysical repository. In the following therefore the radionuclides are regarded as equally dangerous and all are partitioned and transmuted to such a degree, that the definitely discharge mass to a repository is 1 % of that discharged with the directly disposed spent fuel after having generated the same amount of energy [1]. Under this constraint, the needed decontamination factors (DF) have been calculated (table 1). They refer to the self generated minor actinides (MA) and  $^{99}\text{Tc}$  recycling in a 1000 MWe FBR under equilibrium conditions [1].

*Tab.1 Target decontamination factors for partitioning strategies*

	Tc	Np	Pu	Am	Cm
TU recycle in LWR	350	110	230	530	1900
TU recycle in FR	310	64	1060	630	2300

In order to achieve for the MA, especially for Am and Cm (An) the DF values given in table 1, lanthanides (Ln) will have to be carried over to the product. The neutron poisoning in a FBR reactor is not the hinting factor for the Ln concentration but rather the fuel irradiation behaviour itself. Neither in metal alloys nor in mixed oxides, Ln's form solid solutions but segregate in separate phases, with the tendency to grow under thermal treatment. Because of their chemical nature, Am and Cm tend to concentrate in these phases leading to an unacceptable non-uniform heat distribution in the fuel matrix under irradiation. Therefore in case of a heterogeneous fuel concept, with Am + Cm concentrations of up to 20 % a Ln/An separation of about 100 would be needed, which with present extraction techniques is difficult to reach observing an overall decontamination for An as specified in table 1. The situation is more favourable in the case of the homogeneous selfgenerated concept, where the fuel composition under equilibrium conditions is:  $(\text{U}_{0.8}\text{Pu}_{0.186}\text{Am}_{0.007}\text{Cm}_{0.006}\text{Np}_{0.001})\text{O}_{2-x}$  [1]. Assuming a Ln concentration of about 1 % being acceptable for the two fuel types, a Ln/An separation of 10 should be achieved with the proposed partitioning process schemes.

## Irradiation Experiments

An important contribution to the experimental programmes related to the research on transmutation consists of the irradiation of candidate fuels in a reactor or a burner. These fuels are by definition new fuels, with a given fraction of one or more radionuclides to be transmuted. The properties of these fuels have first to be determined, both for the selection of the appropriate candidate fuels, and for the safety analysis to be prepared prior to any irradiation experiment.

Most of the basic data concerning the new fuels, although related to the behaviour under irradiation, can be measured out-of-pile in laboratories equipped for the handling of radionuclide materials. However the radiation creep, the swelling, the densification and the fission gas release can only be studied by irradiation experiments or through computer simulation.

The Institute of Transuranium Elements (ITU) has no nuclear reactor and therefore runs irradiation experiments in the frame of external collaborations or contracts. The METAPHIX programme, conducted in collaboration with CRIEPI (Japan) and CEA (France) concerns the irradiation in the PHENIX reactor of metallic fuel samples containing minor actinides and rare earths [2]. The irradiation of targets for transmutation of minor actinides and fission products in accordance with the heterogeneous recycling route is the subject of the EFTTRA collaboration presented in a separate paper at this meeting [3].

The ITU is also participating with KFK (Germany) and CEA (France) in the irradiation of fuels containing minor actinides in accordance with the homogeneous recycling route. Two experiments are in preparation, namely ACTINEAU planned for 1996 in the OSIRIS reactor and SUPERFACT 2. The ACTINEAU experiment will contain 1 MOX pin with 2 % Am, to be fabricated by ITU, SUPERFACT 2 is a follow-up of the SUPERFACT 1 experiment [4], and concerns the irradiation of (U,Pu)O<sub>2</sub> pins containing 2 % of minor actinides (Am, Np); the start of this irradiation is planned for the end of 1995 in the PHENIX reactor. ITU is in charge of the fabrication of the Am containing pins. Finally, the irradiation of Np containing fuels in the HFR Petten (TRABANT experiment, planned for 1995) and at a later stage in SUPERPHENIX, is foreseen in the CAPRA programme.

## Dosimetry Aspects of MA-Containing Fuels

The inclusion of MA, and particularly americium and curium, in a fuel for subsequent transmutation, will increase the radiation dose levels of these fuels. Knowledge of these dose levels would allow measures to be conceived for the handling of such material. Radiation dose levels have been calculated at fabrication and discharge for the MA-containing fuels irradiated during the SUPERFACT 1 program. In order to assess the accuracy of these predictions, the calculated radiation doses are compared to measured ones. Verification of such predictions are essential since future industrial scale fabrication of MA fuels will be planned on computer predictions.

Under the SUPERFACT 1 program, a series of oxide fuels containing <sup>237</sup>Np and <sup>241</sup>Am at low and high concentrations were prepared at ITU and irradiated in the fast reactor PHENIX [5]. The gamma dose rates of the pins were measured during fabrication using portable ionisation instrumentation. After discharge (cooling 57 months), the gamma and neutron dose rates were measured using a passive neutron-gamma interrogation unit developed for the characterisation of spent fuel inside a hot cell at ITU [6]. The isotopic evolution of the fuels during irradiation and cooling has been studied using the computer code KORIGEN [7] with the cross-sections adjusted to those for the PHENIX reactor. The neutron and gamma dose rates were calculated using the computer program PUDOL [8]. The dosimetry calculations are performed on the basis of the fuel composition, physical properties, cladding and self-shielding in the fuel and cladding. Furthermore, it allows the use of a range of shielding materials for radiation protection purposes.

The high radiation doses from the americium containing mixtures is confirmed through the measurements at fabrication [9]. The presence of 2% and 20%  $^{241}\text{Am}$  in the fuel results in an increase of the gamma dose by 7 and 40 times respectively over the dose from a standard fast reactor fuel. However, the resulting soft gamma ray spectrum from the presence of americium can be easily shielded by 1-2 mm Pb. The use of freshly purified plutonium does not demand for further shielding, due to its soft spectrum, while the buildup of  $^{208}\text{Tl}$  is avoided. The dose rates of these fuels were calculated, for comparison purposes, on the basis of the isotopic composition obtained by chemical analyses. The level of agreement is within 30%, which is an acceptable accuracy for radiation protection purposes.

At discharge, the gamma and neutron dose rates were calculated on the basis of the fuel isotopic composition predicted by KORIGEN [10]. Although a considerable amount of curium is produced during the irradiation, the gamma dose dominates the total dose from the fuel. If the gamma dose due to soft part of the gamma spectrum is excluded, then the gamma dose is determined by the final burn-up achieved by the fuel during irradiation, i.e. by the content in fission products with an effective gamma energy of 0.7 MeV. From the gamma dose point of view, the problems encountered during unloading would not differ much from those with a present day commercial fuel of the same burn-up. The neutron dose at 1 m however, is up to 20 times higher, for the fuels with  $^{241}\text{Am}$  at charge, than a standard fuel. A shielding of 100 mm Pb and 200 mm polyethylene would be required for the handling at 1 m of a single such pin during unloading. The necessity for remote handling, particularly in the case of assemblies, is evident. The gamma dose dominates further the total dose from the fuels with cooling time due to the decay of  $^{242}\text{Cm}$  and  $^{244}\text{Cm}$ .

In order to verify the predictions on spent fuel, the measured and calculated dose rates of the MA fuels after irradiation and 57 months cooling were compared. The dose rates were calculated on the basis of the isotopic composition predicted by KORIGEN. An agreement within 50% is observed between the measured and calculated values. The discrepancy can be attributed to different sources: the reproducibility of the experimental set-up in the calculations; the fuel compositions predicted obtained from KORIGEN predictions. The reliability of KORIGEN, for the source term nuclides, has been checked through the comparison of its predictions with chemical analyses [10]. The agreement is within 25% for the actinides and 50% for the fission products. This agreement, although sufficient for dose rate calculations indicates limitations in its basic nuclear data libraries. The latter should be considered when neutron physics calculations are performed.

The high radiation dose levels encountered during the fabrication of MA fuel requires the construction of a special hot cell laboratory for the handling of large amounts of these elements.

### Partitioning

The feasibility of transmutation strongly depends on an effective partitioning process. Apart from a few studies on pyrochemical reprocessing [11,12], liquid-liquid extraction processes are mainly considered to fulfil this task. At ITU a study has been carried out to compare the partitioning capabilities of three organic molecules, e.g. trialkyl (C6-C8) phosphine oxide (TRPO), n-octyl(phenyl)-N,N-diisobutyl carbamoylmethylphosphine oxide (CMPO) and diisodecyl phosphoric acid (DIDPA). Similar process schemes were applied and tested out for the three different extractants [13].

Genuine HLW from LWR reactor fuel (ca. 30,000 Mwd/t U) was treated in a continuous countercurrent mode by means of centrifugal extractors, installed in a hot cell facility. The decontamination factors obtained for the most relevant isotopes are given in table 2.

Tab. 2 Decontamination factors(DF) determined for the different extractants

isotope	Concentration in the feed (g/l)	DF TRPO	DF CMPO	DF DIDPA
<sup>99</sup> Tc	0.14	> 1760	> 180	-
<sup>144</sup> Nd	0.47	> 22000	> 30000	> 4000
<sup>237</sup> Np	0.05	12.4 (> 4100*)	> 30000	>5
<sup>238</sup> U	0.86	> 5400	> 100000	>20000
<sup>239</sup> Pu	0.02	> 760	> 4000	> 150
<sup>243</sup> Am	0.06	> 900	> 15000	> 10000
<sup>244</sup> Cm	0.007	> 600	> 1500	> 1500

\* HNO<sub>3</sub> concentration in the feed increased from 0.7 to 1.35 M

Except for Tc, CMPO gives the highest decontamination factors. The rather low values for Cm are estimated lower limits, due to a low initial concentration of this element in the feed. The analytical detection limit and the back-ground in the hot cell facility are the limiting factors for the DF value calculated for Cm. With higher concentrations in the feed, to be expected for the above mentioned reference case of a self generated MA and <sup>99</sup>Tc recycle in a 1000 MWe FBR under equilibrium conditions [1], higher DF values would certainly be observed as in the case of Nd for the 3 extractants. It is known, that Ln and An have a very similar behaviour in these 3 extraction processes. The low values determined for Np in the DIDPA and the TRPO (at low HNO<sub>3</sub> concentration) is due to the slow kinetics of the NpO<sub>2</sub><sup>+</sup> reduction to the oxidation state IV required for the extraction of this element.

However with a view to the fabrication of new targets not only a good extraction with high decontamination factors is necessary but also a high recovery rate from extraction process with small overall losses is of great importance in any P&T strategy. For the present comparative study, the distribution of the actinides on the process streams is given in table 3

Tab. 3 Relative distribution (in %) for the main actinide isotopes

process	process stream	<sup>237</sup> Np	<sup>238</sup> U	<sup>239</sup> Pu	<sup>243</sup> Am
TRPO		9.81(0.0*)	0.0	0.2	0.0
CMPO	raffinate	0.0	0.0	0.0	0.0
DIDPA		15.8	0.0	0.5	0.0
TRPO		0.0	0.0	0.0	99.7
CMPO	stripping 1	7.7	0.1	12.3	7.2
DIDPA		0.0	0.0	0.3	97.9
TRPO		89.5	0.1	99.6	0.1
CMPO	stripping 2	2.2	0.4	3.5	6.7
DIDPA		72.6	0.7	91.1	2.1
TRPO		0.1	99.9	0.2	0.1
CMPO	stripping 3	2.6	98.8	1.3	4.9
DIDPA		-	-	-	-
TRPO		0.5(0.1*)	0.1	0.1	0.0
CMPO	used organic	0.1	0.6	0.0	0.3
DIDPA		11.6	99.3	8.1	0.0

\* HNO<sub>3</sub> concentration in the feed increased from 0.7 to 1.35 M

These results show, that for the chosen operation conditions TRPO has the best back-extraction properties. Although for CMPO the organic phase is almost actinide free after stripping, only low amounts of Pu and Am are recovered in the respective stripping solutions, due to an accumulation of these elements in the corresponding extractor stages.

As mentioned above the organic molecules commonly used for partitioning of actinides generally have almost identical extraction properties for An and Ln; thus the An/Ln separation is one of the most challenging tasks in any partitioning and transmutation project. The high neutron capture cross sections of Ln but mainly their tendency to form separate phases upon re-fabrication are the reasons for the absolute necessity for the Ln/An separation.

In extraction processes schemes three main routes can be envisaged to achieve the required separation factors mentioned above.

- use of an additional chromatographic process
- use of an additional extractant with the known capability of separating Ln from An by means of complexing agents
- use of complexing agents in an existing process without changing the primary extractant.

Separation of Ln and An by high performance liquid chromatography (HPLC) on ion exchange columns using  $\alpha$ -hydroxy isobutyric acid in a pH gradient for elution gives a complete Ln/An separation. The feasibility to separate gram amounts of those elements under real conditions was demonstrated at ITU [14]. The drawback of this technique is the batch operation mode as a follow-up of the extraction process, generally conducted continuously either in a mixer settler, column or centrifugal extractor equipment.

A classical example for the use of a second extractant would be the TALSPEAK [15] process where Ln are extracted by di(2-ethylhexyl)phosphoric acid (HDEHP) after complexation of Am and Cm by diethylenetriaminepentaacetic acid (DTPA). An alternative could be the reversed TALSPEAK [16] process with a selective stripping of Am and Cm by DTPA after extraction with HDEHP. Ln/An separation factors around 10 could be achieved in a single extraction stage. A continuous experiment carried out at CEA (CEN Fontenay aux Roses, France) on real HLW using 6 extraction stages and 4 back-extraction stages in a mixer settler device, gave an Am/Cm product containing less than 1 % of Ln; separation factors of 150 for Eu and more than 1000 for Ce were attained [17].

Finally the use of complexing agents in an additional back-extraction step included in an established process would possibly offer the most appropriate solution. Because DIDPA has a chemical structure very similar to HDEHP the process based on this extractant seems to be the most suitable to fulfil this purpose. First test with DTPA gave very promising results [18]. A single stage extraction gave a separation factor of 10 between Am and Nd. It could be calculated, that this value will considerably improve in a continuous multistage process. In this case 99.99 % of Am and Cm would be recovered with a total Ln contamination of about 10 %. Similar results were obtained with diamides and SCN<sup>-</sup> as a complexing agent [19]. In a single extraction step an Am/Eu separation of 9 was obtained.

Tests are presently running at ITU to evaluate the possibility to include a similar stripping step in the TRPO process, which revealed the most promising results in the back-extraction part.

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