C H A P T E R   I I

RADIOCHEMICAL AND NUCLEAR ENGINEERING DATA OF MINOR ACTINIDES AND LONG
LIVED FISSION PRODUCTS.

2.1. MINOR ACTINIDES

2.1.1. Inter relationships of Am. Np and Cm formation in fuel cycle operations and long term storage.

The composition of spent fuel as discussed in the previous chapter under-
goes a very complex series of radiochemical transformations which are
determined by decay chaines of the nuclides produced by neutron absorption
of the initial U and Pu isotopes present in fresh fuel. Our attention will
be focussed on Am. Np and Cm isotopes present in spent fuel at time t=5y
after discharge from the reactor and their evolution as a function of time
(up to t=10.000 years) for various fuel cycle scenarios.
The contribution to the long term radiotoxicity of the radionuclides can be
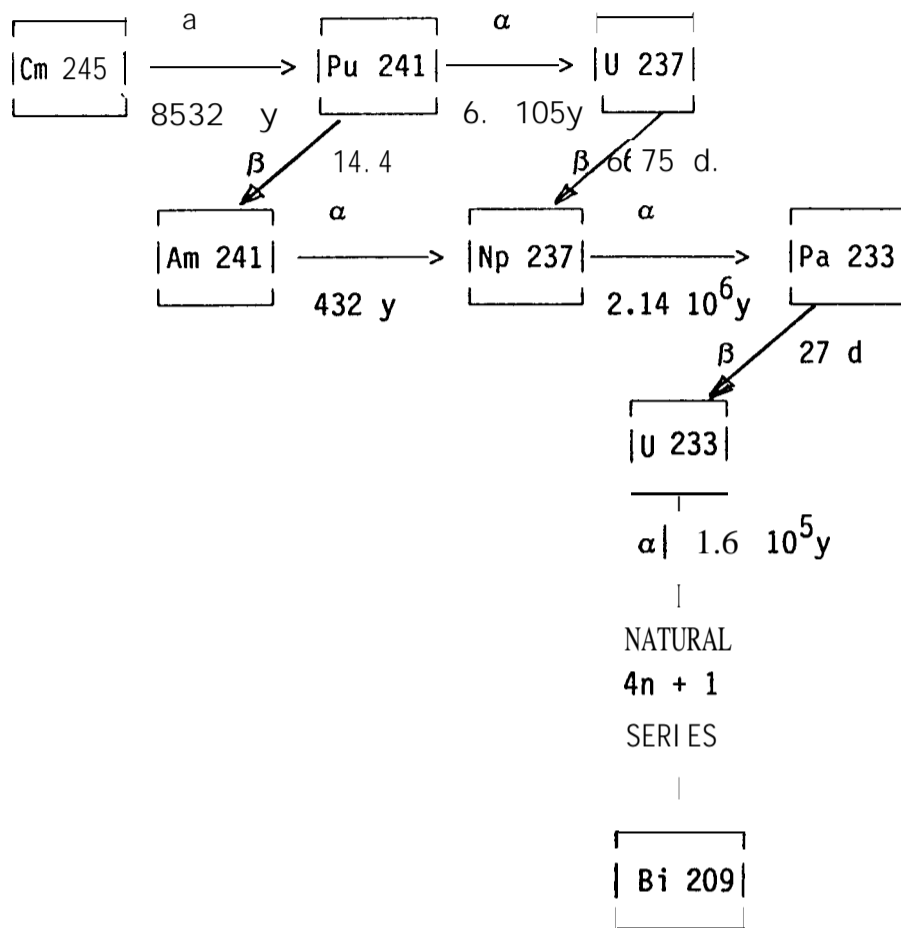deduced from the data of the tables IV, V and VI of chapter I

2.1.1.1.   The $4n+1$ series

The most important decay chain from radiological point of view is the 4n+1
series as shown in fig 2.1.
This series starts in the present context with Cm 245 and decays into
Pu 241, Am 241 and Np 237. From this nuclide onward starts the natural
series 4n+1 whose parent nuclide is U 233 and which decays into a series of
naturally occurring alpha emitters into stable Bi 209. The important
nuclear constants : nuclide emission and half life, are shown in the decay
chain diagramme.

Fig. 2.1.

4 n + 1 series


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┌──────┐   a     ┌──────┐   α    ┌──────┐
│Cm 245│ ──────> │Pu 241│ ─────> │U 237│
└──────┘ 8532 y  └──────┘ 6. 105y└──────┘
              β ╱ 14.4        β ╱α 6. 75 d.
         ┌──────┐   α   ┌──────┐   α    ┌──────┐
         │Am 241│ ────> │Np 237│ ─────> │Pa 233│
         └──────┘ 432 y └──────┘2.14 10⁶y└──────┘
                                    β ╱ 27 d
                               ┌──────┐
                               │U 233│
                               └──────┘
                               α│ 1.6 10⁵y
                               │
                               NATURAL
                               4n + 1
                               SERIES
                               │
                               ┌──────┐
                               │Bi 209│
                               └──────┘
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The impact of Cm 245 is very low because it is one of the heaviest **acti-nides** formed by multiple neutron capture of U and Pu in **UO²-PWR** spent fuel and according to the data of table IV of Chapter I, only present at a concentration level of 0.138 **Ci/THM** (0,804 **g/THM).** It does not contribute significantly to the lower masses because of its long half life (8500 y). However it represents still 0.47 **%** of the total actinide activity after 10.000 years and plays a role as yardstick in the determination of the target OF'S to be aimed at for the other **nuclides.**

The second and much more important **nuclide** of the **4n+1** series is Pu 241 which is the direct parent **nuclide** of Am 241. In the non-reprocessing option all Pu 241 present in spent fuel at t=0 will decay into Am 241 within a time interval of 140 years. In the long term this Am 241 with a half life of 432 y will be transformed into Np 237 and constitute the long term hazard for the environment.

In the reprocessing option at t=5y, the Pu 241 source term will be split into a **majour** fraction (99 %) which is supposed to reenter the fuel cycle either by thermal recycling or by reuse in a fast reactor. One percent of the Pu 241 (98,5 **Ci/THM)** ends up in the HLLW together with about 1000 **Ci/THM** of Am 241.

The beta branching ratio of Pu 241 is 99,99 % towards Am 241 and the alpha branching ratio of 0,0025 % leads to a short lived U 237 fraction which may be completely neglected in further discussions.
The residual Pu 241 content will increase the Am 241 content of HLW from 296 **g/THM** at t=5y to 305 **g/THM** at t=50 years. If an Am separation **would** be carried out on HLLW at t=5y, 97 **%** of the total long term Am 241 content would be removed. The 3 **%** residual amount of Am 241 derives from Pu 241 decay. In order to decrease quantitatively, e.g. by a factor of 1000, the long term hazard of Am 241 it is necessary to reduce the Pu 241 content in the HLLW by a factor of 10 to 50. The overall reduction of the Am 241 impact requires an intervention on the Pu 241 recovery.

The precise moment at which reprocessing takes place, influences the target separation yields which are achievable. The Pu extraction yield can be improved during the conventional reprocessing operation by introducing an additional Pu recovery step on the HLLW stream before the acid recovery evaporation step. It could also be achieved by increasing the number of extraction stages in the HA-HS column.
However it is at present not very clear whether this option of increased Pu extraction is at all possible within the existing or constructed reprocessing plants. It is very probable that additional facilities will be necessary to carry out such step. Advanced reprocessing with P & T objectives should investigate the feasibility of improved Pu extraction in combination with new methods for Am 241 separation from **HLLW.** In the very

long run i.e. hundred-thousands to million years, Np 237 is the most important nuclide because of its very long half life (2.14 10^{6}y) its radiological toxicity (0.03 Bq/l) and its peculiar migration characteristics. Np 237 is formed directly in the fuel during reactor irradiation and in addition continuously produced by alpha decay from Am 241. Direct separation of Np 237 from HLLW at t=5y will reduce its inventory by 437 g/THM. Long term ingrowth of Np 237 amounts to 382 g/THM over a period of 10.000 years. Quantitative separation of Np 237 from HLLW separated during advanced reprocessing will reduce the long term inventory only by a factor of 2.2. (from 820 g/THM to 382 g/THM) if Am 241 is not removed from HLLW. In order to reduce significantly the radiological hazard of the trans-uranium nuclides of the 4n+1 series it is necessary to take appropriate measures aiming at a decrease of the Pu 241 - Am 241 - Np 237 mixture in HLLW. Each of these nuclides have to be extracted to a different level in order to be significant for the waste disposal strategy and coherent with respect to their hazard factors. A systematic analysis of the separation factors should be undertaken to define realistic and meaningful technical targets.

2.1.1.2. *The 4m-3 series*

This series as shown in fig. 2.2 starts from Cm 247 and includes important nuclides eg. Am 243 and Pu 239. The natural 4n+3 series which follows has U 235 as parent nuclide and forms a tail of interconnected decay products. This series is important from radiological point of view for the MOX-fuel recycling scenarios but much less significant for UO^2-PWR fuel in terms of minor actinides.

The contribution of Cm 247 - Pu 243 to the overall minor actinide concentration is negligeable for UO^2-PWR fuel and even very small for MOX fuel (3.15 10-' Ci/THM or 3.39 10^{-2} g/THM). Am 243 is the true first nuclide of the 4n + 3 series as shown in tables IV and V of chapter 1. The Am 243 concentrations in spent fuel and HLW are radiologically significant since Am 243 is the long term parent nuclide of Pu 239 and U 235. In UO^2 PWR fuel the Am243 content is 83,8 g/THM which decays quantitatively to 82.4 g Pu/THM and constitutes a concentration level which is comparable or even slightly higher than the conventional Pu 239 content in HLW (54.7 g/THM).

Fig. 2.2.

4 n + 3 series
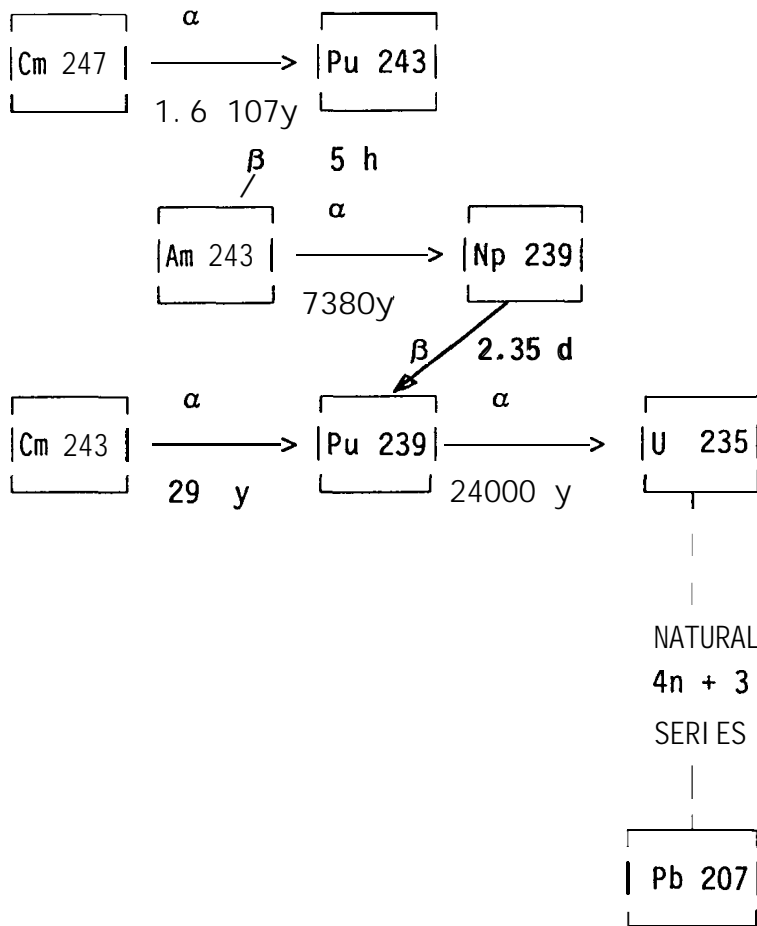
In MOX fuel discharged from a PWR the Am 243 content is 1074 **g/THM and** transforms by decay into 1056 g Pu **239/THM.** The Pu 239 concentrate ion in HLW would in this case only amount to 139 **g/THM.** The P & T option for Am 243 is important in order to minimize the residual Pu 239 content in a repository of HLW.
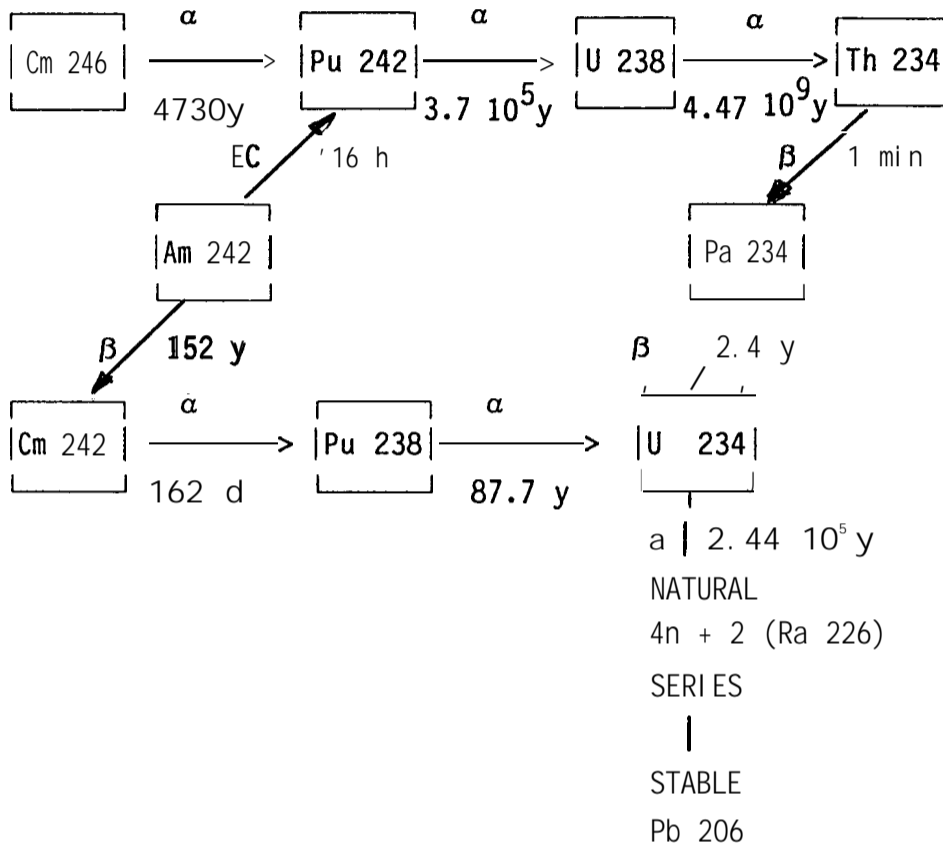
2.1.1.3 The 4n + 2 series

This series deserves special attention because of the Ra 226 formation in its natural tail.

Fig 2.3 shows the 4n + 2 series which contains radiologically important
nuclides eg. Pu 242 , Pu 238 and the most common U isotope U 238 parent of
the 4n + 2 natural series.

Fig. 2.3.

The 4 n + 2 series

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┌─────────┐     α      ┌─────────┐    α     ┌────────┐    α     ┌────────┐
│ Cm 246  │ ────────→  │ Pu 242  │────────→ │ U 238  │────────→ │ Th 234 │
└─────────┘  4730y     └─────────┘ 3.7 10⁵y └────────┘4.47 10⁹y└────────┘
                    EC        16 h                          β      1 min
                ┌─────────┐                          ┌─────────┐
                │ Am 242  │                          │ Pa 234  │
                └─────────┘                          └─────────┘
        β     152 y                            β       2.4 y
   ┌─────────┐    α      ┌─────────┐    α     ┌────────┐
   │ Cm 242  │ ────────→ │ Pu 238  │────────→ │ U  234 │
   └─────────┘  162 d    └─────────┘  87.7 y  └────────┘
                                           a │ 2.44 10⁵y
                                           NATURAL
                                           4n + 2 (Ra 226)
                                           SERIES
                                           │
                                           STABLE
                                           Pb 206
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The 4 n + 2 series — α, β, EC; $3.7\ 10^5$y; $4.47\ 10^9$y; $2.44\ 10^5$y

The production of Cm 246 by multiple neutron capture of U and Pu isotopes
is sufficiently small to ignore it in the analysis of the radiological
impact of the 4 n + 2 series. Pu 242 with its very long **halflife**
($3.7\ 10^5$y) is relatively speaking the most important toxic **radionuclide**
(486 **g/THM)** but is recycled in the conventional reprocessing option. In
the medium half life range (87 y) Pu 238 occupies a special position
because of its heat and neutron production but does not pose any long term
threat if geological disposal in a suitable repository is accepted for a
period of 1000 years.

In the very long term the presence of Ra 226 in secular equilibrium with its parent nuclides will determine the radiological hazard of the 4n + 2 series.

2.1.1.4. The 4n series.

The nuclides of the 4n series decay from Cm 244 to the Th 228 natural series 4n which contains a very strong gamma emitter Tl 208. (2.6 MeV) Fig 2.4 shows the essential steps of the 4n series.

Fig. 2. 4.

The 4 n series
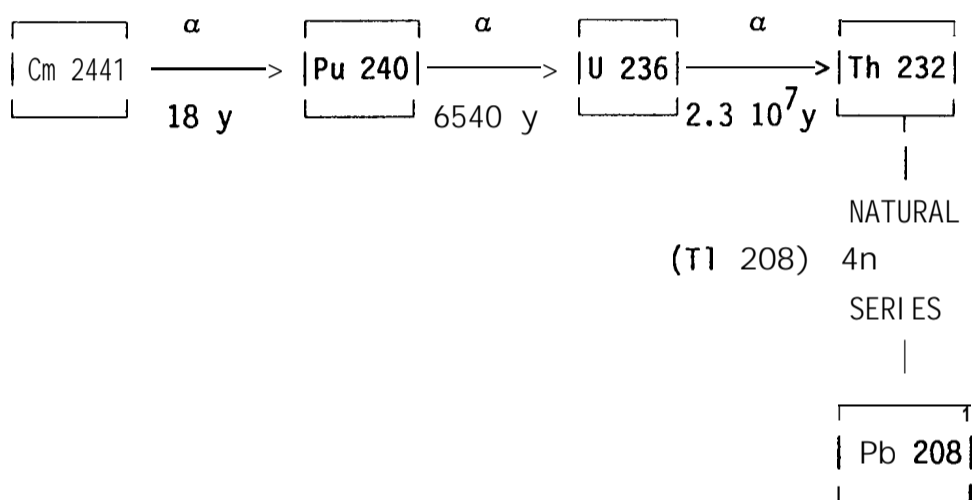
In the context of P & T, Cm 244 is an annoying isotope which has a high a activity (1500 - 1600 Ci/THM) in the early years after discharge, but decays with a half life of 18 years. As a result, it does not influence the long term toxicity except through its daughter isotope Pu 240.

However, Cm 244 disturbs all fuel cycle operations (reprocessing fuel fabrication) when it occurs in a concentrated form in oxygen containing materials. Due to its intense (an) reaction, it produces neutron radiation which interferes with conventional processing methods. For obvious reasons, it would be preferable to leave the Cm fraction with the HLLW until vitrification. But therefore an efficient RE/Am/Cm separation must be available.

Pu 240 is for 99 % recycled in conventional reprocessing which leaves about 40 g/THM in the HLW. U 236 occurs not only as a daughter product of Pu 240 but is independently produced by neutron capture of U 235. Due to the isotopic dilution with U 238 and U 235 very little can be done to alleviate the radiological consequences of the Tl 208 in- growth.

2.1.2 Discussion on the decontamination factors in a P & T option.

The desired decontamination factors for Am, Np and to a lesser extent for Cm, result from an analysis of the production and interrelated decay data coupled to their radiological toxicity or hazard index.

The following cases will be discussed and evaluated on their feasibility and long term interest :

- Quantitative removal of Actinides in order to reduce HLW to a mixture of fission products.

- Partial and selective removal of Actinides with a great potential for long term contamination.

- Selective removal of Actinides which cannot be kept safely within the geologic repository.

In order to simplify the set of data the following assumptions are made :

- The radiological impact of minor actinide separation is insignificant between 0 and 1.000 years.

- The standard HLW contains only 1 **%** of the **majour actinides** U and Pu.

- Vitrification is the standard waste conditioning technique for HLW.

- Geological disposal is supposed to have a technical life time of 10.000 years. Beyond that period the migration is controlled by **geochemical** phenomena in the natural environment.

2.1.2.1. ***Quantitative removal of act in ides from HLW.***

The level of alpha radioactivity which is tolerated in surface storage or without special safety precautions is limited to 10 nCi/g per nuclide and 100 nCi/g as a whole. One metric ton of Heavy metal is nominally reduced to about 400 kg glass-compound which corresponds to a maximum alpha concentration of 40 mCi/THM. The decontamination factors (DF) to be obtained after 1.000 respectively 10.000 years are shown in table II-1 for each of the significantly contributing nuclides.

Table II-1

Actinide concentrations and target DF's
for HLW after 1.000 and 10.000 years

Nuclide	Actinide concentration Ci/THM		Decontamination factors based on 10 n Ci/g	
	1.000 y	10.000 y	1.000 y	10.000 y
U 234	0.0198	0.0195	5	5
Np 237	0.524	0.578	130	144
Np 239	15.2	6.54	$3.8 \ 10^3$	$1.6 \ 10^3$
Pu 239	3.77	5.12	$9.42 \ 10^2$	$1.28 \ 10^3$
Pu 240	8.30	3.20	2.10^3	8.10^2
pu 241	0.128	0.0612	32	15.3
Pu 242	0.0192	0.0206	4.8	5.1
Am 241	273.0	0.0614	$6.8 \ 10^4$	15.3
Am 242	0.04		10	
Am 243	15.2	6.54	$3.8 \ 10^3$	$1.6 \ 10^3$
Cm 242	$3.34 \ 10^{-2}$		8.3	
Cm 245	0.127	0.0611	31.7	15.27
Cm 246	0.194	0.052	48.5	13.0
TOTAL	318	21		

The global DF to be obtained in order to reduce HLW to the "non" radio-active levels amounts to 8.7 10^4 after 10 years and 7.9 10^3 after 1000 years. Such high separation factors are hardly obtainable in industrial circumstances.

However if geological disposal is accepted as a waste management option with a technical lifetime ranging from 1000 to 10.000 years global DF's of 8.10^3 down to 525 are reasonable technical goals to aim at.

The Am 'isotopes 241 and 243 require the highest DF's followed by Pu 239 and 240. In the third position we find Np 237 and 239 and finally the Cm isotopes and U 234.

The relatively high DF values found for Np 239 and Pu 239 are explained by the fact that it are alpha decay products of Am 243. A similar observation is valid for Pu 240 which is a daughter product of the relatively short lived Cm 244 (t1/2 = 18 y). Delayed reprocessing would be beneficial for the reduction of the radiological impact of Pu 240.

2.1.2.2. Partial and selective removal of Actinides

In the previous section we have seen that unrealistically high DF's are required to reduce the alpha content of HLW to the nominal 100 nCi/g thres-hold. A series of alternative scenarios with partial and selective removal of minor **actinides** have to be analyzed in order to come up with a radio-logically significant result.

An obvious route to be investigated is the removal of minor **actinides** except Cm, and its impact on the overall result. If the Cm 242-244-245 and 246 **nuclides** are not removed from HLLW a residual activity of 0.35 **Ci/THM** will buildup in HLW after 1.000 years and 0.11 **Ci/THM** after 10.000 years. These activity levels correspond to 0.5 and 0.1 **%** of the total alpha activity which amounts to 318 **Ci/THM** and respectively 21 **Ci/THM** at the considered time intervals.

Based on these data overall DF's of = 900 resp. = 200 **should** be sufficient for Am isotopes if the technical lifetime of a geological disposal is guaranteed up to 10.000 years.

For Np 237 a theoretical DF of 130-140 is required to reduce this nuclide to the 10 nCi/g level. In the option of a Cm activity of 0.35 Ci/THM i.e. without Cm removal the DF for Np 237 could be reduced to 1 or 2. However such a scenario does not take into account the difference between the migration pattern of Np and Cm and their half lifes. A DF range between 10 and 20 is therefore a reasonable proposal taking into account the important Np 237 contribution to the long term individual dose to man. A DF of 10 to 20 for Np 237 is also coherent with a partial (90%) removal of Cm.

Define the minimum DF's for Pu isotopes is a more complex issue. The data of table II-1 show that the Pu contents in HLW require relatively high DF's but the Pu 239 activity is the result of a combined decay of initially present Pu in HLLW and the ingrowth of Pu 239 from Am 243. If the Am fraction is removed from HLW prior to vitrification the Pu activity would remain at its initial 3.4 Ci/THM level and require only a DF of about 10 based on the residual Cm activity of 0.35 Ci/THM which would remain in this scenario in the HLW.

However such a reasoning does not apply to Pu 240 which is a daughter of Cm 244 with a halflife of 18 y. If the Cm 244 is not removed during advanced reprocessing Pu 240 content will further increase from an initial level of 22 g/THM to 36 g/THM after 50 years and require the OF'S listed in table II-1 to reduce its activity to the 10 nCi/g level.

A DF of 23 is necessary to reduce the Pu 240 activity to that of the Cm fraction if this is not removed during the partitioning step. If a 90 % removal of the Cm fraction would be considered the DF's for Pu 239 and 240 should be increased to 100 respectively 230.

For sake of completeness it has to be mentioned that other criteria have been applied to these question in the early period of R & D in this area [2.1] [2.2].

One of the interesting approaches is the comparison with natural U bodies. The lowest level is Carnotite with 0.2 % U content and typical for very many U ores exploited throughout the world.

The highest is 70 % U in Pitchblende as found in some very rich U deposits. The 0.2 % U ore corresponds to 1 n Ci/g and pitchblende to 800 n Ci/g.

It does not seem a practicable option to try to reduce HLW toxicity to the Carnotite ore level which is freely distributed in the earth crust because the fission products which are still present in HLW would also have to be considered and would preclude an unsurveilled dispersion in the biosphere.

The reference to pitchblende is undoubtedly a more feasible target for P & T processes. Assimilation of partitioned HLW to pitchblende leads to decontamination factors of the same order of magnitude as those of the "non Cm removal". Table II-2 shows the target DF's to be aimed at for UO_2-PWR fuel reprocessed 7 years after discharge in order to reduce the partitioned HLW to radiologically acceptable levels for free dispersion in the bio-sphere within a time interval between 1000 and 10.000 years.

From chemical processing point of view there is no difference between the extraction characteristics of different isotopes from a single element. If the 90 % Cm removal option is considered the proposed DF's are very ambi-tious and cannot be realized for Am 241. The option without Cm removal but with an increased DF for Np seems the most viable P & T proposal.

Table II-2

Realistic target decontamination factors from HLW of some long lived
actinides in case of partial actinide removal.
(UO^2 PWR)

Nuclide	No Cm removal		90% **Cm** removal		**Pitchblende** analog	
	1.000 y	10.000 y	1.000 y	10.000 y	1.000 y	10.000 y
Np 237	1.5	1.6	15	16	1.6	1.8
pu 239	10.	10.	100	100	11.	16.
pu 240	23.	10.	230	100	25.	10.
Am 241	780.		7800		850	
Am 243	43.	18.	430	180	47	20
Cm 245	1	1	10	10		
Cm 246	1	1	10	10		
TOTAL ACTINIDE	900	200	9000	2000		

2.1.2.3. Impact of geologic repository conditions on partitioning targets.

As already discussed in Chapter I the geologic confinement within a mul-
tiple barrier systemof vitrified HLWin a well chosen host rock is capable
of retaining most of the long lived **radionuclides** within a 1000 to 10.000
year period.   Beyond that period uncontrollable natural migration occurs
from the repository structure to the far field geologic strata and from
there to the groundwater and the biosphere. Such a scenario is presently
accepted throughout the world as the most probable long term evolution.
Actinide P & T is not an alternative approach to this long term waste
management option but a complementary technique capable of decreasing the
duration of the radiological impact on the biosphere.
Am 241 which requires the highest DF's in a pure P & T perspective becomes
rather marginal if a geologic repository with a technical confinement of
10.000 years is accepted as a waste management option.

However if Am 241 has not been separated from the HLW it will be the source of Np 237 creating a long term hazard. Separation of Am 241 and Np 237 from reprocessing waste streams must be performed simultaneously with that of Np 237. It would be preferable to limit the amount of Np 237 in the HLLW to a as low as reasonably achievable value but one order of magnitude (factor 15) is already significant in a long term individual-dose-to-man perspective. Fig 2.1 shows the relative contribution of the long lived Actinides and Fission Products in HLW to the total individual dose rate to man [2.3] living in an area close to a repository; in this case a clay repository. The figure shows the relatively minor contribution of the Actinides to the total dose compared to the long lived fission products and stresses the extremely long time frame (2.10^6 to 2.10^8y) within which these actinides exert their influence.

A similar study was made for cladding waste, see fig 2.2. which shows that only Np 237, Pa 231 and Ra 226 appear as significant actinides in the extreme long time intervals.

Pu, Am and Cm isotopes do not produce a very **longterm** hazard as they have already decayed before their daughter products can leave the repository confinement. This very slow migration is due to their intrinsic insolubility in deep groundwater.

However fig. 2.1 and 2.2 stress dramatically the importance of the long lived fission products e.g. I 129, Se 79, **Zr** 73, Cs 135... which have a much greater radiological impact than the **actinides.**

2.1.3. Occurrence of Minor **Actinides** in the process streams of the **conventional PUREX** reprocessing process.

The reprocessing operations include a series of mechanical physical and chemical processes which transform a spent fuel element into a series of important fractions. Fig. 2.3. shows diagrammatically the principal phases of the reprocessing operations with the most important effluent streams and waste products.
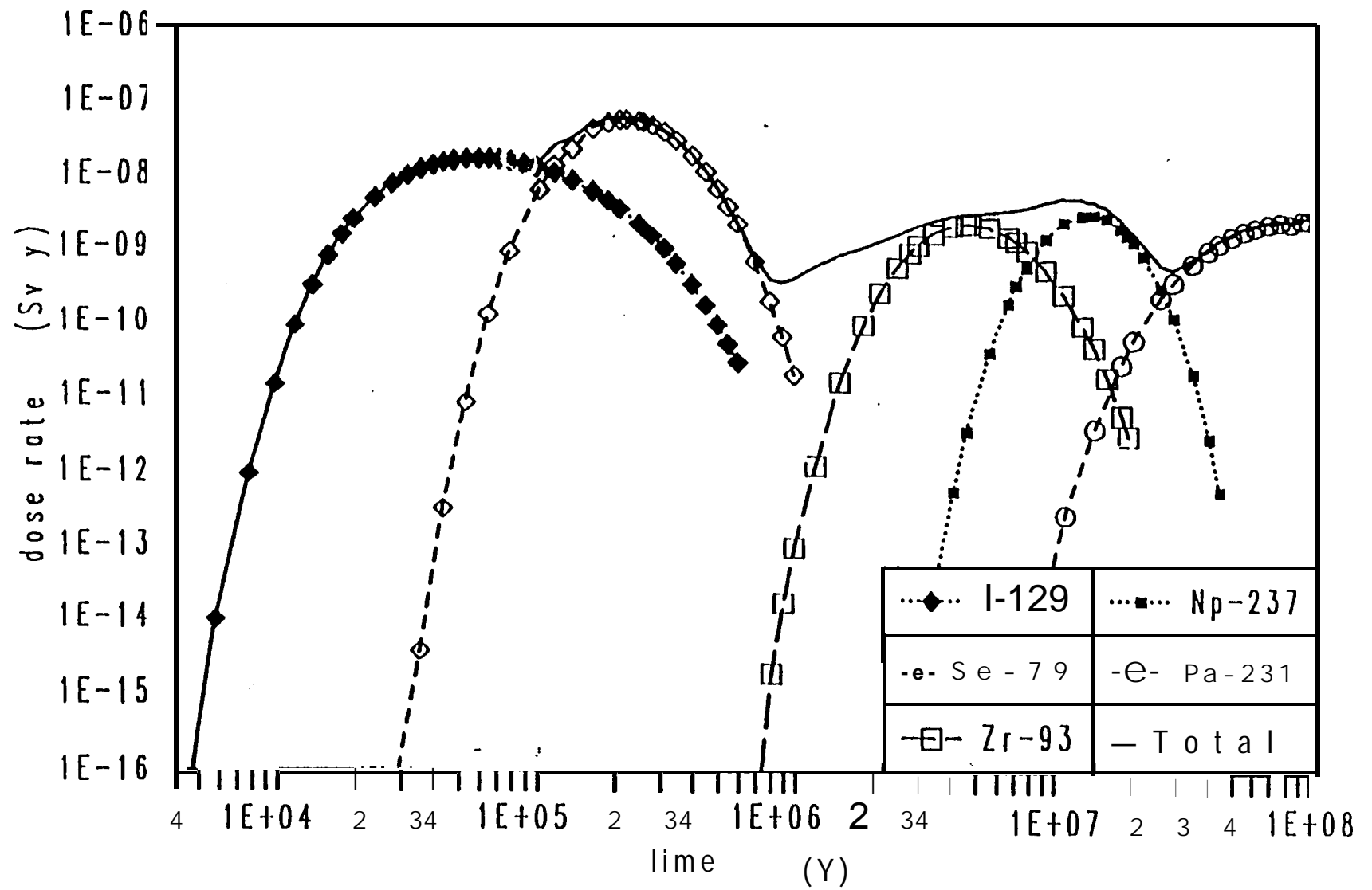
Fig. 2.1   Normal evolution scenario ; total dose rates via the water well pathway   calculated   for the high-level waste
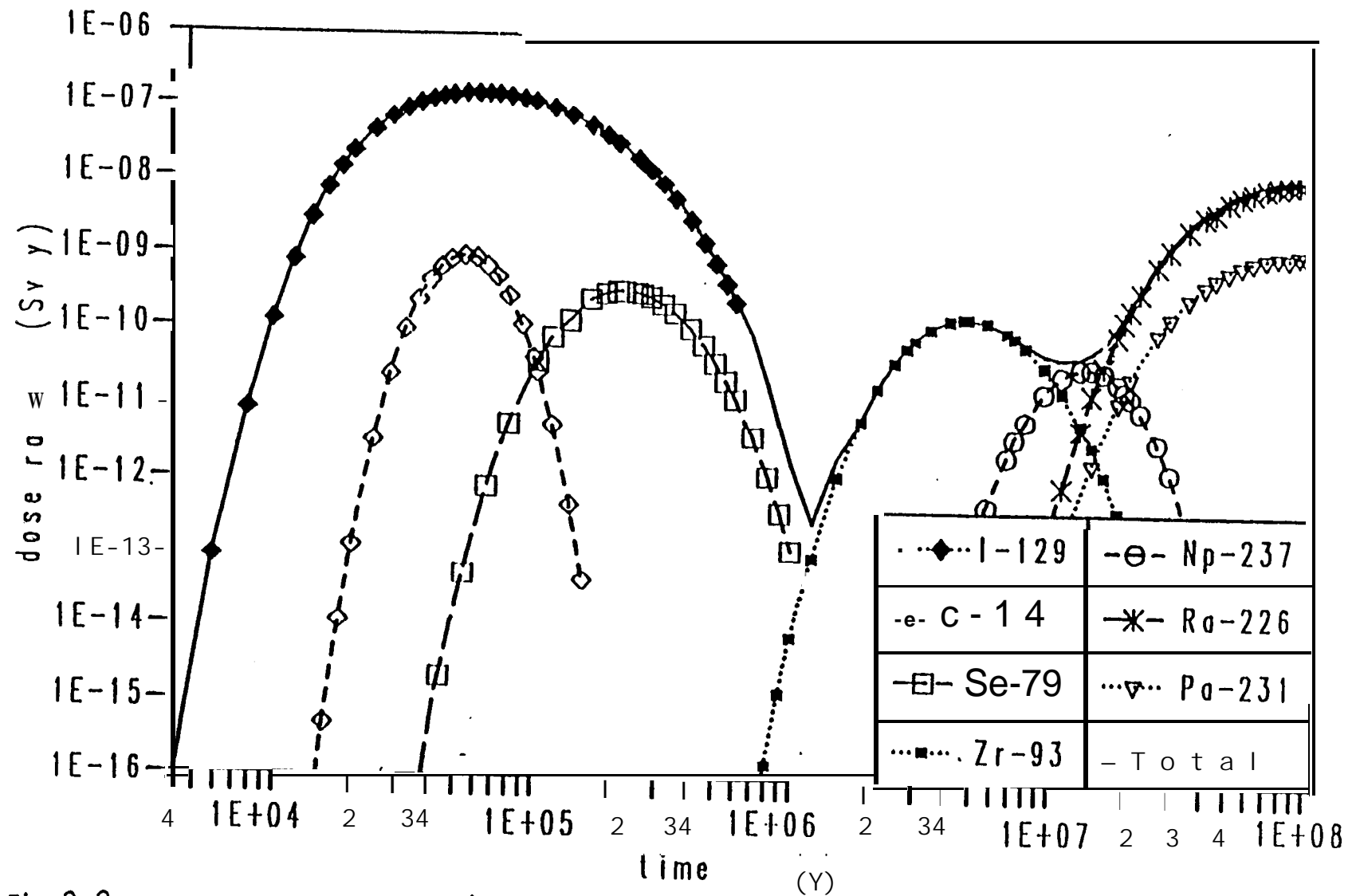
Fig. 2.2 . Norm 1 evolution scenario; total dose rates via the water well pathway calculated for the cladding waste

1. Decanning or shearing processes produce a waste stream of solid products contaminated with U, Pu,Actinides and fission products attached to the hulls made of Zircaloyor stainless steel.

2. Dissolution - clarification generates a sludge type residue with very high specific activity due to mediumshort lived fission products and contains an Actinide impurity especially if MOX fuel is treated.

3. Separation of U Pu from fission products produces the High Level Liquid Waste (HLLW) fraction from the first extraction column containing all the fission products, the minor actinides and 0.1 to 1 % of U and Pu.

4. Spent-solvent washing liquids are generated during all the sucessive steps of reprocessing and are contaminated with Actinides and Fission products. This stream is treated as Medium level waste and conditioned separately.

5. Gaseous fission products escape from the decanning/ shearing and dissolution steps [1) and 2)]. The noble gases Kr and Xe are discharged but Iodine (I 129) is retained in scrubbers and/or solid filtration units.

Each of these waste streams except the gaseous fission products, contain minor **actinides** which have to be considered in order to establish which maximum DF can be obtained.

2.1.3.1.   *Cladding Hulls*

Systematic studies have been performed on the **actinide** composition of hulls from power reactors [2.4] [2.5]. The leached hulls made of stainless steel or **Zircaloy** contain undissolved fuel residues which are attached to the inner surface. A **small** quantity of **Actinides** inside the metallic wall has penetrated the inner surface by alpha recoil and cannot be removed unless complete dissolution of the hulls is carried out. The residual activity due to **majour** and minor **actinides** is shown in table 11.3. The data reported are mean values which give a good order of magnitude but are not very accurate or representative of all spent **fuel** types. The given values take into account a standard quantity of 350 kg **hulls/THM.**
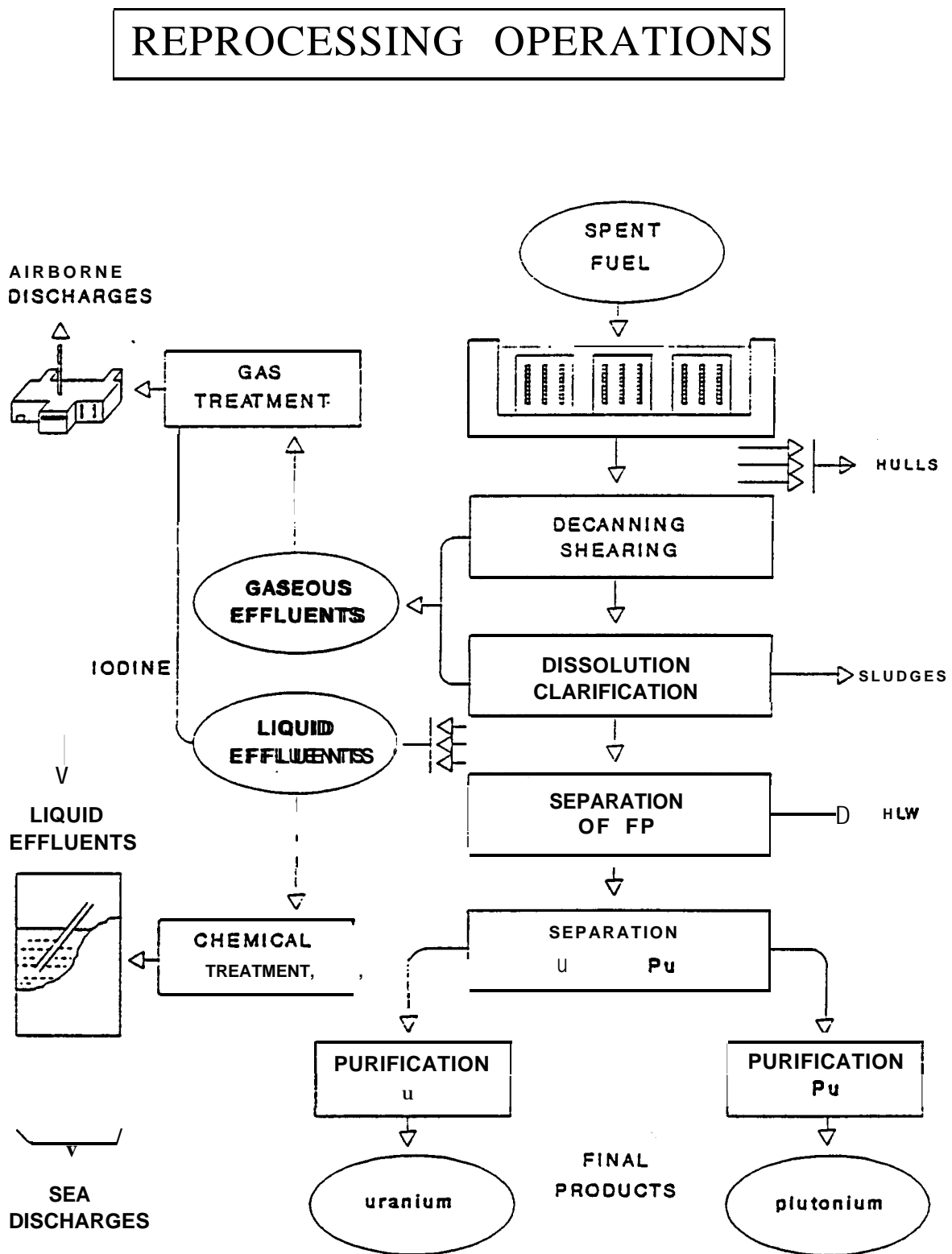
Fig. 2.3.

REPROCESSING OPERATIONS

SPENT FUEL

AIRBORNE DISCHARGES

GAS TREATMENT

HULLS

DECANNING SHEARING

GASEOUS EFFLUENTS

IODINE

DISSOLUTION CLARIFICATION

SLUDGES

LIQUID EFFLUENTS

SEPARATION OF FP

HLW

LIQUID EFFLUENTS

CHEMICAL TREATMENT,

SEPARATION
U   Pu

PURIFICATION
u

PURIFICATION
Pu

FINAL PRODUCTS

SEA DISCHARGES

uranium

plutonium

Figure 2.3

Table 11.3
Residual Actinide Activity of Zircaloy Cladding Waste
[2.4] [2.5] [2.6]

Nuclide	g/THM	Ci/THM	Fraction of Actinide Activity in HLLW
U	398	$0.65 \ 10^{-3}$	$4.1 \ 10^{-2}$
Pu	5-8	1.65	$1.6 \ 10^{-3}$
Np	0.094	$6.7 \ 10^{-5}$	$2 \ 10^{-4}$
Am 241		0.493-0.528	$5 \ 10^{-4}$
Am 243		0.007	$4 \ 10^{-4}$
Cm 242		0.014	$7 \ 10^{-4}$
Cm 244		0.56-0.98	$4 \ 10^{-4}$

The fraction of Pu attached to the hulls is relatively high compared to the minor actinides. Additional rinsing is capable of decreasing the Pu contamination level to 0.15-0.3 Ci/THM. In order to fit within a P & T option, this procedure should be included in the industrial practice. The quantity of minor actinides associated with the hulls corresponds to 0.05 % of that in HLLW. Translated in terms of DF's this corresponds to a DF of ~ 2000 for Am which should not be surpassed since the residual contamination cannot be removed with the presently used techniques for hulls treatment. The only technique capable of separating the Actinides from the hulls material is eg. melting at very high temperature. During this process the actinides concentrate in the slag and can be removed for further leaching or recovery. However by this technique the airborne contamination due to Tritium may become a severe limitation.

2.1.3.2. Clarification residues.

A second stream of solid residues result from the clarification process which is important in order to reduce the "crud" formation at the organic-aqueous solution interface.

The insoluble residues are mainly platinum type metals (Ru, Rh, Pd) and refractory fission products (Me, Tc) which are contaminated with undissolved particles of fuel and Zirconium or stainless steel. If an additional washing step is carried out on the hulls, a similar stream of particles will be added to the clarification sludge.

About 3 kg of residues are collected per THM of LWR fuel irradiated up to 33 GWe/t. The **fissile** material content is **small**: 1 % U, 0.1 % Pu_t and **negligeable** quantities of minor **actinides.**

The impact of the insoluble residues on quantitative recovery of actinides in an advanced reprocessing option is almost **negligeable** except for Pu which remains sometimes trapped within particles of noble metals.

This waste stream becomes significant if MOX fuel is processed. Particles with high enrichment (> 30 % Pu) tend to become insoluble in standard dissolver conditions.

Up to 7 % Pu and 0.4 %Amwere found in the **unsoluble** residues of MOX fuel. Additional information should be gathered to assess the impact of the clarification residues from MOX fuel reprocessing on a coherent P & T option.

Z. 1.3.3. *High leve 1 Liquid Waste (HLLW)*

The High Active Waste stream **(HAW)** leaving the HA-HS column of the PUREX process is the essential source of HLLW. Fig 2-4 shows a simplified flowsheet with the most important extraction columns :

- the high active extraction and scrubbing column **(HA-HS)**
- the **U/Pu** partitioning **column BX**
- the U purification column HC
- the Pu purification column.

A typical HLLW solution is strongly acid *(2-3* M **HNO_3)** and **contai**ns > 99 % of all the fission products, Cm and Am. About 95-97 **%** of the Np enters also the HLLW after a series of extractions and backextractions which are taking place in the U and Pu purification cycles.
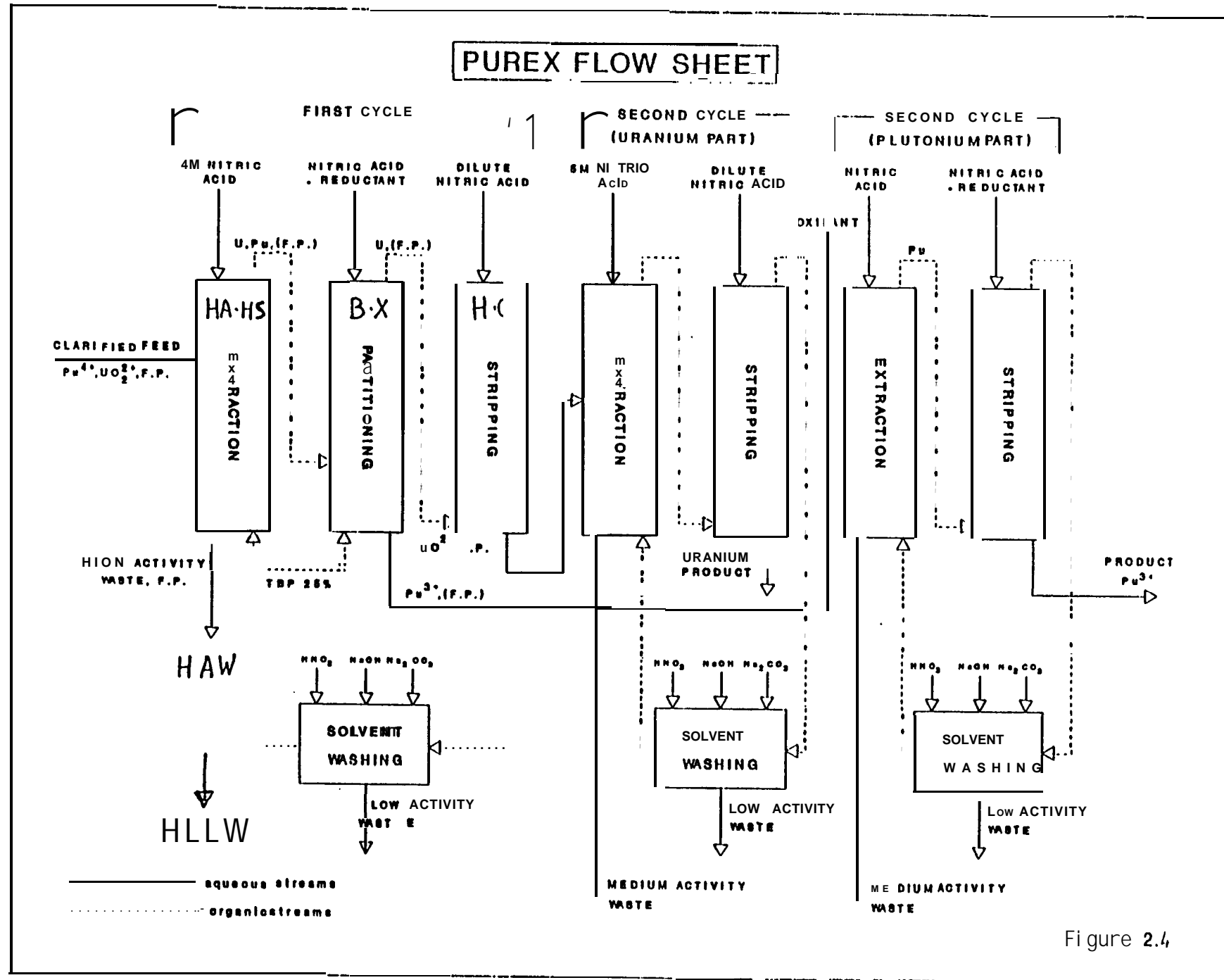
Figure 2.4

Industrial experience has shown that 0.5 % U and 0.7 % Pu enters the HLLW through different pathways [2.7]. In view of a P & T option improved Pu separation should be achieved to reach a target of 0.1 % Pu or less in the HLLW.

Very little experimental work has been done on the composition of real HLLW and most of the data refer to laboratory work or non representative compositions from early reprocessing projects. Table II-4 shows such a "typical" composition, which should be checked taking into account the large experience with UO_2PWR which has been gathered recently throughout the world. A systematic analytical campaign should help in defining more precisely the source term of the minor actinides in HLLW and the concentrations of **lanthanides** which play a very important role in the subsequent actinides extraction processes. This task would also benefit a better process control of the subsequent vitrification process.

During the storage of HLLW insoluble compounds post precipitate and generate a suspension type liquid which cannot be used directly for chemical separations without filtration or **centrifugation.**

Table II-4

Typical HLLW composition resulting from UO_2-PWR
reprocessing. [2.2]

H^+		**2.0M**
NO_3^-		3.6
Fission products :	Group I (Rb, Cs)	0.040
	Group II **(Sr,** Ba)	0,040
	Group III **(RE's)**	0.148
	Zr	0.074
	Mo	0.071
	Tc	0.017
	Group VIII (Ru, Rh, Pd)	0.085
	Te	0.0078
	O t h e r s	0.0042
	Total FP's	0.487
Corrosion products :	Fe	0.054
	Cr	0.0096
	Ni	0.0034
	Total corrosion products	0.067
PO_4^{3-}		0.042
Actinides	: u (0.5%)	0.053
	Np (100%)	0.003
	Pu (0.5%)	0.002
	Am (100 %)	0.009
	Cm (100%)	0.003
	Total **actinides**	0.070
Neutron poison	: Gd	0.150

It has to be noted that gradually more corrosion resistant materials are being used for the storage of HLLW decreasing potentially the level of corrosion products.

The use of salt free reagents for **valency** adjustment of Pu IV and the use of U IV for the Pu reduction are also elements which may influence the composition of HLLW.

Much has to be done in order to have a clear view on the real composition of HLLW which is a very important source term for a P **&** T option.

2.1.4. Status of the extraction **chemistry** of Am, Np and Cm.

2.1.4.1.   Neptunium   extraction.

The present industrial practice with regard to Np is clearly shown in fig. 2.5. and representative of the operations at the UP3 plant of La Hague [2.8]. The total Np input (434 **g/THM)** is split up in two streams : 16.6 % enters directly in the HAW stream and 83.4 % follows the organic phase with U and Pu. In the U resp. Pu purification cycles Np is separated and sent tot the HAW stream as a waste product. About 3 to 5 % remains with the purified U and Pu products.

The conventional PUREX flowsheet of the present generation reprocessing plants permits the recovery of 95 to 97 % but it has to be kept in mind that preparation of Np targets for transmutation requires a quantitative extraction from the HLLW. A separate TBP extraction to remove Np (after **valency** adjustment to VI) from HLLW is theoretically possible but the very strong irradiation of the fission products might interfere with this recovery.

An alternative **flowsheet** is shown in fig. 2.6. and accommodates with a quantitative recovery of Np outside the HLLW solution and prepares it for direct conversion into radiation targets for transmutation.
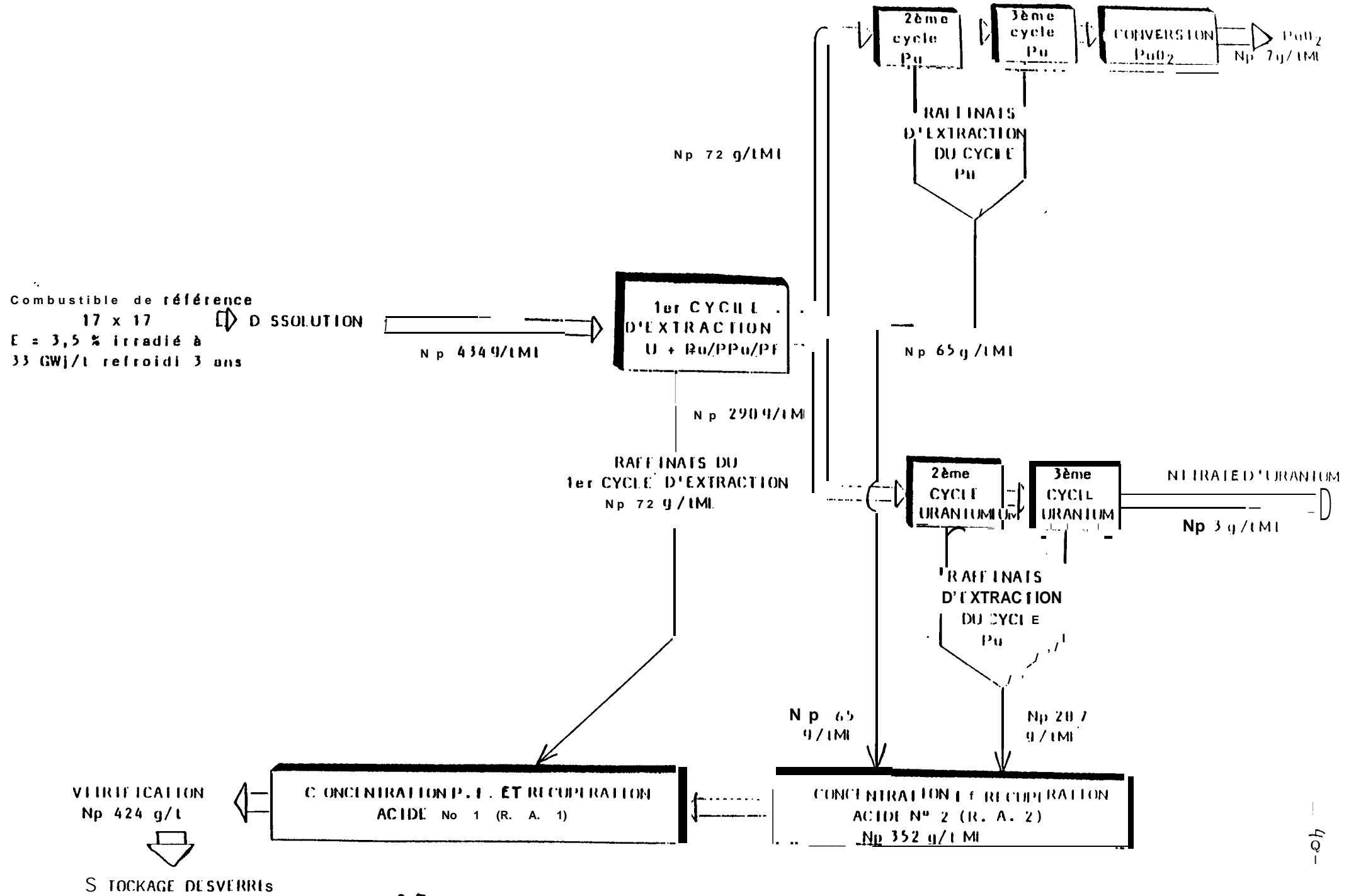
Figure 2.5: Prévisions concernant la répartition du neptunium dans le procédé UP-3

2ème cycle Pu → 3ème cycle Pu → CONVERSION PuO₂ → PuO_2 Np 7 g/tMl

RAFFINATS D'EXTRACTION DU CYCLE Pu

Np 72 g/tMl

Combustible de référence
17 x 17
E = 3,5 % irradié à
33 GWj/t refroidi 3 ans → DISSOLUTION

Np 434 g/tMl

1er CYCLE D'EXTRACTION U + Pu/PPu/PF

Np 65 g/tMl

Np 290 g/tMl

RAFFINATS DU 1er CYCLE D'EXTRACTION
Np 72 g/tMl

2ème CYCLE URANIUM → 3ème CYCLE URANIUM → NITRATE D'URANIUM   Np 3 g/tMl

RAFFINATS D'EXTRACTION DU CYCLE Pu

Np 65 g/tMl   Np 20 7 g/tMl

VITRIFICATION
Np 424 g/t ← CONCENTRATION P.F. ET RECUPERATION ACIDE No 1 (R. A. 1) ← CONCENTRATION ET RECUPERATION ACIDE N° 2 (R. A. 2) Np 352 g/tMl

STOCKAGE DES VERRIs

-46-

Scrub
3 M HNO₃

Extract
0.4 M U)(VI)
0.076g Np(VI)/ℓ
0.9059 Pu(IV)/ℓ
~0.1 M HNO₃

Strippant
0.01 M HNO₃

m

Evaporator product to partitioning
1.172 M U
0.178g Np(IV)/ℓ
2.12g Pu(III)/ℓ
~2 M HNO₃

Uranyl nitrate in solvent
0.244 M U

HS
Scrubbing 60°C

HC
Stripping

15 M HNO₃

Decontamination

0.5 M HNO₃ to strip Np

Aqueous feed
1.6 M U(VI)
0.304g Np(V)/ℓ
3.62 g Pu(IV)/ℓ
2 M HNO₃
Fission products

HA
2 stages

5 stages

Extracting, 45°C

H₂O ← Evaporators

Extract
0.293 M U
0.04459 Np(IV)/ℓ
~0.1 M HNO₃

Plutonium partitioning

Partitioning

Neptunium partitioning

Partially decontaminated product
0.2 M U (VI)
0.0389 Np(VI)/ℓ
0.4529 Pu(IV)/ℓ
0.06 M HNO₃

Reduced product
0.227 M U
0.0345g Np(V)/ℓ
0.411g Pu(III)/ℓ
0.06 M HNO₃

Np Oxidant
0.054 M V(V)
3 M HNO₃

Reducing reactors
>36 min

Solvent
30 v/o TBP

Impure plutonium product
2.12g Pu(III)/ℓ
~1.6 M HNO₃

Impure neptunium product
0.191g Np(IV)/ℓ
0.5 M HNO₃

High-level liquid waste
~2.4 M HNO₃
0.01 M V
Fission products

Solvent
30 v/o TBP
in dodecane

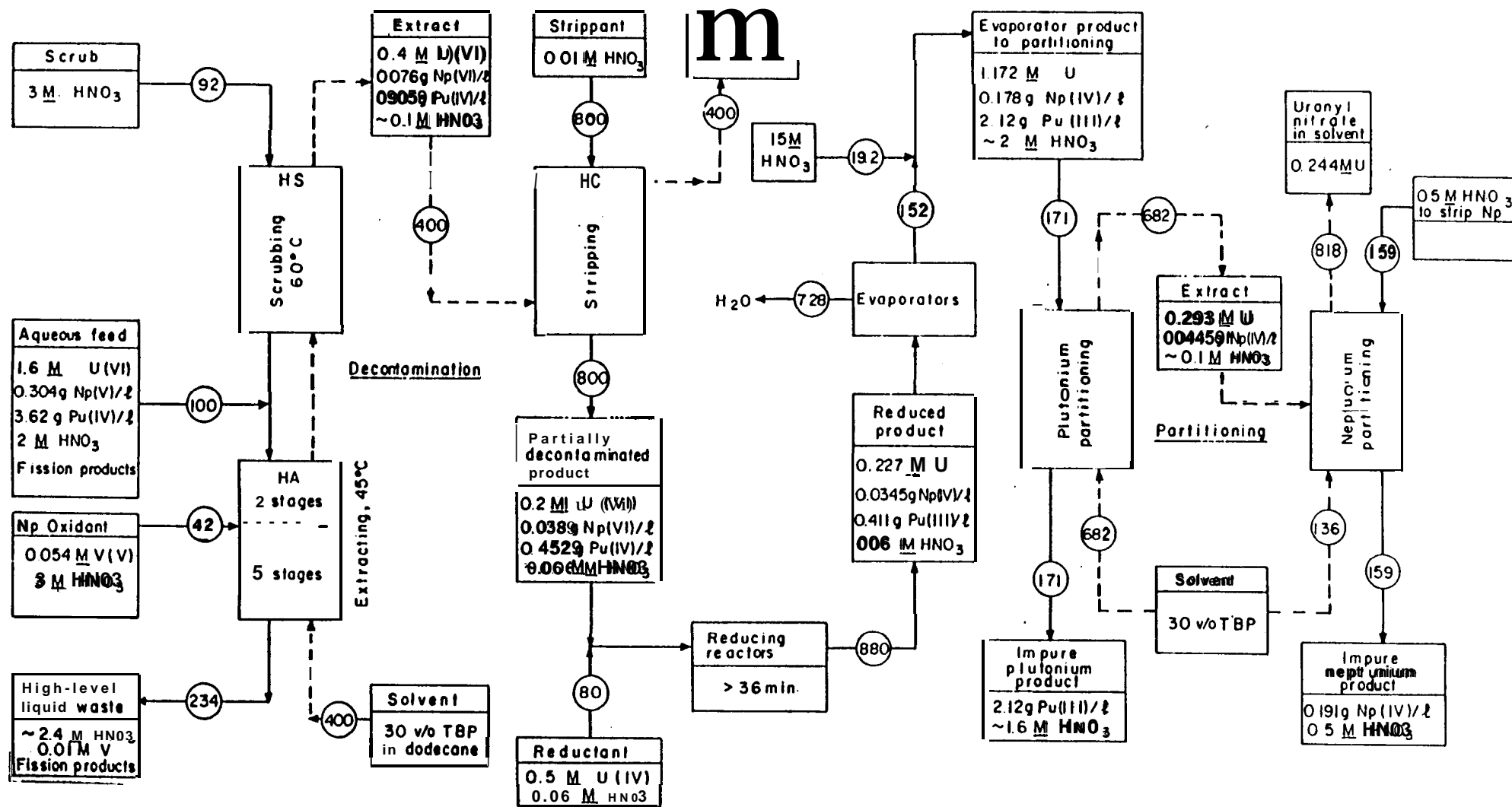**Reductant**
0.5 M U(IV)
0.06 M HNO3

FIG. 2.6 Principal steps in Purex process modified for neptunium recovery. Circles indicate relative volume flow rate; — aqueous; org ---

In this **process** [2.9] Np enters the HA-HS column and is quantitatively taken up in the TBP stream with U and Pu. This transfer is possible because a specific oxidant $(0.05\,M\,V_2O_5)$ is counter currently injected in the HA column at the third stage. All residual **NpV** which might still be present is oxidized to NpVI and coextracted with UVI and **PuIV.** In the Pu partitioning column **(BX)** Np follows quantitatively the **U(VI)** stream and is stripped from TBP with 0.5M **HNO$_3$.** This product stream is directly usable for the preparation of Np targets. However in the overall picture we have to keep in mind that only 45 % of the total Np is available in the HLLW storage or at the reprocessing step, the balance is, as already explained, formed by alpha decay of Am 241. Before proposing any improvement on the extraction flowsheet of Np, it must be proven that Am and Cm (partially) can be extracted from HLLW.

A R & D **programme** has been undertaken at PNC to improve the Np extraction in the **HA/HS** column without addition of salt compounds. By adding NO, **vapour** Np V is faster oxidized to Np VI and would **follow** the **U-Pu-TBP** stream.
The following modifications are required :

- **NO$_2$ sparging** in the Np extraction section;

- decomposition of residual NO$_2$ in the scrubbing section to avoid reduction of Np VI;

- increase of the **HNO$_3$** acid concentration in the scrubbing section.

2.1.4.2. *Americium- Curium extraction from HLLW.*

In the presently designed and operating reprocessing plants, the HAW is directly sent tot the acid recovery evaporator where the initial volume of 5 m^3/THM is reduced to 1000-500 **l/THM.** The HNO$_3$ **concentration is as a rule also reduced** by **addition** of CH$_2$O or **HCOOH.** Finally the HLLW is transferred to the storage tanks where it evaporates ti 11 about 400-300 1 **/THM.** Under these circumstances post-precipitation occurs and some soluble components are at the brink of crystallization.

A general overview of the work carried out in the period 1975-1984 at JRC has been summarized in the final report on the "Chemical separation of **actinides** from high activity liquid wastes" [2.10]. In the framework of this important R & D programme a number of chemical separation techniques have been tested on hot laboratory scale at CEN, FAR and **JRC-Ispra.** Successively we will summarize the three processes and comment on their advantages and drawbacks.

2.1.4.2.1. TBP extraction.

The essential steps of the process are shown in fig. 2.7. It consists of a concentration and partial denigration of HAW from 4 to 1 M HNO_3, followed by selective extraction of Pu and Np. In a second step the 1 M HNO_3 HAW **solution is deacidified by addition** of HCOOH down to 0.2 M HNO_3 with **simultaneous addition** of 0.54 M $Al(NO_3)_3$ and 1 M $NaNO_3$. The trivalent rare earths are coextracted in 30 % TBP dodecane. Selective back extraction of Am, Cm by a stripping solution of 0.05 DTPA + 1 M **Glycollic** acid at pH3.

During the denigration step 25 % Pu and 0.3 **%** Am and Cm precipitate. The recovery yields for Am and Cm in the back extraction were about 99 % but 70 **%** of Ce 144 and 85 **%** of Eu 154 accompany the Am-Cm fraction. Important gamma contamination was also found in the **Actinide** fraction due to Ru 106 and even Cs 137.

The selective separation of Am and Cm from Rare Earths according to the TALSPEAK process was performed with 0.3 M HDEHP - 0.2 M TBP and stripped with 5 M HNO_3. The yields obtained were not sufficiently interesting to be used as reference method for further P & T purposes. In addition it has to be mentioned that the process is technologically complex and introduces large quantities of $Al(NO_3)_3$ and $NaNO_3$ which might interfere with the reference vitrification process.

2.1.4.2.2. HDEHP process.

The process flowsheet is shown in fig. 2.8. The denigration of HAW is directly made with HCOOH till pH2. The solution is filtered to remove
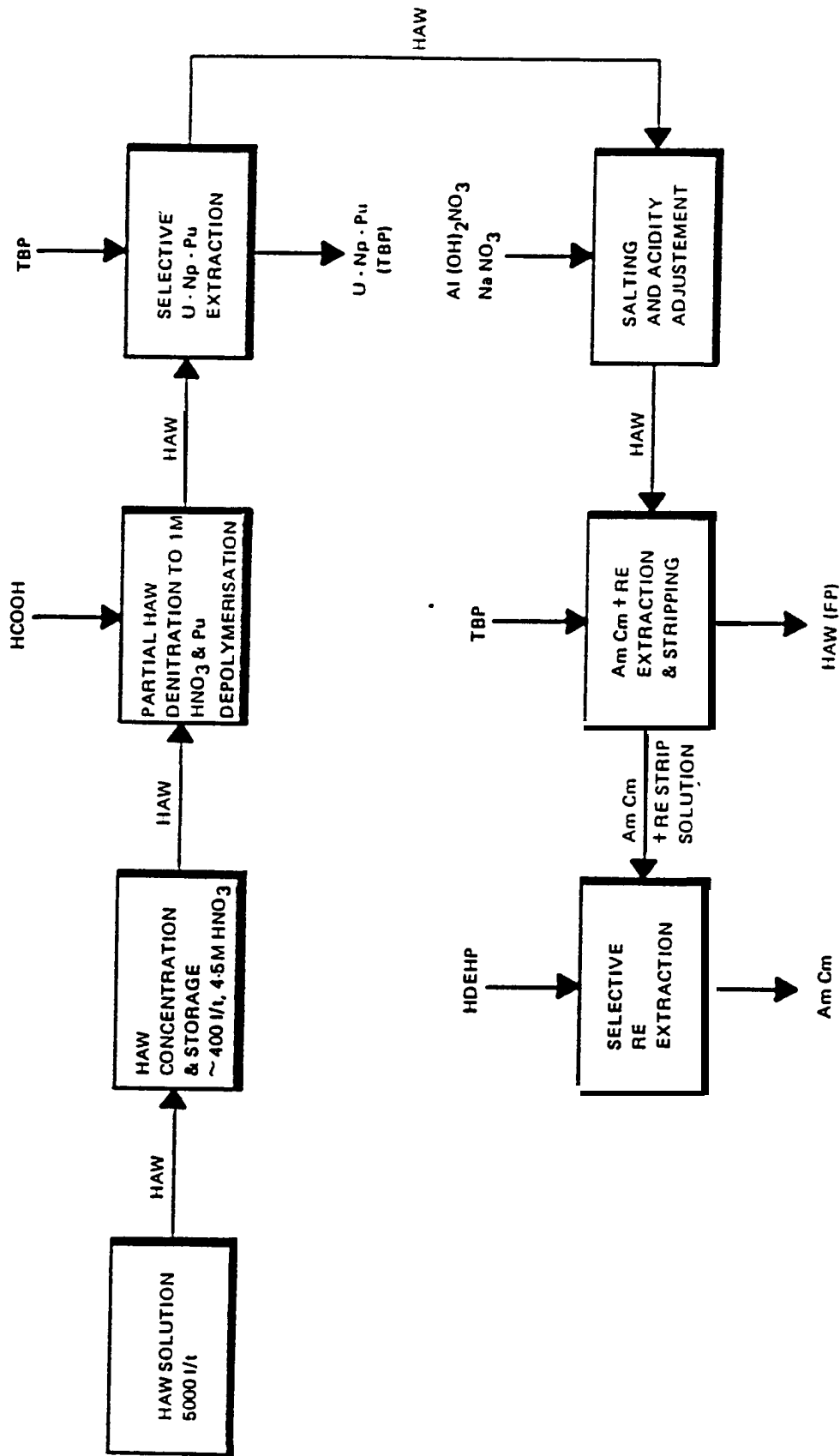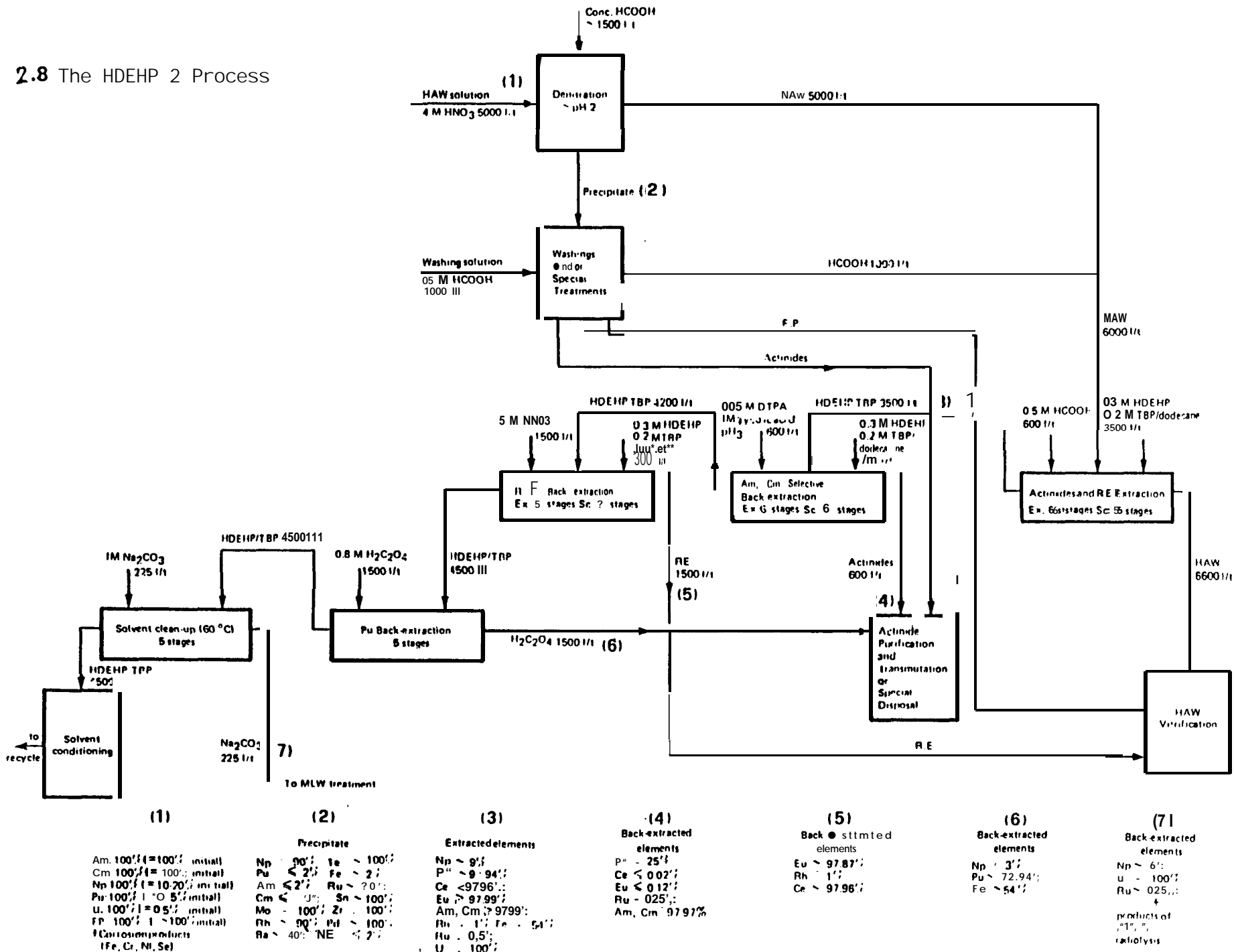
Fig. 2.7.

Fig. 2.7 0   f the TBP 2 Process

2.8 The HDEHP 2 Process

Conc. HCOOH ~ 1500 l/t

HAW solution
4 M HNO₃ 5000 l/t

(1) Denitration ~ pH 2

NAw 5000 l/t

Precipitate (2)

Washing solution
05 M HCOOH 1000 l/t

Washings and or Special Treatments

HCOOH 1000 l/t

F P

Actinides

MAW 6000 l/t

HDEHP TBP 4200 l/t
005 M DTPA
1M glycolic acid pH 3 600 l/t
HDEHP TBP 3500 l/t

5 M NNO3 1500 l/t
0 3 M HDEHP 0 2 M TBP dodecane 300 l/t

0.3 M HDEHP 0.2 M TBP dodecane /m l/t

05 M HCOOH 600 l/t
03 M HDEHP 0 2 M TBP/dodecane 3500 l/t

H F Back extraction Ex 5 stages Sc 2 stages

Am, Cm Selective Back extraction Ex 6 stages Sc 6 stages

Actinides and RE Extraction Ex 66 stages Sc 55 stages

HDEHP/TBP 4500 l/t

IM Na₂CO₃ 225 l/t

0.8 M H₂C₂O₄ 1500 l/t

HDEHP/TBP 4500 l/t

RE 1500 l/t

Actinides 600 l/t

HAW 6600 l/t

(5)

(4)

Solvent clean-up (60 °C) 5 stages

Pu Back-extraction 5 stages

H₂C₂O₄ 1500 l/t (6)

Actinide Purification and transmutation or Special Disposal

HDEHP TBP 4500

Na₂CO₃ 225 l/t (7)

Solvent conditioning

to recycle

HAW Verification

R E

To MLW treatment

(1)	(2) Precipitate	(3) Extracted elements	(4) Back-extracted elements	(5) Back extracted elements	(6) Back-extracted elements	(7) Back-extracted elements
Am 100% (=100% initial)	Np ~ 90% Te ~ 100%	Np ~ 9%	P" - 25%	Eu ~ 97.87%	Np ~ 3%	Np ~ 6%
Cm 100% (= 100% initial)	Pu < 2% Fe ~ 2%	P" ~ 9 94%	Ce ≤ 002%	Rh 1%	Pu ~ 72.94%	u - 100%
Np 100% (= 10-20% initial)	Am ≤ 2% Ru ~ 20%	Ce <9796%	Eu ≤ 012%	Ce ~ 97.96%	Fe ~ 54%	Ru ~ 025%
Pu 100% (~0 5% initial)	Cm < 9% Sn ~ 100%	Eu ~ 97.99%	Ru - 025%			
u. 100% (= 05% initial)	Mo - 100% Zr ~ 100%	Am, Cm ~ 9799%	Am, Cm ~ 97.97%			products of
FP 100% (~100% initial)	Rh ~ 90% Pd ~ 100%	Rh ~ 1% Fe ~ 54%				"1", radiolysis
Corrosion products (Fe, Cr, NI, Se)	Ba ~ 40% NE ~ 2%	Ru ~ 0,5% U ~ 100%				

precipitate. Counter current extraction of Actinides and Rare Earths is done with 0.3 M HDEHP - 0.2 M TBP.dodecane extractant. Counter current back extraction of Am and Cm is done with 1 M glycollic acid 0.05 M DTPA at pH3.

A **full scale hot cell test with representative** HAW solutions was performed at CEN-FAR.

After the denigration step, 7 % of Pu was precipitated but 99 % of Am and Cm could be found in the HNO_3-HCOOH solution. The HDEHP extraction worked quite well with recovery yields of 99.4 % for Am and Cm from HAW. **The back extraction** of Am and Cm in 0.05 DTPA - glycollic acid also proved to be near quantitative. Relatively low residual F.P. **contamination was found in** the Am, Cm fraction.

The HDEHP extractant is very sensitive to pH adjustment and suffers from gamma and alpha irradiation. The degradation of the solvent is about 5 % at 10^8 Rad.

This process looks analytically very attractive but the very strong **deacidification** which is required is a serious drawback since sludge formation is important.

2.1.4.2.3. *OXAL precipitation.*

This process was pioneered at JRC and tested in the hot cell facilities of **Ispra.** Denigration of HCOOH **and precipitation with oxalic acid ($H_2C_2O_2$)** are the main process step. Quantitative precipitation (99.9 %) of Am and Cm was observed in 0.7 to 0.8 M HNO_3. At higher acidities only partial precipitation occurs. About 96 % of Pu and 10 % of different fission products coprecipitated.

The **oxalate** precipitation is a **simple** step but it is not selective and includes all trivalent ions. The method might be used as a pretreatment step to avoid serious radiation damage on the organic extractant.

The corrosion of Stain'less Steel by HCOOH - $H_2C_2O_4$ mixtures is a serious technological drawback which needs carefull thought in designing the facility.

The majour advantage of the process is the absence or at least the very reduced quantity of secundary waste compared to the TBP and HDEHP processes. .

2.1.4.2.4. *The TRUEX process [2. 11]* [2. 12]

A new bidentate extraction reagent CMPO (Octyl-phenyl-N-N-di-iso-butyl-carbamoyl-methyl-phosphine oxide) is efficient in higher nitric acid concentrations than those discussed above. The presence of CMPO together with TBP in normal paraffine hydrocarbon diluent permits the coextraction of III, IV and VI valent actinides in a modified PUREX process called the TRUEX process.

Fig. 2.9. shows a generic TRUEX flowsheet using a mixed solvent of 0.2 M CMPO - 1.4 M TBP in a $C_{12}-C_{14}$ paraffinic diluent.

In order to suppress the extraction of Zr and Mo, oxalic acid is added to the HNO_3 solution. However Rare Earths and Tc are also coextracted to a certain degree and need to be separated afterwards from the Am-Cm fraction. Ion exchange has been proposed for this step.

The fission products and inactive impurities are scrubbed from the CMPO-TBP solvent with 0.25 to 1 M HNO_3. The Am-Cm fraction together with RE is stripped from the loaded solvent with 0.05 M HNO_3. Eight extraction - and four scrub sections are sufficient to reach a DF of > 10^4 from Am. The proposed flowsheet is in principle capable of reducing the HLLW concentration of Am to about 40 n Ci/g.

However one of the weak points in this process is the solvent stripping step which requires the very corrosive HNO_3-HF solution to separate the Pu-Np fraction from the Am-Cm free solvent. The use of corrosion resistant equipment in the frame work of a larger reprocessing complex made of stainless steel asks for specially designed equipment and elimination of fluorides.

Fig. 2.9
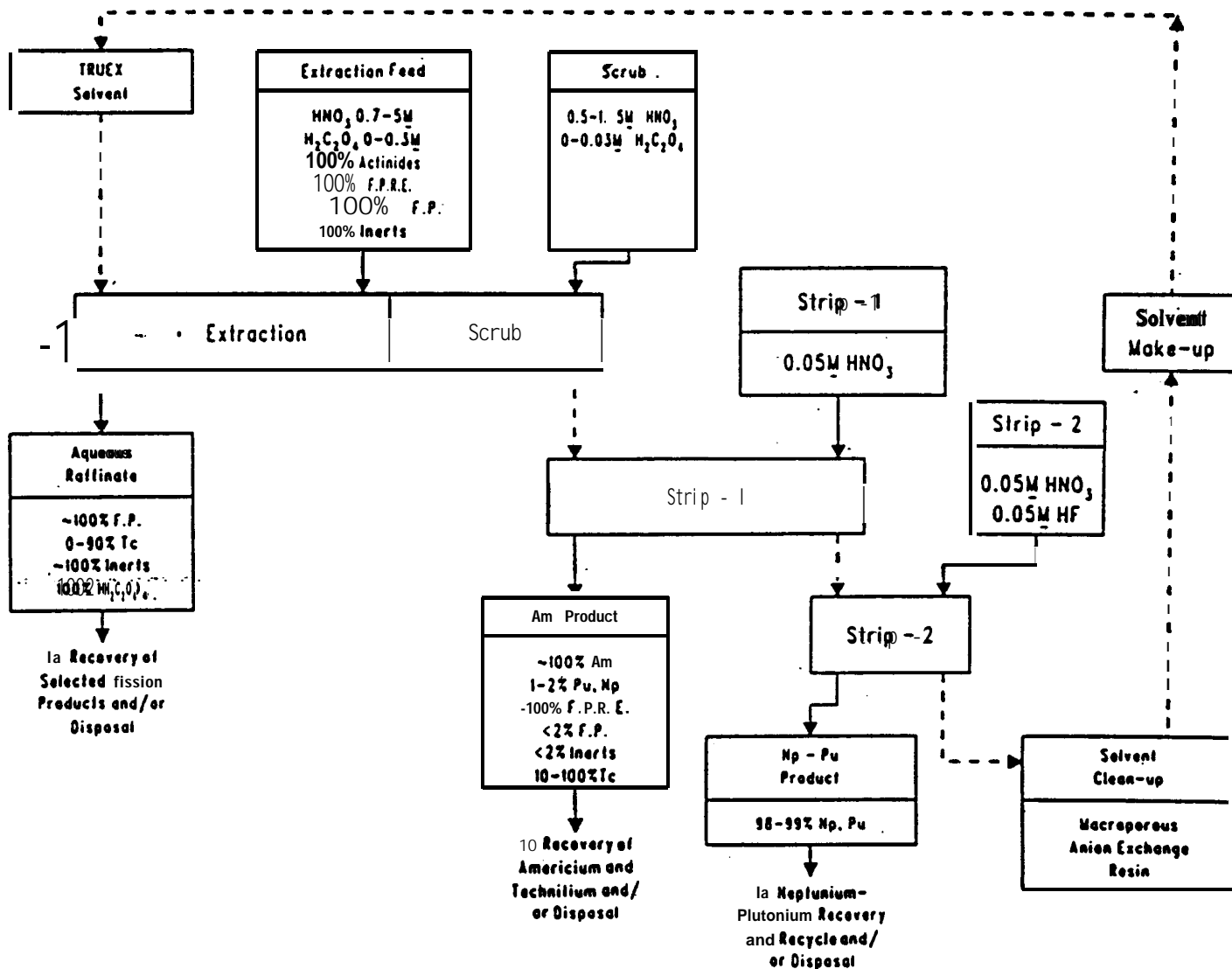
Generic TRUEX Process Flowsheet.

2.1.4.2.5. *Misce 1 laneous deve lopments.*

Several new methods are being studied in order to improve the extractability of minor **actinides.** It is obvious that all methods discussed above suffer from the inability to separate the minor actinides from HLLW in one and a single or at least a few steps. Particularly Am needs a very elaborate separation scheme because of its chemical analogy with the Rare Earths. One of the promising—approaches--consist of—transforming all **actinides** in their **hexavalent** state including Am which is normally unstable as Am VI. By **electro-oxidation** and extraction chromatography separation the isolation of Am is feasible and tests have been performed on laboratory scale [2.13]. A second but completely new venture is the development of a solvent replacing TBP as **majour** extractant in reprocessing : e.g. **N.N. dialkyl** amides [2.14] and beta **diphospor** amides [2.15]. Finally a more conventional approach could also lead to improvements e.g. the development of more specific **extractants** operating at higher acidity. One of those reagents is **di-iso-decyl-phosporic** acid which permits to extract a wide range of actinides from acid medium but more specifically focussed on Neptunium separation [2.16] [2.17]. A general flowsheet is shown in fig. 2.10. Most of Am and Cm can be separated from RE by using the **back-**extraction method similar to the TALSPEAK process.

2.1.5. Technical feasibility and impact of Minor Actinide partition.

As far as the present state of technology is concerned it is not possible to remove the minor actinides quantitatively from HLLW or during the conventional reprocessing step. Many methods have been tried on hot laboratory scale but none have been **upscaled** to a technological level in pilot type facilities.

In the present reprocessing plants the chemical operations are based on the use of TBP and 1.-5 M HNO_3. In such conditions the minor actinides will be entirely diverted to HLLW except for Neptunium.

A first step in the implementation of minor actinide separation could be to slightly modify the PUREX flowsheet in order to isolate Np or to **incorpo-**
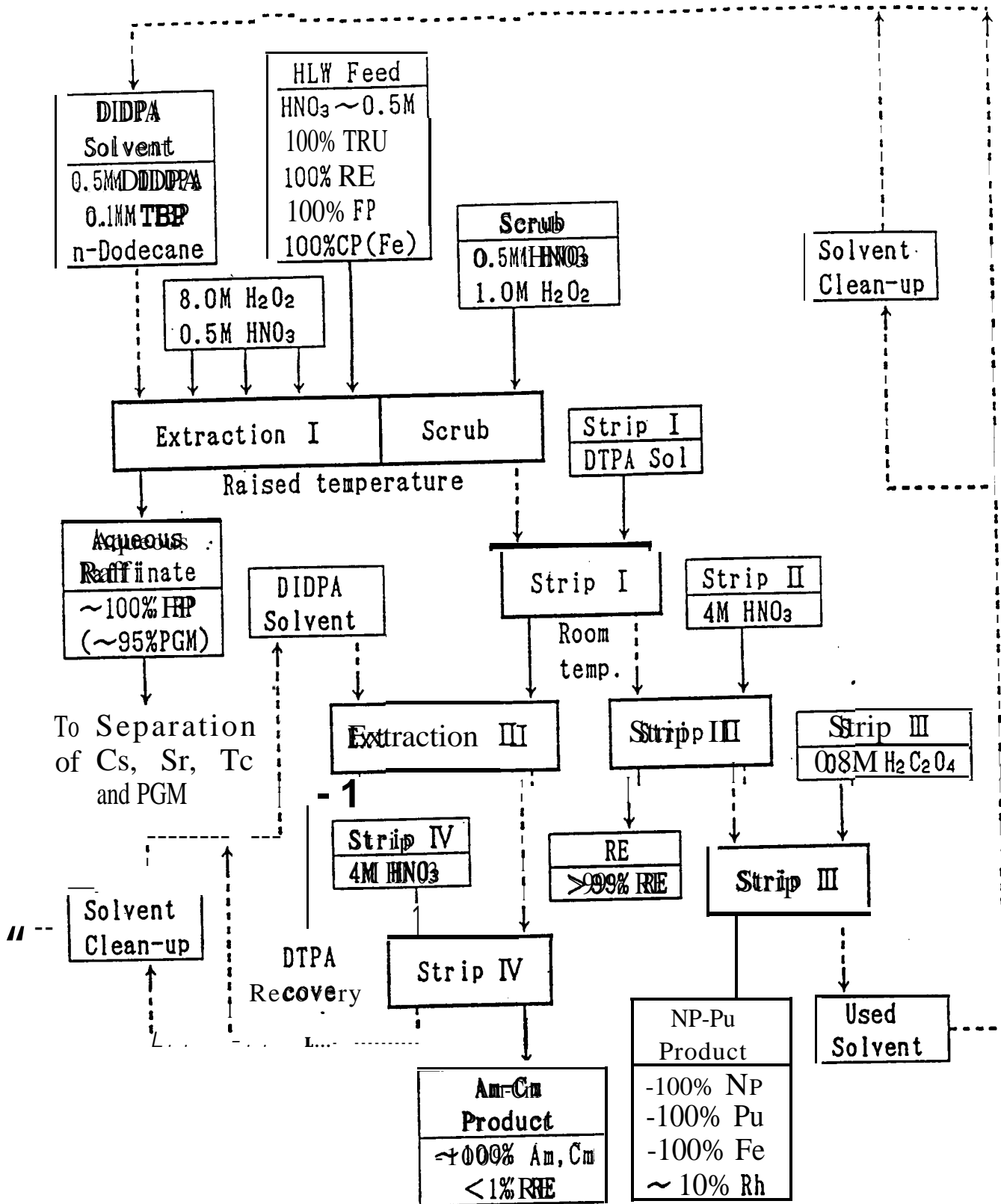
DIDPA
Solvent
0.5M DIDPA
0.1M TBP
n-Dodecane

HLW Feed
HNO₃ ~0.5M
100% TRU
100% RE
100% FP
100% CP(Fe)

Scrub
0.5M HNO₃
1.0M H₂O₂

Solvent
Clean-up

8.0M H₂O₂
0.5M HNO₃

Extraction I | Scrub
Raised temperature

Strip I
DTPA Sol

Aqueous
Raffinate
~100% FP
(~95%PGM)

DIDPA
Solvent

Strip I
Room
temp.

Strip II
4M HNO₃

To Separation
of Cs, Sr, Tc
and PGM

Extraction II

Strip II

Strip III
0.8M H₂C₂O₄

Strip IV
4M HNO₃

RE
>99% RE

Solvent
Clean-up

DTPA
Recovery

Strip IV

Strip III

NP-Pu
Product
-100% NP
-100% Pu
-100% Fe
~ 10% Rh

Used
Solvent

Am-Cm
Product
~100% Am,Cm
<1% RE

Fig.2.10 Process Flowsheet for TRU Separation by Extraction with DIDPA
Followed by Selective Back-Extraction.

rate Np into the HLLW. Such a proposal does not require important tech-
nological changes and can be carried out in the presently designed equip-
ment.

Under these improved extraction conditions the residual **majour actinides**
and all the minor **actinides would** be concentrated in one single solution
from which two ways are practicable : selective extraction and/or vitrifi-
cation. This source term is the basis for further chemical processing and
waste management. The high concentration of HLLW in the waste evaporator
(factor 15) increases considerably the nitrate-salt concentration and the
acidity. Reduction of the acid concentration factor of HAW might produce
an easier type of HLLW to cope with but **will** increase its volume **propor-
tionally.** Acid decomposition by formaldehyde or formic acid are presently
industrial standard and lead to a more moderate acid concentration of 2-3 M
HNO_3. **Thi**s is favorable for corrosion reduction during prolonged storage.

All R & D efforts should be **focussed** on group separation of **Actinides** from
this fai**r**ly acid solution without any further acid decomposition and
without salt addition.

As soon as the acidity drops below 2 M considerable precipitation occurs
and a non **negligeable** fraction of Actinides might co-precipitate and be
taken up in the sludge which enters the vitrification process. Up to now
only the TRUEX process can separate the **actinides** in strong acid medium but
it extracts also the Rare Earths. Under these circumstances a complex
separation and purification flowsheet is required to separate the minor
actinides from the Rare Earths which are strong neutron absorbers. The
chemical stream suitable for target preparation ought to be free of neutron
poisons. Development of more selective and radiation resistant **extrac-**
tants, stable in contact with strong acid media and specific for Am(Cm) is
a **conditio-sine-qua-non** for the success of any partition scheme of **HLLW.**

The use of chlorides or fluorides in any separation scheme should be
avoided in order to protect the hot-cell facilities from early corrosion.
The same applies to chlorine and fluorine atoms incorporated in the **ex-**
tractant molecules or in the solvents (e.g. CCl_4) which will partially
decompose under intense alpha and gamma irradiation.

The Am separation can also be approached from electrochemical viewpoint by using redox reactions to influence the separation scheme. Experience has learned that these reactions are accompanied by strong corrosion except if noble metals or very refractory materials are used as structural materials.

The danger of recycling corrosive chemicals into the reprocessing plant must be avoided by any means.

Aim at very high DF's for minor **actinides** is a scientific and technical goal in itself, but it is not a requirement from waste management or **longterm** safety point of view.

Transform the HLLW into a pure fission product mixture containing less than 10 n Ci/g alpha emitters is a very difficult and probably unnecessary step since the residual fission products constitute themselves the most important **longterm** radiological source term in particular I 129, Tc 99, Se 79, **Zr** 93... The range of target decontamination factors given in table II-2 are technical targets intended to eliminate the **longterm** Np risk and to reduce the Pu inventory in vitrified HLW.

Partitioning of minor actinides is indeed only the first step in a whole process of risk reduction. Transmutation is the next step which must be carried out quantitatively if the whole P & T operation is to yield an overall radiological benefit.

Two terms have to be balanced against each other : on the one hand the radiological cost of increasing the direct irradiation risk due to the extension and complication of the reprocessing operations and on the other hand the radiological benefit of decreasing significantly the long term actinide risk.

According to a recent evaluation of **OECD-NEA** [2.18], the collective dose commitment due to reprocessing operations ranges from 7 man Sv per 800 T spent fuel to 20 man Sv per 1200 T spent fuel. Taking into consideration that improvements will reduce the mean value, a medium collective dose of 10 man **Sv/1000** T HM equiv spent-fuel reprocessing is a reasonable **yard-**

stick.   Increased radiological risk due to partitioning operations can be estimated at 30 % of the total i.e. an additional 3 man.Sv/1000 T or 12 man Sv/4000 T.HM.

The calculated collective dose commitment of 4000 THM/equiv HLW in a geologic repository (clay) amounts to 82 man Sv among which 15 man Sv is due to Np.

It is obvious that an incremental collective dose of 12 man Sv is almost balanced by a credit of 15 man Sv (only due to Np) on a million years horizon.

If however a geologic repository is not accepted as a waste management option increased gain will be obtained from P & T if free dilution of actinides in the groundwater is considered.

The systematic analysis of the different waste streams has shown that the collective dose due to I 129 released from MLW and corresponding to the same quantity of fuel (4000 THM equivalent) is 2400 man Sv.

This comparison shows the overwhelming significance of the fission products and particularly of I 129 in a new concept of P & T complementary to geologic repository of HLW and not as an alternative option for waste management.

The conventional reprocessing cost is presently about 6.000 FF/kg fuel or US 1.000 $/kg fuel.   Additional costs for partitioning are estimated to vary from 10 to 30 %.   The cost to reduce the actinide concentration in HLW to 100-800 n Ci/g levels will amount to US 100 - 300 $ /kg fuel or 380 - 1,140 M$/year for the scheduled conventional reprocessing capacity of 3800 T/year (see chapter I, Table III) in the OECD countries with a positive reprocessing option.

These costs have to be compared with the incremental safety costs asso-ciated with the storage of HLW compared to the actinide free HLW option. This subject need to be further examined in detail.

2.2. LONG LIVED FISSION PRODUCTS

2.2.1. **Occurence** and distribution of long lived fission products.

The fission products which play a very important role in the long term dose to man originating from HLW disposal are Tc 99, **Zr** 93 and Se 79. In cladding waste the same **nuclides** occur but in addition an important C14 **contamination** is found which-has its--impact on--the environment.. .

Last but not least I 129 appears for 99 % in Medium Level Waste and is discharged to the sea or stored on solid **sorbents.**

Hypothysing that in the future Iodine 129 releases to the sea might be curtailed or forbidden, this **nuclide** will have to be disposed of in a geologic repository.

Fig. 2.11 shows the contribution of the different waste streams to the **local** dose to man living in the vicinity of a 4000 THM equivalent HLW repository [2.3].

Iodine is by far the most important contributor (10 % of the **MPC** - large population) followed by cladding and MLW. Vitrified HLW is three orders of magnitude lower than iodine. The reason for this result is the rapid migration of iodine in groundwaters compared to actinides.

The concentration of long lived fission **radionuclides** found in all types of waste are given in table IV and VII of Chapter 1.

Given the importance of I 129 in the overall picture, this **nuclide** will be discussed first.

Fig. 2.11.
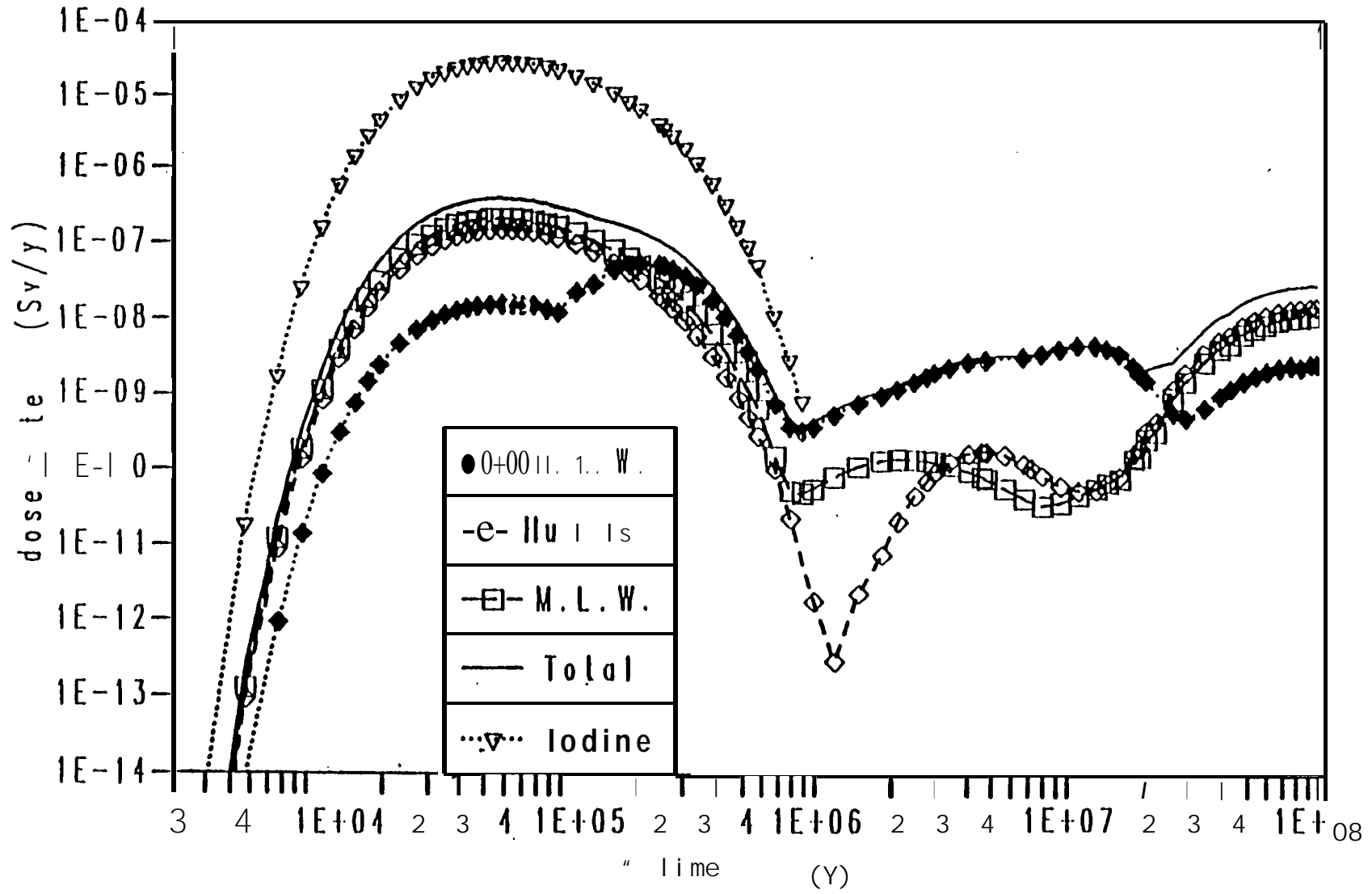
Normal evolution scenario ; total dose rates via the water well pathway calculated for the four considered waste types (total : sum of the dose rates due to HLW, cladding waste and MLW)

2.2.2. Separation of fission products and disposal options.

2.2.2.1. Iodine waste.

Iodine 129 has a half life of 1.7 10^7Y and is produced by fission in the irradiated fuel at a rate of 190 **g/THM.** It is present as molecular iodine, **Cesium** iodide and other oxidized forms.

The separation of ^{129}I from Dissolver Off Gases is a standard procedure at the fuel reprocessing plants, see fig. 2.3, because of the potential local buildup of this **radionuclide** in the biosphere surrounding the plant and its danger to man.

The scrubber liquids contain all iodine compounds (^{127}I, ^{129}I and ^{131}I) and some **nuclides** entrained in the off gas stream as aerosols **(Ru,** Sb, . ..). The saturated liquid can be used directly as the ^{129}I source for conditioning and storage or, as is the case in the UK and France, discharged into the sea under controlled conditions.

The techniques for trapping and conditioning iodine have been studied extensively in the past [2.19]. The most important alternative to caustic scrubbing is the direct sorption on silver impregnated **sorbents.** This option is very attractive from waste management point of view since the iodine is very firmly held by a solid material which can be kept for as long as deemed desirable. In the long term the stored iodine loaded material will have to be disposed of in an underground repository for ultimate confinement. In both fully opposite management options : direct dilution and geologic confinement, the most appropriate one depends on the siting of the reprocessing plant and on the availability of a suitable repository.

The impact of direct discharge into the ocean has been assessed for **re**processing plants located in North Western Europe. The maximum individual thyroid dose due to **molluscs** and crustacea amounts to 0.17 **mSv/y** at a yearly discharge rate of 2 TBq. The regional collective dose remains very small in the first centuries but could reach 150 **man.Sv** after a long period of time. As long as the reprocessing capacity throughout the world remains

at the present level, discharge of iodine-129 effluents could be an acceptable intermediate practice. However, in the long term the accumulation of ^{129}I in world's oceans will increase the doses to mankind. Without sedimentation the global collective dose commitment reaches a value of 2.5 10^4 man.Sv.

The alternative iodine management option with storage of solid sorbents and eventual disposal has to take into account that iodine **is** a very mobile element in the geosphere. In a clay repository the long-lived **actinides** (except ^{237}Np) can be confined for geological periods without noticeable dose to man [2.3] but recent calculations in the framework of the PACOMA project of the **CEC** have shown that iodine-129 cannot be neglected [2.20] [Fig. 2.10].

In case iodine should be retained at the reprocessing plant and that the resulting iodine waste has to be disposed of in a geological repository e.g. (Boom clay in Belgium) the maximum calculated dose rate might rise to a value of 0.54 mSv/y. According to a normal scenario the ^{129}I activity would reach the neighboring aquifer after about 5,000 years and the maximum flux occurs around 5.4 10^4 years with a **radionuclide** flux resulting in an annual dose rate of 0.1 **mSv/year,** which is 10% of the natural background. The waste conditioning form (cement) does not exert any influence on the release rate from a **AgI** type iodine waste source. As a conclusion we can state that geological disposal of ^{129}I in clay is not a suitable and final solution for this problem.

ICRP recommends a dose limit of 1 **mSv/year** and for local contributions to the background 0.1 **mSv/y.** The potential contribution of ^{129}I in iodine waste equals or surpasses that criterion.

Transmutation of ^{129}I into a short-lived ^{130}I decaying into stable ^{130}Xe is an alternative strategy which ought to be assessed in order to investigate its feasibility and economics.

The transformation of iodine trapped in scrubbing liquids or on silver zeolites into pure target material ready for irradiation in a HFR is much

more difficult than could be expected at first glance.   The elements accompanying the iodine must be removed in order to reduce and concentrate the iodine fraction and to reduce the neutron loss due to activation of chemical impurities.

iodine in scrubbing liquids can be removed from the scrubber solution as molecular I_2 by oxidative **sparging;**

- iodine'' present in the **AgI** filter materials is very difficult to extract.

But since the bulk of the iodine is caught in the caustic scrubbers, it is not necessary to recover this residual amount ($\leq$ 2%).

Iodine can easily be transformed into iodate and precipitated with **Ba** or Pb salts.   Because of its chemical stability and insolubility, preference should be given to **Ba(** $IO_3)_2$ as target material which can afterwards also be used as final storage matrix. $Ba(IO_3)_2$ is furthermore thermally stable till **700°C.**

2.2.2.2 *Technetium*

Technetium-99 is the second most important long-lived fission product which cannot be confined within a geologic repository because of its mobility as TcO_4 - coupled to its half-life of 2.1×10^5 years.

^{99}Tc occurs for 50 **%** in the insoluble residues; together with Pu, noble metals and short-lived fission products (^{103}Ru, ^{106}Ru**).**

The reference option presently selected by the major reprocessors is the vitrification of the combined insoluble residues and **HLLW.**   In this scenario all the insoluble residues which contain appreciable amounts of Pd, Rh and Ru are incorporated in a glassy matrix and become practically unrecoverable in the future.   Leaching of the glassy matrix will eventually transfer 'g Tc from the source to the environment. The problem is **obviously** much less preoccupying than I 129 since this level is only reached after 1.1 million years.   However, when comparing with other **nuclides** leached from vitrified HLW, it is still the most important contribution to the **radiologic** burden of HLW after ^{129}I, ^{237}Np and ^{135}Cs**.**

Taking into account the high radioactivity of these fission products, it is very difficult to carry out chemical separations before 25 years cooling [2.2].

By simple chemical treatment (reduction or sulphide precipitation) the soluble "noble metals" including Tc can be separated from HLLW and stored together with the rest of the insoluble residues produced during the clarification.

Storage of this waste stream for several decades would eliminate the major radioactivity due to ^{106}Ru and could be used as a resource for noble metals [2.21]. At that stage the separation of Tc from Ru, Rh and Pd could be performed according to existing precious metal refinery techniques.

A principle advantage of this scenario is the recovery for future generations of important mineral resources which would be available for industrial applications. The residual ^{99}Tc metal could be used as a target for transmutation in HFRs or FBRs. By neutron capture ^{99}Tc is transformed into ^{100}Tc (15.3 s) and decays to stable ^{100}Ru.

Some pyrochemical techniques based on leaching with liquid magnesium and lead at temperatures of 950°C have been reported [2.22]. In Japan work is also in progress on the pyrometallurgical separation of Ru, Rh, Pd, Tc from insoluble residues [2.23]. The separation of Tc along with noble metals from HLLW is being studied in Japan by using active carbon filtration followed by elution with KSCN [2.24].

The transformation of any chemical Tc form into the very insoluble Tc O_2 compound or into metallic Tc is the most obvious way to prepare irradiation targets for long duration irradiation in safe conditions, or even storage.

The quantity of ^{99}Tc produced by the LWR fuel irradiation amounts to 21 kg/GWe year, such relatively large amounts require the development of new large high flux irradiation facilities. The Los Alamos accelerator driven high neutron flux reactor is a typical facility which could transmute Tc 99 on an industrial scale.

2.2.2.3 *Miscellaneous Radionuc 1 ides.*

Among the long lived fission products encountered in HLW a few deserve some attention because of their very long half life. In this case we find Se 79, Zr 93 and Cs 135 with half lives of over a million year.

In MLW and cladding waste C 14 with a half life of 5730 y is a **radiologic** important component.

Table 11.5. summarizes the radiological data for these **nuclides** 1000 years after discharge.

TABLE 11.5

Radiological data of some long lived radionuclides
1000 years after discharge **(ICRP** 61)

	HIGH LEVEL **WAST**			MLW and Cladding
	Se 79	Zr 93	Cs 135	C^{14} "-"
tl/2 (y)	$6.5 \ 10^6$	$1.5 \ 10^6$	$2. \ 10^6$	5730
Ci/THM	0.41 (0.33)	1.8	0.352	0.61
g/THM	5.7	736	324	
g el /THM	9.21_4	3327	448	
Bq/l (*)	2.10	500	300	900
Hazard factor	$7.5 \ 10^5$	$9.4 \ 10^7$	$1.3 \ 10^8$	$2.5 \ 10^7$

(*) ALI x 10^{-4} in **Bq/l**

Se 79 is present as Se O_4 ion (similar to sulfate) in HLLW and ends up in the vitrified waste. It migrates rather easily in aquifers and is one of the early **radionuclides** to reach the biosphere through the aquifer after about 10^5 years. However in a very reducing medium Se would reduced to an insoluble **Selenide** form.

Zr 93 is present in MLLW as a dissolved species and as insoluble precipi-tate in the **unsoluble** fines fraction. Due to its physiochemical **behaviour** (hydrolysis, col loid formation) it does not migrate rapidly and reaches the biosphere only after a million year.

Cs 135 is present in vitrified HLW together with CS137. After 1000 years only Cs 135 remains at a significant concentration. Due to absorption effects with the earth minerals it migrates rather slowly.

Separation of these **radionuclides** from HLLW is very difficult especially for **Cs** 135 because of the overwhelming **Cs** 137 activity which would **complicate** any chemical separation. The isotopic separation **Cs 135/Cs** 137 looks almost impossible to perform at reasonable costs.

It is not excluded to partition the **Zr** 93 from the insoluble residues once all the other **radionuclides** have decayed (after 50 years) but the other stable **Zr** forms will make such an effort futile.

The **C14** contamination of the cladding waste is a very specific radiological hazard for the immediate vicinity of a HLW repository.

Due to the large dilution in **claddings** any attempt to remove **C14** is **difficult** except perhaps melting of the **hulls.** In this case the $^{14}CO_2$ will escape from the molten **zircaloy** and will have to be trapped locally in chemical scrubbers. A **Ba** CO_3 sludge might be the starting point of a P&T approach.

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