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Reprocessing Problems Associated with the
Increasing Burn-up of Future Fuels

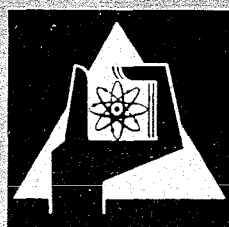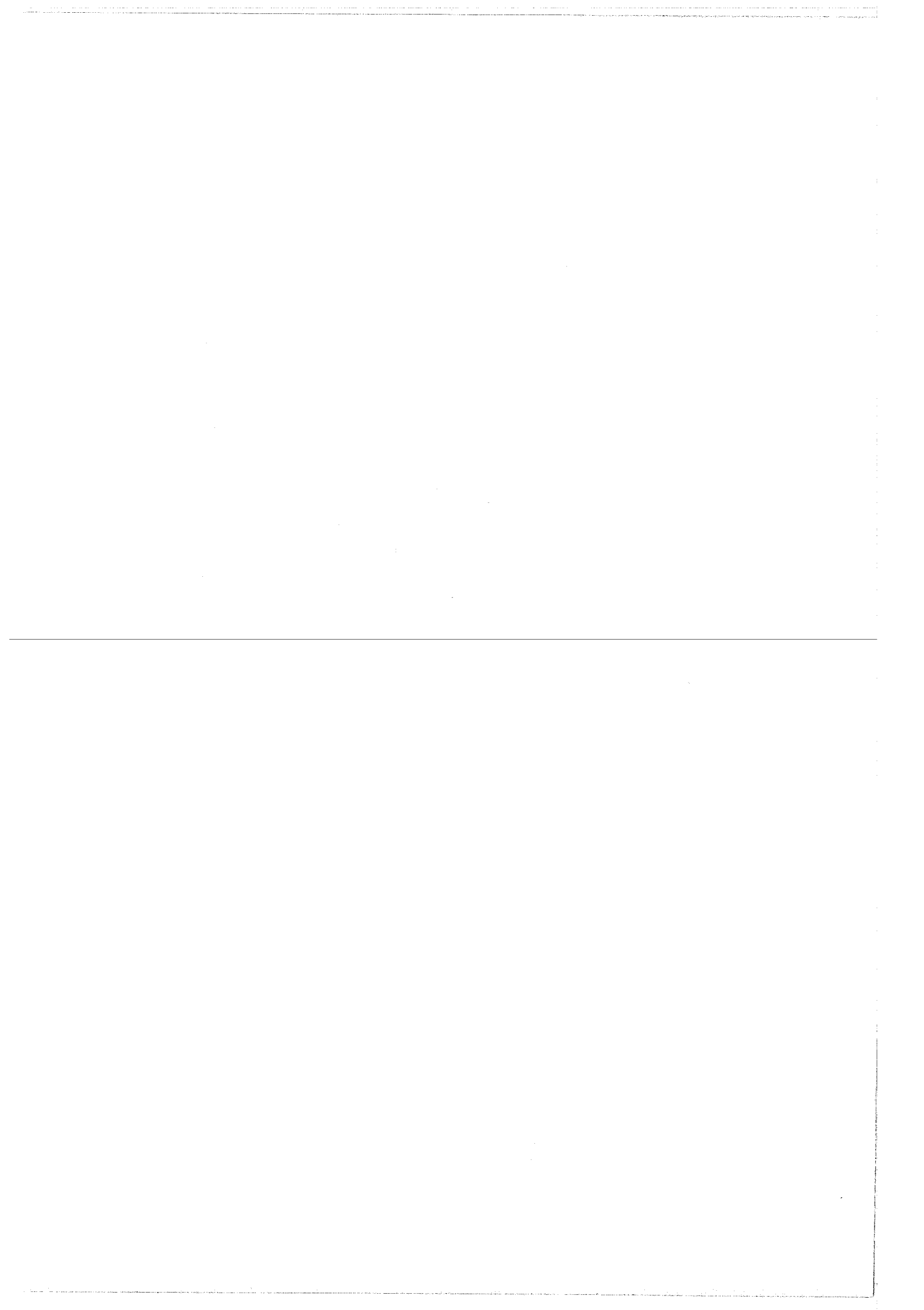F. Baumgärtner

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Reprocessing Problems Associated with the
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## Introduction

Nowadays, the burnup of nuclear fuels reaches up to about
20,000 MWd/to. In the future, the burnup will increase still
further more. Additionally there is a tendency towards shorter
cooling times to perhaps 30 days.

For a realistic discussion of the problems of reprocessing, it
is advisable to estimate at least the order of magnitude of the
future burnup.

If one does exclude from consideration the gas cooled Thorium-
High-Temperature-Reactors which probably will require quite
different chemical treatment, one finds the future burnup for
reprocessing to be in the region of 30,000 - 40,000 MWd/to (1,2).

For the fast breeder, a combined core- and blanket-burnup of
39,000 MWd/to has been listed (1). This corresponds to a common
concept today that core and blanket will be treated jointly.

Concerning the reprocessing problems with this future burnup one
may distinguish primary and secondary consequences of higher
burnup.

As primary consequences we will consider here the objective facts
which will exist independent of the method of reprocessing. This
includes the increased concentration of fission products and alpha
emitting transuranium elements. Both give rise to an increased
radiation intensity which consenquently results in self-heating
of the material.

At the contrary, the secondary consequences we are talking about
are related to a specific technical method of reprocessing.

However, I believe that everybody will agree that under present conditions the aqueous method of reprocessing still constitutes the standard method.

For this reason, I think, it is justified to relate the secondary consequences of higher burnup to the aqueous process, even if this conference deals with the dry processes.

## Primary consequences

The primary consequences of higher burnup create already problems during transport and mechanical disassembling. With fast breeders in particular, the fuel elements of core and blanket still require separate treatment at this stage. Thus, the high fission product concentration of 8-12 % in the core elements and related decay energy density will have to be taken into account. With the core elements of the fast breeder, a power density of the order of 100 - 200 W/kg fuel must be anticipated (3) (with light water reactors it will be less than 10 W/kg fuel). This will require artificial cooling during transport and possibly also during mechanical disassembling (4,5,6).

However, it should be mentioned there is also the opinion that even with fast breeders, the core elements can be handled in the head end of the aqueous process without special cooling (7), if loose bundles of fuel pins are chopped and the rate of through-put is limited to 0.5 to/day.

In the following step of chemical disintegration of the fuel matrix, an increasing rate of disintegration has to be expected.

This effect has been observed already in aqueous processing starting from about 0.5 % burnup (7) and will rise an additional problem namely the correspondingly rapid release of the radio-active off-gases.

But even if there should be no rapid release of the volatile fission products the amount of iodine and tritium will cause some problems in the future.

Iodine-131 is probably the biggest trouble maker in the offgas system (9), because in the reprocessing of fast breeder elements, several hundred curie of iodine-131 per kilogram of fuel must still be expected after thirty days of cooling. Up to now, there has been little practical experience on the removal of such a large amount of iodine activity to such a low level as some micro curies per second in the off-gas stream. With a combination of a caustic scrubber, a heated silver nitrate tower and a charcoal filter an efficiency of 99.99 % of iodine removal in the off gas is expected (7). (In aqueous reprocessing the data on the amount of iodine getting into the offgas system vary between 30 and 95 % (5,10,11,6b).

However, even this efficiency will not be sufficient for short cooled breeder elements. Possibly, the method of retention in the dissolver by means of $Hg^{+2}$, tested in Savannah-River, will have to be employed in addition, (1 ). However, that leads to an increased transfer of the iodine to the organic solvent. Thus, via the solvent, the iodine 131 gets into the solvent washing system, and in a small fraction only, to the high level waste, where it should go. Furthermore, the rate of withdrawal of iodine from the organic phase is low, which again may have the effect of solvent degradation. Because of these difficulties in the aqueous process, there is a certain need for development work in fields of iodine retention and iodine washing in the aqueous process.

Besides iodine, tritium should be considered as well. The fission yield of tritium is known to be around 1 atom of tritium per 10,000 thermal fissions. For fast reactors, the yield of tritium has not been measured experimentally. However, from theoretical considerations, an increase in yield may be expected to occur in fast fission as listed in table 1 (12,13).

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### Tritium in Future Power Reactor Fuels

| $MW_{th}d$ | thermal U-235 | fast U-235 | fast Pu-239 | 80 m stack allowed | effluent allowed | dilution volume |
|---|---|---|---|---|---|---|
| | Ci-T | Ci-T | Ci-T | Ci-T/d | $Ci-T/m^3$ | $m^3$ |
| 20 000 | 260 | 310 | 640 | | | $1-3 \cdot 10^5$ |
| 30 000 | 390 | 470 | 960 | 19 000 | $3 \cdot 10^{-3}$ | $1,6-3,2 \cdot 10^5$ |
| 40 000 | 520 | 620 | 1 280 | | | $2,1-4,5 \cdot 10^5$ |

total aqueous
process effluent
1 to/d - plant
$150 \ m^3$

Table 1.

In Table 2 the anticipated tritium content in the fuel from thermal and fast reactors is shown. However, from the table it is also evident that there are no severe restriction of the tritium is discharged through an exhaust stack of 80 m. Consequently, this means that in the aqueous process, all the overhead aqueous effluent from the general purpose evaporator has to be removed through the exhaust stack. In a plant with a capacity of 1 to/day this is a quantity of some 40 $m^3$ water per day (14) which has to be discharged via the exhaust stack.

Moreover, the table lists the quantities of diluent water that would be required if the tritium-contaminated water had to be discharged into the environment in the liquid form. Considering that the total process effluent of a 1 to/day plant is estimated to be around 150 $m^3$, it is evident from the dilution volume that tritium removal by dilution will be a real possibility only in very rare cases. This situation is not changed in any way, if one considers that only some 50 % of the fission tritium will be found in the process water, while the remaining 50 % escape through the offgas system anyhow (15).

At this point, few remarks on krypton-85 are suitable. Probably any reprocessing method will try to get rid of krypton through the offgas stack. From this point of view, krypton will be less a chemical or a physical problem than a limiting factor on plant capacity which will burden any reprocessing plant.

Furthermore, if we consider that the half lives of Kr-85 and tritium are similar, we come to a comparison between Kr-85 and tritium in the offgas.

The maximum concentration of Kr-85 permitted in air is about four times that of tritium ($3.7 \cdot 10^{-7}$ Ci Kr-85/m$^3$; $7.2 \cdot 10^{-8}$ Ci-T/m$^3$). However, the fission yield of Kr-85 is about 130 times that of tritium. Therefore, the krypton hazard connected with the atmospheric dispersion of nuclear fuel offgases is some ten times higher than that of tritium. Therefore, tritium will not be the limiting isotope but krypton.

Also a remark concerning the non volatile fission products is necessary.

Present experience proves that the high fission product concentration will have an additional effect on the chemical disintegration at least in the aqueous process by formation of an insoluble residue. This residue is an alloy consisting in particular of the fission products ruthenium, molybdenum, rhodium, and technetium together with some $0.2 - 0.5$ % of the plutonium (4,5,8).

Because of the difficulty to filter these insoluble fission products in the aqueous process, Nicholson recommended pulsed columns instead of mixer settlers (7). Pulsed columns offer the possibility of processing also feeds containing larger amounts of solids.

Secondary Consequences
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The problem most frequently cited as the major disadvantage for aqueous reprocessing is radiation damage of the solvent. Partly, this opinion dates back to the time of the 2nd Geneva Conference in 1958, when Cooper and Walling reviewed the process implications of solvent radiolysis (16). Also other experiments seemed to confirm their opinion (17,18,19).

However, a critical check of those results recently made by
CH.A. Blake, Jr., in Oak Ridge claines that these early data
to be of limited value for estimating the effect of solvent
radiation damage on process performance (20). Also, most other
data obtained in laboratory studies require large extrapolations
not to higher values as you might expect, but to lower values
when they are used to predict results during operation of aqueous
fuel reprocessing. In laboratory studies quite often the radiation
exposures were raised up to hnndreds of watthours per liter.
That is quite unrealistic if you compare with those doses to
be expected within the limit of 40,000 MWd/to namely 0.05 to
1.0 watthours per liter per passage (7,20,21,22,23) through the
extractor.

For this reason, we will consider here the probably realistic
radiation effect of doses up to 1 Wh/l. Nevertheless, it is not
yet possible to give a completely clear picture of the situation.

There seems to be a general agreement now that doses up to
several 10 watthours/l have no grave effects on the TBP process,
if the irradiation dose has been received by the solvent over
a prolonged period. Reports from the technical plants at Windscale,
Savannah River and Hanford all agree on this (10,24). From these
results it can be concluded that those degradation products of
TBP and diluents produced at low dose rates are removed to a
sufficient extent in the usual solvent washing systems.

However, the situation does not seem to be absolutely clear if a
dose up to 1 watthour/l is received by the solvent in each
individual passage.

In Karlsruhe we carried out experiments on 20 % TBP dodecane which had been exposed to 1.2 watthours per liter in a mixer chamber under real process conditions (25). You see the result in Table 2.

### Effect of 1,2 Whr/liter on 1 Extraction Cycle
### (flowsheet adjust. to fast breeder fuels)

|  | Zero Whr/l | 1,2 Whr/l |
|---|---|---|
| $DF_{Nb}$ | 1,000 | 40 |
| $DF_{Zr}$ | 1,000 | 10 |
| $DF_{Ru}$ | 3,000 | 2,000 |
| Pu loss | ≤0.1 % | ≤ 1 % |
| reduct.strip. |  | 0.02 % |
| Interface | free | precipitation |

Eight extraction-, eight scrub-, and 16 strip stages were used, and the flowsheet conditions were such as are required for fast breeder fuels with a high plutonium content (up to 10 %).

As you see, the DF for zirconium and niobium decreases in a disastrous way. The DF for ruthenium also becomes lower, however, not that markedly. Furthermore, the loss of plutonium to the waste effluent stream rises to an unacceptable degree.

A similar effect with respect to the DF values of zirconium and ruthenium were reported recently by Faugeras and Talmont on the basis of experience gained in Marcoule and especially with Cyrano, where mixed uranium-plutonium-oxides with a burnup of 25,000 MWd/to were reprocessed (26).

However, the experience from Savannah River and, in particular from Dounreay, sounds quite differently.

In Savannah-River, over the past five years large quantities of high-burnup plutonium have been reprocessed by solvent extraction. The separation of plutonium from the fission products was carried out in the first cycle with 2.5 vol% TBP in kerosene. The essential result sounds: the performance of solvent extraction during five programs is reported to have been excellent (27). The comment especially interesting in our consideration here is that no rapid effects were observed.

Even better information about the usefulness of solvent extraction with TBP at high dose rates is apparent from the reports from Dounreay (28): The calculated radiation dose is reported to have been 1.4 watthours per liter per passage. Even unscheduled shutdowns over 16 to 24 hours are said to have had no remarkable effect either on retained activity in the solvent or on the decontamination factors.

During operation campaigns in Dounreay, various tests for solvent quality are reported to have been made, but no significant variations have been noted. The overall plant decontamination even exceeded the design predictions.

In favour of the aqueous process we hope that this contradictory
results we have to report are contradictions only apparently.
The low DF might only be a temporary effect during the passage
through the first extractor. The degradation effect may be eli-
minated in the following solvent washing system. Then, it would
no longer appear in the overall balance as it is reported from
Dounreay. We are about to study this situation in more detail.

Finally, some further problems of future fuels should be mentioned
with respect to the aqueous process. The higher plutonium concen-
tration will involve problems of criticality and alpha radiolysis
of the solvent also in the second and following cycles of the
aqueous process.

The criticality problem, which becomes a capacity problem for
larger plants, can be overcome with fast extractors as several
authors have discussed in detail (29-35).

The high concentration of plutonium, in particular Pu-238, in
the organic extract may provide a permanent source of solvent
degradation even after the extractant has left the high active
first extractor. The radiation density of Pu 238 is about
$5 \cdot 10^{-3}$ alpha - W/g total Pu (9). The consequence of alpha radio-
lysis at this stage should be a loss of plutonium and uranium
to the waste effluent stream. However, this difficulty in the
stripping process can be completely overcome by a change in
valence state of plutonium (36) as has been proved already in the
aqueous flowsheet of fast breeder fuels.

Furthermore, particularly worth mentioning in this connection is
the fact that according to Faugeras and Talmont (26) it is possible
with a limited quantity of fluoride to remove even the precipitate
at the interface in reprocessing high burned up materials.

This precipitate is an especially awkward effect in mixer settler operation. These examples are by no means complete: they are just an arbitrary selection to show how the solvent extraction process is capable to be adapted to new situations that may arise from high dose rates.

## Summary

The real problems in reprocessing nuclear fuels associated with increased burnup of future uranium- and plutonium oxide fuels are the high fission product concentrations with the corresponding amounts of volatile iodine and tritium. Furthermore, self-heating in the head end stage and rapid off gas release during the dis-integration step will cause problems. On the other hand the aqueous process probably will not fail even with higher burnup and shorter cooling times.

Nevertheless, there is chance for dry methods in the future as well. Future reactor projects like High-Temperature-Gas-Cooled Thorium-Reactors or Fused Salt Reactors may need a nonaqueous method anyway. Non aqueous methods may also take over steps of the reprocessing operation if this would make the overall process more economic.

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