Recycling of MgO, Mo, & ZrO₂ based actinide-bearing matrices: assessment of reprocessing feasibility & waste production

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Abstract

Three U-free matrices were compared with the UO₂ matrix. Mixed with minor actinides (MA) in targets, they were irradiated in the ADS and the SFR.

The study focuses on the feasibility of target reprocessing by hydrometallurgy: dissolution, separation by extraction of U, Pu, Np, Am and Cm, followed by the concentration and vitrification of fission products.

It was shown that UO₂-MA-bearing targets could be reprocessed without major difficulty, whereas among the inert matrix targets, only MgO-MA-bearing target industrial reprocessing could be possible today. There would, however, be a significant production of waste.

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1. Introduction

The objective of this system study was to assess and rank some matrices in terms of their suitability for reprocessing and waste management. Three U-free matrices (MgO, ZrO₂ and Mo metal) were compared with the UO₂ matrix. These matrices mixed with minor actinides (MA) in targets were irradiated in the ADS as defined by the European Project EUROTRANS [1] and the SFR as defined by an INL study in the frame of the GNEP program [2].

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The study was limited to the process aspects of the feasibility of target reprocessing by hydrometallurgy: dissolution, separation by extraction of U, Pu, Np, Am and Cm, followed by the concentration and vitrification of fission products (FP). Other aspects, such as criticality, radiation protection, and nuclear measurement, with an impact on facility design and costs, are not discussed.

2. Reprocessing of MA-bearing Targets

2.1. Matrices of MA-bearing Targets considered

Targets designed for the ADS have been calculated for MgO and Mo-bearing matrices. No UO₂-bearing target for the ADS was available for study, and therefore the composition in UO₂, PuO₂ and MA was estimated. Targets designed for the SFR were made with MgO and UO₂-bearing matrices. No ZrO₂-bearing matrix designed for ADS or SFR was known at the time of the study.

Calculations were carried out in order to evaluate the impact of target reprocessing on fuel reprocessing fluxes, based on future European reprocessing fluxes as presented by the PATEROS European Project. The WP2 studies focus on a few selected scenarios for the implementation of P&T in Europe with an original regional approach [3]. The reprocessing flux of Scenario 2 (reprocessing all European LWR spent fuel, recycling the plutonium in LWR and involving ADS to transmute the MA mixed with plutonium) was selected as it has the highest fluxes.

2.2. General Reprocessing Process

The current reference process for the industrial reprocessing of European and Japanese LWR spent fuels is the well known PUREX process [4], which meets all the process safety and cost objectives. Thus, the reference development scheme to consider for the partitioning of Minor Actinides has to consist of the PUREX process completed by the DIAMEX-SANEX process [5, 6], as presented in Figure 1.

![Flow sheet of the reprocessing process for MA-bearing targets](image-url)
As an alternative process, the assessment of pyrochemical reprocessing for some ADS MA-bearing targets was studied during the FP6 EUROPART Project [7, 8].

2.3. Reprocessing of UO₂ MA-bearing Targets

Handling and mechanical treatments such as decladding and grinding have been implemented at a pilot scale in Marcoule and industrially in La Hague under radioactive conditions on ductile cladding materials (stainless steel or zircalloy), but these operations have not yet been tested with the cladding material used for ADS target fuel or SFR target fuel. Such actions have to be carried out in special front-end facilities.

The front-end mechanical treatment of targets is expected to be similar to the treatment of SFR spent fuel, which is itself not yet developed at the industrial scale. Such development may present difficulties.

Another difficulty will come from the high generation of heat, and of β γ and neutron radiation. The high generation of neutron radiations is due to high burnups applied to MA targets for transmutation, and mainly comes from ²⁴⁴Cm. The consequences include the necessity for high air ventilation flow rates, thermal protection and biological shielding, that will increase the plant investment costs. The mechanical treatments may need to be adjusted to better suit the thermal and radiant constraints. The same difficulty will apply in the target fuel recycling, on retrieval from the reactor and during the transport pre-reprocessing.

These issues may well also be encountered during the front-end mechanical treatment of U-free MA-bearing matrices.

The dissolution of UO₂ MA-bearing targets is similar to that of UOX fuels. There may be more insoluble elements present, which could mean an improvement of dissolution conditions would be necessary. The Pu and minor actinide contents of the targets may result in increased levels of Pu-MA-rich insolubles. Hence, dissolution has to be optimized and potentially completed by a second stage of dissolution. Any losses of transuranic elements to residues must be minimised, to maximise the benefits gained from P&T fuel cycles.

The downstream operations such as PUREX extraction, DIAMEX-SANEX partitioning, FP concentration and vitrification should not present any difficulty.

2.4. Reprocessing of MgO MA-bearing Targets

The dissolution should be very good, as the MgO matrix is soluble in nitric acid with fast dissolution kinetics [9, 10]. Mg is not involved in precipitation.

However the dissolution of PuO₂ may represent the main difficulty. It is known that when the mass ratio Pu/(U+Pu) of PuO₂-UO₂ fuels reaches 35%, the dissolution of PuO₂ is not efficient and the amount of undissolved plutonium increases drastically [11]. The mass composition of unloaded ADS target fuels is 48.8% Pu, 51.1% MA including 44.4% of Am, 0.1% of U. Even if there is a high concentration of AmO₂ diluting the PuO₂ (which is estimated to help the dissolution as UO₂ does), this dissolution should be checked as it has never been examined with the minor actinides in dilution.

Moreover, the dissolution of minor actinides could present difficulties. The first dissolution tests of the irradiated pellets AmO₂-MgO in the Ecrix H experiment revealed the presence of large insolubles. Dissolution of a pellet under standard reprocessing conditions resulted in 10% of undissolved product [12]. In such cases, the use of a complementary dissolution by Ag(II) oxidant ions would be required, as is the case in the Ag(II) process used at La Hague for the dissolution of non-standard PuO₂. Other oxidizing ions, such as Ce (IV) and Co (II), can also be used [13]. The same difficulties would be encountered in the dissolution of the two other U free matrices.

Thus, the dissolution of MgO-MA bearing targets could be carried out without major difficulties, as the difficulties identified have manageable solutions. The downstream operations, such as PUREX extraction, DIAMEX-SANEX partitioning and FP concentration, should not reveal any difficulty.
Concerning vitrification, Mg is not known to create complications during the vitrification process, but the MgO content is limited to 1 to 7.5% weight of the matrix glass composition to prevent a decrease of the matrix leaching resistance [14]. In the current reference glass R7-T7, produced by the AREVA NC La Hague plants, the MgO content is limited to 1% weight of matrix glass to prevent a significant increase of leaching alteration rates [15]. All tests to improve quality in MgO derivative R7T7 glass have so far failed. Tests of the AVM reference glass produced by AREVA NC Marcoule, with a different composition in which up to 7.5% of MgO may be allowed, showed lower resistance to leaching.

A separate reprocessing of CERCER MgO MA-bearing targets would lead to the production of a very large number of high-activity glass containers. A reprocessing in dilution with other reactor spent fuels may lead to a drastic reduction of the production of these high-activity glass containers. Waste flow calculations indicate that the number of R7T7 glass containers is multiplied by 75 for the MgO matrix compared to the UO2 matrix, with a separate reprocessing, and multiplied by 2 with a reprocessing in dilution of all European LWR spent fuel, according to the PATEROS scenario.

A selective separation process before reprocessing or after FP concentration would be a useful alternative, but the technique remains unknown to date.

2.5. Reprocessing of Mo MA-bearing Targets

During the spent nuclear fuel dissolution process, Mo is soluble in nitric acid. However, with high molybdenum concentrations, formation of Mo containing precipitates also including actinides will occur over time.

Spent fuel composed mainly of uranium oxide is dissolved in 3–3.5 M nitric acid at 90° to over 100 °C. A continuous dissolution is obtained by a nitric acid flow. The resulting nitric acid solutions have a typical residence time of a few hours and can precipitate when molybdenum and zirconium fission products are present at concentrations higher than 1 g/L, giving the formation of a zirconium molybdate hydrate or ZMH. This precipitation leads to the formation of fouling layers. For higher concentrations of Mo (i.e. Mo:Zr ratio > 2:1), it appears that MoO2 forms preferentially, and precipitates.

The formation of ZMH precipitates has been studied in many parts of the world over the last thirty years [16, 17, 18 and 19]. From the latest studies at CEA Marcoule [20], concerning the nucleation and crystal growth experiments under the usual conditions for the industrial dissolution process of spent nuclear fuel in nitric acid, the data of the different critical super-saturations was obtained for different acidities from 1.5 to 3 N, and temperatures (80, 87 & 94 °C). From this data, severe fouling and precipitation in the dissolver during CERMET Mo target dissolution can be predicted. It has also been established that dissolution in 5-7 M nitric acid is advised for high Mo concentrations, Mo being more soluble in higher acid solutions.

Calculations of the process flux have been made for a separate reprocessing and for a reprocessing in dilution with all European spent fuels. The separate reprocessing calculations lead to a concentration of Mo of 175 g/L, compared to the maximum of 1 g/L needed to prevent precipitation and fouling under the dissolution conditions. Obviously, such dissolution is not feasible. The diluted reprocessing leads to a concentration of Mo of 9 g/L which again is not workable, as even if a dilution may help to reach 1 g/L, the flow rate would have to be pushed to 14 m³/h, i.e. 9 times the flow rate of UP3.

A selective separation of Mo before reprocessing is required to reprocess Mo matrices by the PUREX-DIAMEX-SANEX separation processes.

2.6. Reprocessing of ZrO2 MA-bearing Targets

The ZrO2 matrix is not soluble in hot concentrated nitric acid, as indicated by two tests, the first of which was performed by the INL [9] and the other by the CEA [21]. The experiments have continued at the CEA on other
reagents such as HNO$_3$/HF, HF, H$_2$SO$_4$, and H$_2$SO$_4$/HF at temperatures of 105 to 110 °C. Only HNO$_3$ 3.5M/HF 3.3M and HNO$_3$ 7M/HF 1M lead to a total dissolution of zircon.

The treatment of the ZrO$_2$-MA-bearing targets is impossible in an industrial-type plant, for which the effluents must be free from fluoride ions in order to prevent corrosion of the dissolver and of the evaporators used for acid effluents with Zr.

3. Conclusion

In terms of reprocessing feasibility and waste production, this system study has shown that:

- The UO$_2$-MA-bearing targets could be reprocessed without major difficulty, enabling the production of a regular glass waste to contain the fission products (R7T7 glass).
- The MgO-MA-bearing targets could be reprocessed without major difficulty in dilution with all European LWR fuels, but still with a significant impact on waste production: for the treatment of ADS Pu-AM-MgO target fuels, the production of R7T7 glass would be doubled compared to the treatment of ADS Pu-AM-UO$_2$ target fuels.
- The Mo-MA-bearing targets could not be reprocessed even in dilution with other irradiated fuels, due to the high precipitation of molybdenum during dissolution and the absence of an effective separation process to implement before reprocessing.
- The ZrO$_2$-MA-bearing targets could not be dissolved without the addition of HF to HNO$_3$, which makes its treatment impossible in a La Hague-type plant where the effluents must be free from fluoride ions (corrosion of the dissolver and the evaporators made of Zr).

Consequently, among the inert matrix targets, only the industrial reprocessing of MgO-Ma-bearing matrices would be possible today in the existing reprocessing plants.

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