

COMMISSARIAT A L'ENERGIE ATOMIQUE  
CENTRE D'ETUDES DE SACLAY  
M I S T

Service des Bases de Données Spécialisées  
F91191 GIF SUR YVETTE CEDEX

FR 9 2000 18  
CEA-CONF-10559

ADVANCED PUREX PROCESS FOR THE NEW REPROCESSING PLANTS  
IN FRANCE AND IN JAPAN

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Communication présentée à : 3. International Conference on Nuclear Fuel Reprocessing  
and Waste Management

Sendai (JP)  
14-18 Apr 1991

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#### INTRODUCTION

In the late Seventies, COGEMA decided to build two reprocessing plants at La Hague :

- The completely new UP3 plant, with a capacity of 800 tons per year of spent fuel from LWR's, which was put in operation in two steps, in November 1989 and August 1990 respectively.

- The UP2 800 plant, an extension of the existing UP2 facility, to achieve the same annual capacity of 800 tons in the beginning of 1993, by the commissioning of a new head end and high active chemical process facilities.

In the early Eighties, Japanese utilities formed the Japan Nuclear Fuel Service Co (JNFS), which is in charge of the construction and the operation of the first commercial reprocessing plant in Japan to be erected in Rokkasho Village, Aomori Prefecture. Following a thorough worldwide examination of available processes and technologies, JNFS selected the French technology developed for UP3 and UP2 800 for the plants's main facilities and especially for the "heart" of the process, i.e the head end and the extraction process, with partial

incorporation of some British and German technologies.

The Technology Transfer Agreement signed on 30 April, 1987 by JNFS and SGN covered the CEA's process know-how and associated technologies and COGEMA's operating experience for the main facility. Other facilities, such as uranium-plutonium mixed denitration and waste solidification facilities were not included in the scope of the agreement; they will be based on Japanese technology.

For these three new plants, the 40-year old PUREX process which is used worldwide for spent fuel reprocessing, has been significantly improved. This paper describes some of the innovative features of the selected processes.

#### PROCESS SELECTION CRITERIA

A modern reprocessing plant is characterized by the utilization of an efficient complex process, designed to meet the end-product specifications, to achieve high recovery of these products, to comply with radioactive release restrictions, and also to reduce the volume of wastes and to process all wastes for final disposal.

1

Process selection criteria draw upon operating experience from existing French plants at La Hague and Marcoule, while taking into account the objectives of safety and availability as a major concern.

A number of basic principles were applied :

- wherever possible, continuous processes were selected over batch processes.

- close attention was paid to the reliability and flexibility of the process to avoid rework of out-of-spec products, as much as possible. This implies adequate safety margins during normal operation to respond to minor disturbances, as well as a suitable process control system.

- in addition, with respect to equipment, the highest achievable reliability was considered necessary, because maintenance is always costly, restricting and waste producing.

- As far as criticality safety is concerned, geometrically safe equipment was selected wherever possible over concentration or mass limitation of fissile material, to facilitate continuous operations and to reduce the constraints of regulatory procedures.

The main process and technology decisions, as well as the associated R & D program, are the result of intensive efforts from the very beginning of the project by all concerned (CEA as process licensor, COGEMA as owner/operator and SGN as architect engineer).

#### MAIN FEATURES OF THE PROCESS

The head end process comprises :

- . fuel dissolution by chop and leach process, using a geometrically safe continuous rotary dissolver, fed from a horizontal shear.

- . special devices to trap iodine from the dissolver off gas and to remove iodine from the dissolution liquor.

- . clarification of the dissolution liquor by centrifugation.

Two lines are provided, though one line is large enough to handle a nominal capacity of four tons per day.

The chemical process includes :

- . the first extraction cycle with U/Pu partition

- . 2 purification cycles for both uranium and plutonium

- . evaporation units for liquid effluent concentration and acid recovery systems

- . a solvent distillation unit.

Annular pulsed columns (geometrically safe) and mixer settlers are used in the first extraction cycle. Partition is performed using mixer settlers in UP3 and annular pulsed columns in the UP2 800 and Rokkasho reprocessing plants, allowing a higher plutonium concentration. Geometrically safe cylindrical pulsed columns are used in the plutonium purification cycles, as well as slab mixer settlers for plutonium barriers. Mixer settlers are used in the uranium purification cycles.

The process features a number of innovations of which the major ones are:

- iodine desorption from the dissolution liquor to prevent the dissemination of iodine in the overall process

- technetium barrier in the first extraction cycle to limit interaction between Tc and hydrazine in U-Pu partition.

- efficient tritium decontamination in the first extraction cycle to prevent tritium from spreading downprocess.

- plutonium barriers on the solvent streams wherever the stripping of plutonium is performed in pulsed columns

- diluent washing on all the aqueous streams from extraction cycles to prevent any tributylphosphate entrainment to the evaporators

- regeneration of the solvent streams from the extraction cycles in solvent wash systems using sodium carbonate, caustic soda and nitric acid. An additional purification is provided by a solvent distillation unit.

- plutonium oxidation by using nitrous fumes in packed columns
- decontamination of the uranium-stream from residual plutonium and neptunium in the uranium purification cycles, using both adequate reducing agents and precise adjustment of the operating parameters.
- careful selection of reducing agents for plutonium stripping (U/Pu partition, Pu purification cycles, Pu barriers), to obtain high chemical performance and process reliability
- production of uranous nitrate by catalytic reduction with hydrogen.

Some of these processes are discussed in greater detail below.

#### CONTINUOUS DISSOLUTION

The technology of the continuous rotary dissolver has been described elsewhere.

The following points are noteworthy concerning the chemical process :

- Dissolution kinetics in continuous dissolution conditions :
  - . Laboratory tests have been performed to measure the dissolution rate of irradiated fuel cut pieces (fuel pellets inside zircalloy clad) to check that the residence time in the dissolver allows effective and complete dissolution of the oxide with a sufficient safety margin.
  - . on the other hand, laboratory tests with irradiated fuel oxide powder showed a very fast dissolution rate. Full scale pilot plant tests conducted with unirradiated representative material, served to demonstrate that foam generation could be controlled safely and to develop an adequate pressure control system inside the dissolver.
  - From the chemistry standpoint, the continuous formation of nitrous acid prevents the formation of Pu VI and facilitates iodine desorption in the form of elemental iodine.

The first UP3 campaign results confirmed the test data and showed that the fissile material losses in the hulls are lower than expected.

#### IODINE MANAGEMENT

Special attention was paid to iodine behavior in order to remove it as efficiently as possible.

The objective of this process is to route iodine, as much as possible, to the dissolver off gas system, where it is trapped and consequently iodine removal from the dissolution solution is necessary to prevent it from spreading downprocess. (see Fig.1)

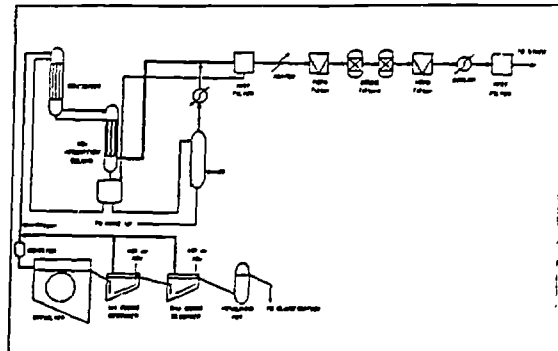


Figure 1 : Dissolver offgas treatment in the Rokkasho plant

#### Iodine trapping

- In UP3 and UP2 800, the major part of iodine is scrubbed in a caustic soda tower and the residual iodine is removed by using silver impregnated solid sorbents.
- In the Rokkasho plant, iodine removal is based on German technology with silver impregnated solid sorbents.
- In both cases, the dissolution off gas system includes a condenser and a NOx absorption column before iodine removal.
- In addition, to prevent iodine build-up in the dissolver, the iodine contained in the recovered acid from the NOx absorption column is removed by air sparging at boiling temperature in a packed counter-current column, before recovered acid is recycled to the dissolver.

### Iodine desorption from dissolution liquor

Most of the iodine is desorbed in the dissolver itself during dissolution. At the dissolver exit, the dissolution liquor flows continuously through an additional desorption system to remove the residual iodine.

A desorber is a slab vessel equipped with internals, which behaves as a multistage cross-current gas-liquid contactor. Desorption is performed at boiling temperature with NO<sub>x</sub> sparging in order to adjust the Redox potential for improving iodine removal.

### CLARIFICATION.

The dissolution liquor is clarified by centrifugation.

A new Robatel DPC 900 pendular centrifuge was developed and extensively tested by the CEA, to improve the performance of the DPC 800 used in UP2 400 since 1976.

The new DPC 900 is characterized by:

- an increase of the centrifugal acceleration field to improve process performance.
- efficient in situ rinsing of the cake to minimize losses of fissile material and to reduce the volume of waste.

Each of the two head end lines is equipped with one centrifuge, but both centrifuges can be operated in series to perform double clarification.

Active tests during the first campaign were successful using first only one centrifuge, and then both centrifuges in series.

In both cases, the clarified solutions were processed efficiently in the first extraction cycle without any trouble, i.e. without any significant build-up of interfacial cruds in the contactors.

### TECHNETIUM BEHAVIOUR IN THE FIRST EXTRACTION CYCLE

Technetium catalyses the oxidation of hydrazine by nitric acid. It is therefore a cause of hydrazine overconsumption in U-Pu partition and of potential problems in operation.

To limit hydrazine consumption, it is necessary to obtain a sufficient decontamination factor for technetium before partition, especially when processing high burnup fuels with higher technetium content.

A conventional first cycle extraction-scrub system does not provide any technetium decontamination factor. The main extraction mechanism is coextraction of technetium with extractable cations, mainly zirconium, plutonium and uranium.

In the extraction section, technetium is quantitatively coextracted with zirconium, which is significantly extracted in the absence of uranium. In the scrub section, zirconium is effectively stripped but technetium leaves in the solvent, due to the coextraction with uranium and to a lesser degree with plutonium.

To achieve technetium decontamination without introducing complexing agents, it was necessary to provide a second scrub section, (see Fig. 2) operated at high acidity (4 N) and to reflux the aqueous scrub to a separate "complementary extraction" section to recover uranium and plutonium from the scrub solution, without any interference from zirconium, thus avoiding coextraction of technetium. The loaded solvent is recycled to the main extraction column.

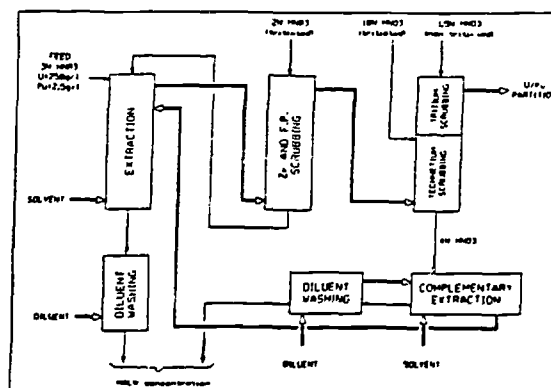


Figure 2 : First extraction cycle : Technetium and tritium scrubbing

Data for process modelling and simulation were obtained from R & D work and the flowsheet was thoroughly tested and adjusted in the laboratory.

The DF values measured during the first UP3 campaign were about 3, in agreement with the expected value.

Technetium scrub is performed in a separate pulsed column in the upper part of which tritium is also removed from the solvent (see section 7).

In the same upper part, the nitric acid content in the solvent is decreased before entering partition, by using a non tritiated low acid scrub solution. The acidity in the technetium scrub section is adjusted by introducing concentrated tritiated nitric acid.

#### TRITIUM DECONTAMINATION

To prevent tritium from spreading throughout the process and to facilitate tritium management, it was decided to differentiate two process areas, high-tritiated and low-tritiated, with two independent acid recovery units.

To achieve this goal, tritium must be removed from the solvent in the first extraction cycle, before partition.

Tritium is easily stripped from the solvent by scrubbing with non tritiated acid solution. Since the effective tritium distribution coefficient is very low, tritium decontamination can be achieved with only one theoretical stage with the selected scrubbing conditions.

From the high-tritiated acid recovery unit, concentrated tritiated nitric acid is recycled mainly to dissolution, while tritiated water is discharged into the sea after possible additional treatment by evaporation.

#### PLUTONIUM BARRIERS

Complementary plutonium stripping systems are provided at the solvent outlet of all the plutonium stripping columns, i.e. both for partition and plutonium purification cycles.

This complementary stripping is performed by using uranous nitrate stabilized with hydrazine, in specially designed mixer settlers.

To achieve the highest possible mass transfer and chemical efficiency, these mixer settlers are of the pump mix type and operate in a continuous organic phase, with internal recycling of a controlled flow of aqueous phase from the settler to the corresponding mixer.

In the plutonium purification cycles, the mixer settlers are reduced in height to make them geometrically safe, and are wide enough to handle the required throughputs.

The aim of these plutonium barriers is to drastically limit the amount of plutonium in the downstream of the process.

#### SELECTION OF REDUCING AGENTS FOR PLUTONIUM STRIPPING

Two reducing reagents are used in the new French and Japanese reprocessing plants : uranous nitrate (U IV) and hydroxylammonium nitrate (HAN). Both are used together with a stabilizer, hydrazinium nitrate (HN). These three reagents comply with salt-free process principles.

Uranium-plutonium partition is performed by using U IV. This technique is well proven and has been used for the last 30 years in French reprocessing plants.

As compared with HAN, U IV is a less demanding reagent for temperature and acidity. It also allows for higher concentration factors. The choice of U IV is therefore the most suitable for U-Pu partition.

By contrast, for the plutonium purification cycles, HAN was selected because the required conditions for plutonium stripping with this reagent (fairly high temperature, low acidity) are easily met and U IV presents a number of drawbacks : lack of stability at high plutonium concentration, and significant introduction of uranium in the plutonium purification cycles.

Moreover, in the plutonium purification cycles, significant concentration factors are obtained thanks to the contribution of the extraction-scrub section.

The use of HAN in pulsed columns proved to be both reliable and highly efficient in the first campaign of UP3.

#### SOLVENT DISTILLATION

To secure optimized operation of the process, care is taken to remove the TBP dissolved or entrained in the aqueous streams from the extraction cycles.

This removal is easily achieved by washing these aqueous streams with pure diluent, using either pulsed columns or mixer-settlers.

At the outlet of these washing operations, the diluent streams are small and are all joined to the solvent streams of the corresponding extraction operations, in order to avoid specific additional treatment (see Fig.3 ). As a result, the organic phase holdup increases and its TBP content decreases, making it necessary to re-adjust the TBP grade of the solvent. It is therefore also necessary to withdraw the excess solvent in each extraction cycle.

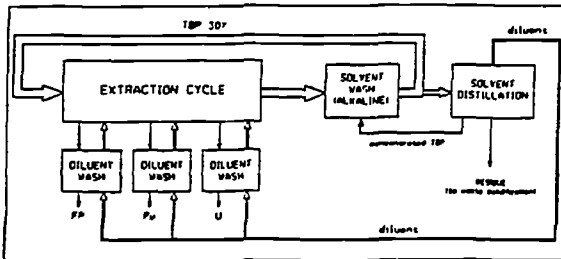


Figure 3 : Solvent management diagram

The excess solvent is treated by distillation, primarily to recover pure diluent and concentrated TBP for recycling purposes. In addition, solvent distillation ensures the decontamination of the processed solvent, as well as the elimination of heavy degradation products of the solvent, which are at least partly responsible of the loss of selectivity of the irradiated solvent.

This process is operated :  
 - at reduced pressure to keep the solvent at moderate temperature,  
 - with thin-film evaporators in order to limit the residence time.

These operating conditions were selected to avoid any significant degradation of the solvent and fouling of the evaporator.

The equipment includes (see Fig.4):  
 - dehydration by distillation under reduced pressure,

- an evaporation system which evaporates (and decontaminates) the solvent and produces an active residue. The composition of this residue is mainly TBP and heavy degradation products,

- a rectification tower, which fractionates the distillates into two parts : pure diluent and concentrated TBP.

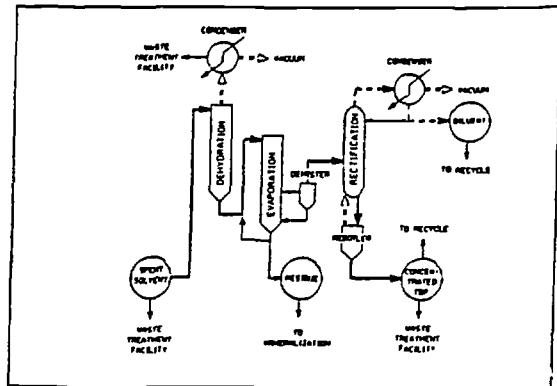


Figure 4 : Solvent distillation process

The first UP3 campaign results demonstrated the validity of the process and, in particular the recyclability of the recovered products as well as the low volume of residue. The distillation unit helps to lower the plant solvent activity level and consequently to improve the extraction process efficiency.