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ADVANCED PUREX PROCESS FOR THE NEW FRENCH REPROCESSING PLANTS

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ABSTRACT

The paper describes the main process innovations of the new Cogema reprocessing plants of La Hague (UP3 and UP2 800). Major improvements of process like the use of rotary dissolvers and annular columns, and also entirely new processes like solvent distillation and plutonium oxidizing dissolution, yield an advanced Purex process. The results of these innovations are significant improvements for throughput, end-products purification performances and waste minimization. They contribute also to limit personnel exposure. The main results of the first three years of operation are described.

INTRODUCTION

Reprocessing is the back-end of the nuclear fuel cycle, designed to recover valuable fissile materials, and to condition safely the radwaste ready for disposal.

A modern reprocessing plant is characterized by:

• the use of a complex chemical process to meet end-product specifications. These end-products are uranium, plutonium as well as all the conditioned waste;

• on-line processing of all the waste;

• stringent safety criteria to guarantee personnel and environmental protection under all circumstances;

• the highest achievable reliability and maintenance capabilities to ensure production availability.

For its new commercial reprocessing plants (UP3 and UP2 800), in order to meet the requirements listed before, Cogema decided to include many engineering innovations as well as new processes and key-components developed by the CEA.

Process innovations are extensive and concern most of the operations already implemented in previous reprocessing plants like the chop and leach process and the extractions, but also new processes like solvent distillation, electro-chemical dissolution of plutonium oxide, etc. In the following pages a selection of new processes, which have been fully operated for three years, is described.

The paper is focused on the main plant, as there is an other paper devoted to the waste management in this conference.

HEAD-END PROCESS

Even though one line is enough to process the design capacity, the head-end of UP3 includes two lines for each operation in order to guarantee availability[1]. This head-end process is illustrated in figure 1.

Fuel assembly preparation

Baskets containing fuel assemblies are transferred from the storage pool by a basket cart moving in a channel between the storage pool and the head-end facility (fuel feed cell).

Each fuel element is lifted and handled vertically from the basket by a tilting crane. The fuel assemblies are identified by video recording of their serial numbers.

Then the fuel assembly is transferred to the burn-up monitoring pit where it is monitored by gamma and neutron detectors before being tilted horizontally to feed the shearing machine.

Shearing

The shearing machines of UP3 are designed to process at high throughputs both PWR and BWR fuel assemblies.

Their magazine, which receives the fuel assemblies from the tilting crane, are horizontal. Two gags hold the bundle firmly during cutting of the rods to prevent the long rods from slipping. End-pieces and rods are cut by two systems of blades and associated counter-blade. A deflector helps to guide the chopped pieces towards the dissolver chute, while the end-pieces are routed to the end-piece rinser system.

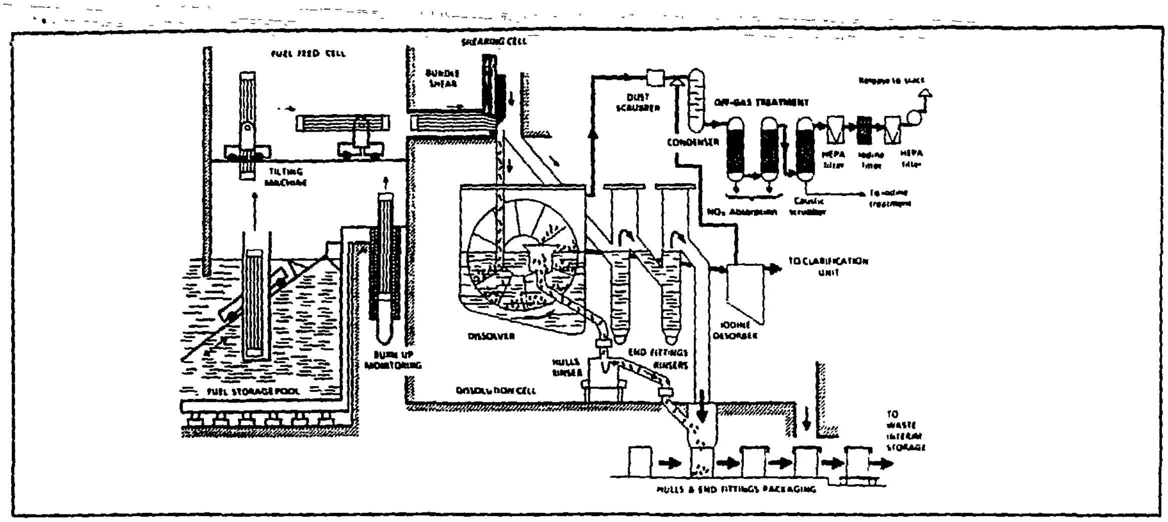

Figure 1: Shearing & Dissolution

All the mechanical pieces subject to wear can be remotely removed and replaced, including the blade-holder cart for blade maintenance.

Dissolution

Dissolution is performed in a continuous rotary dissolver, consisting of a geometrically safe slab tank containing a wheel with twelve buckets, fed successively and sequentially with the chopped pieces. In the lower part, buckets are immersed in the solution, and at the top the buckets are unloaded as late as possible to complete their drainage. In figure 2, the dissolver is shown with the cover and the wheel lifted, as if for maintenance operation.

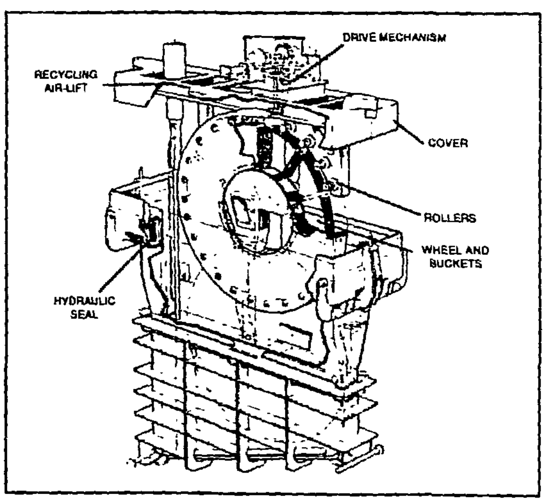

Figure 2: Continuous Dissolver

The slab tank is made of zirconium and is fitted with external stiffeners to prevent any distortion incompatible with criticality safety requirements. The tank is equipped with process pipes and chutes, a pulsator designed to push metallic scraps towards the bottom of the tank, heating and cooling devices including foam breakers just above the liquid level.

The cover ensures the containment of dissolver off-gas by the mean of a hydraulic seal. It supports also a recycling air lift, which sucks up metallic scraps which may fall to the bottom of the tank and recycles them in an immersed bucket.

Off-gas treatment and iodine management

The dissolution off-gas treatment comprises a dust scrubber, a condenser, nitrous fume absorption columns, a caustic scrubber which retains most of the iodine, and HEPA filters designed to remove the residual iodine and aerosols before the gases are discharged through the stack. Nitric acid recombined in DOG system is recycled in the dissolution process.

The liquids leaving the dissolver are treated in a desorber to remove the residual iodine from the dissolution liquor and to route the iodine into the DOG system. This desorber is a slab evaporator with several compartments designed to flush out the iodine in the presence of NOx injection (gas/liquid crosscurrent system).

On-line rinsing and conditioning of hulls and end-pieces

Hulls from the dissolver are countercurrently leached by water in a rinser which acts also as an hydraulic seal to ensure containment of the dissolver off-gases. End-pieces are washed successively with nitric acid and water.

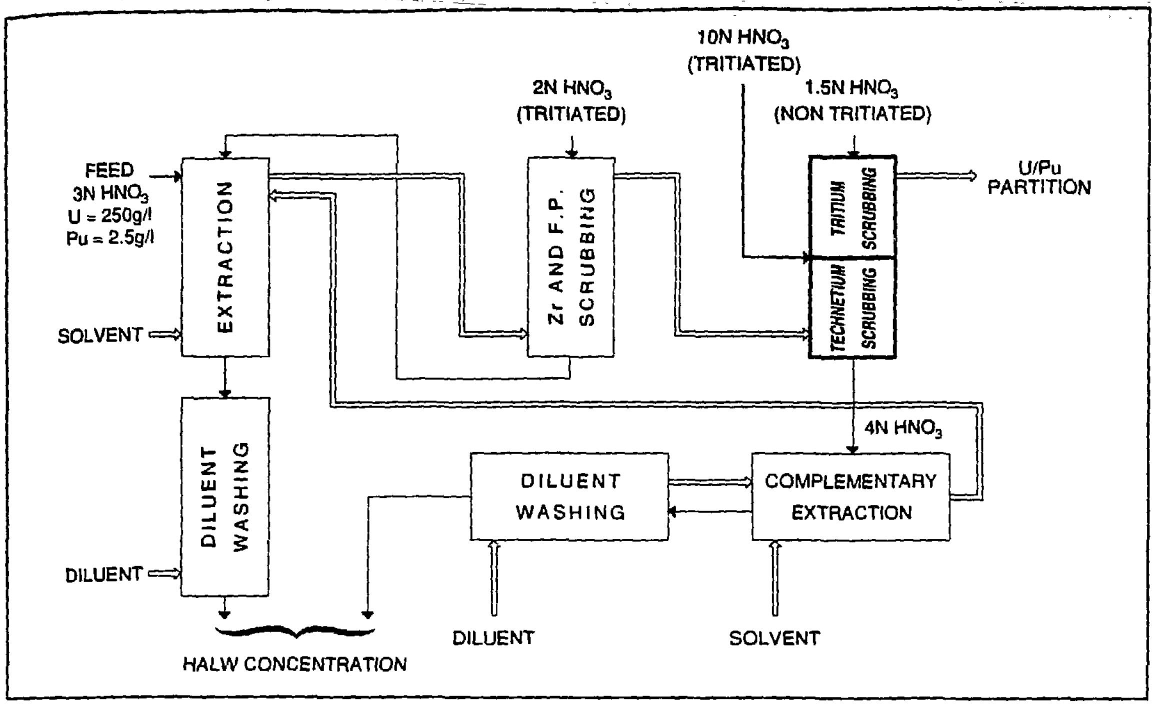

Figure 3: First Extraction Cycle: Technetium and Tritium Scrubbing

Without delay, the rinsed hulls and end-pieces are discharged in drums for final monitoring of residual fissile material content. Hulls and end-pieces are finally embedded in cement.

CHEMICAL PROCESS

Extractions

While based on the well known Purex process, i. e. liquid-liquid extraction with 30% TBP (TriButyl Phosphate) in a C_{12} paraffin, and retaining some proven technologies like mixer-settlers for uranium purification cycles, the extractions use many innovative features[3]:

- Uranium-plutonium first codecontamination extraction cycle (figure 3):

From the process viewpoint, the first decontamination cycle is characterized by the use of two separated scrubbing systems. The first one is dedicated to the separation of the bulk of fission products, while the second is devoted to the separation of tritium and also technetium, the chemical properties of which are unwanted in the downflow process.

The uranium-plutonium partition is operated by stripping plutonium reduced to trivalent state. This reduction is performed by using uranous nitrate, stabilized by hydrazine nitrate.

The major equipment innovation in the first extraction cycle is the use of annular pulsed columns for extraction, fission product scrubbing, technetium scrubbing and diluent washing of the extraction raffinate. Annular geometry allows the plant to process all the production through one line ever safe for criticality. New specially designed baffle plates guarantee high performances in a large range of throughputs, as well as perenniality towards ageing.

- Plutonium purification cycles:

Plutonium purification cycles use cylindrical pulsed columns fitted with disc-ring packing. This packing has properties analogous to the packing used for the first cycle columns, and is efficient on a wide range of throughputs and shows a high capability to withstand ageing. Stripping of plutonium is performed by using hydroxylamine nitrate (HAN), which allows to concentrate the plutonium through its purification cycles. HAN, like uranous nitrate has the distinction to achieve plutonium reduction without introducing any substance (like iron in the case of ferrous sulphamate reduction), liable to increase the amount of solid waste.

Further purifications of solvent for residual plutonium are performed in plutonium barriers, i. e. specially designed extra flat mixer-settlers, operating with uranous nitrate. The alpha contamination of the solvent at the outlet of plutonium barriers is extremely low (about 1 µg/l).

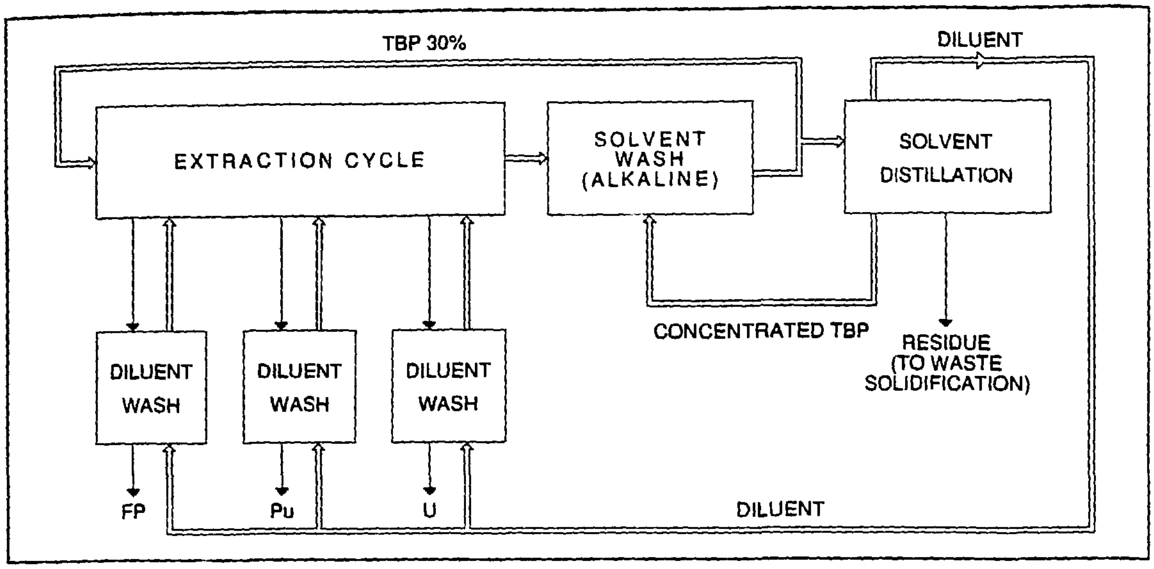

Figure 4: Solvent Management Diagram

Solvent clean-up and management

- Solvent alkaline clean-up:

This operation is performed in specially designed mixer-settlers and include sodium carbonate, nitric acid and caustic soda washings. A filtration step is also provided. To enhance their efficiency, the alkaline washings are performed in several stages, counter-currently arranged.

- Solvent management:

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 achieved by washing these aqueous streams with pure diluent. At the outlet of these washing operations, the diluent streams are all mixed with the solvent streams of the corresponding extraction operations. As a result, the organic phase hold-up increases and its TBP content decreases, making it necessary to readjust the TBP grade of the solvent. It is therefore also necessary to withdraw the excess solvent in each extraction cycle. The management of the solvent is designed to provide the maximum renewal to the most irradiated solvent, which is the one used in the first codecontamination cycle (figure 4).

- Solvent distillation (figure 5):

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, by removing heavy degradation products, which are at least partly responsible of the loss of selectivity of the irradiated solvent. Since TBP can be degradated by high temperatures, and can cause fouling in evaporators, it was necessary to find operating conditions which prevent troubles:

- operation at reduced pressure to keep the solvent at moderate temperature,
- use of thin-film evaporators in order to limit the residence time,
- special packing for the distillation tower.

This distillation unit is designed to minimize nuclear maintenance: the removal of separated fractions is operated by using atmospheric seals, the recirculation in the evaporator is operated by air-lifts...

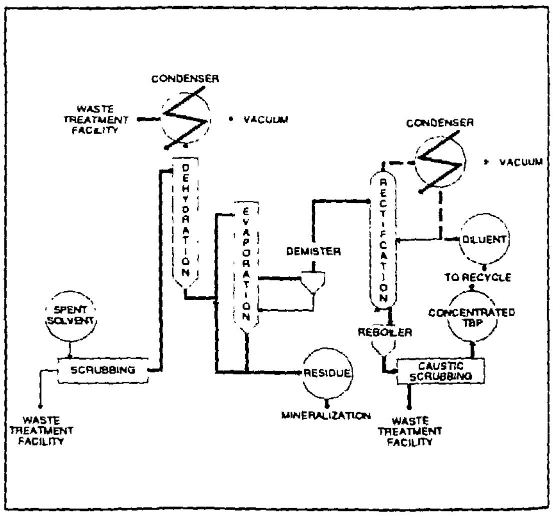

Figure 5: Solvent Distillation Process

Liquid waste processing

The containment of the beta-gamma activity is realized through the effective separation of the main fission product flow and the implementation of a tritium barrier in the first extraction cycle. The acid solutions containing the fission products are routed to the high level waste concentration unit, which separates the highly active flow, routed to the vitrification unit, from the tritiated acid, directed to a tritiated acid recovery unit. The recovered acid is then recycled upstream to the dissolution unit.

In a similar way, the acid solutions (mainly the extraction raffinates) coming from the purification cycles are routed to a low tritiated acid recovery unit, the recovered acid being recycled.

The alkaline solutions are collected and evaporated, the concentrate being routed to the vitrification unit. Other aqueous effluents are either processed in the waste treatment facility or released to the sea, according to their activity level.

Plutonium dioxide dissolution

In the new Cogema reprocessing plants, the well proven process of oxalic precipitation has been retained for plutonium conversion, with some improvements relating mainly to technology. The major process innovation of the tail-end is the dissolution of plutonium dioxide.

In the past, it was assumed that plutonium dioxide could not be fully dissolved in nitric medium without adding fluoride ions.

An entirely new process, fluoride free, has been developed for this dissolution and is operated at the UP3 plant. The principle of this process is the dissolution of PuO_2 in nitric medium with the addition of electrogenerated Ag (II).

Insoluble PuO_2 reacts with Ag (II) to give soluble PuO_2^+. The pentavalent plutonium is then oxidized to hexavalent state.

The electrogeneration of Ag (II) is carried out using a platinum grid anode, a cathodic compartment filled with concentrated HNO_3 including a diaphragm and a cooled tantalum cathode, and a stirrer for circulation of the solution.

A criticality safe electrolytic dissolver has been built at a capacity of 1 kg of plutonium per batch, leading to 6 litres of concentrated plutonium. With a current of 80 A, the dissolution is achieved within four hours. It has been successfully operated since 1990 for removal of americium from aged plutonium dioxide.

PLANT OPERATION RESULTS AND CONCLUSIONS

Main process

From the start-up of the UP3 plant to the end of March 1993, the cumulated production is 1210 t of reprocessed uranium. The annual schedules have all been observed and, as the 1993 and 1994 ones are respectively 600 t and 800 t, the plant is now approaching its design capacity.

For the head-end, the results are very satisfactory: daily throughputs over 4 t/d for PWR and 3 t/d for BWR are currently sustained for significant periods. The trapping of iodine in the DOG by the liquid washing is excellent and, as a consequence, the loading rate of zeolite filters for the residual iodine is much lower than expected.

The monitoring of the drums of hulls and end-pieces shows an average loss of fissile material of about 0.1 % (to be compared to a 0.45 % design value).

The performances of the chemical process are outstanding:

- Decontamination:

The first codecontamination cycle provides excellent beta-gamma decontamination factors (DF > 5.10^4) for both plutonium and uranium streams.

As a result, most of the time, the design values for beta gamma DF are obtained at the outlet of the second cycle for both uranium and plutonium.

The uranium-plutonium partition reaches an outstanding efficiency, as there is less than 10 µg of Pu per kg of uranium at the outlet of the first cycle.

With a neptunium DF comprised between 10^2 and $2.5\ 10^2$, the 2nd uranium purification allows also uranium to reach its design alpha decontamination.

- Flexibility:

The UP3 plant first cycle comprises four pulsed columns and various different mixer-settler banks. This complex extraction unit shows an excellent flexibility, as it has been successfully operated at throughputs ranging from 2 t/d up to 4.4 t/d.

Throughput flexibilities of the uranium and plutonium purification cycles are similar.

- Plutonium losses

Both in raffinates and in unloaded solvent, the plutonium losses are extremely low. As a matter of fact, the figures given are almost never actual plutonium concentrations, but technical limits of the routinely used analytical methods.

Liquid waste management

The excellent results described above have consequences which make more sense than the satisfaction of surpassing the purification targets for the uranium and plutonium end-products.

The extremely high DF obtained at the first cycle, not only for beta-gamma, but also for alpha emitters allow to·

- concentrate virtually all the radioactivity in the highly active liquid waste (HALW);
- make management of the "further waste" streams more simple;
- make easier the maintenance operations, and therefore limir the volume and activities of the waste generated by these operations.

The HALW are now vitrified in the T7 facility, started July 1992. At the end of March 1993, 286 glass canisters have been produced, corresponding to 550 t of reprocessed uranium.

The liquid waste routed to the waste treatment facility, shows that both flowrates and radioactive content are far lower than expected.

The efficiency of the various systems dedicated to the cleaning of solvent, i. e.: plutonium barriers, improved alkaline washings and the new distillation unit lead to a first cycle solvent which retains the qualities of a fresh solvent. In particular, unlike any previous reprocessing plant, there is no significant ruthenium retention. The plutonium retention in the solvent is also extremely low, at the limit of detection. As a consequence, the organic residue of the distillation of the solvent is far lower than the expected value (5% of the feed) and shows a level of contamination extremely low.

All these results prompted Cogema to reconsider the principles of the liquid waste management, with the aim of minimizing drastically the volumes of TRU waste and HALW. Studies, waste sorting, building of new concentration units shall enable Cogema to concentrate practically all the fission product and TRU waste into the glass matrix, without increase of the glass volume generated by ton of reprocessed uranium, to suppress the production of bituminized waste, and in parallel to reduce the volume of technological waste.

On short notice, the volume of waste not compatible with shallow land disposal will be significantly lower than the volume of waste resulting of direct disposal of spent fuel. Reprocessing is therefore the best technically feasible solution for the long lived waste[3].

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